*Supporting Information for*

# Reactivity of a *β*-Diketiminate-Supported Magnesium Alkyl toward Small Molecules

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## EXPERIMENTAL SECTION

**General Procedures.** All reactions and manipulations were carried out under an atmosphere of dry dinitrogen with rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glove box. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $S_8$ was purified by sublimation. $\{[HC(C(Me)N\text{-}2,6\text{-}^{i}Pr_2C_6H_3)_2]Mg(^{n}Bu)\}_2$[1] was prepared according to the literature method. All other chemicals were purchased from Aldrich Chemical Co. and Energy Chemical Co. and used as received unless otherwise noted. **Caution**! Most selenium compounds are toxic; care should be exercised to avoid contact with skin. All operations in this procedure should be conducted in a well-ventilated hood. Infrared spectra were obtained from KBr pellets on an Avatar 360 Fourier transform spectrometer. $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker AV 600 spectrometer at 600 and 150 MHz, respectively. All chemical shifts were reported in $\delta$ units with reference to the residual protons of the deuterated solvents, which were internal standards, for proton and carbon chemical shifts. Melting points were measured on an X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

**Preparation of $\{[HC(C(Me)N\text{-}2,6\text{-}^{i}Pr_2C_6H_3)_2]Mg(\mu\text{-}S^{n}Bu)\}_2$ (2).** $S_8$ (0.032 g, 0.125 mmol) was added to a benzene (5 mL) solution of $\{[HC(C(Me)N\text{-}2,6\text{-}^{i}Pr_2C_6H_3)_2]Mg(^{n}Bu)\}_2$ (**1**; 0.500 g, 0.5 mmol) with stirring at room temperature. After stirring at room temperature for 10 h, the solution was filtered. The volume of the filtrate was reduced to 2 mL, and the compound **2** crystallized at room temperature in

2 days as colorless crystals. Yield: 0.405 g (76%). M.p.: 116-118 $^{o}$C. $^{1}$H NMR (600 MHz, $C_6D_6$): $\delta$ = 7.21 (t, 2H, $^{3}J$ = 7.2 Hz, phenyl *H*), 7.16 (benzene), 7.12 (d, 4H, $^{3}J$ = 7.2 Hz, phenyl *H*), 4.73 (s, 1H, *H*C{C(CH$_3$)N-2,6-$^{i}$Pr$_2$C$_6$H$_3$}$_2$), 3.31 (m, 4H, C*H*Me$_2$), 2.47 (t, 2H, $^{3}J$ = 7.2 Hz, SC*H*$_2$C$_3$H$_7$ ), 1.56-1.53 (m, 2H, SCH$_2$C*H*$_2$C$_2$H$_5$), 1.52 (s, 6H, HC{C(C*H*$_3$)N-2,6-$^{i}$Pr$_2$C$_6$H$_3$}$_2$), 1.34-1.31 (m, 2H, SC$_2$H$_4$C*H*$_2$CH$_3$), 1.21-1.16 (m, 24H, CH(C*H*$_3$)$_2$), 0.90 (t, 3H, $^{3}J$ = 7.2 Hz, Bu-C*H*$_3$) ppm. $^{13}$C{$^{1}$H} NMR (150 MHz, $C_6D_6$): $\delta$ = 169.07 (HC{*C*(CH$_3$)-N-2,6-$^{i}$Pr$_2$C$_6$H$_3$}$_2$), 145.53 (phenyl *C*), 142.44 (phenyl *C*), 126.8 (benzene), 125.22 (phenyl *C*), 123.65 (br, phenyl *C*), 94.53 (H*C*{C(CH$_3$)N-2,6-$^{i}$Pr$_2$C$_6$H$_3$}$_2$), 37.34 (S*C*H$_2$C$_3$H$_7$), 31.55 (SCH$_2$*C*H$_2$C$_2$H$_5$), 28.28 (*C*H(CH$_3$)$_2$), 28.02 (*C*H(CH$_3$)$_2$), 26.64 (CH(*C*H$_3$)$_2$), 24.38 (CH(*C*H$_3$)$_2$), 24.17 (CH(*C*H$_3$)$_2$), 24.11 (ArCH(*C*H$_3$)$_2$), 23.37 (HC{C(*C*H$_3$)N-2,6-$^{i}$Pr$_2$C$_6$H$_3$}$_2$), 22.60 (SC$_2$H$_4$*C*H$_2$CH$_3$), 13.87 (Bu-*C*H$_3$) ppm. IR (KBr): $\nu$ = 2957 (m), 2925 (m), 2865 (m), 1620 (m), 1544 (m), 1459 (s), 1433 (s), 1401 (s), 1363 (s), 1258 (m), 1172 (m), 1101 (m), 1018 (m), 929 (m), 790 (m) cm$^{-1}$. A reproducible microanalysis could not be obtained for the compound as the solvent molecule (benzene) in the crystal lattice were slowly lost upon isolation of the compoud as a dry crystalline solid. However, it is diffcult to completely remove them by placing crystalline samples of the compound under vaccum for several hours.

