Nucleophilic Magnesium Silanide and Sila-amidinate Derivatives

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Dedication: Dedicated to Dr. Helmar Görls on the occasion of his 65th birthday.

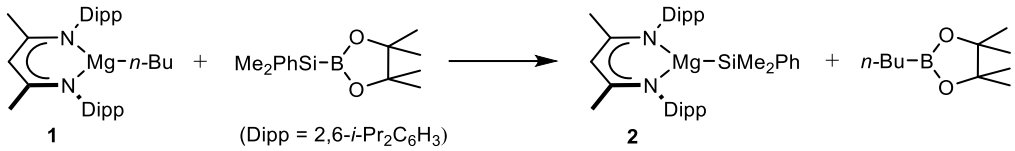
Abstract

Density functional theory (DFT) calculations demonstrate that the previously reported reaction of [(BDI)Mgn-Bu] (BDI = HC{(Me)CN-Dipp}$_2$; Dipp – 2,6-di-iso-propylphenyl) with the silaborane, Me$_2$PhSi-Bpin, provides the magnesium silanide derivative, [(BDI)MgSiMe$_2$Ph], through the intermediacy of a short lived silyl-pinacolato-organoborate species. The nucleophilic character of the resultant silanide anion is assayed through a series of reactions with RN=C=NR (R = i-Pr, Cy, t-Bu) and p-tolN=C=Np-tol. When performed in a strict 1:1 stoichiometry, all four reactions result in silyl addition to the carbodiimide carbon center and formation of the corresponding β-diketiminato magnesium sila-amidinate complexes. Although performance of the reaction of [(BDI)MgSiMe$_2$Ph] with two equivalents of p-tolylcarbodiimide also results in the formation of a sila-amidinate anion, the second equivalent is observed to engage with the nucleophilic γ-methine carbon of the BDI ligand to provide a tripodal di-imino-iminoamidate ligand. This behaviour is judged to be a consequence of the enhanced electrophilicity of the N-aryl substituted carbodiimide reagent, a viewpoint supported by a further reaction with the N-isopropyl sila-amidinate complex, [(BDI)Mg(i-PrN)$_2$CSiMe$_2$Ph]. This latter reaction not only provides an identical di-imino-iminoamidate ligand but also results in twofold insertion of p-tolN=C=Np-tol into a Mg-N bond between the magnesium center and the sila-amidinate anion.

Introduction

Di- and mono-organomagnesium compounds, R$_2$Mg and RMgX, provide some of the commonest and most longstanding sources of organic nucleophiles.[1] While much of this chemistry has historically focused on their use as stoichiometric reagents, more recent research has also begun to delineate a broadly-based catalytic reactivity.[2-28] In contrast, the chemistry of magnesium silanide reagents has received comparatively limited interest despite the clear utility of such species as sources of triorganosilyl anions.[29-31] While Oestreich and co-workers have recently demonstrated that triorganosilylmagnesium halides are accessible by *in situ* oxidation of magnesium metal to MgBr$_2$ and lithium silanide transmetallation,[32, 33] true silicon-centered Grignard analogues,[34] that are prepared from

elemental magnesium and a triorganosilyl halide, are limited to Ritter's synthesis of $Me_3SiMgBr{\cdot}L$ and $Me_3SiMgI{\cdot}L$ (L = tetramethylethylenediamine or pentamethyldiethylenetriamine).[35] More commonly, the synthesis of silylmagnesium compounds has been achieved either by redox transmetallation of $(R_3Si)_2Hg$ and magnesium,[36-38] or by salt metathesis between a sterically encumbered silylpotassium reagent and a magnesium halide.[39-46] As part of a broader exploration of magnesium compounds in which the alkaline earth is directly bonded to an element of group 13 or 14,[47-54] we have previously reported that reaction of the β-diketiminato organomagnesium, [(BDI)MgBu] (**1**; BDI = HC{(Me)CN-Dipp}$_2$ where Dipp = 2,6-di-*iso*-propylphenyl), with the silaborane, Me_2PhSi-Bpin, provides facile access to the heteroleptic magnesium silanide, [(BDI)MgSiMe$_2$Ph] (**2**, Scheme 1).[55]



Scheme 1: Synthesis of compound **2**.

Although we also exploited this reactivity for the catalytic 'disilacoupling' of amines and boranes,[55] and Crimmin and co-workers have very recently reported that compound **2** and several related iminoanilido- or guanidinato-magnesium silyls behave as potent reagents for the defluorosilylation of industrially relevant fluoroolefins,[56] no further assay of the reactivity of compound **2** has yet been performed. In this contribution, we present a theoretical consideration of the mechanism of formation of compound **2** and report its reactivity with a range of representative carbodiimides.

Experimental Section

General Experimental Procedures

All reactions of air- and moisture-sensitive compounds were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of argon. NMR experiments involving air-sensitive compounds were conducted in J. Young tap NMR tubes made up and sealed in a glovebox under argon. NMR spectra were recorded on a Bruker AV300 Ultrashield instrument for ^{1}H (300.2 MHz), a Bruker 400 Ultrashield instrument for ^{29}Si (79.5 MHz) or an Agilent ProPulse instrument for ^{1}H (500 MHz), ^{13}C (126 MHz) and ^{29}Si (99 MHz) spectra at room temperature. The ^{1}H/^{13}C NMR spectra were referenced relative to residual solvent resonances, while ^{29}Si NMR spectra were referenced to an external standard (Me_4Si). Solvents (toluene, pentane and hexane) were dried using an MBraun solvent purification system and stored over 4 Å molecular sieves under argon. THF for use in air- and moisture-sensitive reactions was dried over sodium or potassium/benzophenone and distilled before use. C_6D_6 was purchased from Sigma-Aldrich and dried over a potassium mirror, vacuum transferred into a sealed ampoule and stored in a glovebox under argon. Di-*n*-butylmagnesium (Mg*n*-Bu$_2$ 1.0 M solution in *n*-

heptane) and carbodiimides were purchased from Sigma-Aldrich and used without further purification. The β-diketiminato magnesium alkyl complex, [(BDI)Mg*n*Bu] (BDI = CH{C(Me)NDipp}$_2$, Dipp = 2,6-*i*-Pr$_2$C$_6$H$_3$) (**1**), and di-methylphenylsilyl boronic acid pinacol ester (pinBSiMe$_2$Ph, pin = pinacolato) were synthesized by literature procedures.[57, 58] Yields are non-optimized and refer to isolated crystalline material. Elemental analysis was performed by Elemental Microanalysis, Okehampton, UK or by Mr Stephen Boyer of London Metropolitan Enterprises. For details of the X-ray studies, computational analyses and coordinates of calculated species see the Supporting Information.

Synthesis of [(BDI)Mg{(*i*PrN)$_2$C(SiMe$_2$Ph)}] (3)

