

**Exposing Elusive Cationic Magnesium-Chloro Aggregates in Aluminate
Complexes Through Donor Control**

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SUPPORTING INFORMATION

Table S1 Selected bond lengths (Å) and angles (°) of the anionic moieties of complexes **1-4**

	1	2	3	4
N1-Al1	1.8172(16)	1.817 (3)	1.812(4)	1.819(3)
N1-C1	1.441(2)	1.438(4)	1.447(6)	1.442(4)
N1-Si1	1.7343(16)	1.741(2)	1.743(4)	1.735(3)
Al1-Cl1	2.1483(7)	2.1640(14)	2.168(2)	2.1524(14)
Al1-Cl2	2.1582(7)	2.1469(13)	2.150(2)	2.1396(13)
Al1-Cl3	2.1648(7)	2.1520(14)	2.154(2)	2.1646(14)
C1-N1-Si1	116.59(12)	117.54(19)	118.0(3)	116.5(2)
Al1-N1-Si1	121.98(9)	122.75(14)	125.8(2)	123.75(14)
C1-N1-Al1	121.43(12)	119.66(19)	116.0(3)	119.6(2)
N1-Al1-Cl1	113.00(6)	116.67(10)	113.06(16)	111.25(10)
N1-Al1-Cl2	111.32(6)	110.17(9)	112.34(15)	111.41(9)
N1-Al1-Cl3	112.50(6)	109.52(9)	113.25(16)	114.80(10)
Cl1-Al1-Cl2	107.19(3)	105.99(6)	107.22(9)	108.54(6)
Cl1-Al1-Cl3	106.74(3)	104.40(6)	104.00(8)	104.75(6)
Cl2-Al1-Cl3	105.65(3)	109.81(6)	106.35(9)	105.65(6)

Table S2 Selected bond lengths of cationic moieties of complexes **1-4** (D = Lewis donor atom).

	1 (D = O)		2 (D = N)	3 (D = N)			4 (D = O)		
	Mg1	Mg2	Mg1	Mg1	Mg2	Mg3	Mg1	Mg2	Mg3
Mg-Cl4	2.4819(8)	2.5196(8)	2.3229(13)	2.508(2)	2.495(2)	-	2.4868(14)	2.4932(16)	-
Mg-Cl5	2.4759(8)	2.5309(8)	-	-	2.483(2)	2.497(2)	-	2.4908(15)	2.5086(14)
Mg-Cl6	2.5083(8)	2.4997(8)	-	2.460(2)	-	2.491(2)	2.4793(13)	-	2.4988(13)
Mg-Cl7	-	-	-	2.606(2)	2.576(2)	2.544(2)	2.5487(14)	2.5449(15)	2.5847(13)
Mg-Cl8	-	-	-	2.555(2)	2.555(2)	2.600(2)	2.5706(13)	2.5440(13)	2.5401(13)
Mg-D1	2.1063(14)	-	-	-	-	-	2.044(3)	-	-
Mg-D2	2.0840(15)	-	2.219(3)	2.186(4)	-	-	2.048(3)	-	-
Mg-D3	2.0688(15)	-	2.198(3)	2.220(4)	-	-	-	2.022(4)	-
Mg-D4	-	2.0674(15)	2.169(3)	-	2.190(4)	-	-	2.032(3)	-
Mg-D5	-	2.0906(15)	2.173(3)	-	2.200(4)	-	-	-	2.040(3)
Mg-D6	-	2.0678(15)	-	-	-	2.176(4)	-	-	2.021(3)
Mg-D7	-	-	-	-	-	2.169(4)	-	-	-

Table S3 Selected bond angles of cation of complex **1**.

O-Mg-Cl(trans)		O-Mg-Cl(cis)		O-Mg-Cl(cis)		Cl-Mg-Cl		O-Mg-O		Mg-Cl-Mg	
O1-Mg1-Cl5	174.70(5)	O1-Mg1-Cl4	89.66(4)	O4-Mg2-Cl5	93.05(5)	Cl4-Mg1-Cl5	85.06(3)	O1-Mg1-O2	86.69(6)	Mg1-Cl4-Mg2	78.05(2)
O2-Mg1-Cl6	177.46(5)	O1-Mg1-Cl6	95.51(4)	O4-Mg2-Cl6	93.71(5)	Cl4-Mg1-Cl6	85.87(3)	O1-Mg1-O3	92.26(6)	Mg1-Cl5-Mg2	77.95(2)
O3-Mg1-Cl4	177.72(5)	O2-Mg1-Cl4	95.40(5)	O5-Mg2-Cl4	90.73(5)	Cl5-Mg1-Cl6	84.65(3)	O2-Mg1-O3	85.92(6)	Mg1-Cl6-Mg2	77.94(3)
O4-Mg2-Cl4	176.14(5)	O2-Mg1-Cl5	93.27(5)	O5-Mg2-Cl6	93.27(5)	Cl4-Mg2-Cl5	83.15(3)	O4-Mg2-O5	93.03(6)		
O5-Mg2-Cl5	173.36(5)	O3-Mg1-Cl5	93.02(5)	O6-Mg2-Cl4	92.46(5)	Cl4-Mg2-Cl6	85.25(2)	O4-Mg2-O6	88.37(6)		
O6-Mg2-Cl6	176.11(5)	O3-Mg1-Cl6	92.73(5)	O6-Mg2-Cl5	92.93(5)	Cl5-Mg2-Cl6	83.69(2)	O5-Mg2-O6	89.90(6)		

Table S4 Selected bond angles of cation of complex **2**.

N_{ax}-Mg-Cl		N_{eq}-Mg-Cl		N_{ax}-Mg-N_{eq}		N_{eq}-Mg-N_{eq}	
N2-Mg1-Cl4	178.28(9)	N3-Mg1-Cl4	98.18(8)	N2-Mg1-N3	80.24(10)	N3-Mg1-N4	115.88(11)
		N4-Mg1-Cl4	99.64(9)	N2-Mg1-N4	81.71(11)	N3-Mg1-N5	122.09(11)
		N5-Mg1-Cl4	99.11(8)	N2-Mg1-N5	81.22(10)	N4-Mg1-N5	114.87(10)

Table S5 Selected bond angles of cation of complex **3**.