**Preparation of [HC(C(Me)N-2,6-$^{i}$Pr$_2$C$_6$H$_3$)$_2$]Mg(Se$^{n}$Bu)(THF) (3).** A mixture of Se$_8$ (0.079 g, 0.125 mmol) and {[HC(C(Me)N-2,6-$^{i}$Pr$_2$C$_6$H$_3$)$_2$]Mg($^{n}$Bu)}$_2$ (**1**; 0.500 g, 0.5 mmol) in benzene (5 mL) with a few drops of THF was stirred at room temperature for 10 h, then the solution was concentrated to dryness under vacuum.

Benzene (2 mL) was added to the residue, and then diffusion of n-hexane into the solution gave colorless crystals of **3**. Yield: 0.480 g (74%). M.p.: 140-142 $^{o}$C. $^{1}$H NMR (600 MHz, $C_6D_6$): $\delta$ = 7.26 (s, 6H, phenyl *H*, overlapping peaks), 4.80 (s, 1H, *H*C{C($CH_3$)N-2,6-$^{i}Pr_2C_6H_3$}$_2$), 3.72 (br, 4H, THF), 3.62-3.10 (m, 4H, C*H*$Me_2$), 2.19 (t, 2H, $^{3}J$ = 7.2 Hz, SeC*H*$_2C_3H_7$ ), 1.65 (s, 6H, HC{C(C*H*$_3$)N-2,6-$^{i}Pr_2C_6H_3$}$_2$), 1.57-1.52 (m, 6H, $SeCH_2CH_2C_2H_5$ + THF), 1.34-1.30 (m, 2H, $SeC_2H_4CH_2CH_3$), 1.29-1.19 (m, 24H, CH(C*H*$_3$)$_2$), 0.83 (t, 3H, $^{3}J$ = 7.2 Hz, Bu-C*H*$_3$) ppm. $^{13}$C{$^{1}$H} NMR (150 MHz, $C_6D_6$): $\delta$ = 168.63 (HC{*C*($CH_3$)-N-2,6-$^{i}Pr_2C_6H_3$}$_2$), 144.98 (phenyl *C*), 142.44 (phenyl *C*), 125.23 (phenyl *C*), 123.65 (br, phenyl *C*), 94.50 (H*C*{C($CH_3$)N-2,6-$^{i}Pr_2C_6H_3$}$_2$), 69.72 (THF), 39.19 (Se*C*$H_2C_3H_7$), 31.55 ($SeCH_2CH_2C_2H_5$), 28.28 (*C*H($CH_3$)$_2$), 28.02 (br, *C*H($CH_3$)$_2$), 25.04 (THF), 24.95 (CH(*C*$H_3$)$_2$), 24.22 (br, CH(*C*$H_3$)$_2$), 24.11 (CH(*C*$H_3$)$_2$), 23.82 (CH(*C*$H_3$)$_2$), 23.62 (HC{C(*C*$H_3$)N-2,6-$^{i}Pr_2C_6H_3$}$_2$), 22.74 ($SeC_2H_4CH_2CH_3$), 13.63 (Bu-*C*$H_3$) ppm. IR (KBr): $v$ = 2958 (m), 2926 (m), 2865 (m), 1621 (w), 1502 (s), 1458 (s), 1433 (s), 1402 (s), 1382 (s), 1308 (s), 1258 (m), 1179 (s), 1144 (s), 1077 (s), 1018 (m), 958 (m), 794 (m) cm$^{-1}$. Anal. Calcd for $C_{37}H_{58}N_2OSeMg$: C, 68.35; H, 8.99; N, 4.31. Found: C, 68.53; H, 9.08; N, 4.16.