A solution of **1** (50 mg, 0.10 mmol) and pinBSiMe$_2$Ph (26 mg, 0.10 mmol) in C$_6$D$_6$ (0.5 mL) was added via pipette to a J. Young NMR tube. Complete conversion to compound **2** was obtained after approximately 12 hours at room temperature. *N*,*N*′-di-*iso*-propylcarbodiimide (13.96 µL, 0.10 mmol) was added to the reaction mixture and complete conversion to compound **3** was obtained after 15 minutes at room temperature. The solvent was removed and crystals suitable for single crystal X-ray diffraction analysis were obtained by cooling a hexane/toluene solution to –30 °C (20 mg, 29%). Elemental analysis (%). Calculated for C$_{44}$H$_{66}$MgN$_4$Si: C, 75.13; H, 9.46; N, 7.96. Found: C, 75.19; H, 9.42; N, 7.67. ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K) δ 7.39 – 7.34 (m, 2H, *o*-(C$_6$*H*$_5$)Si), 7.20 – 7.13 (6H, Dipp-Ar), 7.10 (m, 3H, *m*, *p*-(C$_6$*H*$_5$)Si), 4.85 (s, 1H, C*H*{C(CH$_3$)NDipp}$_2$), 3.52 (m, $^3J_{H,H}$ = 5.9 Hz, 2H, NC*H*), 3.47 (m, $^3J_{H,H}$ = 6.8 Hz, 4H, Dipp-C*H*(CH$_3$)$_2$), 1.68 (s, 6H, CH{C(C*H*$_3$)NDipp}$_2$), 1.33 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, Dipp-CH(C*H*$_3$)$_2$), 1.25 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, Dipp-CH(C*H*$_3$)$_2$), 0.76 (d, $^3J_{H,H}$ = 5.9 Hz, 12H, NC(H)(C*H*$_3$)$_2$), 0.45 (s, 6H, Si(C*H*$_3$)$_2$Ph) ppm. ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 298 K) δ 181.9 (Si*C*N), 169.4 (CH{*C*(CH$_3$)NDipp}$_2$), 145.8 (*i*-Dipp-Ar), 142.7 (*o*-Dipp-Ar), 139.0 (*i*-(*C*$_6$H$_5$)Si), 134.0 (*o*-(*C*$_6$H$_5$)Si), 129.2 (*m*-(*C*$_6$H$_5$)Si), 128.4 (*p*-(*C*$_6$H$_5$)Si), 125.2 (*p*-Dipp-Ar), 123.9 (*m*-Dipp-Ar), 94.6 (*C*H{C(CH$_3$)NDipp}$_2$), 46.3 ((Si(CH$_3$)$_2$Ph)C(N*C*(H)(CH$_3$)$_2$)$_2$), 28.3 (Dipp-*C*H(CH$_3$)$_2$), 27.6 (NC(H)(*C*H$_3$)$_2$), 25.5 (Dipp-CH(*C*H$_3$)$_2$), 24.6 (Dipp-CH(*C*H$_3$)$_2$), 24.4 (CH{C(*C*H$_3$)NDipp}$_2$), 1.9 (Si(*C*H$_3$)$_2$Ph) ppm. ^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$, 298 K) δ –16.8 ppm.

Synthesis of [(BDI)Mg{(C$_6$H$_{11}$N)$_2$C)N)$_2$C(SiMe$_2$Ph)}] (4)

A solution of **1** (50 mg, 0.10 mmol) and pinBSiMe$_2$Ph (26 mg, 0.10mmol) in C$_6$D$_6$ (0.5 mL) was added via pipette to a J. Young NMR tube. Complete conversion to compound **2** was obtained after approximately 12 hours at room temperature. *N*,*N*′-di-cyclohexylcarbodiimide (21 mg, 0.1 mmol) was added to the reaction mixture and complete conversion to compound **4** was obtained after 15 minutes at room temperature. After removal of volatiles, crystals suitable for single crystal X-ray diffraction analysis were obtained by cooling a pentane solution to –30 °C (0.03 g, 39%). Elemental analysis, calculated for C$_{50}$H$_{74}$MgN$_4$Si: C, 76.64; H, 9.52; N, 7.15%. Found: C, 76.62; H, 9.50; N, 6.98%. ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K) δ 7.44 (m, 2H, *o*-(C$_6$*H*$_5$)Si), 7.23 – 7.14 (6H, Dipp-Ar), 7.14 – 7.10 (3H, *m*,*p*-(C$_6$*H*$_5$)Si), 4.88 (s, 1H, C*H*{C(CH$_3$)NDipp}$_2$), 3.52 (m, $^3J_{H,H}$ = 6.8 Hz, 4H, Dipp-C*H*(CH$_3$)$_2$), 3.16

– 3.08 (m, 2H, NC*H*), 1.70 (s, 6H, CH{C(CH_3)NDipp}$_2$), 1.55 – 1.48 (8H, CH_2), 1.40 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, Dipp-CH(CH_3)$_2$), 1.30 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, Dipp-CH(CH_3)$_2$), 1.03 – 0.83 (12H, CH_2), 0.50 (s, 6H, Si(CH_3)$_2$Ph) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K) δ 181.8 (Si*C*NCH), 169.4 (CH{*C*(CH$_3$)NDipp}$_2$), 145.9 (*i*-Dipp-Ar), 142.7 (*o*-Dipp-Ar), 134.0 (*i*-(*C*$_6$H$_5$)Si), 129.1 (*o*-(*C*$_6$H$_5$)Si), 125.2 (*m*-(*C*$_6$H$_5$)Si), 123.9 (*p*-Dipp-Ar), 94.6 (*C*H{C(CH$_3$)NDipp}$_2$), 54.8 (N*C*H), 38.5 (*C*H$_2$), 28.4 (s, *C*H(CH$_3$)$_3$), 26.3, 25.9 (*C*H$_2$), 25.5 (Dipp-CH(*C*H$_3$)$_2$), 24.6 (Dipp-CH(*C*H$_3$)$_2$), 24.4 (CH{C(*C*H$_3$)NDipp}$_2$), 1.4 (Si(*C*H$_3$)$_2$Ph) ppm. ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 298 K) δ –18.0 ppm.

Synthesis of [(BDI)Mg{(*t*-BuN)$_2$C(SiMe$_2$Ph)}] (5)

A solution of **1** (50 mg, 0.10 mmol) and pinBSiMe$_2$Ph (26 mg, 0.10 mmol) in C_6D_6 (0.5 mL) was added via pipette to a J. Young NMR tube. Complete conversion to compound **2** was obtained after approximately 12 hours at room temperature. *N*,*N*′-di-*tert*-butylcarbodiimide (19.32 µL, 0.10 mmol) was added to the reaction mixture and complete conversion to compound **5** was obtained after 15 minutes at room temperature. After removal of volatiles, crystals suitable for single crystal X-ray diffraction analysis were obtained by cooling a hexane/toluene solution to –30 °C (0.06 g, 82%). Elemental analysis (%). Calculated for $C_{46}H_{70}MgN_4Si$: C, 75.53; H, 9.65; N, 7.66. Found: C, 75.50; H, 9.87; N, 7.66. ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 7.58 (m, $^3J_{H,H}$ = 7.9, 1.4 Hz, 2H, *o*-(C$_6$*H*$_5$)Si), 7.28 – 7.06 (6H, Dipp-Ar), 7.01 (3H, *m*, *p*-(C$_6$*H*$_5$)Si), 4.90 (s, 1H, C*H*{C(CH$_3$)NDipp}$_2$), 3.59 – 3.44 (m br, 4H, Dipp-C*H*(CH$_3$)$_2$), 1.65 (s, 6H, CH{C(C*H*$_3$)NDipp}$_2$), 1.38 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, Dipp-CH(C*H*$_3$)$_2$), 1.29 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, Dipp-CH(C*H*$_3$)$_2$), 1.19 – 0.99 (m, 18H, C(*C*H$_3$)$_3$), 0.67 (s, 6H, Si(C*H*$_3$)$_2$Ph) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K) δ 180.5 (Si(CH$_3$)$_2$Ph)*C*(NC(H)(CH$_3$)$_2$)$_2$), 169.6 (CH{*C*(CH$_3$)NDipp}$_2$), 146.0 (*i*-Dipp-Ar), 142.9 (*o*-Dipp-Ar), 141.7 (*i*-(*C*$_6$H$_5$)Si), 135.1 (*o*-(*C*$_6$H$_5$)Si), 129.0 (*m*-(*C*$_6$H$_5$)Si), 128.4 (*p*-(*C*$_6$H$_5$)Si), 95.6 (*C*H{C(CH$_3$)NDipp}$_2$), 51.1 (*C*(CH$_3$)$_3$)), 34.6 (Dipp-*C*H(CH$_3$)$_2$), 28.2 (Dipp-*C*H(CH$_3$)$_2$), 26.0 (Dipp-CH(*C*H$_3$)$_2$), 24.9 (C(*C*H$_3$)$_3$)), 6.5 (s, Si(*C*H$_3$)$_2$Ph) ppm. ^{29}Si{H} NMR (99 MHz, C_6D_6, 298 K) δ – 20.1 ppm.