N-Mg-Cl(μ_3-trans)	N-Mg-Cl(μ_2-cis)	Cl(μ_2)-Mg-Cl(μ_3)	Cl(μ_2)-Mg-Cl(μ_2)	Mg-Cl(μ_3)-Mg
N2-Mg1-Cl8 176.27(14)	N2-Mg1-Cl4 95.05(13)	Cl4-Mg1-Cl7 80.89(6)	Cl4-Mg1-Cl6 157.72(9)	Mg1-Cl7-Mg2 79.19(6)
N3-Mg1-Cl7 179.30(14)	N2-Mg1-Cl6 100.04(13)	Cl4-Mg1-Cl8 81.26(7)	Cl4-Mg2-Cl5 157.00(9)	Mg1-Cl7-Mg3 78.71(6)
N5-Mg2-Cl7 179.05(14)	N3-Mg1-Cl4 99.02(13)	Cl6-Mg1-Cl7 81.48(7)	Cl5-Mg3-Cl6 157.21(9)	Mg2-Cl7-Mg3 80.03(6)
N4-Mg2-Cl8 178.38(13)	N3-Mg1-Cl6 98.77(13)	Cl6-Mg1-Cl8 83.64(7)	Cl(μ_3)-Mg-Cl(μ_3)	Mg1-Cl8-Mg2 80.54(7)
N6-Mg3-Cl8 178.73(15)	N4-Mg2-Cl4 97.17(12)	Cl4-Mg2-Cl7 81.73(7)	Cl7-Mg1-Cl8 84.61(6)	Mg1-Cl8-Mg3 78.64(6)
N7-Mg3-Cl7 178.17(14)	N4-Mg2-Cl5 99.92(12)	Cl4-Mg2-Cl8 81.49(6)	Cl7-Mg2-Cl8 85.21(6)	Mg2-Cl8-Mg3 79.38(6)
N-Mg-Cl(μ_3-cis)	N5-Mg2-Cl4 99.12(13)	Cl5-Mg2-Cl7 81.42(6)	Cl7-Mg3-Cl8 84.95(7)	Mg-Cl(μ_2)-Mg
N2-Mg1-Cl7 95.30(13)	N5-Mg2-Cl5 97.88(13)	Cl5-Mg2-Cl8 81.62(6)	N-Mg-N	Mg1-Cl4-Mg2 82.62(7)
N3-Mg1-Cl8 96.07(13)	N6-Mg3-Cl5 98.63(14)	Cl5-Mg3-Cl7 81.79(7)	N2-Mg1-N3 84.01(16)	Mg2-Cl5-Mg3 82.77(7)
N5-Mg2-Cl8 95.33(13)	N6-Mg3-Cl6 98.98(14)	Cl5-Mg3-Cl8 80.48(7)	N4-Mg2-N5 83.95(16)	Mg1-Cl6-Mg3 82.56(7)
N4-Mg2-Cl7 95.52(12)	N7-Mg3-Cl5 99.97(13)	Cl6-Mg3-Cl7 82.13(7)	N6-Mg3-N7 84.40(17)	
N6-Mg3-Cl7 95.83(13)	N7-Mg3-Cl6 96.04(13)	Cl6-Mg3-Cl8 82.11(7)		
N7-Mg3-Cl8 94.85(13)				

Table S6 Selected bond angles of cation of complex **4**.

O-Mg-Cl(μ_3-trans)	O-Mg-Cl(μ_2-cis)	Cl(μ_2)-Mg-Cl(μ_3)	Cl(μ_2)-Mg-Cl(μ_2)	Mg-Cl(μ_3)-Mg
O1-Mg1-Cl7 178.02(9)	O1-Mg1-Cl4 96.33(9)	Cl4-Mg1-Cl7 82.36(5)	Cl4-Mg1-Cl6 157.67(5)	Mg1-Cl7-Mg2 80.19(4)
O2-Mg1-Cl8 175.42(9)	O1-Mg1-Cl6 98.20(8)	Cl4-Mg1-Cl8 81.05(4)	Cl4-Mg2-Cl5 157.80(6)	Mg1-Cl7-Mg3 80.02(4)
O3-Mg2-Cl8 175.12(15)	O2-Mg1-Cl4 98.66(9)	Cl6-Mg1-Cl7 82.62(4)	Cl5-Mg3-Cl6 156.29(5)	Mg2-Cl7-Mg3 80.07(4)
O4-Mg2-Cl7 178.60(10)	O2-Mg1-Cl6 98.22(9)	Cl6-Mg1-Cl8 80.95(4)	Cl(μ_3)-Mg-Cl(μ_3)	Mg1-Cl8-Mg2 79.80(4)
O5-Mg3-Cl7 175.84(9)	O3-Mg2-Cl4 94.13(13)	Cl4-Mg2-Cl7 82.31(5)	Cl7-Mg1-Cl8 83.67(4)	Mg1-Cl8-Mg3 80.45(4)
O6-Mg3-Cl8 176.13(10)	O3-Mg2-Cl5 103.45(14)	Cl4-Mg2-Cl8 81.46(5)	Cl7-Mg2-Cl8 84.28(4)	Mg2-Cl8-Mg3 80.94(4)
O-Mg-Cl(μ_3-cis)	O4-Mg2-Cl4 97.58(10)	Cl5-Mg2-Cl7 82.12(5)	Cl7-Mg3-Cl8 83.56(4)	Mg-Cl(μ_2)-Mg
O1-Mg1-Cl8 94.67(8)	O4-Mg2-Cl5 97.60(9)	Cl5-Mg2-Cl8 81.33(4)	O-Mg-O	Mg1-Cl4-Mg2 82.41(5)
O2-Mg1-Cl7 91.76(8)	O5-Mg3-Cl5 96.17(9)	Cl5-Mg3-Cl7 80.99(4)	O1-Mg1-O2 89.91(11)	Mg2-Cl5-Mg3 82.60(4)
O3-Mg2-Cl7 97.25(13)	O5-Mg3-Cl6 100.34(9)	Cl5-Mg3-Cl8 81.06(4)	O3-Mg2-O4 84.15(15)	Mg1-Cl6-Mg3 83.06(4)
O4-Mg2-Cl8 94.32(9)	O6-Mg3-Cl5 99.26(9)	Cl6-Mg3-Cl7 81.52(4)	O5-Mg3-O6 90.77(12)	
O5-Mg3-Cl8 93.03(8)	O6-Mg3-Cl6 97.42(9)	Cl6-Mg3-Cl8 81.18(4)		
O6-Mg3-Cl7 92.68(9)				

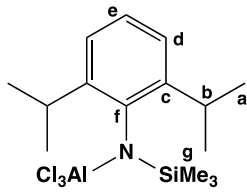
Table S7 Crystallographic data and refinement details for complexes **1-5**.

Compound	1	2	3^a	4	5
Formula	C ₃₉ H ₇₄ O ₆ Mg ₂ Cl ₆ NSiAl	C ₂₇ H ₅₆ MgCl ₄ N ₅ SiAl	C ₃₃ H ₇₄ Mg ₃ Cl ₈ N ₇ SiAl	C ₄₅ H ₈₆ O ₆ Mg ₃ Cl ₈ NSiAl	C ₉ H ₂₃ Cl ₂ MgN ₃
Formula weight	969.42	671.96	980.59	1148.74	268.51
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P 2 ₁ /n	P 2 ₁ /n	P 2 ₁ /c	P 2 ₁ /n	P 2 ₁ /c
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073
<i>a</i> /Å	19.5415(9)	17.4285(12)	19.692(2)	13.3260(3)	8.3278(4)
<i>b</i> /Å	13.8802(5)	13.2180(7)	16.2309(12)	14.1674(3)	29.5439(14)
<i>c</i> /Å	19.5602(8)	17.5260(12)	16.9709(15)	32.6193(8)	11.9786(5)
β /°	110.428(5)	114.337(8)	107.610(11)	95.436(2)	101.773(5)
Volume/Å ³	4971.9(4)	3678.7(5)	5170.0(8)	6130.7(2)	2885.2(2)
<i>Z</i>	4	4	4	4	8
Reflns. collected	54746	40914	11759	57615	15977
Unique reflns.	12079	4860	11759	14559	6762
R _{int}	0.0392	0.1136	^a	0.0383	0.0218
Obs. Reflns. [<i>I</i> > 2σ(<i>I</i>)]	9222	4509	6255	10691	5779
Goodness of fit	1.052	1.022	0.798	1.065	1.0452

$R[F^2 > 2\sigma], F$	0.0406	0.0586	0.0508	0.0651	0.0356
R_w (all data), F^2	0.1011	0.1135	0.0992	0.1620	0.0765
Largest diff. peak/hole $e/\text{\AA}^{-3}$	0.69/-0.60	0.79/-0.81	0.48/-0.39	0.97/-0.77	0.42/-0.49
CCDC number	1431065	1431066	1431067	1431068	1443823

^a Crystals of compound **3** were found to be twinned. The raw data was processed as originating from two crystals related by the matrix 1.0017 - 0.0014 0.7028 -0.0009 -1.0026 0.0008 0.0002 -0.0005 -1.0013 to give a hklf 5 formatted file. Refinement against this file gave a model that was far superior than a model refined against a dataset with no twin treatment. The BASF parameter refined to 0.3918(6).