**Preparation of [HC(C(Me)N-2,6-$^{i}Pr_2C_6H_3$)$_2$]Mg(Se$_2$$^{n}$Bu)(THF) (4). Method A.** This compound was obtained as yellow crystals from the reaction of {[HC(C(Me)N-2,6-$^{i}Pr_2C_6H_3$)$_2$]Mg($^{n}$Bu)}$_2$ (**1**; 0.500 g, 0.5 mmol) and $Se_8$ (0.158 g, 0.250 mmol) in benzene (5 mL) with a few drops of THF and recrystallization from a benzene/n-hexane solution by a procedure similar to that described in the synthesis of **3**. Yield:

0.408 g (56%). M.p.: 152-154 $^{o}$C. $^{1}$H NMR (60 $^{1}$H NMR (600 MHz, $C_6D_6$): $\delta$ = 7.15 (br, 6H, phenyl *H*), 4.82 (s, 1H, *H*C{C($CH_3$)N-2,6-$^{i}Pr_2C_6H_3$}$_2$), 3.89 (m, 4H, THF), 3.32-3.24 (m, 4H, C*H*Me$_2$), 2.00 (t, 2H, $^{3}J$ = 7.2 Hz, SeC*H*$_2$C$_3$H$_7$), 1.66 (m, 4H, THF), 1.65 (s, 6H, HC{C(C*H*$_3$)N-2,6-$^{i}Pr_2C_6H_3$}$_2$), 1.54-1.51 (m, 2H, SeCH$_2$C*H*$_2$C$_2$H$_5$), 1.30-1.28 (m, 2H, SeC$_2$H$_4$C*H*$_2$CH$_3$), 1.24 (d, 12H, $^{3}J$ = 7.2 Hz, CH(C*H*$_3$)$_2$), 1.21 (d, 12H, $^{3}J$ = 7.2 Hz, CH(C*H*$_3$)$_2$), 0.79 (t, 3H, $^{3}J$ = 7.2 Hz, Bu-C*H*$_3$) ppm. $^{13}$C{$^{1}$H} NMR (150 MHz, $C_6D_6$): $\delta$ = 168.73 (HC{*C*($CH_3$)-N-2,6-$^{i}Pr_2C_6H_3$}$_2$), 145.22 (phenyl *C*), 142.33 (phenyl *C*), 125.22 (phenyl *C*), 123.67 (br, phenyl *C*), 123.21 (phenyl *C*), 94.55 (H*C*{C($CH_3$)N-2,6-$^{i}Pr_2C_6H_3$}$_2$), 70.05 (THF), 32.51 (Se*C*H$_2$C$_3$H$_7$), 31.55 (SeCH$_2$*C*H$_2$C$_2$H$_5$), 28.28 (*C*H(CH$_3$)$_2$), 28.05 (br, *C*H(CH$_3$)$_2$), 25.05 (THF), 24.33 (CH(*C*H$_3$)$_2$), 24.24 (CH(*C*H$_3$)$_2$), 24.11 (CH(*C*H$_3$)$_2$), 23.98 (CH(*C*H$_3$)$_2$), 23.03 (HC{C(*C*H$_3$)N-2,6-$^{i}Pr_2C_6H_3$}$_2$), 22.75 (SeC$_2$H$_4$*C*H$_2$CH$_3$), 13.46 (Bu-*C*H$_3$) ppm. IR (KBr): $\nu$ = 2958 (m), 2925 (m), 2866 (m), 1620 (m), 1549 (m), 1461 (m), 1441 (s), 1380 (s), 1321 (m), 1277 (m), 1178 (s), 1145 (s), 1057 (s), 933 (m), 792 (m) cm$^{-1}$. Anal. Calcd for $C_{37}H_{58}N_2OSe_2Mg$: C, 60.95; H, 8.02; N, 3.84. Found: C, 61.06; H, 8.15; N, 3.75.

**Method B.** $Se_8$ (0.061 g, 0.097 mmol) was added to a benzene (5 mL) solution of [HC(C(Me)N-2,6-$^{i}Pr_2C_6H_3$)$_2$]Mg(Se$^{n}$Bu)(THF) (**3**; 0.500 g, 0.775 mmol) with stirring at room temperature. After stirring at room temperature for 5 h, the solution was filtered. The volume of the filtrate was reduced to 2 mL, the crystals of **4** were isolated at room temperature in the glovebox after addition of a few drops of n-hexane. Yield: 0.333 g (59%).

