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SUPPORTING INFORMATION

Unsupported Metal Silyl Ether Coordination

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1. Supporting Experimental Data

1.1. General Experimental Procedures

All experiments were conducted under an inert nitrogen atmosphere using standard Schlenk and glovebox techniques (MBraun, Labmaster SP). All solvents were degassed with nitrogen, dried over activated aluminium oxide (Solvent Purification System: Pure Solv 400−4−MD, Innovative Technology) and stored over 3Å molecular sieves. Chlorobenzene and bromobenzene were dried over calcium hydride, distilled under N_2 atmosphere and stored over molecular sieves 3Å. Hexamethyldisiloxane (Acros, 98%+) was refluxed over sodium, distilled under N_2 atmosphere and stored over molecular sieves 3Å. C_6D_6 and C_6D_5Br (99.6% D, Sigma Aldrich) were dried over 3Å molecular sieves. *n*PrMgCl in Et_2O (2M, Sigma Aldrich), $AlMe_3$ (97%, Sigma Aldrich), AlI_3 (99.99%, Abcr), $AlCl_3$ (99.99%, Abcr), borane-dimethyl sulfide (94%, Alfa Aesar), $B(C_6F_5)_3$ (Boulder Scientific) and $[Ph_3C^+][(C_6F_5)_4B^-]$ (Boulder Scientific) were used as received. [(BDI)Mg*n*Pr]$_2$[S1] and $[(BDI)Al^+Me][(C_6F_5)_4B^-]$[S2] were synthesized according to a literature procedure. NMR spectra were recorded with a Bruker Avance III HD 400 MHz or a Bruker Avance III HD 600MHz spectrometer. The spectra were referenced to the respective residual signals of the deuterated solvents. Elemental analysis was performed with a Euro EA 3000 (Euro Vector) analyzer. All crystal structures have been measured on a SuperNova (Agilent) diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector.

1.2. Synthesis

Synthesis of $[(BDI)Mg^{+}\cdot O(SiMe_3)_2][B(C_6F_5)_4^{-}]$

$[(BDI)Mg\textit{n}Pr]_2$ (0.2446 g, 0.2524 mmol) and $[Ph_3C^{+}][B(C_6F_5)_4^{-}]$ (0.4527 g, 0.4908 mmol) were dissolved in chlorobenzene (1.5 ml) and the solution was stirred until it was almost colorless (circa 1 min). Hexamethyldisiloxane (0.9 ml) was carefully added to the solution. After 18h the glass wall of the reaction vessel was scratched with a spatula initiating crystallization. The supernatant was decanted and the colorless crystals were washed with hexamethyldisiloxane (4 x 2 ml) and dried under vacuum. The product was obtained as a colorless crystalline material. Yield: 76%, 0.4806 mg, 0.3745 mmol. Decomposition temperature: 60°C. ^{1}H NMR (600 MHz, C_6D_5Br, 298K) δ 7.22 – 7.13 (m, 2H, Ar*H*), 7.10 – 7.04 (m, 4H, Ar*H*), 4.93 (s, 1H, CC*H*C), 2.74 (br, 4H, C*H*Me$_2$), 1.61 (s, 6H, CC*H$_3$*), 1.25 – 1.08 (m, 6H, CHC*H$_3$*), 1.07 (d, $^{3}J_{HH}$ = 6.6 Hz, 12H, CHC*H$_3$*), 1.04 – 0.88 (m, 6H, CC*H$_3$*), 0.09 – -0.08 (br m, 18H, Si(C*H$_3$*)$_3$) ppm. ^{13}C NMR (151 MHz, C_6D_5Br, 298K) δ 173.8 (s, N*C*(CH$_3$)), 149.1 (br d, $^{1}J_{CF}$ = 242 Hz, B(*C$_6$*F$_5$)$_4$), 142.0 (s, Ar*C*), 140.2 – 135.9 (m, B(*C$_6$*F$_5$)$_4$), 129.1 (s, Ar*C*), 127.8 (br s, Ar*C*), 125.3 (br s, Ar*C*), 97.1 (s, C*C*HC), 29.6 (br s, *C*HMe$_2$), 24.7 (br s, CH*C*H$_3$, NC(*C*H$_3$)), 2.7 (br s ,Si(*C*H$_3$)$_3$), 1.6 (br s ,Si(*C*H$_3$)$_3$) ppm. ^{19}F NMR (376 MHz, C_6D_5Br, 298K) δ -131.4 (d, $^{3}J_{FF}$ = 19 Hz, 8F, *o*-C*F*), -161.2 (t, $^{3}J_{FF}$ = 21 Hz, 4F, *p*-C*F*), -165.6 (t, $^{3}J_{FF}$ = 21 Hz, 8F, *m*-C*F*) ppm. ^{11}B NMR (128 MHz, C_6D_5Br, 298K) δ -15.9 (s, *B*(C$_6$F$_5$)$_4$) ppm. ^{29}Si NMR (79 MHz, C_6D_5Br, 253K) δ 33.5 (s, O(*Si*Me$_3$)$_2$) ppm. Anal. Calcd for $C_{59}H_{59}MgSiON_2BF_{20}$ (M = 1283.39 g/mol): C, 55.22; H, 4.63; N, 2.18. Found: C, 54.93; H, 4.48; N, 1.86.

1.3 Selected NMR Spectra

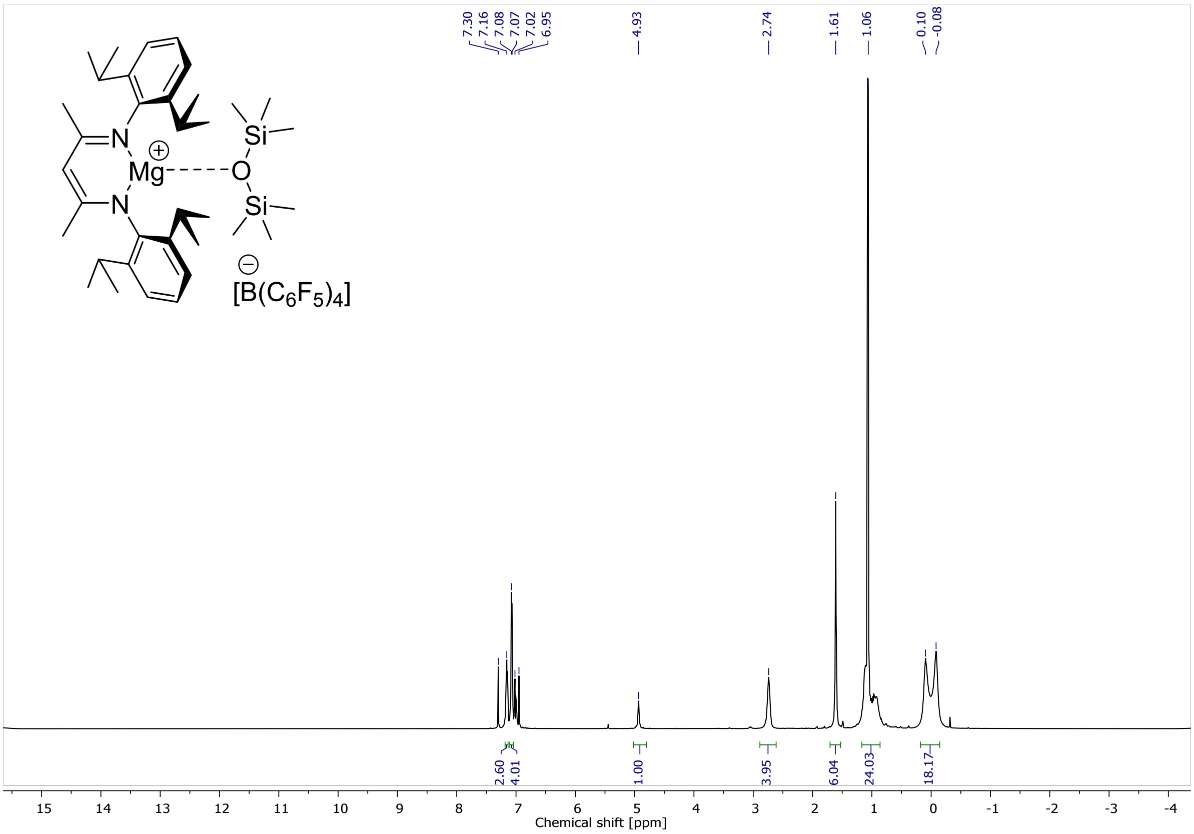


Figure S1. ^{1}H NMR spectrum of $[(BDI)Mg^+\cdot O(SiMe_3)_2][B(C_6F_5)_4^-]$ in C_6D_5Br