Table S8 ¹H (top) and ¹³C (bottom) NMR data for anionic moieties of complexes **1-4**.

	1 (OC ₄ D ₈)	2 (OC ₄ D ₈)	3 (OC ₄ D ₈)	4 (OC ₄ D ₈)	free amine (OC ₄ D ₈)
a	1.13 26.1/25.2	1.15 26.3/25.2	1.14 26.2	1.13 26.1/25.2	1.17 24.1
b	3.88 27.8	3.88 27.9	3.88 27.9	3.89 27.8	3.51 28.9
c	- 147.6	- 147.6	- 147.6	- 147.6	- 145.5
d	6.83 123.0	6.78 123.2	6.85 123.0	6.84 123.0	6.98 123.4
e	6.74 122.2	6.75 122.5	6.75 122.3	6.74 122.2	6.93 124.3
f	- 147.6	- 147.4	- 147.6	- 147.6	- 140.6
g	0.04 3.1	0.05 3.1	0.04 3.1	0.05 3.1	0.12 1.0

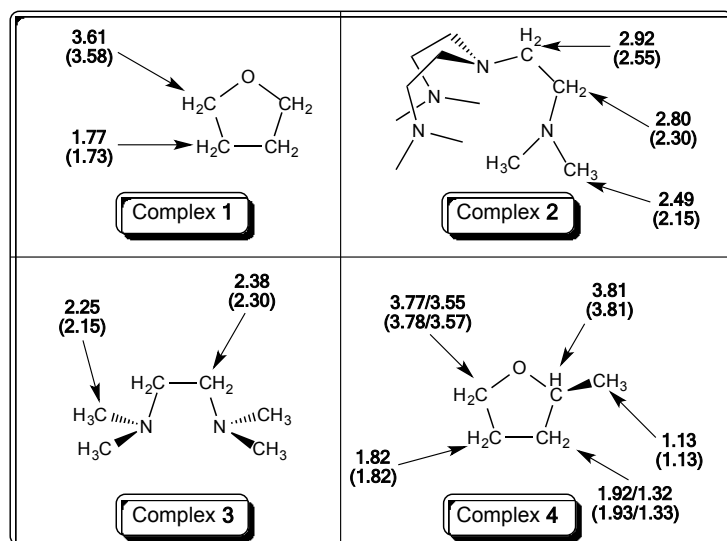


Figure S1 ^1H NMR resonances of donors in ppm (value in parentheses represents free donor) recorded in d_8 -THF at 21°C.

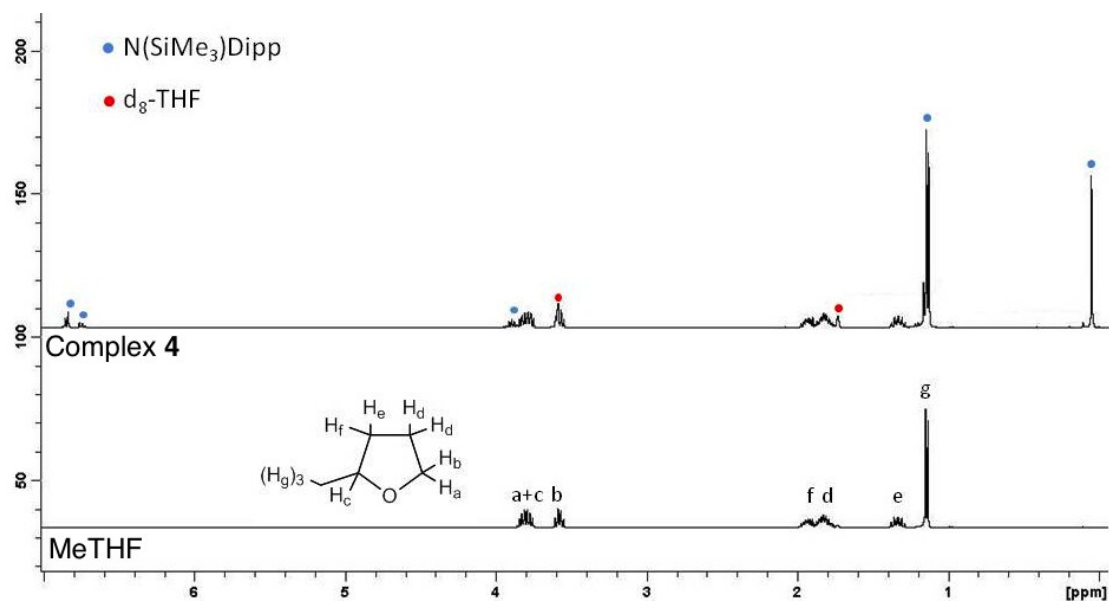


Figure S2 ^1H NMR spectra of Complex 4 (top) and free MeTHF, recorded in d_8 -THF at 21°C.

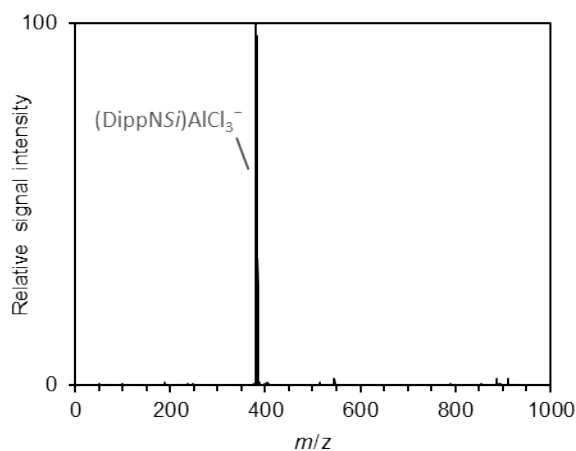


Figure S3 Negative-ion mode ESI mass spectrum of a 20-mM solution of $[(\text{Dipp})(\text{Me}_3\text{Si})\text{NAlCl}_3]^- [\text{MgCl} \cdot \text{Me}_6\text{TREN}]^+$ (**2**) in THF ($\text{Si} = \text{SiMe}_3$).

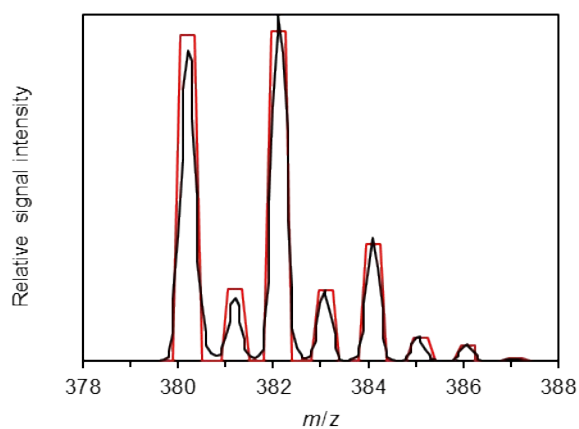


Figure S4 Comparison of observed (black) and simulated (red) isotope pattern of $[(\text{Dipp})(\text{Me}_3\text{Si})\text{NAlCl}_3]^-$.

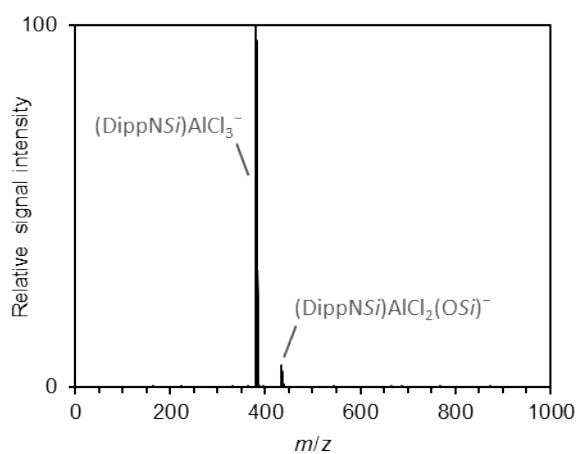


Figure S5 Negative-ion mode ESI mass spectrum of a 20-mM solution of $[(\text{Dipp})(\text{Me}_3\text{Si})\text{NAlCl}_3]^- [\text{Mg}_2(\mu^2\text{-Cl})_3 \cdot 6\text{THF}]^+$ (**1**) in THF.