**Preparation of [HC(C(Me)N-2,6-$^{i}Pr_2C_6H_3)_2$]Mg(SPh)(THF)•THF (5•THF).** A THF (2 mL) solution of PhSSPh (0.219 g, 1.0 mmol) was added to a THF (3 mL) solution of {[HC(C(Me)N-2,6-$^{i}Pr_2C_6H_3)_2$]Mg($^{n}$Bu)}$_2$ (**1**; 0.500 g, 0.5 mmol) with stirring at room temperature. After the solution was stirred at room temperature for 2 h, the solution was filtered. The volume of the filtrate was reduced to 2 mL and cooled to -20 °C, yielding pale yellow crystals **5•THF**, which were isolated by filtration. Yield: 0.550 g (79%). $^1$H NMR (600 MHz, $C_6D_5N$): $\delta$ = 7.28–7.20 (m, 6H, phenyl ), 6.91 (d, 2H, $J_{HH}$ = 7.2 Hz, phenyl ), 6.77 (m, 3H, phenyl ), 5.06 (s, 1H, *H*C{C(CH$_3$)NAr}$_2$), 3.63 (m, 8H, THF), 3.28 (m, 4H, C*H*Me$_2$), 1.82 (s, 6H, HC{C(C*H$_3$*)NAr}$_2$), 1.62 (m, 8H, THF), 1.25-1.11 (m, 24H, CH(C*H$_3$*)$_2$) ppm. The solid-state structures of the complex has been further confirmed by single crystal X-ray diffraction, which is identical to that reported.[2]

Oily PhS$^{n}$Bu can be isolated from the filtrate by silica gel chromatography (hexane). Yield: 0.46 g (68 %). $^1$H NMR ($CDCl_3$): $\delta$ = 7.33-7.27 (m, 3H, phenyl *H*), 7.16 (t, 2H, $^3J$ = 7.8 Hz, phenyl *H*), 2.92 (t, 2H, $^3J$ = 7.2 Hz, C*H*$_2$), 1.66-1.60 (m, 2H, C*H*$_2$), 1.48-1.42 (m, 2H, C*H*$_2$), 0.92 (t, 2H, $^3J$ = 7.2 Hz, C*H*$_3$). By $^1$H NMR spectroscopy, the compound is spectroscopically identical to the previous report.[3]

**Preparation of [HC(C(Me)N-2,6-$^{i}Pr_2C_6H_3)_2$]Mg(SePh)(THF)•THF (6•THF).** This compound was prepared as pale yellow crystals from the reaction of {[HC(C(Me)N-2,6-$^{i}Pr_2C_6H_3)_2$]Mg($^{n}$Bu)}$_2$ (**1**; 0.500 g, 0.5 mmol) and PhSeSePh (0.312 g, 1.0 mmol) in THF (5 mL) and recrystallization from a THF solution by a similar procedure as that in the synthesis of **5•THF**. Yield: 0.615 g (83%). $^1$H NMR

(600 MHz, $C_6D_5N$): $\delta$ = 7.25–7.17 (m, 6H, phenyl ), 6.87 (m, 2H, phenyl), 6.74 (m, 3H, phenyl), 4.84 (s, 1H, *H*C{C($CH_3$)NAr}$_2$), 3.57 (m, 8H, THF), 3.04 (m, 4H, C*H*Me$_2$), 1.67 (s, 6H, HC{C(C*H*$_3$)NAr}$_2$), 1.55 (m, 8H, THF), 1.24-1.07 (m, 24H, CH(C*H*$_3$)$_2$) ppm. The solid-state structures of the complex has been further confirmed by single crystal X-ray diffraction, which is identical to that reported.[2]

Oily PhSe$^n$Bu can be isolated from the filtrate by silica gel chromatography (hexane). Yield: 0.62 g (73%). $^1$H NMR ($CDCl_3$): $\delta$ = 7.49 (m, 2H, phenyl), 7.26-7.24 (m, 3H, phenyl), 2.90 (t, 2H, $^3J$ = 7.2 Hz, C*H*$_2$), 1.71-1.66 (m, 2H, C*H*$_2$), 1.46-1.40 (m, 2H, C*H*$_2$), 0.91 (t, 2H, $^3J$ = 7.2 Hz, C*H*$_3$). By $^1$H NMR spectroscopy, the compound is spectroscopically identical to the previous report.[4]