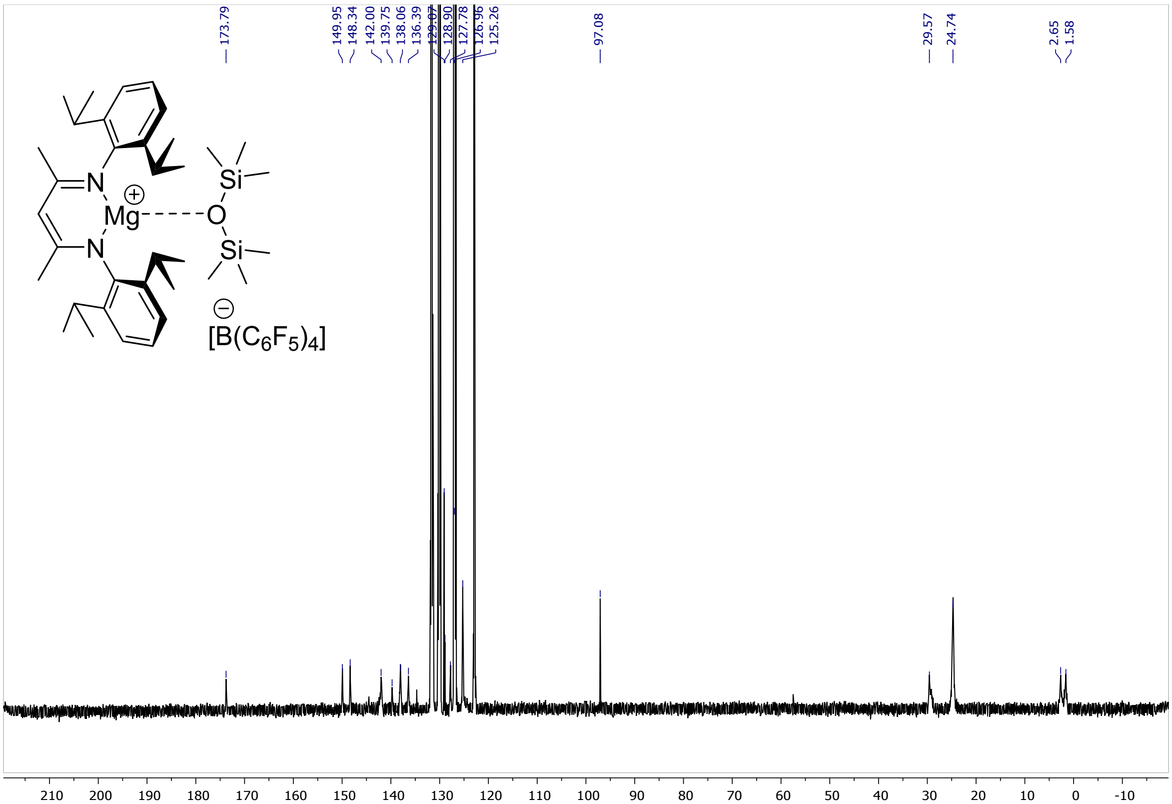


Figure S2. ^{13}C{^{1}H} NMR spectrum of $[(BDI)Mg^+\cdot O(SiMe_3)_2][B(C_6F_5)_4^-]$ in C_6D_5Br

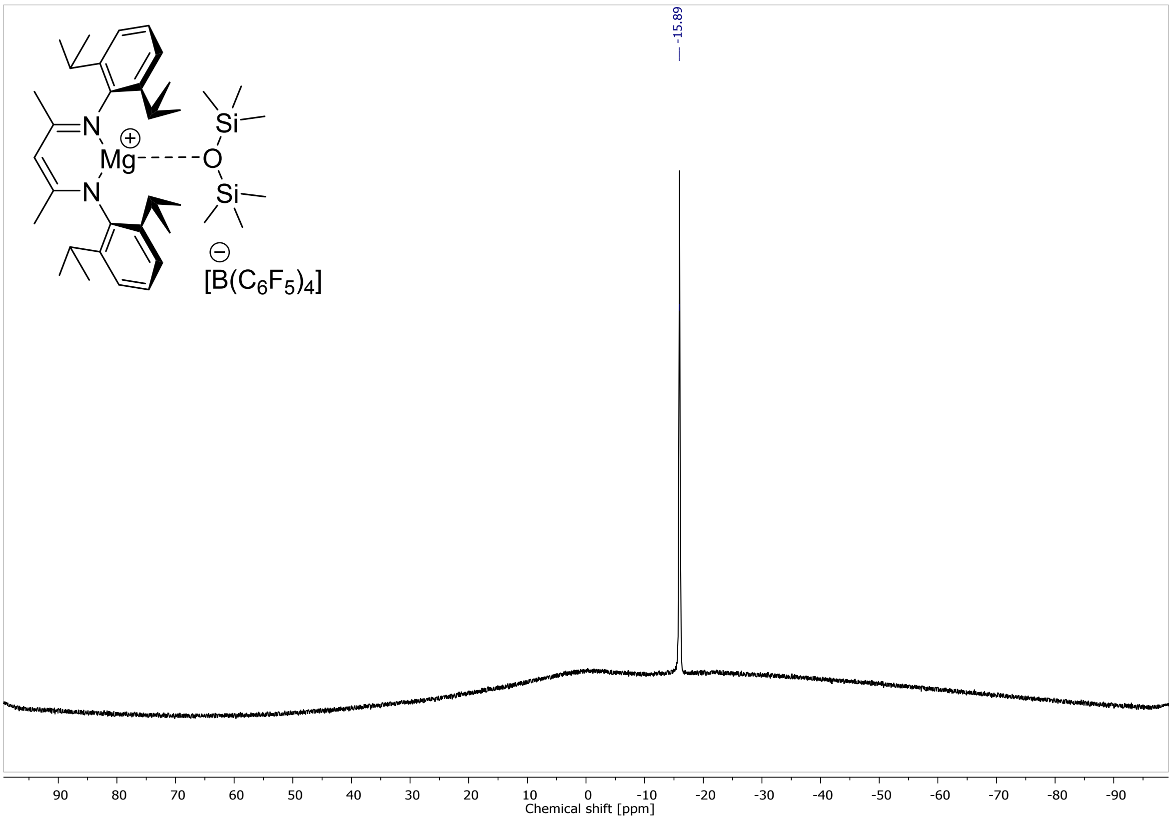


Figure S3. ^{11}B NMR spectrum of [(BDI)Mg$^+$·O(SiMe$_3$)$_2$][B(C$_6$F$_5$)$_4$$^-$] in C$_6D_5$Br

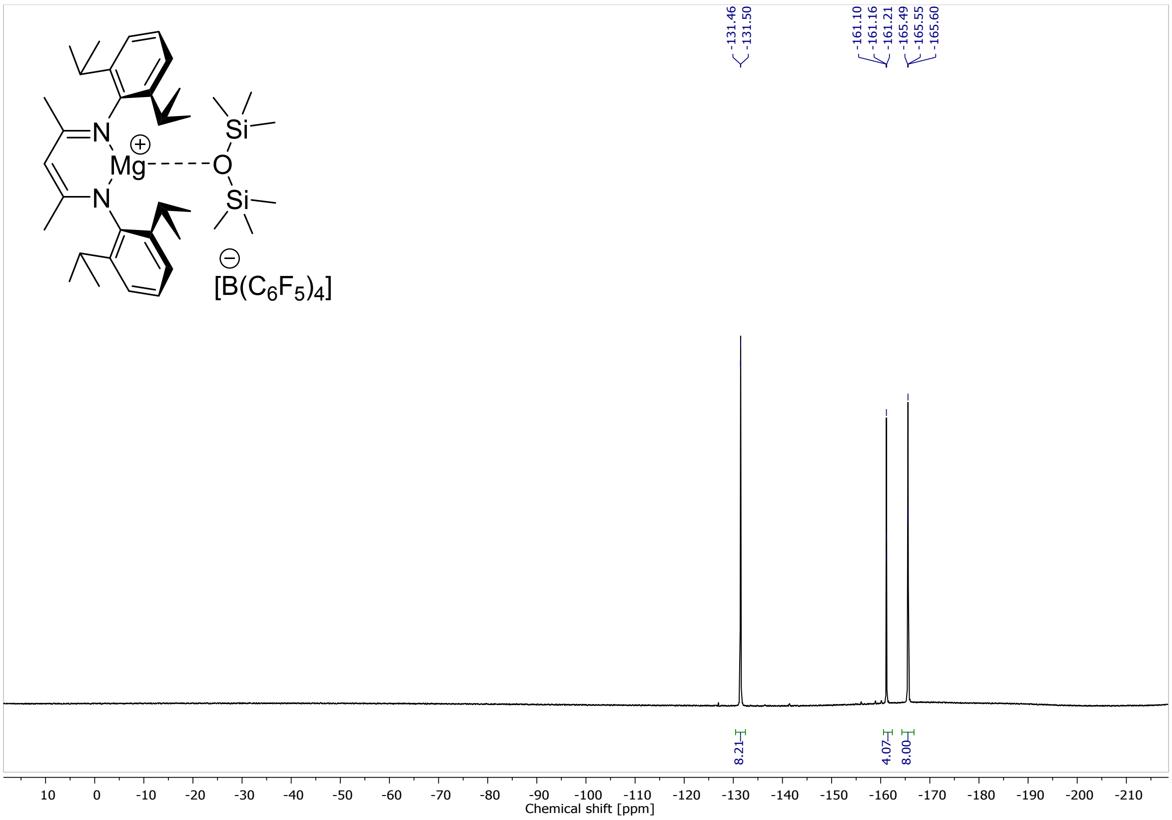


Figure S4. ^{19}F NMR spectrum of [(BDI)Mg$^+$·O(SiMe$_3$)$_2$][B(C$_6$F$_5$)$_4$$^-$] in C$_6D_5$Br