Synthesis of [(BDI)Mg{(*p*-CH$_3$C$_6$H$_4$N)$_2$C(SiMe$_2$Ph)}] (6)

A solution of **1** (50 mg, 0.10 mmol) and pinBSiMe$_2$Ph (26 mg, 0.10mmol) in C_6D_6 (0.5 mL) was added via pipette to a J. Young NMR tube. Complete conversion to compound **2** was obtained after approximately 12 hours at room temperature. *N*,*N*′-di-*p*-tolylcarbodiimide (22 mg, 0.10 mmol) was added to the reaction mixture and complete conversion to compound **6** was obtained after 15 minutes at room temperature. After removal of volatiles, crystals suitable for single crystal X-ray diffraction analysis were obtained by cooling a pentane solution to –30 °C (0.02 g, 25%). Elemental analysis (%). Calculated for $C_{52}H_{66}MgN_4Si$: C, 78.12; H, 8.32; N, 7.01. Found: C, 77.93; H, 8.10; N, 6.94. ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 7.18 – 7.16 (6H, Dipp-Ar), 7.11 – 7.08 (2H, *o*- (C$_6$*H*$_5$)Si), 7.07 – 7.02 (1H, (*p*-C$_6$*H*$_5$)Si), 7.00 – 6.95 (2H, (*m*-C$_6$*H*$_5$)Si), 6.69 (d, $^3J_{H,H}$ = 8.1 Hz, 4H, N(C$_6$*H*$_4$(CH$_3$))), 6.38 (d, $^3J_{H,H}$ = 7.8 Hz, 4H, N(C$_6$*H*$_4$(CH$_3$))), 4.95 (s, 1H, C*H*{C(CH$_3$)NDipp}$_2$), 3.36 (m, $^3J_{H,H}$ = 6.8 Hz, 4H, Dipp-

C*H*$(CH_3)_2$), 2.08 (s, 6H, N(C_6H_4(C*H*$_3$))), 1.73 (s, 6H, CH{C(*C*H_3)NDipp}$_2$), 1.20 (d, $^3J_{H,H}$ = 7.1 Hz, 12H, Dipp-CH(C*H*$_3$)$_2$), 1.10 (d, $^3J_{H,H}$ = 6.8 Hz, 12H Dipp-CH(C*H*$_3$)$_2$), –0.06 (s, 6H, Si(C*H*$_3$)$_2$Ph) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K) δ 185.4 (Si*C*N), 169.8 (CH{*C*(CH$_3$)NDipp}$_2$), 147.1 (Si*C*N), 145.6 (CH{*C*(CH$_3$)NDipp}$_2$), 142.7 (*i*-Dipp-Ar), 133.9 ((*C*$_6$H$_5$)Si), 128.0 (*p*-(*C*$_6$H$_5$)Si), 125.0 (*p*-(*C*$_6$H$_5$)CH$_3$), 124.0 (Dipp-Ar), 95.6 (*C*H{C(CH$_3$)NDipp}$_2$), 28.8 (Dipp-*C*H(CH$_3$)$_2$), 24.6 (Dipp-CH(*C*H$_3$)$_2$), 24.4 (Dipp-CH(*C*H$_3$)$_2$), 24.3 (CH{C(*C*H$_3$)NDipp}$_2$), 23.8 (Dipp-CH(*C*H$_3$)$_2$), 23.2 (CH{C(*C*H$_3$)NDipp}$_2$), 20.9 (N(C_6H_4(*C*H$_3$))), 1.3 (Si(*C*H$_3$)$_2$Ph) ppm. ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 298 K) δ –11.3 ppm.

Synthesis of [(CH{C(Me)NDipp}$_2$(*p*-CH$_3$C$_6$H$_4$N)$_2$C)Mg{(*p*-CH$_3$C$_6$H$_4$N)$_2$C(SiMe$_2$Ph)}] (7).

A solution of **1** (50 mg, 0.10 mmol) and pinBSiMe$_2$Ph (26 mg, 0.10mmol) in C_6D_6 (0.5 mL) was added via pipette to a J. Young NMR tube. Complete conversion to compound **2** was obtained after approximately 12 hours at room temperature. *N*,*N*′-di-*p*-tolylcarbodiimide (44 mg, 0.20 mmol) was added to the reaction mixture and complete conversion to compound **7** was obtained after 15 minutes at room temperature. After removal of volatiles, crystals suitable for single crystal X-ray diffraction analysis were obtained by cooling a pentane solution to –30 °C (0.03 g, 29%). Despite multiple attempts a microanalysis could not be obtained for this compound. ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 8.07 (d, *J* = 9.9 Hz, 2H *o*-N(C_6H_4(CH$_3$))C*H*), 7.28 (d, *J* = 8.0 Hz, 2H *m*-N(C_6H_4(CH$_3$)) C*H*), 7.01 (m, 11H, C*H*, Ar, Ph, Dipp), 6.92 (d, *J* = 8.5 Hz, 2H *o*-N(C_6H_4(CH$_3$))C*H*), 6.87 (d, *J* = 8.1 Hz, 2H *m*-N(C_6H_4(CH$_3$))C*H*), 6.47 (d, *J* = 7.9 Hz, 4H *o*,*m* N(C_6H_4(CH$_3$))C*H*), 5.87 (d, *J* = 8.1 Hz, 4H *o*,*m*-N(C_6H_4(CH$_3$))C*H*), 5.39 (s, 1H, C*H*{C(CH$_3$)NDipp}$_2$), 3.18 – 3.07 (m, 2H Dipp-C*H*(CH$_3$)$_2$), 2.88 – 2.78 (m, 2H, Dipp-C*H*(CH$_3$)$_2$), 2.34 (s, 3H, N(C_6H_4(C*H*$_3$))), 2.24 (s, 3H, N(C_6H_4(C*H*$_3$))), 2.11 (s, 6H, N(C_6H_4(C*H*$_3$))), 1.58 (s, 6H, CH{C(*C*H$_3$)NDipp}$_2$), 1.32 (d, *J* = 6.8 Hz, 6H, Dipp-CH(C*H*$_3$)), 1.12 (d, *J* = 6.7 Hz, 6H, Dipp-CH(C*H*$_3$)), 0.91 (d, *J* = 6.8 Hz, 6H, Dipp-CH(C*H*$_3$)), 0.80 (d, *J* = 6.7 Hz, 6H , Dipp-CH(C*H*$_3$), –0.01 (s, 6H, Si(C*H*$_3$)$_2$Ph) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K) δ 144.3 (Si*C*N), 140.4 (CH{*C*(CH$_3$)NDipp}$_2$), 139.9 (CH{*C*(CH$_3$)NDipp}$_2$), 138.9 (CH{*C*(CH$_3$)NDipp}$_2$), 130.4 (Dipp-Ar), 128.2 (*s*, *p*-(*C*$_6$H$_5$)CH), 127.8 (*p*-(*C*$_6$H$_5$)CH), 127.0 ((*C*$_6$H$_5$)Si), 126.7 (*p*-(*C*$_6$H$_5$)Si), 125.6 (*p*-(*C*$_6$H$_5$)CH), 123.4 (Dipp-Ar), 122.9 (*p*-(*C*$_6$H$_5$)CH), 29.3 (Dipp-*C*H(CH$_3$)$_2$), 28.1 (Dipp-*C*H(CH$_3$)$_2$), 25.6 (Dipp-*C*H(CH$_3$)$_2$), 24.7 (CH{C(*C*H$_3$)NDipp}$_2$), 24.6 (CH{C(*C*H$_3$)NDipp}$_2$), 24.1 (CH{C(*C*H$_3$)NDipp $_2$), 23.6 (CH{C(*C*H$_3$)NDipp}$_2$), 21.1 (N(C_6H_4(*C*H$_3$)), 20.9 (N(C_6H_4(*C*H$_3$)), 1.5 (Si(*C*H$_3$)$_2$Ph) ppm. ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 298K) δ –12.4 ppm.