**Preparation of [HC(C(Me)N-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$]Mg(N(H)C(Ph)=CHC$_3$H$_7$)(DME) (7).** A benzene (2 mL) solution of PhCN (0.103 g, 1.0 mmol) was added dropwise to a benzene (3 mL) solution of {[HC(C(Me)N-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$]Mg($^n$Bu)}$_2$ (**1**; 0.500 g, 0.5 mmol) with stirring at room temperature. After 1.5 h, the solution was filtered. The volume of the filtrate was reduced to 2 mL, the colorless crystals of **7** were isolated at room temperature in the glovebox after addition of a few drops of DME. Yield: 0.520 g (75%). M.p.: 98-100 $^o$C. $^1$H NMR (600 MHz, $C_6D_6$): $\delta$ = 7.28-7.27 (m, 2H, phenyl *H*), 7.16 (br, 4H, phenyl *H*), 7.10 (br, 2H, phenyl *H*), 6.88 (t, 1H, $^3J$ = 7.2 Hz, phenyl *H*), 6.71 (m, 2H, phenyl *H*), 4.72 (s, 1H, *H*C{C($CH_3$)N-2,6-$^i$Pr$_2$C$_6$H$_3$}$_2$), 4.29 (t, 1H, $^3J$ = 6.6 Hz, C(Ph)=C*H*C$_3$H$_7$), 3.25 (m, 4H, C*H*Me$_2$), 3.02 (m, 10H, DME), 2.32 (s, 1H, N*H*), 1.83 (m, 2H, C(Ph)=CHC*H*$_2$CH$_2$CH$_3$), 1.58 (s, 6H, HC{C(C*H*$_3$)N-2,6-$^i$Pr$_2$C$_6$H$_3$}$_2$), 1.43 (m, 2H, C(Ph)=CHCH$_2$C*H*$_2$CH$_3$), 1.33-1.21 (br, 12H, CH(C*H*$_3$)$_2$),

1.16 (d, 12H, $^{3}J$ = 7.2 Hz, CH(C$H_3$)$_2$), 0.97 (t, 3H, $^{3}J$ = 7.2 Hz, Bu-C$H_3$) ppm. $^{13}$C{$^{1}$H} NMR (150 MHz, $C_6D_6$): $\delta$ = 168.93 (HC{*C*(CH$_3$)-NAr}$_2$), 151.91 (NH*C*=CHC$_3$H$_7$)Ph), 145.68 (phenyl *C*), 142.46 (phenyl *C*), 128.09 (phenyl *C*), 127.95 (phenyl *C*), 125.40 (phenyl *C*), 125.30 (phenyl *C*), 125.20 (phenyl *C*), 123.91 (br, phenyl *C*), 94.35 (H*C*{C(CH$_3$)N-2,6-$^{i}$Pr$_2$C$_6$H$_3$}$_2$), 91.67 (NHC=*C*HC$_3$H$_7$)Ph), 72.57 (DME), 59.41 (DME), 29.73 (C(Ph)=CH*C*H$_2$CH$_2$CH$_3$), 28.04 (*C*H(CH$_3$)$_2$), 27.88 (*C*H(CH$_3$)$_2$), 24.78 (CH(*C*H$_3$)$_2$), 24.59 (CH(*C*H$_3$)$_2$), 24.28 (CH(*C*H$_3$)$_2$), 24.14 (CH(*C*H$_3$)$_2$), 24.08 (C(Ph)=CHCH$_2$*C*H$_2$CH$_3$), 23.73 (HC{C(*C*H$_3$)N-2,6-$^{i}$Pr$_2$C$_6$H$_3$}$_2$), 14.37 (Bu-*C*H$_3$) ppm. IR (KBr): $\nu$ = 2957 (m), 2922 (m), 2864 (m), 1627 (w), 1594 (m), 1513 (m), 1457 (m), 1430 (s), 1400 (s), 1312 (s), 1257 (m), 1176 (m), 1141 (m), 1056 (m), 1021 (m), 931 (m), 757 (m) cm$^{-1}$. Anal. Calcd for $C_{44}H_{65}N_3O_2Mg$: C, 76.33; H, 9.46; N, 6.07. Found: C, 76.18; H, 9.32; N, 6.15.

**Preparation of {κ$^3$-N,N',N''-(ArNCMe)$_2$[N(Ph)CS]CH}Mg[(Ph)NC($^{n}$Bu)S] (8).** A benzene (2 mL) solution of PhNCS (0.270 g, 2.0 mmol) was added dropwise to a benzene (3 mL) solution of {[HC(C(Me)N-2,6-$^{i}$Pr$_2$C$_6$H$_3$)$_2$]Mg($^{n}$Bu)}$_2$ (**1**; 0.500 g, 0.5 mmol) with stirring at room temperature. After 10 minutes, the solution was filtered. The volume of the filtrate was reduced to 2 mL, and the compound **8** crystallized at room temperature in 2 days as pale yellow crystals. Yield: 0.548 g (71%). M.p.: 60-62 $^{o}$C (dec.). $^{1}$H NMR (600 MHz, $C_6D_6$): $\delta$ = 8.07 (d, 2H, $J$ = 7.8 Hz, phenyl *H*), 7.37 (t, 2H, $J$ = 7.8 Hz, phenyl *H*), 7.16 (br, 5H, phenyl *H*), 7.08-7.06 (m, 4H, phenyl *H*), 6.94 (m, 2H, phenyl *H*), 6.67 (m, 2H, phenyl *H*), 6.15 (s, 1H, C*H*), 5.38-5.36 (m, 2H, phenyl *H*), 2.99-2.91 (m, 4H, C*H*Me$_2$), 2.06 (t, $J$ = 7.2 Hz, 2H,