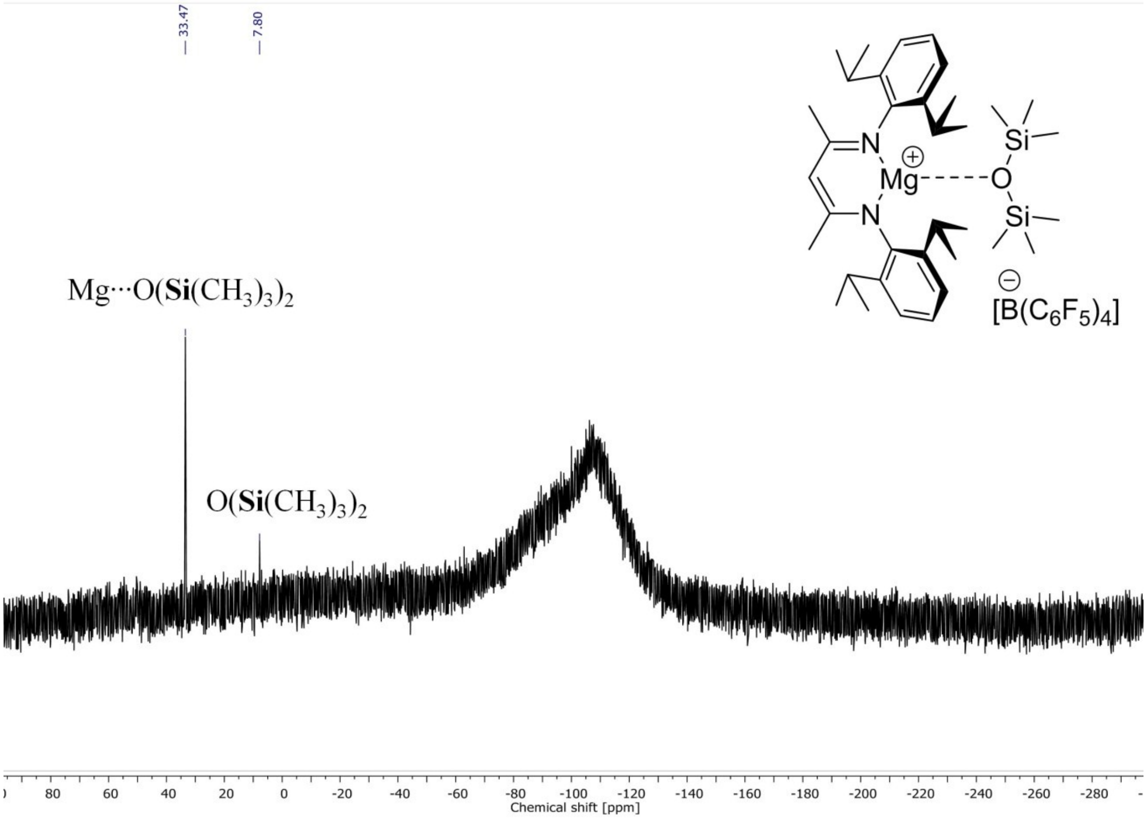


Figure S5. ^{29}Si NMR spectrum of [(BDI)Mg^{+}·O(SiMe$_3$)$_2$][B(C$_6$F$_5$)$_4$$^{-}$] in C$_6D_5$Br at 253K.

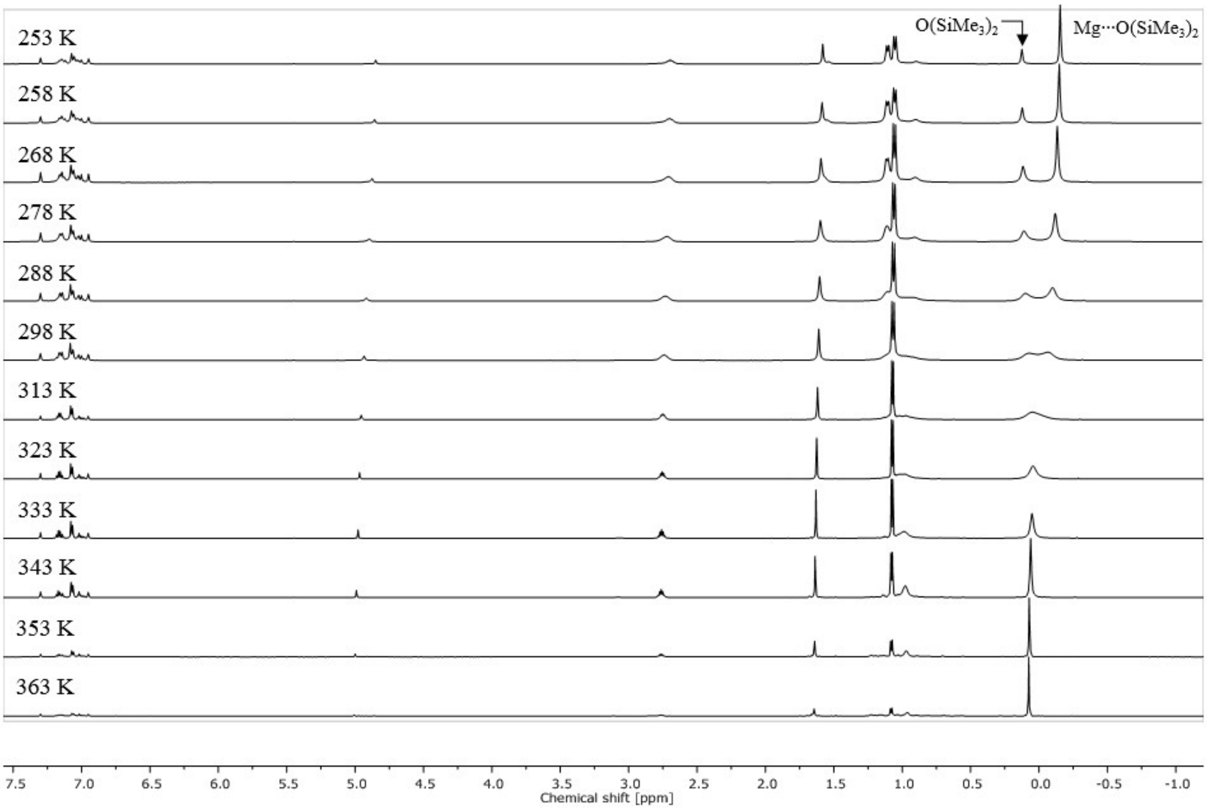


Figure S6. ^{1}H NMR spectra of [(BDI)Mg^{+}·O(SiMe$_3$)$_2$][B(C$_6$F$_5$)$_4$$^{-}$] in C$_6D_5$Br at various temperatures. ^{1}H NMR signal of uncoordinated O(SiMe$_3$)$_2$: δ = 0.12 ppm

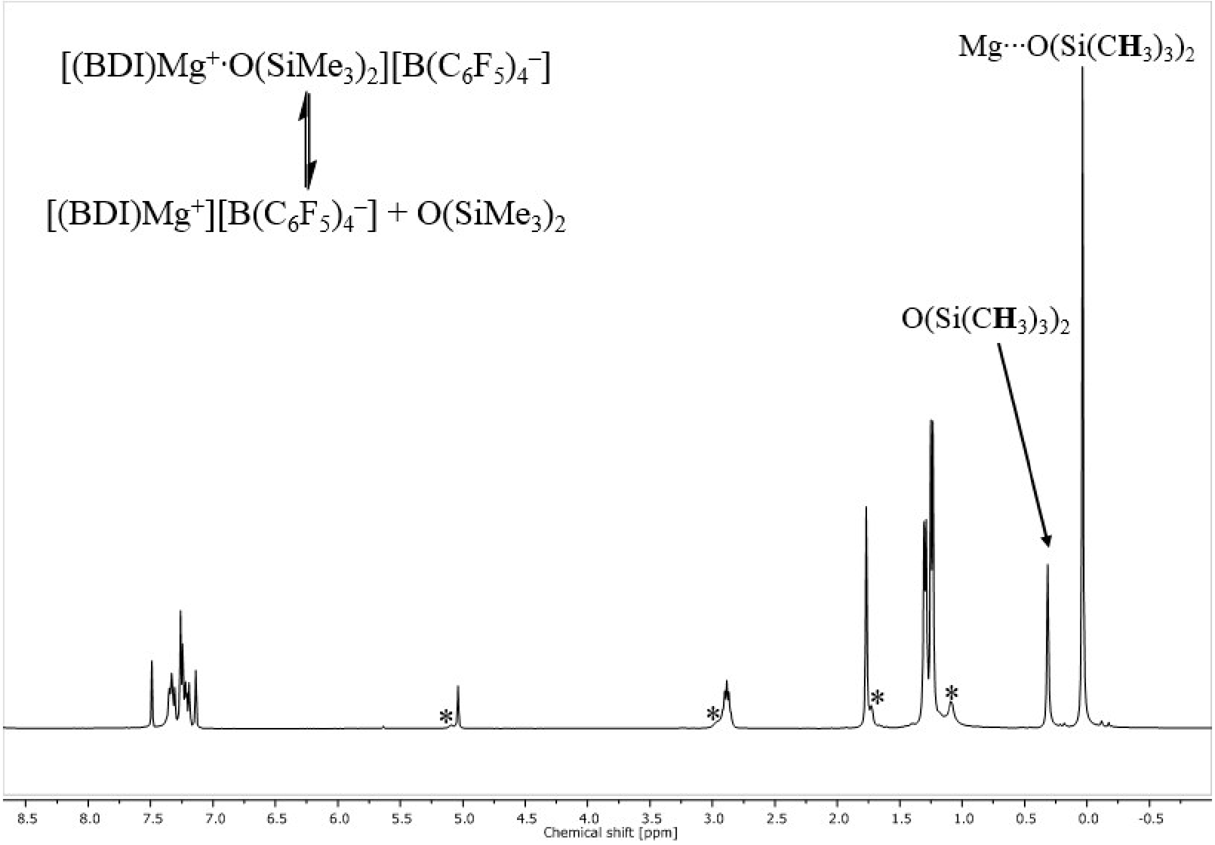


Figure S7. ^{1}H NMR spectrum of [(BDI)Mg$^+$·O(SiMe$_3$)$_2$][B(C$_6$F$_5$)$_4$$^-$] in C$_6D_5$Br at 253K. Resonances for free [(BDI)Mg$^+$][B(C$_6$F$_5$)$_4$$^-$] are indicated by *.