Synthesis of [(CH{C(Me)NDipp}$_2$(*p*-CH$_3$C$_6$H$_4$N)$_2$C)Mg{(*p*-CH$_3$C$_6$H$_4$N)$_2$C)$_3$}{(*i*PrN)$_2$C(SiMe$_2$Ph)}] (8)

A solution of **1** (50 mg, 0.10 mmol) and pinBSiMe$_2$Ph (26 mg, 0.10 mmol) in C_6D_6 (0.5 mL) was added via pipette to a J. Young NMR tube. Complete conversion to compound **2** was obtained after approximately 12 hours at room temperature. *N*,*N*′-di-*iso*-propylcarbodiimide (13.96 µL, 0.10 mmol)

was added to the reaction mixture and complete conversion to compound **3** was obtained after 15 minutes at room temperature. *N*,*N*′-di-*p*-tolylcarbodiimide (22 mg, 0.10 mmol) was subsequently added to the reaction mixture. After removal of volatiles, crystals suitable for single crystal X-ray diffraction analysis were obtained by cooling a pentane/hexane solution to –30 °C. This compound could not be obtained as a bulk sample in sufficient quantity to enable microanalysis or analysis by ^{13}C or ^{29}Si NMR spectroscopy. ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 8.06 (s, 2H, *o*-N(C_6H_4(CH_3))), 7.37 (d, $^{3}J_{H,H}$ = 7.8 Hz, 2H, *m*-N(C_6H_4(CH_3))), 7.28 – 6.72 (16H, C*H*, Ar, Ph, Dipp, *o*-N(C_6H_4(CH_3))), 6.93 (d, $^{3}J_{H,H}$ = 2.9 Hz, 2H, *m*-N(C_6H_4(CH_3))), 6.82 (d, $^{3}J_{H,H}$ = 5.4 Hz, 2H, *m*-N(C_6H_4(CH_3))), 6.63 (d, $^{3}J_{H,H}$= 6.9 Hz, 2H, *m*-N(C_6H_4(CH_3))), 6.50 (d, $^{3}J_{HH}$= 7.5 Hz, 2H, *m*-N(C_6H_4(CH_3))), 5.37 (s, 1H, C*H*{C(CH_3)NDipp}$_2$), 3.60 – 3.52 (m, $^{3}J_{H,H}$ = 13.9 Hz, 1H, , Dipp-C*H*(CH_3)$_2$), 3.47 – 3.39 (m, $^{3}J_{H,H}$ = 5.4 Hz, 2H, N-*i*pr-C*H*(CH_3)$_2$), 3.01 – 2.95 (m, 1H, NDipp-C*H*(CH_3)$_2$), 2.93 – 2.88 (m, 1H, Dipp-C*H*(CH_3)$_2$), 2.69 – 2.62 (m, 1H, Dipp-C*H*(CH_3)$_2$), 2.36 (s, 3H, N(C_6H_4(C*H*$_3$))), 2.30 (s, 3H, N(C_6H_4(C*H*$_3$))), 2.23 (s, 3H, N(C_6H_4(C*H*$_3$))), 2.14 (s, 3H, N(C_6H_4(C*H*$_3$))), 2.08 (s, 3H, N(C_6H_4(C*H*$_3$))), 2.00 (s, 3H, N(C_6H_4(C*H*$_3$))) 1.91 (d, *J* = 6.9 Hz, 3H, NCH(C*H*$_3$)$_2$), 1.65 (s, 3H, CH{C(C*H*$_3$)NDipp}$_2$), 1.53 (s, 3H, CH{C(C*H*$_3$)NDipp}$_2$), 1.38 (d, *J* = 6.5 Hz, 3H, NCH(C*H*$_3$)$_2$), 1.17 (d, *J* = 6.6 Hz, 3H, NDipp-CH(C*H*$_3$)), 1.12 (d, *J* = 6.7 Hz, 3H, NCH(C*H*$_3$)$_2$), 1.06 (d, *J* = 15.4, 6.0 Hz, 3H, Dipp-CH(CH_3)}$_2$)), 0.98 (d, *J* = 6.7 Hz, 3H, NCH(C*H*$_3$)$_2$), 0.94 (s, 3H, Si(C*H*$_3$)$_2$Ph), 0.86 – 0.82 (m, 6H, Dipp-CH(CH_3)}$_2$), 0.75 (d, *J* = 6.7 Hz, 3H, CH{C(*C*H$_3$)NDipp}$_2$), 0.52 – 0.45 (m, 9H, CH{C(*C*H$_3$)NDipp}$_2$), –0.13 (s, 3H, Si(C*H*$_3$)$_2$Ph) ppm.

Results and discussion

Computational study of the formation of compound 2. Our initial report of the synthesis of compound **2** envisaged the reaction shown in Scheme 1 to occur as a σ-bond metathesis involving synchronous Si-B/Mg-C cleavage and Mg-Si/B-C bond formation. Although this provisional model was devised by analogy with our earlier observations of a variety of alkaline earth-mediated catalyses, it contradicts a significant volume of reports for reactions in which an Mg-C or Mg-N bonded compound is reacted with a borane, diborane or silane reagent.[6, 7, 9, 12, 13, 22, 47, 59] In many such cases, B-X bond activation has been deduced to proceed through the initial assembly of an isolable or short-lived borate or silicate intermediate formed by the nucleophilic attack of the magnesium-bound nucleophile at the electrophilic p-block element center. It was, thus, considered probable that the synthesis of compound **2** proceeds in a similar stepwise manner. This revised viewpoint is now borne out by density functional theory (DFT, Figure 1(a)) calculations, which were performed on the complete system and with energies corrected for the toluene solvent and dispersion effects, and to include a larger basis set description. (see Supplementary Information for full details of computational methodology). The overall formation of compound **2** is mildly exergonic (ΔG_f = –15.3 kcal mol^{-1}) and takes place through the intermediacy of a short lived silyl-pinacolato-organoborate species, **I(1-2)**. Consistent with the mild experimental

conditions, the facile reaction is initiated by nucleophilic attack at the three-coordinate boron center of the silaborane reagent by the *n*-butyl nucleophile *via* transition state **TS(1-2)1** ($\Delta G^{\ddagger}$ = 7.9 kcal mol^{-1}). The previously trigonal boron center is perturbed towards a distorted tetrahedral geometry during the assembly of this transition state, a process which is facilitated by the close interaction of one of the pinacolate oxygen atoms with magnesium (Mg-O, 2.34 Å). Complete transfer of the *n*-butyl group from magnesium to boron provides the intermediate, **I(1-2)**, that may be considered as an ion pair in which contact between the magnesium center and the resultant borate anion is maintained by a further augmented Mg-O_{pin} interaction (1.99 Å). The validity of this latter metric may be assessed by comparison with analogous distances observed in several crystallographically-characterized pinacolatoborate derivatives of the {(BDI)Mg} unit. Most pertinently, a Mg-O_{pin} distance of 1.9461(8) Å was observed for the isolable diboranate species, [(BDI)Mg{pinB-Bpin(Bu)}], which was synthesized by a similar reaction of B_2pin_2 and compound **1**.[45] Although, B-B heterolysis and formation of magnesium boryl species required the addition of an exogenous base,[47, 49, 52, 53] the transformation of **I(1-2)** to compound **2** is facile. Traversal of **I(TS1-2)2** ($\Delta G^{\ddagger}$ = 7.3 kcal mol^{-1}) occurs with the maintenance of the aforementioned Mg-O_{pin} interaction (1.98 Å) and the transfer of the {$PhMe_2Si$} unit from boron to magnesium is foreshadowed by a pronounced elongation of the Si-B bond from 2.14 Å in **I(1-2)** to 2.36 Å at the transition state. **I(TS1-2)2** is further characterized by the development of the Mg-Si interaction (3.92 Å), which initiates the group transfer step and which may be rationalized as an effective β-silicon elimination of pinB-*n*-Bu to yield compound **2**.