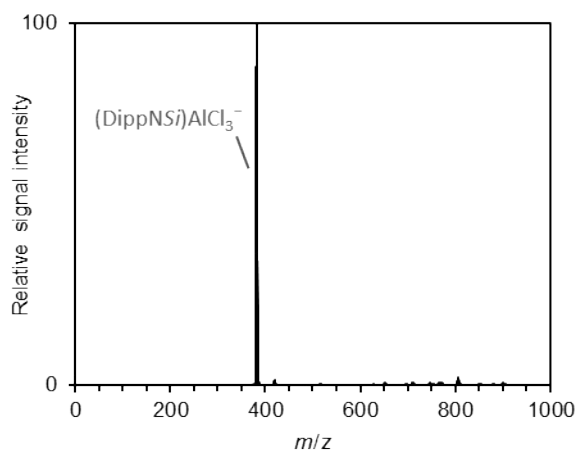


Figure S6 Negative-ion mode ESI mass spectrum of a saturated solution ($c \leq 10$ mM) of $[(\text{Dipp})(\text{Me}_3\text{Si})\text{NAlCl}_3]^- [\text{Mg}_3(\mu^3\text{-Cl})_2(\mu^2\text{-Cl})_3 \cdot 3\text{TMEDA}]^+$ (**3**) in THF.

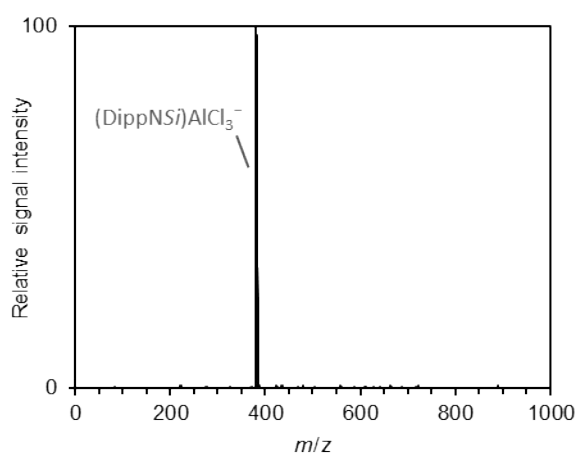


Figure S7 Negative-ion mode ESI mass spectrum of a 20-mM solution of $[(\text{Dipp})(\text{Me}_3\text{Si})\text{NAlCl}_3]^- [\text{Mg}_3(\mu^3\text{-Cl})_2(\mu^2\text{-Cl})_3 \cdot 6\text{MeTHF}]^+$ (**4**) in THF.

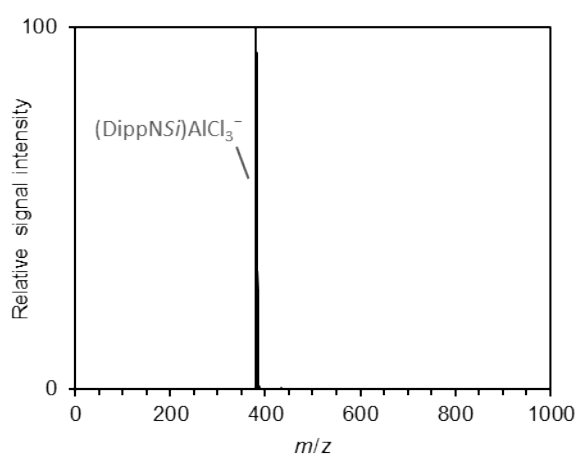


Figure S8 Negative-ion mode ESI mass spectrum of a 20-mM solution of $[(\text{Dipp})(\text{Me}_3\text{Si})\text{NAlCl}_3]^- [\text{Mg}_2(\mu^2\text{-Cl})_3 \cdot 6\text{THF}]^+$ (**1**) in MeTHF.

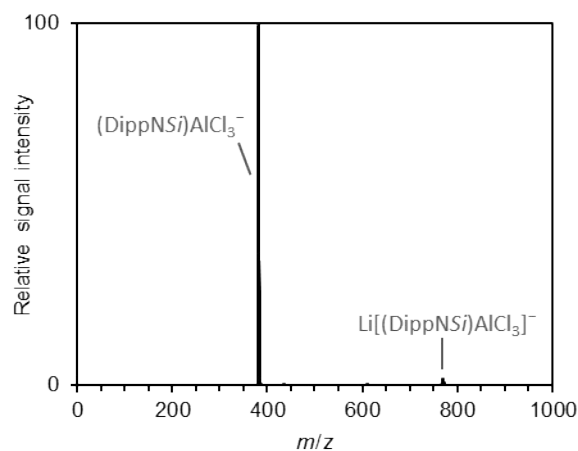


Figure S9 Negative-ion mode ESI mass spectrum of a 20-mM solution of $[(\text{Dipp})(\text{Me}_3\text{Si})\text{NAlCl}_3]^- [\text{Mg}_3(\mu^3\text{-Cl})_2(\mu^2\text{-Cl})_3 \cdot 6\text{MeTHF}]^+$ (**4**) in MeTHF.

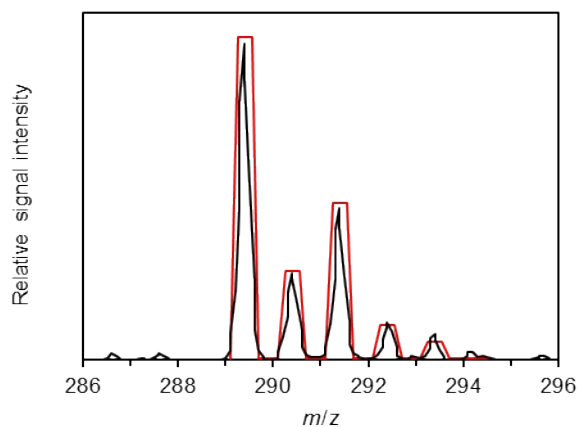


Figure S10 Comparison of observed (black) and simulated (red) isotope pattern of $\text{MgCl}(\text{L})^+$ ($\text{L} = \text{Me}_6\text{TREN}$).

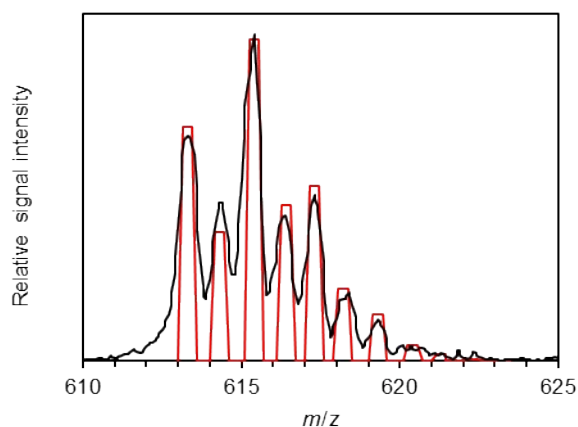


Figure S11 Comparison of observed (black) and simulated (red) isotope pattern of $\text{Mg}_2\text{Cl}_3(\text{L})_2^+$ ($\text{L} = \text{Me}_6\text{TREN}$).