(Ph)NC(C$H_2$C$_3$H$_7$)S), 1.76 (s, 6H, HC{C(C$H_3$)NAr}$_2$), 1.58-1.56 (m, 2H, (Ph)NC(CH$_2$C$H_2$C$_2$H$_5$)S), 1.47 (d, $J$ = 7.2 Hz, 6H, CH(C$H_3$)$_2$), 1.23-1.21 (m, 2H, (Ph)NC(C$_2$H$_4$C$H_2$CH$_3$)S), 1.07 (d, $J$ = 7.2 Hz, 6H, CH(C$H_3$)$_2$), 0.97 (d, $J$ = 7.2 Hz, 6H, CH(C$H_3$)$_2$), 0.82 (d, $J$ = 7.2 Hz, 6H, CH(C$H_3$)$_2$), 0.59 (t, $J$ = 7.3 Hz, 3H, Bu-C$H_3$). $^{13}$C{$^1$H} NMR (150 MHz, C$_6$D$_6$): $\delta$ = 203.29 (S*C*N(Ph)Mg), 188.57 (S*C*(Bu)NPh), 177.13 (HC{*C*(CH$_3$)NAr}$_2$), 149.60 (phenyl *C*), 148.48 (phenyl *C*), 142.02 (phenyl *C*), 140.46 (phenyl *C*), 139.20 (phenyl *C*), 128.24 (phenyl *C*), 128.10 (phenyl *C*), 127.95 (phenyl *C*), 127.7 (phenyl *C* and benzene), 126.69 (phenyl *C*), 125.22 (phenyl *C*), 124.84 (phenyl *C*), 123.92 (phenyl *C*), 123.63 (phenyl *C*), 123.23 (phenyl *C*), 122.61 (phenyl *C*), 79.47 (H*C*{C(CH$_3$)NAr}$_2$), 38.21 ((Ph)NC(*C*H$_2$C$_3$H$_7$)S)), 30.59 ((Ph)NC(CH$_2$*C*H$_2$C$_2$H$_5$)S), 29.20 (*C*H(CH$_3$)$_2$), 27.83 (*C*H(CH$_3$)$_2$), 26.11 (CH(*C*H$_3$)$_2$), 24.54 (CH(*C*H$_3$)$_2$), 24.25 (CH(*C*H$_3$)$_2$), 24.06 (CH(*C*H$_3$)$_2$), 23.58 (NC*C*H$_3$), 22.00 ((Ph)NC(C$_2$H$_4$*C*H$_2$CH$_3$)S), 13.37 (Bu-*C*H$_3$) ppm. IR (KBr): $\nu$ = 2956 (m), 2924 (m), 2857 (m), 1641 (m), 1620 (m), 1590 (m), 1543 (m), 1491 (m), 1454 (m), 1431 (s), 1384 (s), 1362 (s), 1261 (m), 1165 (m), 1025 (w), 791 (m) cm$^{-1}$. A reproducible microanalysis could not be obtained for the compound as the solvent molecule (benzene) in the crystal lattice were slowly lost upon isolation of the compoud as a dry crystalline solid. However, it is diffcult to completely remove them by placing crystalline samples of the compound under vaccum for several hours.

**Preparation of {[HC(C(Me)N-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$]Mg(μ-Im)}$_2$ (9·0.5C$_7$H$_8$).** 1-methylimidazole (0.082 g, 1.0 mmol) was added to a THF (5 mL) solution of {[HC(C(Me)N-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$]Mg($^n$Bu)}$_2$ (**1**; 0.500 g, 0.5 mmol) with stirring at room