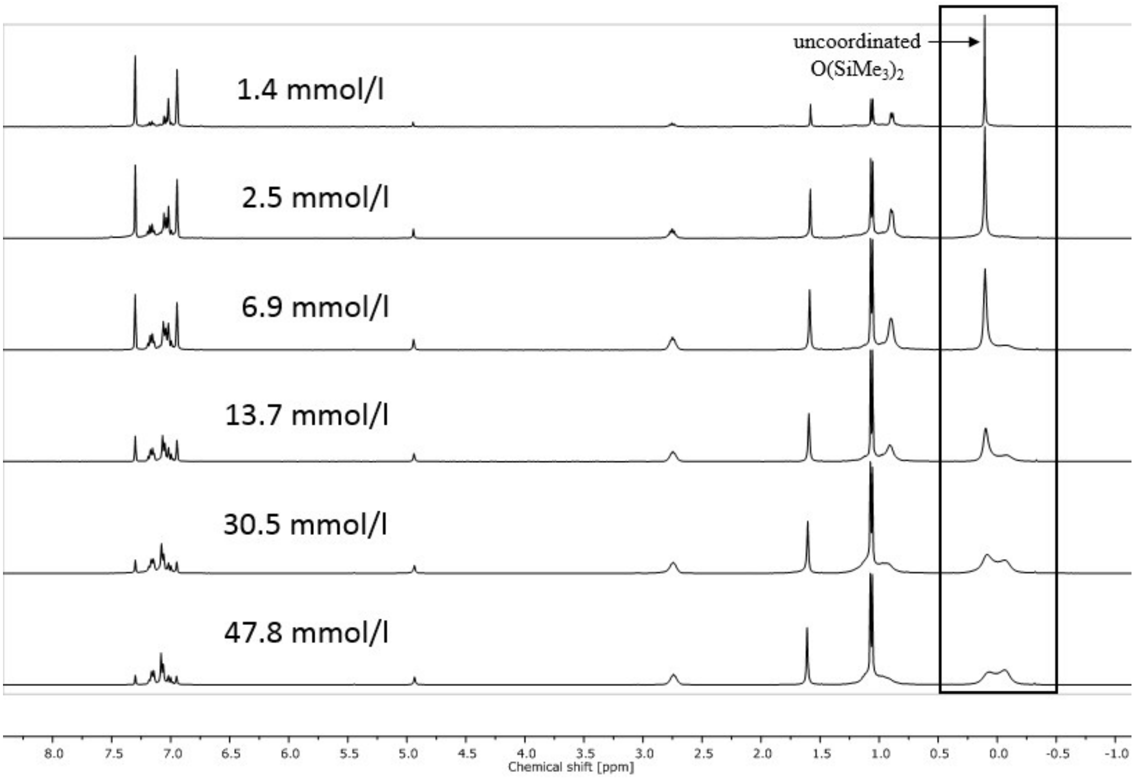


Figure S8. ^{1}H NMR spectra of [(BDI)Mg$^+$·O(SiMe$_3$)$_2$][B(C$_6$F$_5$)$_4$$^-$] in C$_6D_5$Br (298K) with varying concentrations. ^{1}H NMR signal of uncoordinated O(SiMe$_3$)$_2$: $\delta = 0.12$ ppm.

1.4 Single Crystal X-Ray Diffraction

Single crystal X–ray diffraction data were collected on a SuperNova diffractometer (Rigaku Oxford diffraction) with Atlas S2 detector using a CuK$_\alpha$ microfocus source. The crystal was maintained at 100 K during data collection. Using Olex2,[S3] the structure was solved by Direct Methods (ShelXT)[S4] and refined with ShelXL[S5] using Least Squares minimization. The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding mode. Complex [(BDI)Mg$^+$·O(SiMe$_3$)$_2$][B(C$_6$F$_5$)$_4^-$] crystallized with one complete ion pair and one cocrystallized chlorobenzene solvent molecule in the asymmetric unit. Crystal structure data for [(BDI)Mg$^+$·O(SiMe$_3$)$_2$][B(C$_6$F$_5$)$_4^-$] 1822421 has been deposited with the Cambridge Crystallographic Data Centre.

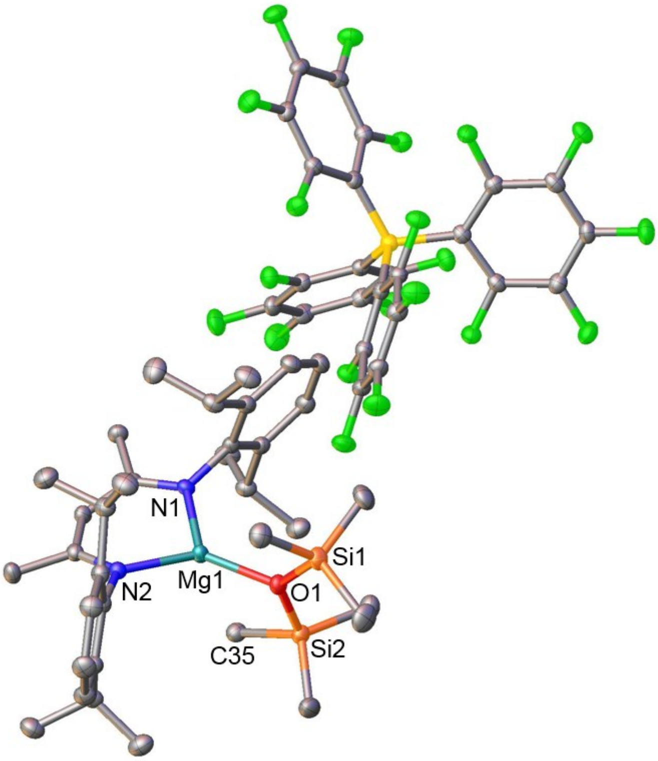


Figure S9. ORTEP representation of [(BDI)Mg$^+$·O(SiMe$_3$)$_2$][B(C$_6$F$_5$)$_4^-$] (probability level 50%). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Mg1-O1 1.9926(11), Mg1-N1 2.0013(13), Mg1-N2 1.9934(13), Si1-O1 1.7239(11), Si2-O1 1.7113(12), Mg1-C35 2.6370(17), N2-Mg1-N1 99.64(5), Si1-O1-Mg1 125.22(6), Si2-O1-Mg1 107.31(6), Si2-O1-Si1 127.08(6), C35-Si2-O1-Mg1 -1.21(8), C35-Si2-O1-Si1 -174.23(9)

Table S1. Crystal data.

Identification code	$[(BDI)Mg^{+}\cdot O(SiMe_3)_2]$ $[B(C_6F_5)_4^{-}]$
Empirical formula	$C_{65}H_{64}BClF_{20}MgN_2OSi_2$
Formula weight	1395.93
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	13.3518(6)
b/Å	14.4685(7)
c/Å	17.3377(7)
α/°	98.233(4)
β/°	97.872(4)
γ/°	90.686(4)
Volume/Å^3	3281.9(3)
Z	2
ρ_{calc}g/cm^3	1.413
μ/mm^{-1}	1.848
F(000)	1436.0
Crystal size/mm^3	0.25 × 0.17 × 0.14
Crystal color	colorless
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.176 to 147.188
Index ranges	$-16 \le h \le 16$, $-11 \le k \le 17$, $-21 \le l \le 16$
Reflections collected	20747
Independent reflections	12606 [R_{int} = 0.0244, R_{sigma} = 0.0363]
Data/restraints/parameters	12606/0/865
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0365, wR_2 = 0.0951
Final R indexes [all data]	R_1 = 0.0409, wR_2 = 0.0995
Largest diff. peak/hole / e Å^{-3}	0.46/-0.71

1.5 Attempts to isolate coordination complexes of $O(SiMe_3)_2$ with Lewis acids

General procedure for the Lewis acids $AlMe_3$, BH_3, $B(C_6F_5)_3$) and [(BDI)Al^+Me] [$B(C_6F_5)_4^-$]

A rigorously dried NMR tube was charged with the respective Lewis acid ($AlMe_3$ 10 µL, 52 µmol; $Me_2S{\cdot}BH_3$ 10 µL, 105 µmol; $B(C_6F_5)_3$ 51.2 mg, 100 µmol) and C_6D_6 (0.5 ml) was added. After measuring NMR spectra (^1H, ^{11}B, ^{19}F, ^{27}Al) of the Lewis acid in C_6D_6, one equivalent of $O(SiMe_3)_2$ was added. Remeasurement of NMR data did not show any change in the chemical shifts (^1H, ^{11}B, ^{19}F, ^{27}Al) of the respective Lewis acids or $O(SiMe_3)_2$ Lewis base. All attempts to crystallize $O(SiMe_3)_2$ adducts (cooling and layering with hexane) failed.

As the Lewis acid [(BDI)$AlMe^+$][$B(C_6F_5)_4^-$] (20.0 mg, 17.6 µmol) is not soluble in C_6D_6, the procedure above was slightly modified and 0.5 ml of a mixture of chlorobenzene/C_6D_6 (5/1; v/v) was used instead.