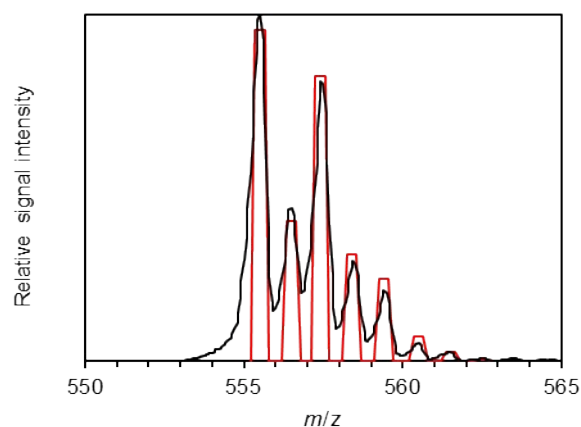


Figure S12 Comparison of observed (black) and simulated (red) isotope pattern of $\text{MgCl}(\text{L})_2 \cdot \text{HCl}^+$ ($\text{L} = \text{Me}_6\text{TREN}$).

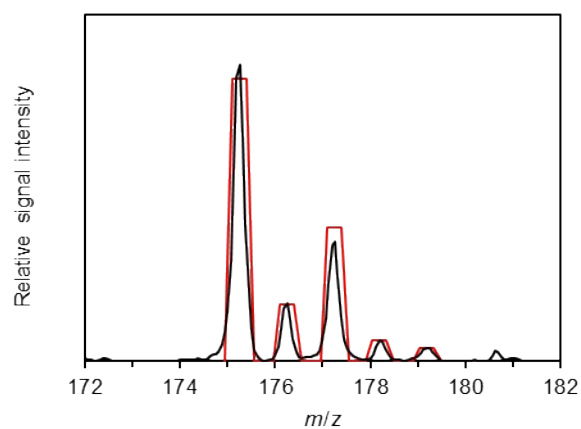


Figure S13 Comparison of observed (black) and simulated (red) isotope pattern of $\text{MgCl}(\text{TMEDA})^+$.

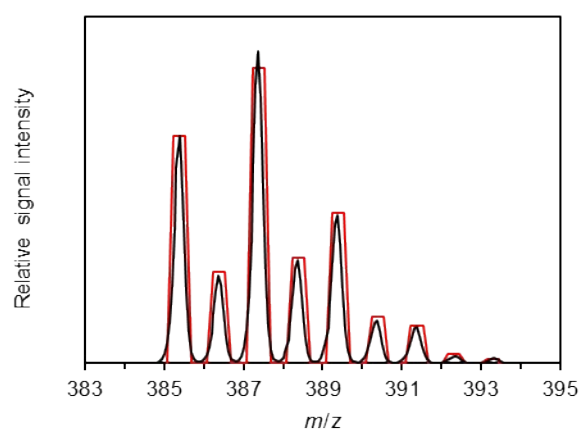


Figure S14 Comparison of observed (black) and simulated (red) isotope pattern of $\text{Mg}_2\text{Cl}_3(\text{TMEDA})_2^+$.

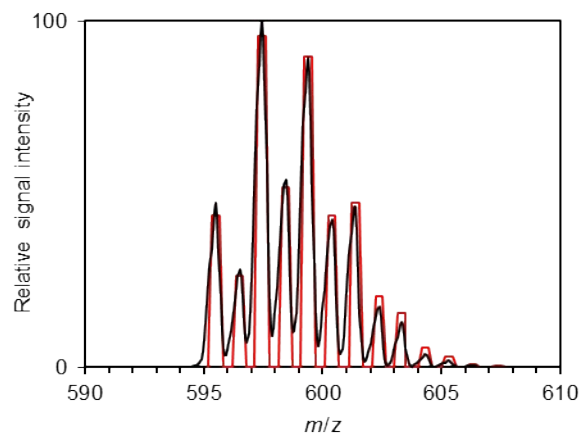


Figure S15 Comparison of observed (black) and simulated (red) isotope pattern of $\text{Mg}_3\text{Cl}_5(\text{TMEDA})_3^+$.

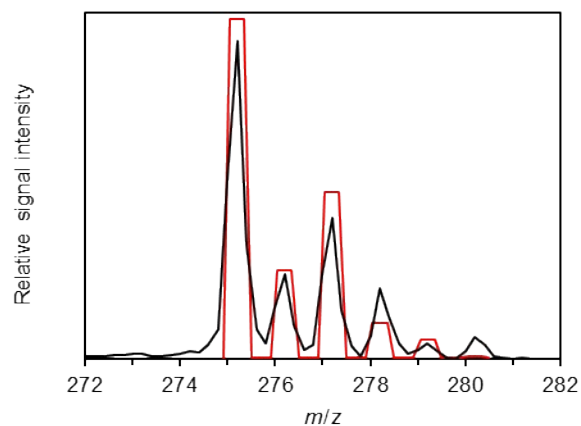


Figure S16 Comparison of observed (black) and simulated (red) isotope pattern of $\text{MgCl}(\text{THF})_3^+$.

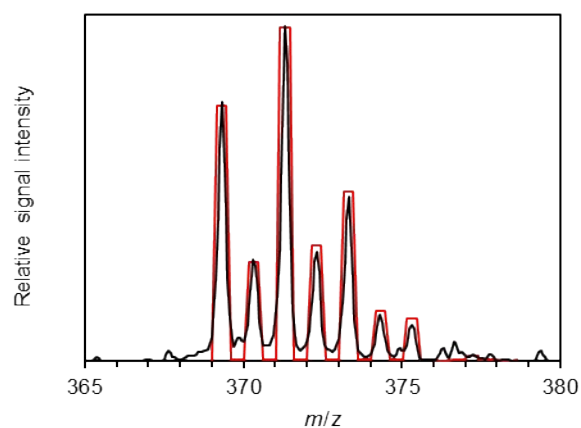


Figure S17 Comparison of observed (black) and simulated (red) isotope pattern of $\text{Mg}_2\text{Cl}_3(\text{THF})_3^+$.

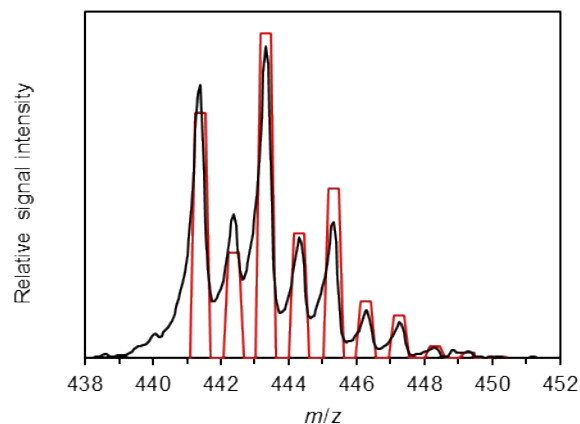


Figure S18 Comparison of observed (black) and simulated (red) isotope pattern of $\text{Mg}_2\text{Cl}_3(\text{THF})_4^+$.

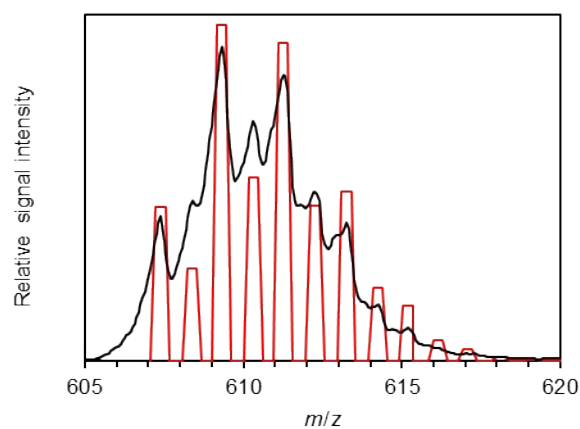


Figure S19 Comparison of observed (black) and simulated (red) isotope pattern of $\text{Mg}_3\text{Cl}_5(\text{THF})_5^+$.