temperature. The resultant mixture was stirred at 60 °C for overnight, the solution was filtered. The volume of the filtrate was reduced to 2 mL, and the colorless crystals of **9** were isolated at room temperature in the glovebox after addition of a few drops of toluene. Yield: 0.378 g (72%). M.p.: 130-132 °C (dec.) $^1$H NMR (600 MHz, $C_4D_8O$): $\delta$ = 7.13-7.02 (m, 5H, toluene *H* ), 6.92 (br, 2H, N(Me)C*H*CHNC), 6.91-6.87 (m, 8H, phenyl *H* ), 6.81 (br, 2H, N(Me)C*H*CHNC), 6.70-6.71 (m, 4H, phenyl *H* ), 4.85 (s, 2H, *H*C{C(CH$_3$)N-2,6-$^i$Pr$_2$C$_6$H$_3$}$_2$), 3.75 (s, 6H, N(C*H*$_3$)NCHNC), 3.56-3.54 (m, 4H, C*H*Me$_2$), 2.73-2.69 (m, 4H, C*H*Me$_2$), 2.31 (s, 3H, toluene C*H*$_3$), 1.56 (s, 12H, HC{C(C*H*$_3$)N-2,6-$^i$Pr$_2$C$_6$H$_3$}$_2$), 1.28 (d, 12H, *J* = 7.2 Hz, CH(C*H*$_3$)$_2$), 1.09 (d, 12H, *J* = 7.2 Hz, CH(C*H*$_3$)$_2$), 0.90 (d, 12H, *J* = 7.2 Hz, CH(C*H*$_3$)$_2$)，-0.58 (d, 12H, *J* = 7.2 Hz, CH(C*H*$_3$)$_2$) ppm. $^{13}$C{$^1$H} NMR (150 MHz, $C_4D_8O$): $\delta$ = 185.42 ($C_q$, $C_\alpha$ of *C*-Mg, *C*$_3$H$_4$N$_3$), 167.66 (HC{*C*(CH$_3$)-N-2,6-$^i$Pr$_2$C$_6$H$_3$}$_2$), 145.91 (phenyl *C*), 142.48 (phenyl *C*), 141.35 (phenyl *C*), 137.42 (phenyl *C*), 129.02 (phenyl *C*), 128.67 (phenyl *C*), 128.03 (phenyl *C*), 125.04 (*C*H of *C*$_3$H$_4$N$_3$), 124.16 (phenyl *C*), 123.63 (phenyl *C*), 122.75 (phenyl *C*), 122.41 (phenyl *C*), 118.70 (*C*H of *C*$_3$H$_4$N$_3$), 93.40 (H*C*{C(CH$_3$)NAr}$_2$), 35.67 (Im *C*H$_3$), 28.45 (*C*H(CH$_3$)$_2$), 28.09 (*C*H(CH$_3$)$_2$), 26.70 (CH(*C*H$_3$)$_2$), 24.79 (CH(*C*H$_3$)$_2$), 24.66 (CH(*C*H$_3$)$_2$), 24.53 (CH(*C*H$_3$)$_2$), 23.51 (CH(*C*H$_3$)$_2$), 22.50 (HC{C(*C*H$_3$)N-2,6-$^i$Pr$_2$C$_6$H$_3$}$_2$), 21.35 (toluene *C*H$_3$) ppm. IR (KBr): $\nu$ = 2956 (m), 2923 (m), 2864 (m), 1616 (m), 1545 (m), 1516 (m), 1459 (m), 1431 (m), 1408 (s), 1313 (m), 1255 (m), 1172 (m), 1102 (m), 1020 (m), 930 (m), 790 (m) cm$^{-1}$. Anal. Calcd for $C_{73}H_{100}Mg_2N_8$: C, 77.03; H, 8.86; N, 9.84. Found: C, 76.95 H, 8.75; N, 9.91.

***X*-ray Crystallography.** Single-crystal X-ray diffraction measurements were carried out on an Agilent SuperNova EosS2 diffractometer using graphite monochromated Cu Kα radiation (λ = 1.54184 Å) or Mo Kα radiation (λ = 0.710 Å). The crystals were kept at 150 (10) K during data collection. The structures were solved by the Superflip[5] structure solution program in Olex2[6] and refined using Full-matrix Least Squares based on $F^2$ with program SHELXL-97[7] and the SHELXL-2014 within Olex2. Crystal data and experimental data for **2-4** and **7-9** are summarized in Table S1.

For compounds **2** and **8**, the solvent molecules were disordered and could not be modeled properly; thus, the program *SQUEEZE*[8], a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data.