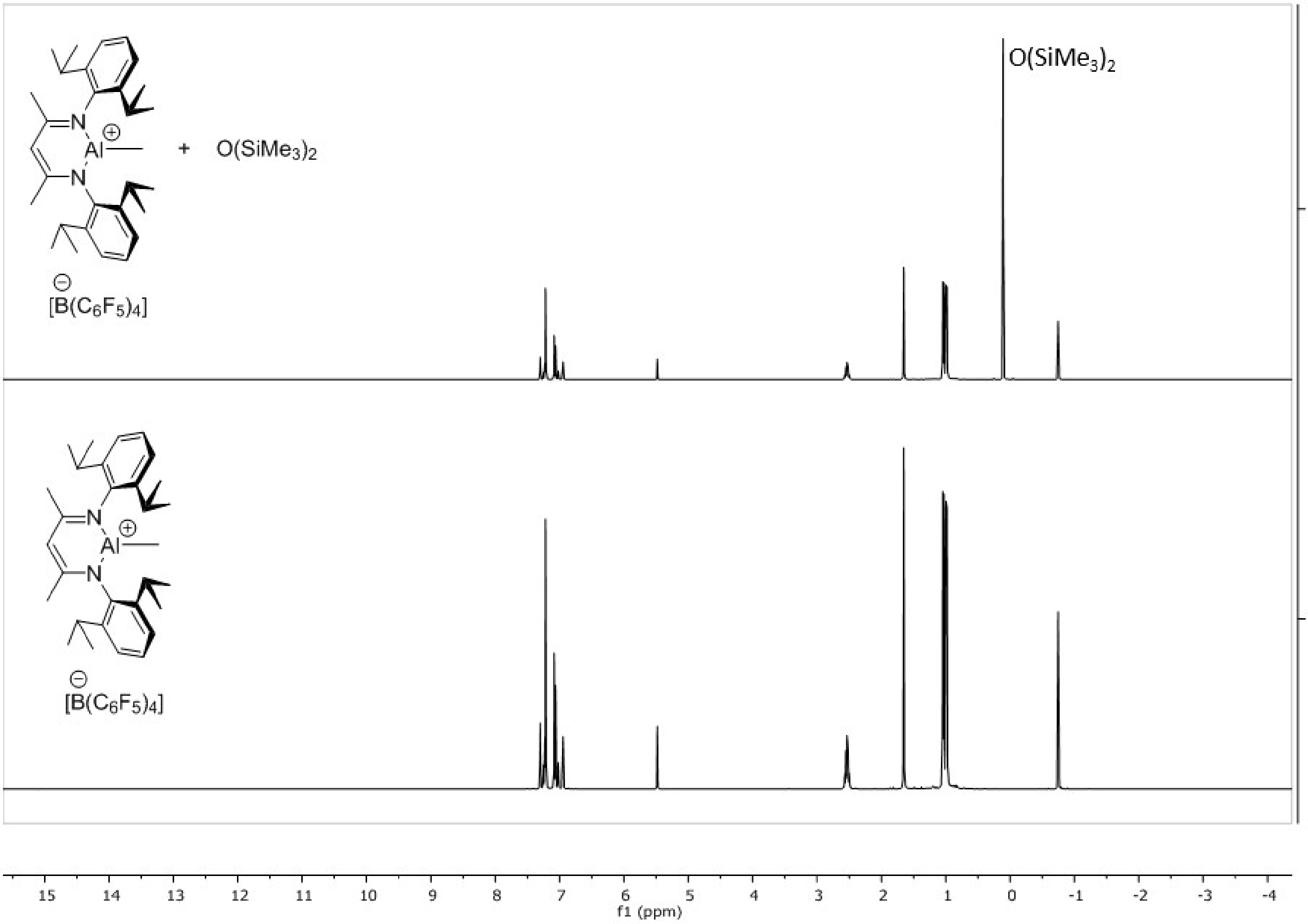


Figure S10. ^1H NMR spectra of [(BDI)$AlMe^+$][$B(C_6F_5)_4^-$] without $O(SiMe_3)_2$ (bottom) and after addition of 1eq of $O(SiMe_3)_2$ (top) in C_6D_5Br.

General procedure for the Lewis acids $AlCl_3$ and AlI_3

A rigorously dried NMR tube was charged with $AlCl_3$ (13.3 mg, 100 μmol) which was suspended in chlorobenzene/C_6D_6 (5/1; v/v). Upon addition of three equivalents of $O(SiMe_3)_2$ (63.9 μL, 300 μmol) at room temperature, the colorless suspension turned pale yellow within 16 h of shaking. NMR spectroscopy revealed formation of $(Me_3Si)OAlCl_2$ and $ClSiMe_3$.[S6]

$(Me_3Si)OAlCl_2$: ^1H NMR (C_6D_6, 600 MHz, 298 K): δ 0.30 (s, 9H) ppm. ^{27}Al NMR (C_6D_6, 156 MHz, 298 K): δ 93.0 ppm. ^{29}Si NMR (C_6D_6, 119 MHz, 298 K): δ 33.2 ppm.

$ClSiMe_3$: ^1H NMR (C_6D_6, 600 MHz, 298 K): δ 0.28 (s, 9H) ppm. ^{29}Si NMR (C_6D_6, 119 MHz, 298 K): δ 30.2 ppm.

A rigorously dried NMR tube was charged with AlI_3 (20.4 mg, 50 μmol) which was dissolved in chlorobenzene/C_6D_6 (5/1; v/v). After addition of one equivalent of $O(SiMe_3)_2$ (10.7 μL, 50 μmol) the solution was shaken for 2 d at room temperature. NMR spectroscopy revealed formation of $(Me_3Si)OAlI_2$ and $ISiMe_3$. [S6]

$(Me_3Si)OAlI_2$: ^1H NMR (C_6D_6, 600 MHz, 298 K): δ 0.59 (s, 9H) ppm. ^{27}Al NMR (C_6D_6, 156 MHz, 298 K): δ 63.2 ppm.

Me_3SiI: ^1H NMR (C_6D_6, 600 MHz, 298 K): δ 0.45 (s, 9H) ppm. ^{29}Si NMR (C_6D_6, 119 MHz, 298 K): δ 8.9 ppm.

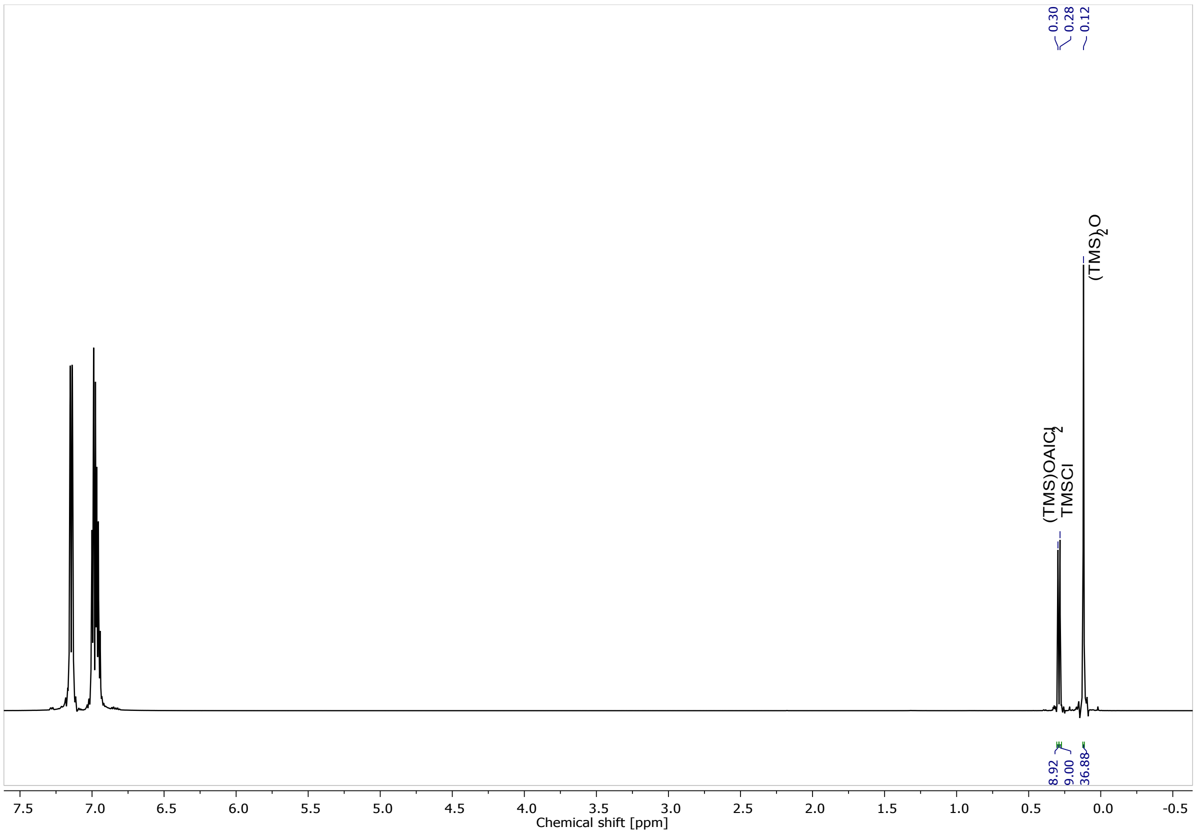


Figure S11. ^1H NMR spectrum of $AlCl_3$ and $O(SiMe_3)_2$ (3 equiv.) in C_6H_5Cl/C_6D_6 (5/1; v/v)