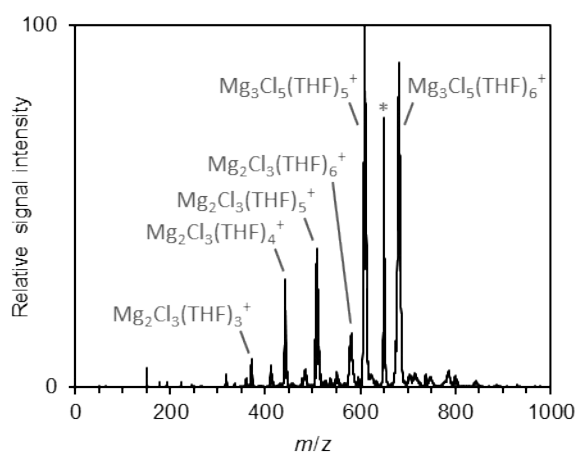


Figure S20 Positive-ion mode ESI mass spectrum of a 20-mM solution of $[(\text{Dipp})(\text{Me}_3\text{Si})\text{NAlCl}_3]^- [\text{Mg}_3(\mu^3\text{-Cl})_2(\mu^2\text{-Cl})_3 \cdot 6\text{MeTHF}]^+$ (**4**) in THF. The peak marked with an asterisk corresponds to an unknown contamination.

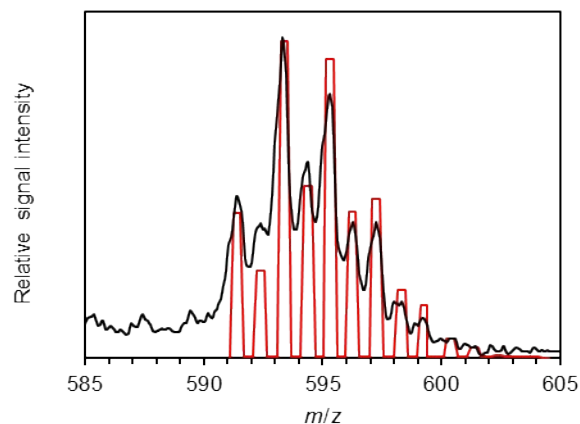


Figure S21 Comparison of observed (black) and simulated (red) isotope pattern of $\text{Mg}_3\text{Cl}_5(\text{MeTHF})_4^+$.

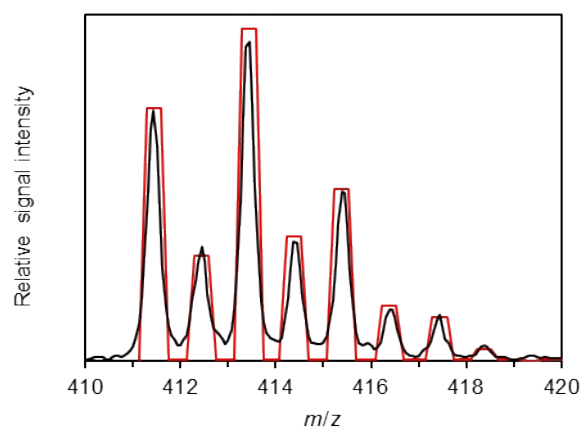


Figure S22 Comparison of observed (black) and simulated (red) isotope pattern of $\text{Mg}_2\text{Cl}_3(\text{MeTHF})_3^+$.

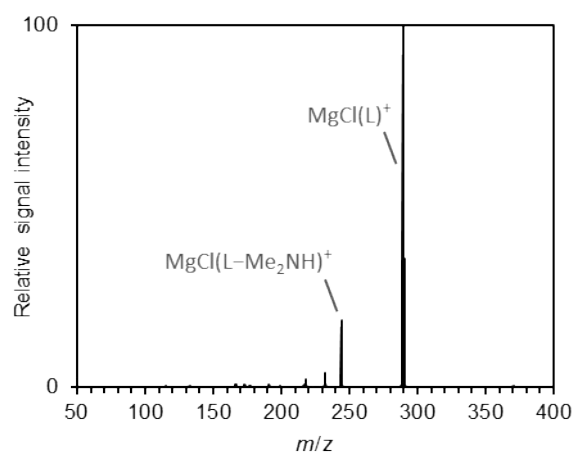


Figure S23 Mass spectrum of mass-selected $\text{MgCl}(\text{L})^+$ (m/z 289) and its fragment ions produced upon collision induced dissociation ($V_{\text{exc}} = 0.45$ V, $\text{L} = \text{Me}_6\text{TREN}$).

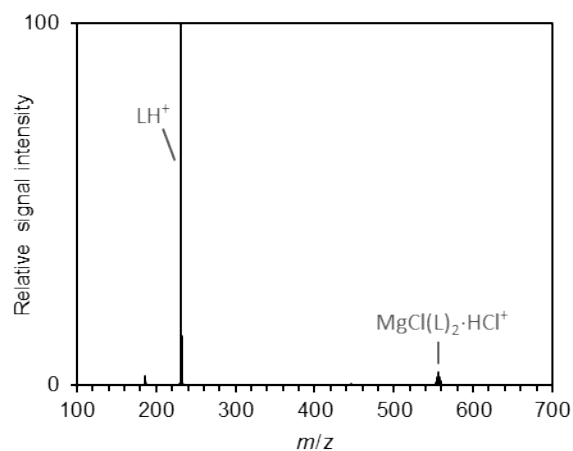


Figure S24 Mass spectrum of mass-selected $MgCl(L)_2 \cdot HCl^+$ (m/z 557) and its fragment ions produced upon collision induced dissociation ($V_{exc} = 0.40$ V, $L = Me_6TREN$).

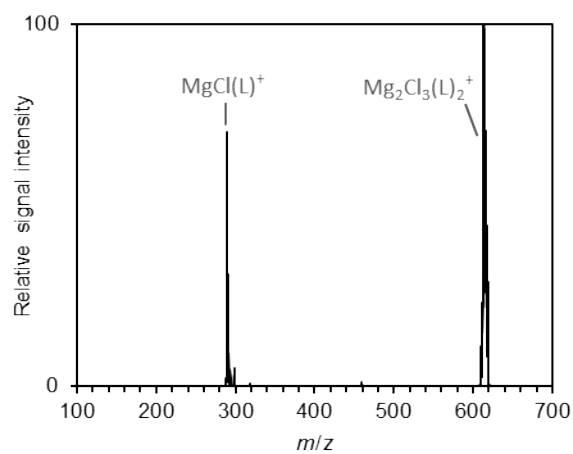


Figure S25 Mass spectrum of mass-selected $Mg_2Cl_3(L)_2^+$ (m/z 615) and its fragment ions produced upon collision induced dissociation ($V_{exc} = 0.30$ V, $L = Me_6TREN$).

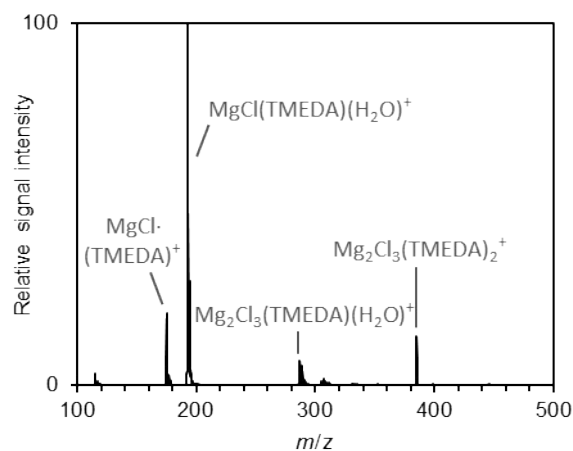


Figure S26 Mass spectrum of mass-selected $\text{Mg}_2\text{Cl}_3(\text{TMEDA})_2^+$ (m/z 387) and its fragment ions produced upon collision induced dissociation ($V_{\text{exc}} = 1.20$ V). The H_2O -containing ions result from an ion-molecule reaction with traces of background water present in the ion trap.