Inspection of the Natural Bond Orbitals (NBO) for compound **2** emphasizes the polarization intrinsic to the Mg-Si σ-bond (Figure 1(b)). The contribution to the primary NBO associated with Mg-Si bonding is dominated by the silicon center (77% on Si and 23% on Mg), an observation underscored by the calculated NBO charges (Mg +1.27; Si +0.81). Albeit the local environment of each of the p-block centers is rather different, the differential between these latter values may be compared to the relevant NBO charges calculated for the terminally-bonded group 13 species, [(BDI)Mg-Bpin(DMAP)] (Mg, +1.28; B +0.32: DMAP = 4-dimethylaminopyridine) and [(BDI)Mg-Al{N(Dipp)Si(Me)$_2$CH$_2$}$_2$] (Mg, +1.45; Al +0.83),[47, 54] both of which comprise the identical {(BDI)Mg} unit as **2** and demonstrate unambiguous nucleophilic character at the p-block element center.

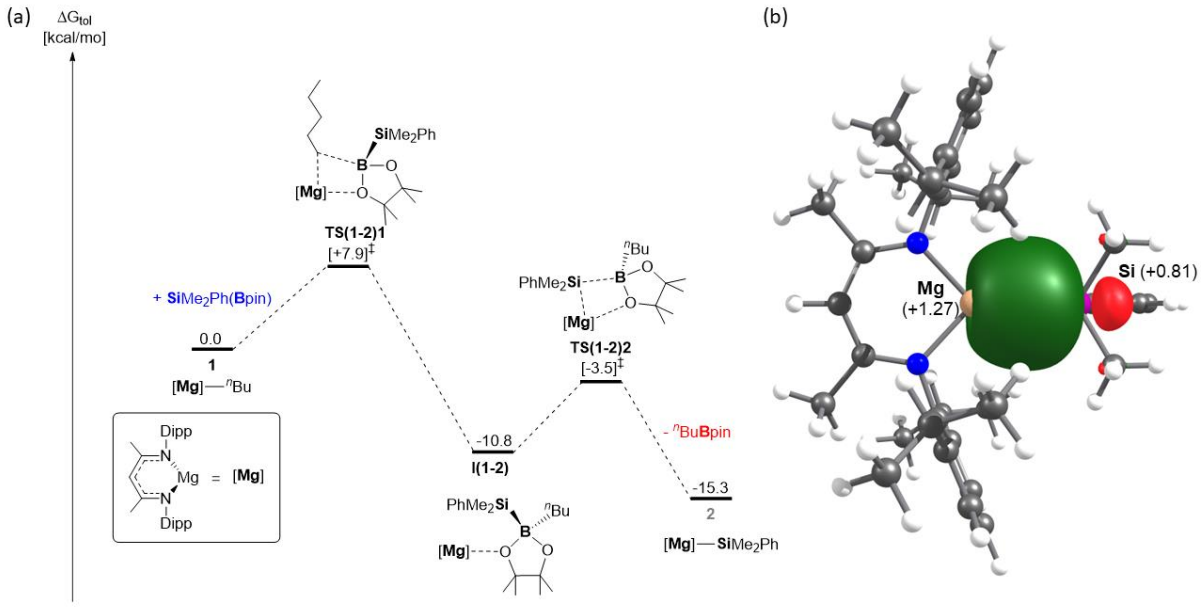
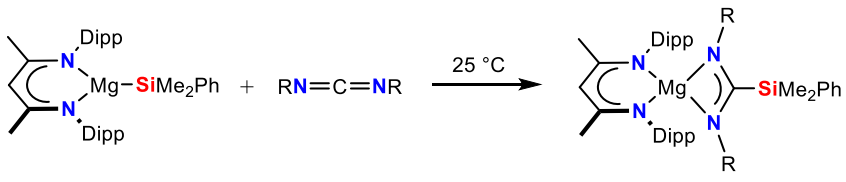


Figure 1: (a) DFT calculated free energy profile (BP86-D3(BJ)-toluene/BS2//BP86/BS1, in kcal mol^{-1}) for the reaction of **1** with $PhMe_2Si$-Bpin; (b) Calculated Natural Bond Orbital (NBO) surface of the Mg-Si bonding orbital of compound **2** (NBO charges shown in parenthesis).

Reactivity of 2 with carbodiimides. Although these results implicate a latent nucleophilic character for the triorganosilyl ligand, Crimmin and co-workers' study of the reactivity of compound **2** with a selection of fluoroalkenes was limited by undesirable ligand-based reactivity ascribed to the nucleophilic γ-methine carbon center of the BDI ligand. Reactions of carbodiimide reagents with polar σ-organometallics to provide *C*-alkylated or *C*-arylated amidinates are ubiquitous.[60-62] Although the formation of *C*-silylated amidinate anions through carbodiimide insertion into the M-Si bond of polar silanide derivatives should be similarly facile, the only available precedent is provided by Piers' report of the rare earth silanides, $[Et(Me_3Si)_2SiMI_2(THF)_3]$ (M = Y or Gd) with RN=C=NR (R = *i*-Pr, Cy).[63] The potential for compound **2** as a reagent for the selective formation of Si-*C* σ-bonds was, therefore, examined through a series of reactions with *N*,*N*'-diorganocarbodiimides of varying steric demands and electronic character.



2 (Dipp = 2,6-*i*-$Pr_2C_6H_3$) **3**, R = *i*-Pr; **4**, R = Cy; **5**, R = *t*-Bu; **6**, R - *p*-tol

Scheme 2: Synthesis of compounds **3** – **6**.

In each case, compound **2** reacted smoothly at room temperature with either *N*,*N*'-di-*iso*-propylcarbodiimide, *N*,*N*'-di-cyclohexylcarbodiimide or *N*,*N*'-di-*tert*-butylcarbodiimide to provide the corresponding *N*,*N*'-dialkyl-*C*-sila-amidinate derivatives, compounds **3** – **5** (Scheme 2). In each case, the reactions were characterized in the resultant ^{1}H NMR spectra by the disappearance of the (3H) silyl methyl proton resonances of **2** at δ 0.06 and 0.43 ppm and the emergence of a single (6H) methyl signal at δ 0.45 (**3**), 0.43 (**4**) and 0.67 ppm (**5**). The most diagnostic features of the ^{13}C{^{1}H} NMR spectra were downfield signals observed at δ 181.9 (**3**), 181.8 (**4**) and 180.5 (**5**) ppm, which bear reasonable comparison to chemical shifts observed in Piers' diamagnetic yttrium derivatives (δ 188.2 ppm and 187.3 ppm for the *N*-R = *i*-Pr and Cy derivatives, respectively) and are correspondingly assigned as the *C*-Si carbon resonances of the newly formed amidinate anions. The ^{29}Si{^{1}H} NMR spectra of **3 - 5** were similarly consistent and comprised single resonances at δ(^{29}Si) –16.8 (**3**), –18.0 ppm (**4**) and –20.1 ppm **(5**). Albeit internally consistent, these frequencies diverge considerably from those assigned to the comparable C-*Si*(SiMe$_3$)$_2$Et environments (δ(^{29}Si) *ca.* –54 ppm) in Piers and co-workers' yttrium derivatives. Although these previously reported data were assigned on the basis of an observable ^{3}J(^{29}Si-^{89}Y) coupling of 5 Hz for the *N*,*N*'-dicyclohexyl derivative, it is notable that these spectra also comprised a further resonance at *ca.* –13 ppm, which was attributed to the silylmethyl environment of the C-Si(*Si*Me$_3$)$_2$Et unit. Taking account of the closer comparison of these latter signals to the resonant frequencies observed for **3** – **5**, and the otherwise similar electronic disposition of the sila-amidinate anions in all five compounds, it is reasonable to suggest that these earlier data were possibly miss-assigned and that the observed coupling was reflective of a four-bond rather than a three-bond interaction between the silicon and yttrium nuclei.