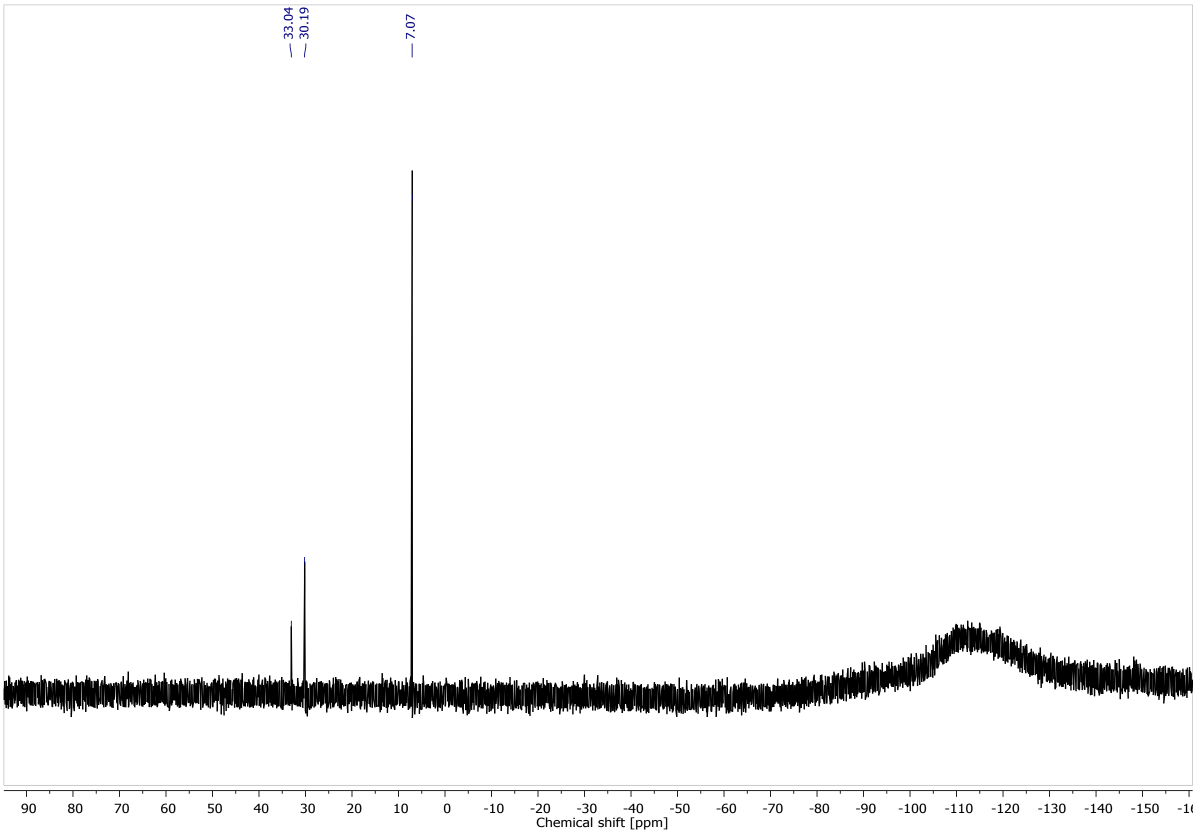


Figure S12. ^{29}Si NMR spectrum of $AlCl_3$ and $O(SiMe_3)_2$ (3 equiv.) in C_6H_5Cl/C_6D_6 (5/1; v/v)

1.6 Crystal structures of compounds with incorporated $O(SiMe_3)_2$

The Cambride Structural Database (CSD)[S7] has been searched for solid state structures incorporating the fragment $O(SiMe_3)_2$. This lead to a total of 40 structures. In 38 of these entries, metal complexes are included in the unit cell. In these cases the silylether is merely a non-coordinating cocrystallized solvent molecule.

The CSD REF-codes of entries containing $O(SiMe_3)_2$ are the following:

ABAKEU, AWAREW, BAPMUC, BEQKUF, CAZQEC, CAZQIG, CELZEB, CIPLAP, COGZEE, COHBIL, ECIYAT, ECIYEX, ENUXOC, EPOSOT, EPOSUZ, ERIZUC, FACKID, FESCOX, FEYRAD, FUSTAQ, GIBQAK, GOMNAZ, HESQEB, HMDSIX, HMDSIX01, HUGTOT, ILOHEW, KEPRII, MUPREV, NOFCES, PIZSUN, RABJIO, TEVTIZ, TOCWUF, UWOYUC, VIMWUK, VUPMUP, WAVGOQ, YUVXOD.

1.7 Thermodynamic parameters

The coordination of $O(SiMe_3)_2$ to $[(BDI)Mg^+][B(C_6F_5)_4^-]$ forming $[(BDI)Mg^+\cdot O(SiMe_3)_2][B(C_6F_5)_4^-]$ is in C_6D_5Br solution in an equilibrium with its educts which can be observed by ^{1}H NMR (see Figure S1 and S6).

$$[(BDI)Mg^+]\ [B(C_6F_5)_4^-] + O(SiMe_3)_2 \rightleftarrows [(BDI)Mg^+\cdot O(SiMe_3)_2] + [B(C_6F_5)_4^-]$$

In the temperature range between 253 K and 278 K, it was possible to observe sufficiently separated signals for integration of the ratio between coordinated and free $O(SiMe_3)_2$; bromobenzene solidifies at 243 K. This allowed for a rough estimation of the equilibrium constants at these temperatures. These values (Table S2) were used to determine the thermodynamic parameters ΔH^0 and ΔS^0 using the following equations:

$$\Delta G^0 = -RTlnK_{eq}\ \textbf{(1)} \qquad \textbf{and} \qquad \Delta G^0 = \Delta H^0 - T\Delta S^0\ \textbf{(2)}$$

$$\textbf{(1) in (2)} \qquad RTlnK_{eq} = T\Delta S^0 - \Delta H^0$$

Table S2. K_{eq} values at their respective temperatures determined by ^{1}H-NMR

T [K]	253	258	268	278
K_{eq}	9.24	8.23	4.67	2.92

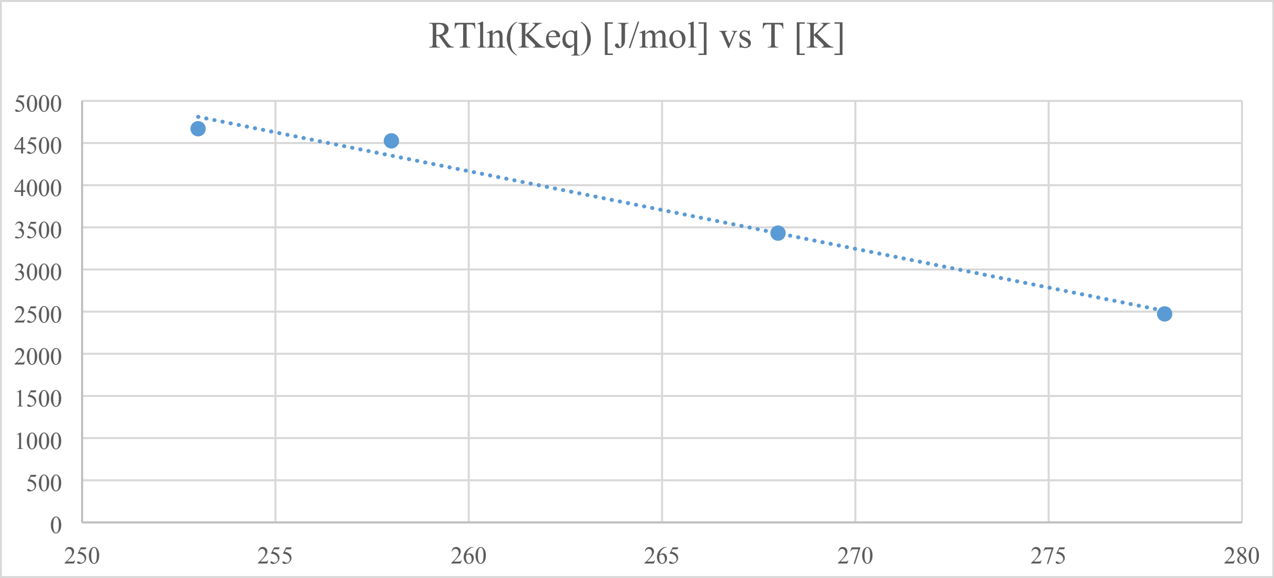


Figure S13. Plot of RTln(K_{eq}) [J/mol] (vertical) against T [K] with a linear least-squares best fit.

Determined thermodynamic values:

$\Delta H^0 = -28.1\,\frac{kJ}{mol}$ $\Delta S^0 = -92.1\,\frac{J}{mol\,K}$

2. Computational Details

All geometry optimizations were carried out using Gaussian 16 Rev. A.03.[S8] All structures were fully optimized on ωB97XD/6-311+G** and ωB97X/6-311+G**[S9]-[S12] levels of theory. The first level includes corrections for dispersion (Table 2) but the latter not (Table 3). All structures were determined to be true minima by the absence of imaginary frequencies (NIMAG=0). For all ligands and cationic model complexes the frequency calculation was carried out at the same level as the optimization. For the full systems (including the [B(C_6F_5)$_4^-$] anion) optimizations were carried out on a ωB97XD/6-31G* level of theory while final energies were determined by single point calculations using the larger 6-311+G** basis set. Charges were determined via NBO analysis[S13] by Gaussian 16 Rev. A.03. Topological analysis were carried out using AIMAll V16.[S14-15] Molecules were drawn and evaluated using "Molecule V2.3".[S16] The Cartesian coordinates of the molecules are available as data files: S1 (Ligands and cationic model complexes @ ωB97XD), S2 (Ligands and cationic model complexes @ ωB97X), S3 (Cationic complexes including [B(C_6F_5)$_4^-$]).