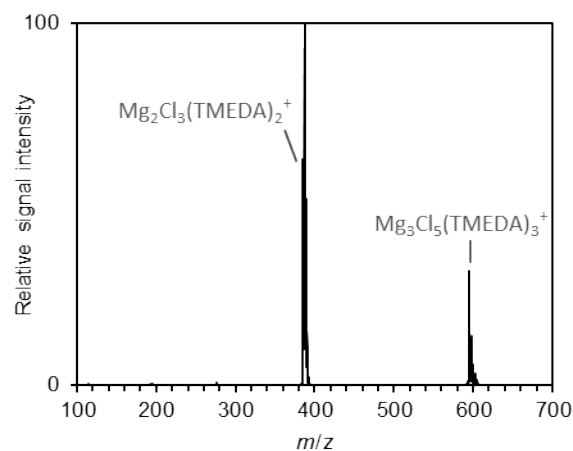


Figure S27 Mass spectrum of mass-selected $\text{Mg}_3\text{Cl}_5(\text{TMEDA})_3^+$ (m/z 599) and its fragment ions produced upon collision induced dissociation ($V_{\text{exc}} = 0.60$ V).

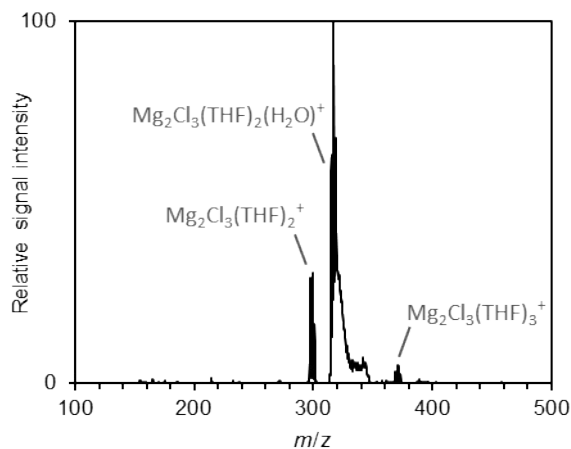


Figure S28 Mass spectrum of mass-selected $\text{Mg}_2\text{Cl}_3(\text{THF})_3^+$ (m/z 371) and its fragment ions produced upon collision induced dissociation ($V_{\text{exc}} = 0.40$ V). The H_2O -containing ion results from an ion-molecule reaction with traces of background water present in the ion trap.

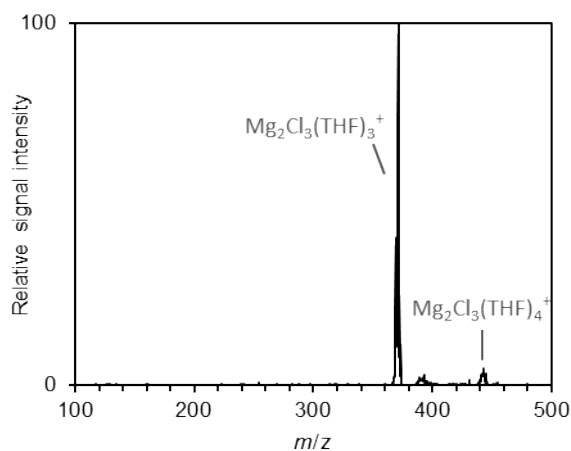


Figure S29 Mass spectrum of mass-selected $\text{Mg}_2\text{Cl}_3(\text{THF})_4^+$ ($m/z = 442$) and its fragment ions produced upon collision induced dissociation ($V_{\text{exc}} = 0.40$ V).

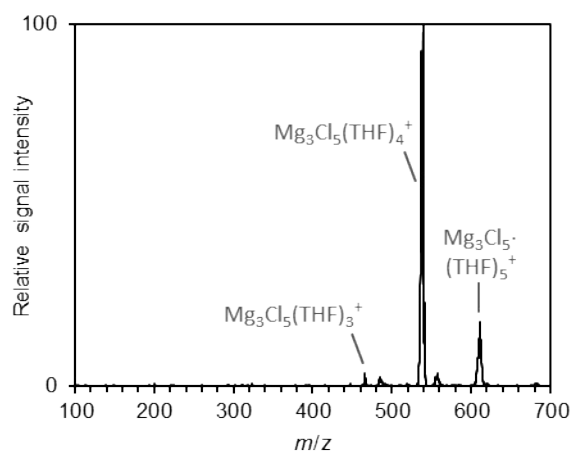


Figure S30 Mass spectrum of mass-selected $\text{Mg}_3\text{Cl}_5(\text{THF})_5^+$ ($m/z = 610$) and its fragment ions produced upon collision induced dissociation ($V_{\text{exc}} = 0.45$ V).

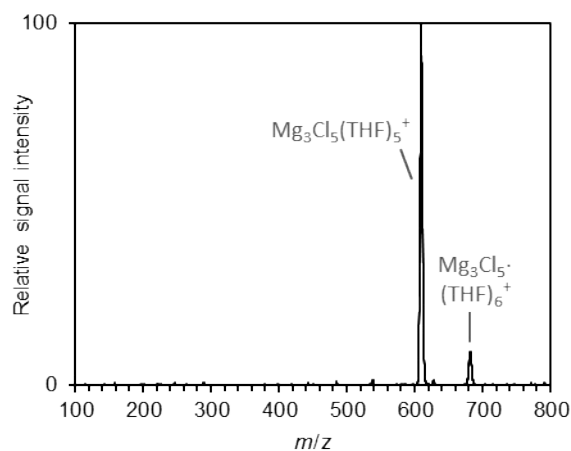


Figure S31 Mass spectrum of mass-selected $\text{Mg}_3\text{Cl}_5(\text{THF})_6^+$ ($m/z = 681$) and its fragment ions produced upon collision induced dissociation ($V_{\text{exc}} = 0.27$ V).

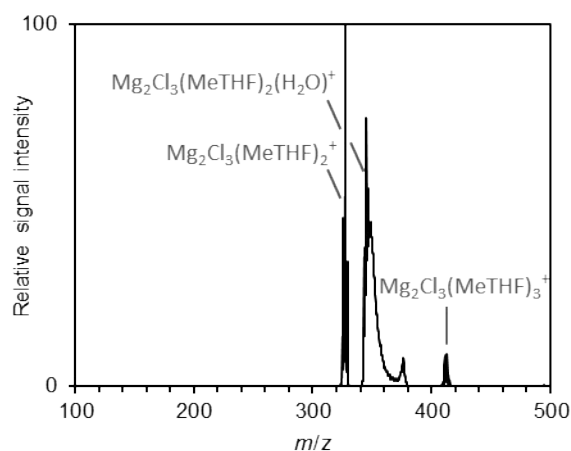


Figure S32 Mass spectrum of mass-selected $\text{Mg}_2\text{Cl}_3(\text{MeTHF})_3^+$ ($m/z = 413$) and its fragment ions produced upon collision induced dissociation ($V_{\text{exc}} = 0.40$ V). The H_2O -containing ion results from an ion-molecule reaction with traces of background water present in the ion trap.