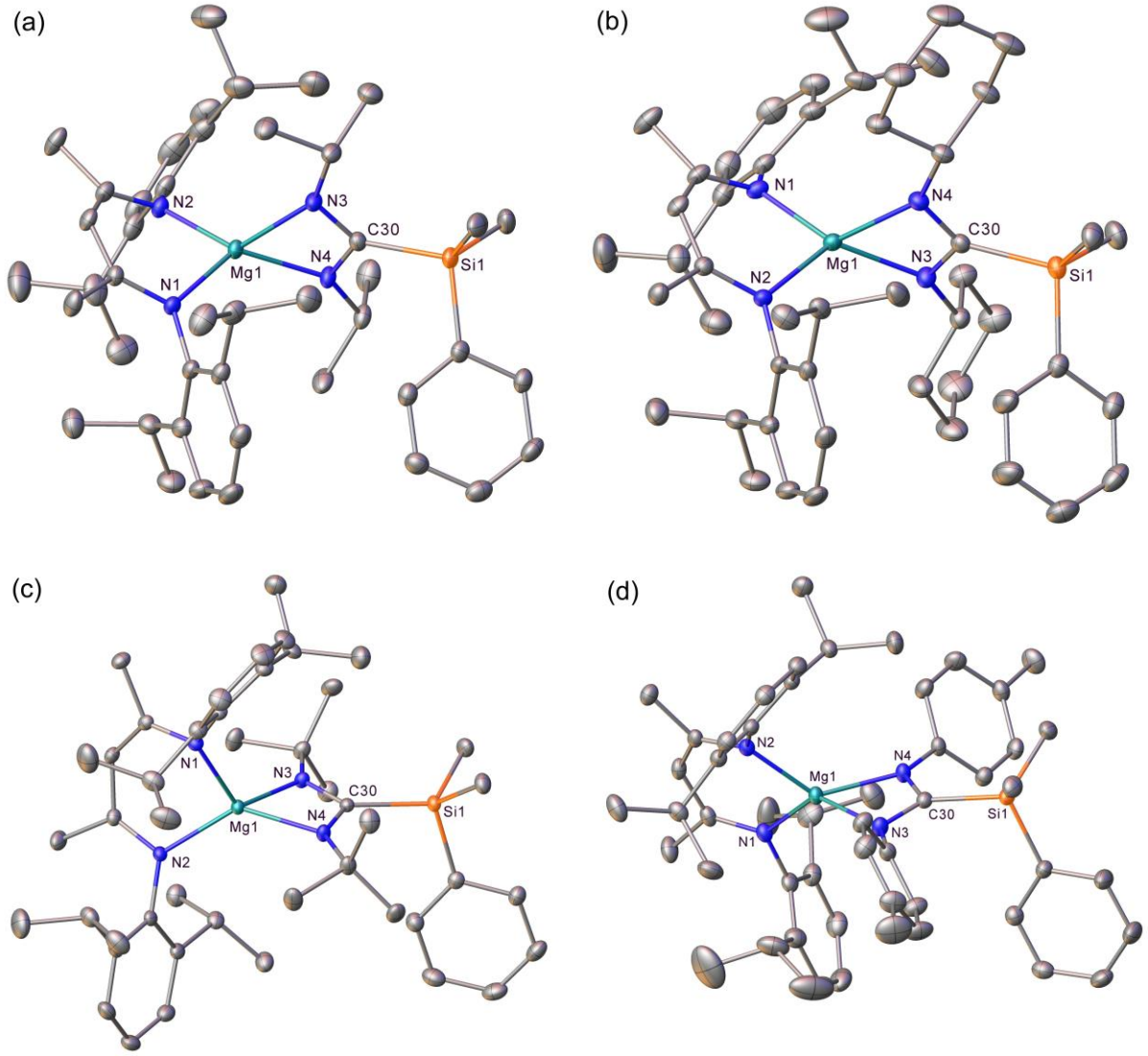


Figure 2: Molecular structures of (a) compound **3**, (b) compound **4**, (c) compound **5** and (d) compound **6**. Ellipsoids are depicted at 30% probability. Hydrogen atoms have been removed for clarity.

Table 1: Selected bond lengths (Å) and angles (°) for compounds **3** – **6**.

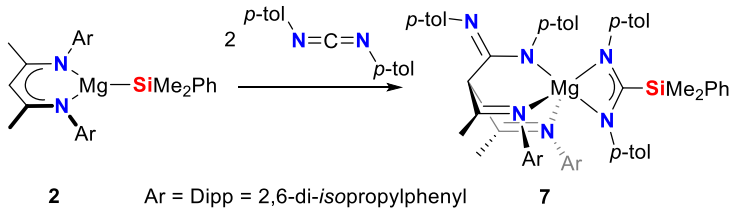
	3	**4**	**5**	**6**
Mg1-N1	2.053(2)	2.0370(10)	2.0482(19)	2.048(2)
Mg1-N2	2.023(2)	2.0516(10)	2.0570(18)	2.027(2)
Mg1-N3	2.058(2)	2.0422(11)	2.0721(18)	2.086(2)
Mg1-N4	2.037(2)	2.0655(11)	2.0257(19)	2.055(2)
C30-N3	1.344(3)	1.3429(16)	1.348(3)	1.346(3)
C30-N4	1.347(3)	1.3371(16)	1.347(3)	1.343(3)
C30-Si1	1.932(3)	1.9381(12)	1.968(2)	1.936(2)
N1-Mg1-N2	93.73(9)	94.54(4)	94.90(7)	93.99(8)
N3-Mg1-N4	65.91(8)	65.62(4)	64.95(7)	64.91(8)
Mg1-N3-C30	90.14(14)	91.03(7)	91.74(12)	91.06(13)
Mg1-N4-C30	90.98(15)	90.19(7)	93.80(12)	92.47(14)
N3-C30-Si1	127.47(18)	119.36(9)	127.40(15)	123.60(16)
N4-C30-Si1	120.33(18)	127.88(9)	123.17(15)	124.71(17)

The structures of compounds **3** – **5** were confirmed by single crystal X-ray diffraction analysis (Figures 2(a) – (c)). Despite the variation in steric demands enforced by the *N*-alkyl groups of the sila-amidinate ligands, the structures show very little variation among the bond lengths and angles associated with the binding of the magnesium centers and across the NCN cores of the newly formed anions (Table 1). While these latter data are effectively identical to those reported by Piers and co-workers in their study of rare earth $[Et(Me_3Si)_2SiC(NR)_2]^-$ (R = *i*-Pr, Cy) derivatives,[63] the most relevant measurements are also closely comparable to those of the variety of *C*-alkylated magnesium amidinates that have been described,[64-79] These observations suggest that neither the incorporation of the *C*-silyl function nor variation of the *N*,*N*'-alkyl substituents induce any significant perturbation to the electronic structure of the delocalized amidinate framework.

Reaction of compound **2** with *N*,*N*'-di-*p*-tolycarbodiimide also proceeded smoothly to provide the analogous *N*-aryl sila-amidinate derivative, compound **6**, which was isolated as colorless crystals suitable for X-ray diffraction analysis (Scheme 2). The resultant structure (Figure 2(d)) revealed that the introduction of *N*-aryl substitution of the amidinate ligand induces no noteworthy adjustments to either the bonding of the magnesium center or across the amidinate ligand (Table 1). The newly formed Si-C bond of **6** was characterized in solution by the observation of signals at δ 185.4 ppm and δ –11.3 ppm in the respective $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra. While these frequencies are somewhat deshielded in comparison to the analogous data arising from compounds **3** – **5**, the solution NMR data

provided by **6** were again consistent with the maintenance of the solid state structure in solution. The silylmethyl protons provided a single upfield resonance (δ –0.06 ppm) in the ^{1}H NMR spectrum, while the symmetrically chelated disposition of both ligands was clearly apparent from the observation of single sets of sharp signals for all the relevant sila-amidinate and BDI proton environments.