Table S3. Energies for ωB97X calculations.[a]

Molecule	**ωB97X**	**ZPE**	**G_{corr}**
C_6H_6	-232.23619	63.6506	0.073995
OEt_2	-233.666171	86.3858	0.108242
$O(SiMe_3)_2$	-893.875963	143.1887	0.184085
O*t*Bu$_2$	-390.927067	156.8829	0.214826
[(BDI)Mg$^+$···C_6H_6]	-1671.513708	468.7223	0.674866
[(BDI)Mg$^+$···OEt_2]	-1672.966376	491.527	0.708429
[(BDI)Mg$^+$···$O(SiMe_3)_2$]	-2333.181886	549.1145	0.792385
[(BDI)Mg$^+$···O*t*Bu$_2$]	-1830.236079	562.6021	0.819638

[a] ωB97X energies as well as the correction term for the Gibbs free energy ($G_{corr)}$) are given in Hartree, zero point energies (ZPE) are given in kcal·mol^{-1}.

Table S4. Energies for ωB97XD calculations (including corrections for dispersion).[a]

Molecule	**ωB97XD**	**ZPE**	**G_{corr}**
C_6H_6	-232.220942	63.45	0.073663
OEt_2	-233.655667	86.04	0.107602
$O(SiMe_3)_2$	-893.869474	142.67	0.184072
O*t*Bu$_2$	-390.912098	156.30	0.213898
[(BDI)Mg$^+$···C_6H_6]	-1671.457476	468.11	0.675488
[(BDI)Mg$^+$···OEt_2]	-1672.910781	491.39	0.710926
[(BDI)Mg$^+$···$O(SiMe_3)_2$]	-2333.136913	549.08	0.796234
[(BDI)Mg$^+$···O*t*Bu$_2$]	-1830.182089	561.31	0.818366
[(BDI)Mg$^+$] [B(C_6F_5)$_4^-$]	-4375.5473417	537.97	0.750319
[(BDI)Mg$^+$···C_6H_6] [B(C_6F_5)$_4^-$]	-4607.777896	603.70	0.847671
[(BDI)Mg$^+$···OEt_2] [B(C_6F_5)$_4^-$]	-4609.229757	627.2073	0.880746
[(BDI)Mg$^+$···$O(SiMe_3)_2$] [B(C_6F_5)$_4^-$]	-5269.430076	684.8398	0.964698
[(BDI)Mg$^+$···O*t*Bu$_2$] [B(C_6F_5)$_4^-$]	-4766.472553	698.228	0.988350

[a] ωB97XD energies as well as the correction term for the Gibbs free energy ($G_{corr)}$) are given in Hartree, zero point energies (ZPE) are given in kcal·mol^{-1}.

Table S5. NPA charges and selected geometrical parameters for ligands and their complexes with (BDI)Mg$^+$ at the ωB97XD/6-311+G** level.

Compound	Fragment X	Charge X	O-X (Å)	X-O-X (°)
C_6H_6	C	-0.210		
	H	+0.210		
OEt_2	O	-0.612		
	Et	+0.306	1.409	113.1
O*t*Bu$_2$	O	-0.662		
	*t*Bu	+0.331	1.433	127.1
$O(SiMe_3)_2$	O	-1.255		
	$SiMe_3$	+0.628	1.656	145.5
	Si[c]	+1.873		
	Me[c]	-0.415		
$(BDI)Mg^+\cdot C_6H_6$	Mg	+1.820		
	C_6H_6	+0.050	2.368[b]	
	C[a]	-0.259	2.452	
	H[a]	+0.262		
$(BDI)Mg^+\cdot OEt_2$	Mg	+1.830	1.986	
	OEt_2	+0.066		
	O	-0.757		
	Et	+0.410	1.445	116.6
(BDI)Mg$^+\cdot$O*t*Bu$_2$	Mg	+1.837	2.000	
	O*t*Bu$_2$	+0.051		
	O	-0.828		
	*t*Bu	+0.440	1.485	126.9
$(BDI)Mg^+\cdot O(SiMe_3)_2$	Mg	+1.852	1.992	
	$O(SiMe_3)_2$	+0.047		
	O	-1.367		
	$SiMe_3$	0.707	1.739	129.9
	Si[c]	+1.860		
	Me[c]	-0.385		

[a] Closest Mg···CH contact
[b] Mg···centroid
[c] Average value

Comparison of bond lengths (DFT/X-ray) in (BDI)Mg

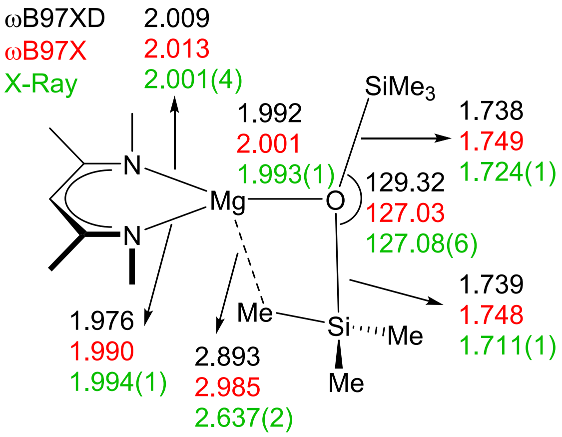


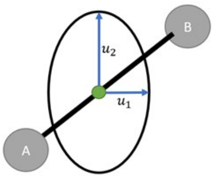
Figure S14. Comparison between structures of [(BDI)Mg$^+\cdot O(SiMe_3)_2$] calculated at the ωB97XD level (including dispersion) in black and ωB97X (without dispersion) in red and the crystal structure in green (distances in Å).

Table S6. Atoms-In-Molecules Analysis (AIM) of selected complexes and ligands.[a]

Bond	**ρ [au]**	**Δ [au]**	**ε [a.u.]**	**DI [a.u.]**
(BDI)Mg$^+$·O(SiMe$_3$)$_2$				
Mg-N	0.0570 0.0532	+0.3600 +0.3950	0.1000 0.1142	0.1852 0.2071
Mg-O	0.0453	+0.3519	0.0592	0.1564
O-Si	0.1036 0.1039	+0.6249 +0.6231	0.0190 0.0202	0.3426 0.3419
O(SiMe$_3$)$_2$				
O-Si	0.1247 0.1247	+0.8703; +0.8703	0.0125; 0.0124	0.3948 0.3942
(BDI)Mg$^+$·OEt$_2$				
Mg-N	0.0584 0.0572	+0.4086 +0.3947	0.1123 0.1078	0.2105 0.2033
Mg-O	0.0449	+0.3560	0.1210	0.1458
O-CH$_2$	0.2293 0.2280	-0.2097 -0.2096	0.0505 0.0475	0.8083 0.8068
OEt$_2$				
O-CH$_2$	0.2612 0.2612	-0.4136 -0.4136	0.0465 0.0465	0.8692 0.8691
(BDI)Mg$^+$·OtBu$_2$				
Mg-N	0.0538 0.0561	+0.3643 +0.3865	0.1035 0.1111	0.1895 0.2011
Mg-O	0.0447	+0.3416	0.1169	0.1455
O-C	0.2114 0.2103	-0.3017 -0.2904	0.0197 0.0179	0.7638 0.7585
OtBu$_2$				
O-C	0.2454 0.2454	-0.4377 -0.4377	0.0200 0.0200	0.8230 0.8229

[a] ρ represents the electron density at the bond critical point (atomic units). Δ represents the negative Laplacian of ρ at the bond critical point (atomic units). ε represents the ellipticity parameter (arbitrary units). DI represents the delocalization index (arbitrary units).

Bond ellipticity



The bond ellipticity ε can be calculated from the eigenvalues λ_1 and λ_2 of the Hessian of ρ (electron density).[S17] In the eigenplane spanned by the eigenvectors u_1 and u_2, the eigenvalues λ_1 and λ_2 give the curvature of ρ near the BCP. The ellipticity is defined as:

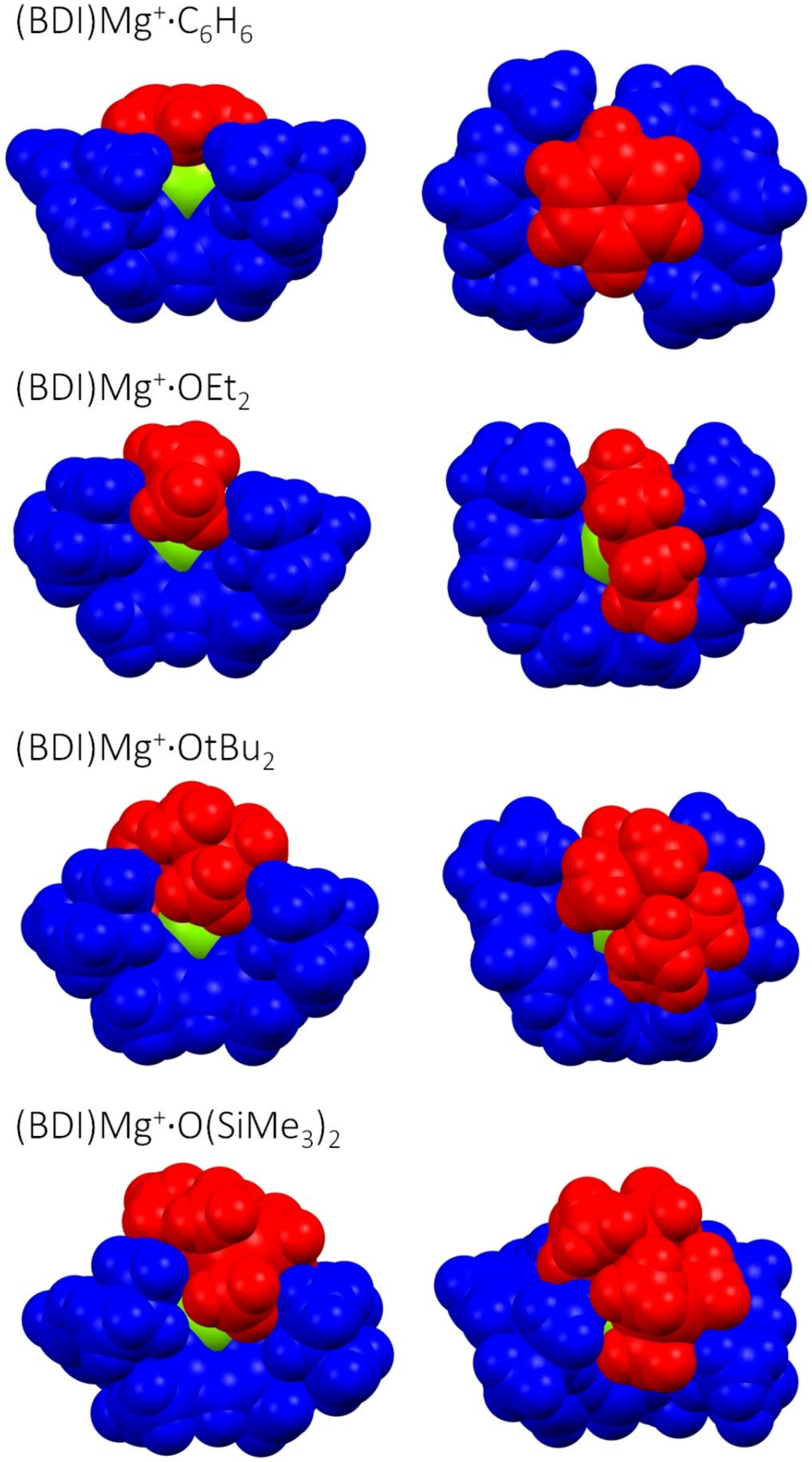
$$\varepsilon = \frac{\lambda_1}{\lambda_2} - 1$$

Typical values of ε are
C-C = 0.014
C=C = 0.298
C≡C = 0.000

Benzene = 0.176

The Delocalization Index (DI)

The DI is calculated from the Fermi hole density and can be correlated to the bond order. Here the electronegativity is closely related with the correspondence between DI and formal bond order. For more information on the mathematical and physical description see Firme *et al*.. [S18]
In general it can be said that a formal single bond between two atoms of same electronegativity has an DI of close to one (polar bonds have a smaller DI). A formal double bond has a DI of close to two while a formal triple bond has an DI approximately 3.



$(BDI)Mg^{+}\cdot C_6H_6$

$(BDI)Mg^{+}\cdot OEt_2$

$(BDI)Mg^{+}\cdot OtBu_2$

$(BDI)Mg^{+}\cdot O(SiMe_3)_2$

Figure S15. Space-filling models of the calculated cationic complexes (without anion interaction) using van der Waals atomic radii (blue = BDI, green = Mg, red = solvent).

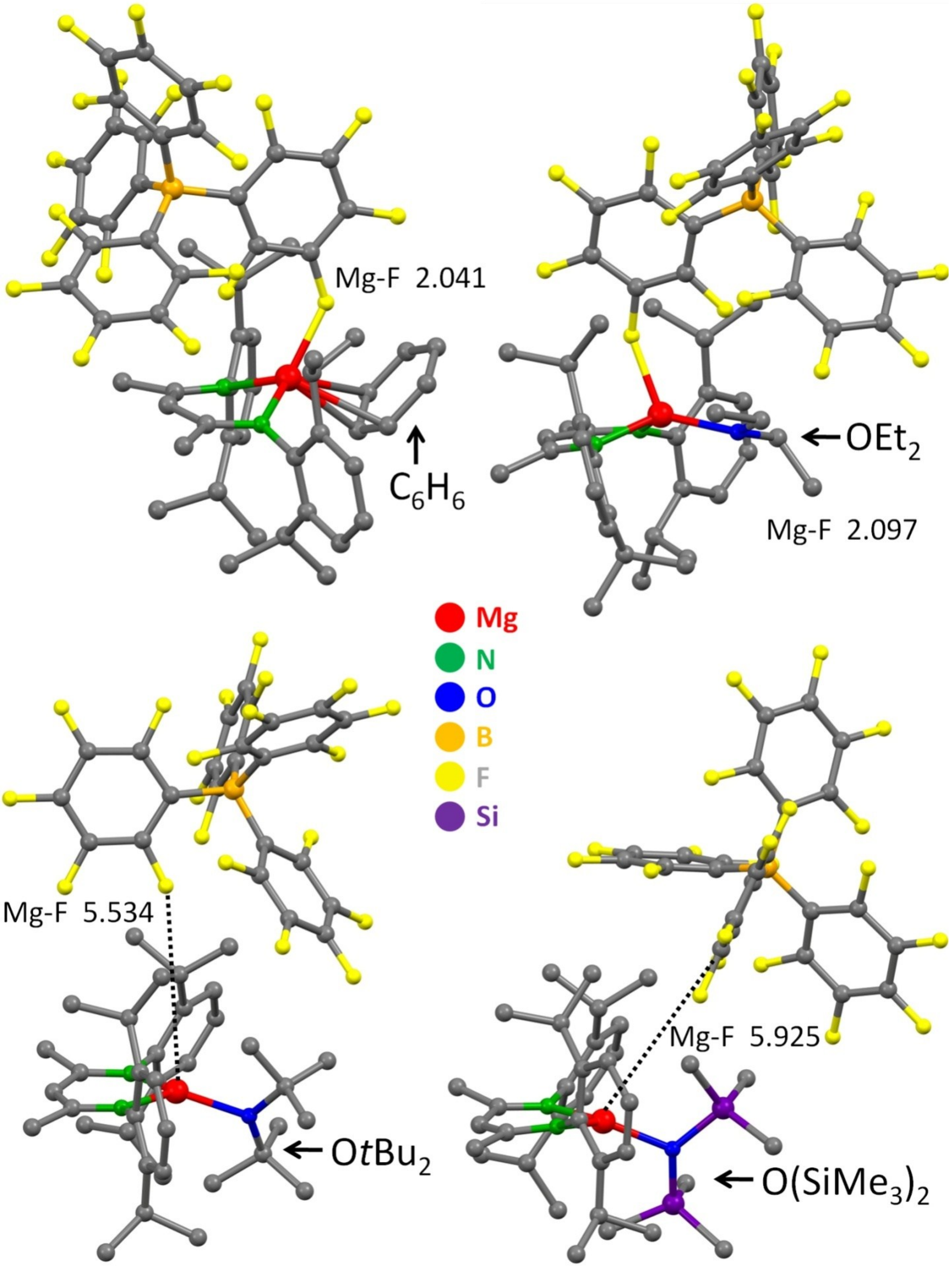


Figure S16. Calculated structures of cation-anion pairs showing the shortest Mg···F contact (Å). This cation-anion contact (Mg···F) increases along the row: C_6H_6 < OEt_2 < O*t*Bu_2< $O(SiMe_3)_2$

3. References

[S1] J. Pahl, S. Brand, H. Elsen, S. Harder, *Chem. Commun.* 2018, accepted article, DOI: 10.1039/C8CC04083D.

[S2] C. E. Radzewich, I. A. Guzei, R. F. Jordan, *J. Am. Chem. Soc.* 1999, **121**, 8673–8674.

[S3] O. V. Dolomanov, L. J. Bourhis, R.J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.,* 2009, **42**, 339–341.

[S4] G. M. Sheldrick, *Acta Cryst. A,* 2015, **71**, 3–8.

[S5] G. M. Sheldrick, *Acta Cryst. C,* 2015, **71**, 3–8.

[S6] H. Schmidbaur, *J. Am. Chem. Soc.,* 1963, **85**, 2336–2337.

[S7] These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures; CCDC: C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Cryst. B,* 2016, **72**, 171-179.

[S8] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16 Rev. A.03, Wallingford CT, **2016**.

[S9] J. Chai and M. Head-gordon, *Phys. Chem. Chem. Phys.,* 2008, **10**, 6615–6620.

[S10] W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986**.**

[S11] R. C. Binning and L. A. Curtiss, *J. Comput. Chem.,* 1990, **11**, 1206–1216.

[S12] T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. v. R. Schleyer, *J. Comp. Chem.*, 1983, **4**, 294–301.

[S13] A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.,* 1985, **83**, 735–746.

[S14] R. F. W. Bader, *Chem. Rev.* **1991**, *91*, 893–928

[S15] AIMAll V16, T. A. Keith, **2016**

[S16] N. van Eikema Hommes, *Molecule*, Erlangen, **2016**.

[S17] *“Atoms in Molecules, An Introduction”,* Paul Popelier, Pearson Education Limited, **2000**, ISBN: 0-582-36798-0”.

[S18] C. L. Firme, O. A. C. Antunes, P. M. Esteves, *Chemical Physical Letters*, **2009**, 468, 129-133.