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**Table S1.** Crystal data and experimental parameters for compounds **2**-4 and **7-9**

| Compound | **2** | **3** | **4** | **7** | **8** | **9·0.5$C_7H_8$** |
|---|---|---|---|---|---|---|
| Formula | $C_{66}H_{100}Mg_2N_4S_2$ | $C_{37}H_{58}MgN_2OSe$ | $C_{37}H_{58}MgN_2O\ Se_2$ | $C_{44}H_{65}MgN_3O_2$ | $C_{47}H_{60}MgN_4S_2$ | $C_{73}H_{100}Mg_2N_8$ |
| Fw | 1062.24 | 650.12 | 729.11 | 692.30 | 769.45 | 1138.22 |
| crystal system | monoclinic | triclinic | monoclinic | triclinic | monoclinic | triclinic |
| space group | $P\ 2_1/n$ | $P$ -1 | $P\ 2_1/c$ | $P$ -1 | $P\ 2_1/c$ | $P$ -1 |
| $a$ (Å) | 12.01460(10) | 9.3835(3) | 23.0510(5) | 8.9221(2) | 21.2566(2) | 13.3001(5) |
| $b$ (Å) | 20.5390(2) | 12.6275(3) | 10.0565(2) | 10.1350(2) | 17.0216(2) | 14.3346(5) |
| $c$ (Å) | 14.3234(2) | 15.4945(5) | 16.8071(4) | 23.6908(5) | 13.6278(2) | 21.0947(8) |
| $\alpha$ (deg) | 90 | 86.019(2) | 90 | 100.865(2) | 90 | 72.837(3) |
| $\beta$ (deg) | 100.3880(10) | 80.490(2) | 108.036(3) | 95.075(2) | 105.9520(10) | 75.308(3) |
| $\gamma$ (deg) | 90 | 84.668(2) | 90 | 101.435(2) | 90 | 63.308(4) |
| $V$ (Å$^3$) | 3476.62(7) | 1800.14(9) | 3704.65(15) | 2044.39(8) | 4740.95(10) | 3398.4(2) |
| Z | 2 | 2 | 4 | 2 | 4 | 2 |
| $\rho_{calc}$ (g/cm$^3$) | 1.015 | 1.199 | 1.303 | 1.125 | 1.076 | 1.112 |
| μ/mm$^{-1}$ | 1.142 | 1.090 | 2.875 | 0.659 | 1.393 | 0.661 |
| radiation | CuKα | MoKa | CuKα | CuKα | CuKα | CuKα |
| size (mm) | 0.20 × 0.20 × 0.2 | 0.15 × 0.15 × 0.15 | 0.1 0× 0.10 × 0.05 | 0.10 × 0.10× 0.10 | 0.20 × 0.10 × 0.10 | 0.30 × 0.20 × 0.20 |
| $F$(000) | 1160 | 696 | 1520 | 756 | 1651 | 1236 |
| 2$\theta$ range (deg) | 7.61 to 146.152 | 6.838 to 58.994 | 9.676 to 144.04 | 7.666 to 145.948 | 6.758 to 146.846 | 8.166 to 143.752 |
| reflns collected | 25706 | 31682 | 34408 | 30124 | 35040 | 62621 |
| indep. reflns | 6800 ($R_{int}$ = 0.0239) | 8759 ($R_{int}$ = 0.0281) | 7141 ($R_{int}$ = 0.0322) | 8024 ($R_{int}$ = 0.0389) | 9328 ($R_{int}$ = 0.0324) | 13121 ($R_{int}$ = 0.0543) |
| reflns obs. [$I > 2\sigma(I)$] | 5849 | 7370 | 6343 | 7334 | 6872 | 11966 |
| data/restr/paras | 6800 /0/349 | 8759/1/394 | 7141 /59/458 | 8024 /0/468 | 9328 /48 /518 | 13121 /0/ 771 |
| GOF | 1.054 | 1.029 | 1.039 | 1.042 | 1.047 | 1.020 |

| | | | | | | |
|---|---|---|---|---|---|---|
| R1/wR2 [$I >= 2\sigma(I)$] | 0.0418 / 0.1095 | 0.0395/ 0.0912 | 0.0434 / 0.1114 | 0.0443 / 0.1224 | 0.0567 / 0.1491 | 0.0395 / 0.1047 |
| R1/wR2 (all data) | 0.0491 / 0.1154 | 0.0508/ 0.0966 | 0.0503/ 0.1160 | 0.0474 / 0.1255 | 0.0767 / 0.1575 | 0.0432 / 0.1084 |
| largest diff. peak/hole / e $Å^{-3}$ | 0.283 / -0.186 | 0.712/ -0.638 | 0.821 / -0.622 | 0.307 / -0.232 | 0.885 / -0.424 | 0.334 / -0.288 |
| CCDC | 1874067 | 1874068 | 1874069 | 1874070 | 1874071 | 1874072 |