While the γ-methine signal of the BDI ligand of isolated crystalline samples of **6** provided the expected (1H) singlet signal at δ 4.95 ppm, ^{1}H NMR analysis of the initial *in situ*-formed solutions revealed the formation of small quantities of a second reaction product (**7**), which was manifested most clearly as an apparent BDI γ-methine resonance at δ 5.39 ppm. Further investigation revealed this new species to be the reaction product of compound **6** with a second equivalent of *N*,*N*'-di-*p*-tolycarbodiimide. The completely selective synthesis of compound **7** was, thus, most readily achieved by performance of the reaction between compound **2** and *N*,*N*'-di-*p*-tolycarbodiimide in the requisite 1:2 stoichiometry (Scheme 3). Although the solution data indicated that the integrity of the sila-amidinate ligand observed in compound **6** had been maintained [δ(^{29}Si) –12.4 ppm], two further singlet resonances at δ 2.34 and 2.24 ppm observed in the ^{1}H NMR spectrum could also be assigned to compound **7**. Each of these latter signals provided an integration of 3H, relative to a 6H singlet signal at δ 2.11 ppm assigned to the equivalent *p*-methyl protons of the symmetrically-disposed silamidinate anion. The origin of these observations was resolved by a single crystal X-ray diffraction analysis of **7**. In mitigation of the observation by Crimmin and co-workers that the potential of compound **2** as a source of the {$PhMe_2Si$}$^{-}$ anion is compromised by the potentially nucleophilic character of the BDI anion,[56] compound **7** is a further magnesium derivative of the {($PhMe_2SiC(p$-Me-$C_6H_4N)_2$}$^{-}$ anion in which a C=N bond of the additional equivalent of carbodiimide has added in a 1,4-fashion across the group 2 metal center and the γ-methine carbon of the BDI ligand (Figure 3(a)).



2 Ar = Dipp = 2,6-di-*iso*propylphenyl **7**

Scheme 3: Synthesis of compound **7**.

Although similar reactivity of metallated β-diketiminate anions toward heteroallenes and related multiply-bonded small molecules is by no means unprecedented,[80] exemplary behaviour of magnesium derivatives is currently limited to the addition of CO_2,[59] diphenylketene,[81] PhN=C=S[82] and the internal alkynes, PhC≡CPh and PhC≡CMe.[83] The five-coordinate magnesium center of compound **7** is, thus, ligated by the bidentate sila-amidinate anion and a κ^{3}-*N*,*N*',*N*''-bound tripodal anion. While the bond lengths and angles about the {$SiCN_2$} core of the sila-amidinate are effectively unchanged in

comparison to the analogous measurements observed in **6**, an elongation of the Mg-N bonds [Mg1-N5 2.109(2); Mg1-N6 2.118(2) Å] may be attributed to the increased coordination number of magnesium. The C-N bonds comprising the donor nitrogen atoms [C2-N1, 1.288(3); C4-N2 1.288(3), C30-N4 1.349(3) Å] and the exocyclic C30-N3 imine bond [1.295(3) Å] vary significantly across the newly formed tripodal ligand. These data indicate the anion is best described as a localised di-imino-iminoamidate, the negative charge of which is localized on the *p*-tolyl-amidate nitrogen; a deduction also borne out by consideration of the relevant Mg-N bonds [Mg1-N1, 2.1703(19); Mg1-N2 2.2351(19); Mg1-N4 2.0890(18) Å].

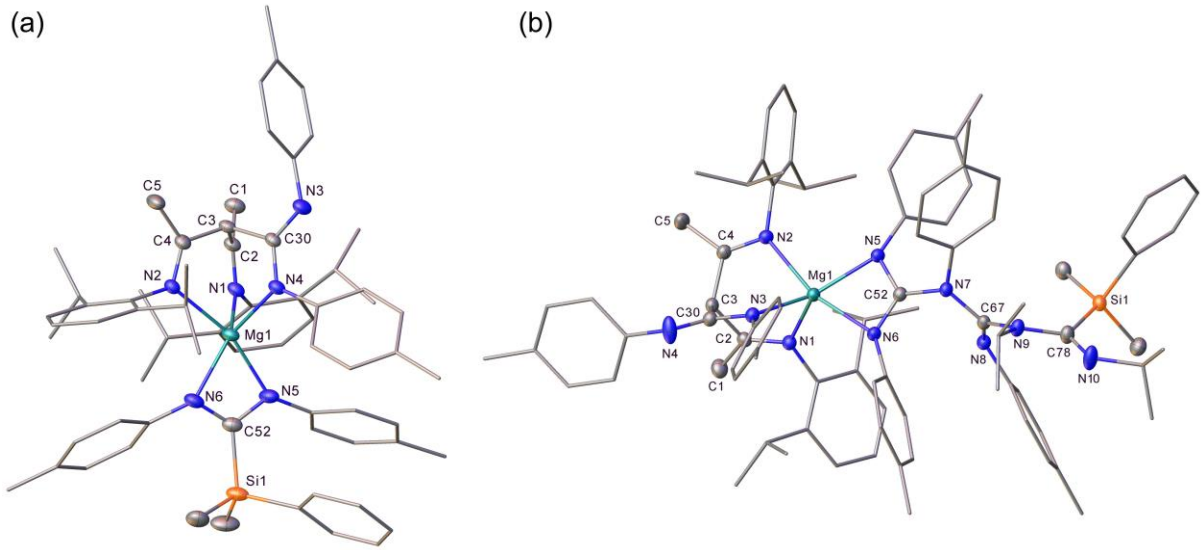


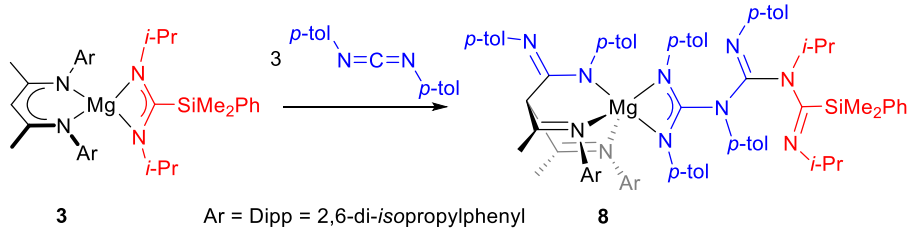
Figure 3: Molecular structures structures of (a) compound **7** and (b) compound **8**. Ellipsoids (where shown) are depicted at 30% probability. Hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (°): **7**: Mg1-N1 2.1703(19), Mg1-N2 2.2351(19), Mg1-N4 2.0870(18), Mg1-N5 2.109(2), Mg1-N6 2.118(2), N1-C2 1.288(3), N1-C6 1.450(3), N2-C4 1.288(3), N3-C30 1.295(3), N4-C30 1.349(3), N4-C38 1.411(3), N5-C52 1.325(3), N6-C52 1.345(3), Si1-C52 1.939(2), N1-Mg1-N2 88.19(7), N4-Mg1-N1 88.12(7), N4-Mg1-N2 85.67(7), N4-Mg1-N5 109.04(8), N4-Mg1-N6 144.76(8), N5-Mg1-N1 102.50(8), N5-Mg1-N2 161.85(8), N5-Mg1-N6 63.48(8), N6-Mg1-N1 126.83(8), N6-Mg1-N2 98.36(8); **8**: Mg1-N1 2.1562(13), Mg1-N2 2.2711(12), Mg1-N3 2.0812(13), Mg1-N5 2.0978(12), Mg1-N6 2.1409(12), N1-C2 1.2858(19), N1-C6 1.4407(18), N2-C4 1.2766(19), N2-C18 1.4540(18), N3-C30 1.3420(18), N3-C31 1.4209(19), N4-C30 1.284(2), N5-C52 1.3440(17), N6-C52 1.3084(18), N7-C52 1.4346(17), N7-C67 1.4091(18), N8-C67 1.283(2), N9-C67 1.4015(18), N9-C78 1.4267(19), N10-C78 1.277(2), Si1-C78 1.9448(16), N1-Mg1-N2 87.34(5), N3-Mg1-N1 87.02(5), N3-Mg1-N2 85.79(5), N3-Mg1-N5 140.66(5), N3-Mg1-N6 108.59(5), N5-Mg1-N1 131.78(5), N5-Mg1-N2 100.19(5), N5-Mg1-N6 63.53(5), N6-Mg1-N1 101.24(5), N6-Mg1-N2 163.43(5).

Re-examination of the reactions to derive compounds **3** – **5** provided no evidence for similar elaboration of the BDI ligand in the presence of an excess of any of the *N*-alkyl carbodiimides. This observation,

and the negligible structural variations observed across the sila-amidinate derivatives **3** – **6**, indicate that the formation of compound **7** is unlikely to be a consequence of any electronic adjustment to the sila-amidinate anion or resultant enhancement of the BDI ligand nucleophilicity. A very recent kinetic and computational study of their reactivity with reference nucleophiles has allowed the quantification of the relative electrophilic character of a variety of heteroallenes in terms of an electrophilicity parameter, *E*.[84] While *N*,*N*'-diphenylcarbodiimide (*E* = –20.14) was found to be a hundred-fold less electrophilic than, for example, both carbon disulphide (*E* = –17.70) and phenyl isothiocyanate (*E* = –18.15), the electrophilicity of *N*,*N*'-dicyclohexylcarbodiimide was so low that no suitable reference nucleophiles could be identified for the experimental quantification of its reactivity and its approximate electrophilicity ($E \approx -30$) could only be derived by quantum chemical calculations. Similar deductions may be drawn from our own calculations of the frontier orbital energies of the carbodiimide substrates employed in the synthesis of compounds **3** – **7** (see Supporting Information) and from which the LUMO energy of *N*,*N*'-di-*p*-tolycarbodiimide was computed to lie *ca*. 1.5 eV lower than any of the variously substituted *N*-alkylated analogues. In addition, whereas the transformation of compound **6** to compound **7** was calculated to be significantly exergonic (ΔG = –16.5 kcal mol^{-1}), formation of analogous di-imino-iminoamidate anions through reactions of compounds **3** – **5** with further equivalents of *N*,*N*'-di-*i*-propylcarbodiimide (ΔG_f = +12.2 kcal mol^{-1}), *N*,*N*'-di-cyclohexylcarbodiimide (ΔG_f = +20.1 kcal mol^{-1}) and *N*,*N*'-di-*t*-butylcarbodiimide (ΔG_f = +24.5 kcal mol^{-1}), respectively, were found to be thermodynamically non-viable (Figure S17). On this basis, therefore, we suggest that the formation of **7** is a consequence of the enhanced electrophilicity of the central carbodiimide carbon center as a result of its more electron-withdrawing *N*-aryl substitution.

As an examination of this hypothesis, we carried a further reaction between equimolar quantities of compound **3** and *N*,*N*'-di-*p*-tolycarbodiimide. Although the resultant ^{1}H NMR spectrum presented a complex series of aliphatic resonances and evidence for the formation of a predominant new compound (**8**) characterized by a singlet resonance at δ 5.37 ppm, examination of the BDI γ-methine region also indicated incomplete consumption of the *N*-isopropyl-sila-amidinate (**3**). While a bulk sample could not be obtained, single crystal X-ray diffraction analysis performed after fractional crystallization of the reaction products from pentane/hexane solution to –30 ^{o}C revealed that **8** was again a product of 1,4-addition of the carbodiimide to the ligated BDI ligand (Figure 3(b)). Compound **8**, therefore, contains a tripodal di-imino-iminoamidate anion identical to that observed in **7**, but which has formed in addition to reaction with a further two molecules of *N*,*N*'-di-*p*-tolycarbodiimide at one of the donor nitrogen atoms of the *N*-isopropyl-sila-amidinate ligand of compound **3** (Scheme 4). This latter process provides an unusual di-*N*,*N*'-*p*-tolyl guanidinate anion, which may be considered to result from the net oligomerization of three carbodiimide molecules by the magnesium silanide derivative, **2**. The metric data arising from the di-imino-iminoamidate ligand of **8** are very similar to those observed in **7**, while examination of the various C-N bonds within the guanidinate ligand indicates that the

primary chain of atoms propagating from the non-magnesium-ligated N7 atom is best viewed as a silyl-terminated sequence of alternating singly bonded nitrogen and carbon centers, with each carbon bearing a pendent *N*-*p*-tolyl imine function. We have previously observed that similar reactions of group 2 amidinate complexes with organic isocyanates, isothiocyanates and carbon disulphide enable the catalytic construction of imidazolidine and thiazolidine heterocycles.[8,85,86] The threefold insertion of carbodiimide to provide compound **8** is, however, to the best of our knowledge, unprecedented. Although we have not yet examined this chemistry any further, we suggest that the contrasting outcome of the reactions to form compounds **7** and **8** is a likely consequence of the enhanced nucleophilic character of the *N*-alkyl sila-amidinate anion of **3** in comparison to that of **6**, in conjunction with the superior electrophilicity of the *N*,*N'*-*p*-tolyl-substituted carbodiimide.



3 **8**

Scheme 4: Synthesis of compound **8**.

Conclusions

Computational analysis of the reaction of [(BDI)MgBu] with pinBSiMe$_2$Ph indicates that formation of the resultant magnesium silanide occurs in a stepwise fashion. In a similar manner to previously reported metathesis reactions of B-X units with organomagnesium reagents, ligand exchange occurs via an initially formed silyl-organoborate, albeit conversion of this latter species to the magnesium silanide and alkyl borane products is too facile ($\Delta G^{\ddagger}$ = 7.3 kcal mol^{-1}) to allow its experimental observation. The polar nature of the resultant Mg-Si bond is demonstrated through reactions with a range of organic carbodiimides. While reactions with *N*-alkyl substituted reagents are straightforward and provide the corresponding heteroleptic magnesium sila-amidinate compounds, introduction of *p*-tolylcarbodiimide results in more complex behaviour, demonstrating the non-innocence of the β-diketiminate spectator ligand.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information, including NMR spectra and details of the computational and single crystal X-ray diffraction analysis, is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01537. Accession Codes CCDC 2015263-2015268 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting

The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Notes

The authors declare no competing financial interest.

Acknowledgements

We thank the Petroleum Technology Development Fund (PTDF) of Nigeria for the provision of a PhD scholarship for BO-E. We also thank the EPSRC for research grant EP/R020752/1, the EPSRC's Centre for Doctoral Training in Catalysis (EP/L016443/1) for providing a PhD studentship for LJM and the European Commission Erasmus+ programme for allowing MD to spend two months in MSH's group. This research made use of the Balena High Performance Computing (HPC) Service at the University of Bath.

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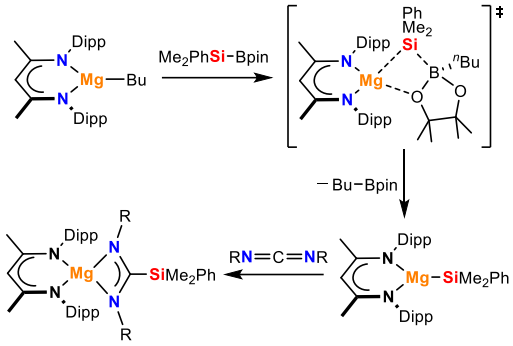

Computational analysis of the reaction of [(BDI)MgBu] with pinBSiMe$_2$Ph indicates that formation of the resultant magnesium silanide occurs in a stepwise fashion. The polar nature of the resultant Mg-Si bond is demonstrated through reactions with a range of organic carbodiimides.