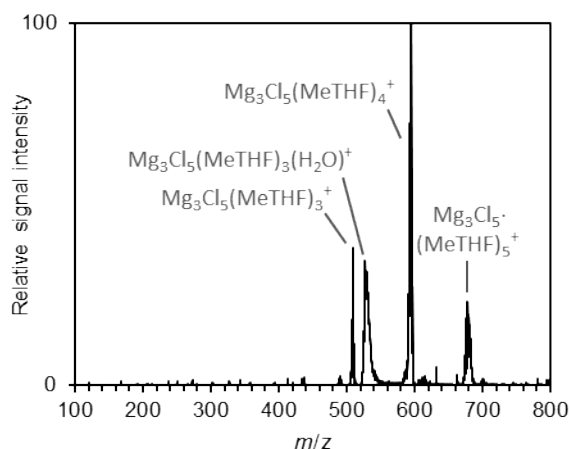


Figure S33 Mass spectrum of mass-selected $\text{Mg}_3\text{Cl}_5(\text{MeTHF})_5^+$ (m/z 679) and its fragment ions produced upon collision induced dissociation ($V_{\text{exc}} = 0.40$ V). The H_2O -containing ion results from an ion-molecule reaction with traces of background water present in the ion trap.

Experimental

General experimental

All reactions and manipulations were carried out under a protective dry argon atmosphere using standard Schlenk techniques or an argon-filled glovebox. Diethyl ether and THF were dried by heating to reflux over sodium-benzophenone and distilled under nitrogen or argon prior to use. $\text{DippN}(\text{H})\text{SiMe}_3$ ^[1] and Me_6TREN ^[2] were prepared according to literature methods. TMEDA and MeTHF were distilled over CaH_2 and stored over 4 Å molecular sieves prior to use. $n\text{BuLi}$, AlCl_3 and $n\text{BuMgCl}$ were purchased from Aldrich and used as received. NMR spectra were recorded on a Bruker AVANCE 400 NMR spectrometer, operating at 400.13 MHz for ^1H and 100.62 MHz for ^{13}C . All ^{13}C spectra were proton decoupled. ^1H and ^{13}C spectra were referenced to the appropriate solvent signal. Elemental analyses were carried out on a Perkin-Elmer 2400 elemental analyser.

Synthesis of $[(2,6\text{-}i\text{Pr}_2\text{Ph})(\text{Me}_3\text{Si})\text{NAlCl}_3]^- [\text{Mg}_2(\mu^2\text{-Cl})_3 \cdot 6\text{THF}]^+, 1$

$n\text{BuLi}$ (2.5 mL, 4.0 mmol, 1.6 M in hexane) was added to a solution of $\text{DippN}(\text{H})\text{SiMe}_3$ (0.72 mL, 4.0 mmol) in diethyl ether (10 mL) and the reaction mixture was stirred at room temperature for 20 min to give a light yellow solution. This solution was then transferred by syringe to a solution of AlCl_3 (0.532 g, 3.99 mmol) in diethyl ether (10 mL) to form a colourless suspension (LiCl) and the reaction mixture was stirred for 2h at room temperature. The suspension was filtered and the diethyl ether removed *in vacuo* and replaced by THF (10 mL). $n\text{BuMgCl}$ (2.0 mL, 4.0 mmol, 2.0 M in THF) was added to the solution and this was left to stir for 2h

at room temperature. Colourless crystals were obtained overnight after slow diffusion of hexane. Yield: 1.70 g (44 % of 50% possible). Elemental analysis (%) for $C_{39}H_{74}O_6Mg_2Cl_6NSiAl$: calcd: C 48.32, H 7.69, N, 1.44; found: C 48.26, H 7.56, N 1.39.

Synthesis of $[(2,6-iPr_2Ph)(Me_3Si)NAICl_3]^- [MgCl \cdot Me_6TREN]^+$, **2**

The same procedure for the synthesis of **1** was adopted but with Me_6TREN (1.04 mL, 3.95 mmol) added prior to the $nBuMgCl$ solution. The THF solution was filtered to remove a small amount of colourless precipitate which formed upon stirring. Colourless crystals were obtained by slow diffusion of diethyl ether. Yield: 1.76 g (65 %). Elemental analysis (%) for $C_{27}H_{56}MgCl_4N_5SiAl$: calcd: C 48.26, H 8.40, N, 10.42; found: C 48.29, H 8.37, N 10.04.

Synthesis of $[(2,6-iPr_2Ph)(Me_3Si)NAICl_3]^- [Mg_3(\mu^3-Cl)_2(\mu^2-Cl)_3 \cdot 3TMEDA]^+$, **3**

A solution of **1** (0.969 g, 1.00 mmol) in THF (5 mL) was prepared and TMEDA (0.3 mL, 2 mmol) was added, giving a colourless solution. After stirring for 2 hours, toluene was slowly added until a slight suspension was noticed. This was heated to reform a solution and slowly cooled in a Dewar of hot water to give colourless crystals. Yield: 0.20 g (21% of 67% possible). Elemental analysis (%) for $C_{33}H_{74}Mg_3Cl_8N_7SiAl$: calcd: C 40.42, H 7.61, N, 10.00; found: C 40.05, H 7.64, N 9.87.

Synthesis of $[(2,6-iPr_2Ph)(Me_3Si)NAICl_3]^- [Mg_3(\mu^3-Cl)_2(\mu^2-Cl)_3 \cdot 6MeTHF]^+$, **4**

The same procedure for the synthesis of **1** was adopted but with $MeTHF$ as the solvent. $nBuMgCl$ (0.5 M in $MeTHF$) was pre-prepared from $nBuCl$ and Mg , standardized and used in this reaction. Yield: 1.43 g (31% of 33% possible). Elemental analysis (%) for $C_{45}H_{86}O_6Mg_3Cl_8NSiAl$: calcd: C 47.05, H 7.55, N, 1.22; found: C 47.04, H 7.55, N 1.79.

X-ray crystallography

Crystallographic data were collected on Oxford Diffraction instruments with $Mo\ K\alpha$ radiation. Structures were solved using *SHELXS-97*,^[3] and refined on F^2 against all independent reflections by the full-matrix least-squares method using the *SHELXL-97*^[3] or *OLEX 2* programs.^[4] All non-hydrogen atoms were refined using anisotropic thermal parameters. Crystals of compound **3** were found to be twinned. The raw data was processed as originating from two crystals related by the matrix 1.0017 -0.0014

0.7028 -0.0009 -1.0026 0.0008 0.0002 -0.0005 -1.0013 and the reflection data was presented as a hklf 5 formatted file. Refinement against this file gave a model that was far superior in terms of R factors, displacement ellipsoid shapes and residual electron density peaks than a model refined against a dataset with no twin treatment. The BASF parameter refined to 0.3918(6). A THF ligand in compound **1** and five of the methyl-THF groups of compound **4** were modeled as disordered over two sites. Appropriate bond length restraints were applied to the C-C and C-O distances of these disordered groups. For the disordered groups of **4**, restraints were also applied to the displacement ellipsoids.

Selected crystallographic details and refinement details are provided in table S7. CCDC-1431065 – CCDC-1431068 and CCDC-1443823 contain the supplementary crystallographic data for this structure. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Mass spectrometry

Sample solutions were transferred into a gas-tight syringe and injected into the ESI source of a quadrupole-ion trap mass spectrometer (HCT, Bruker Daltonik) at a flow rate of 8 $\mu\text{L min}^{-1}$. The ESI source, which before had been extensively flushed with dry THF at a temperature of 300°C to free it from residual traces of water, was operated at an ESI voltage of ± 3000 V and with nitrogen as nebulizer gas (5 L min^{-1} flow rate) and drying gas (0.7 bar backing pressure). Mild conditions identical to those reported previously were chosen to prevent unwanted decomposition processes during the ESI process and the ion transfer into the quadrupole ion trap (drying gas at 60 °C, low potential differences along the flight path of the ions).^[5, 6] The helium-filled quadrupole ion trap (estimated pressure $p(\text{He}) \approx 2$ mTorr) was typically operated at a trap drive of 40, which permits the efficient detection of ions of medium m/z ratios. Typically, ESI mass spectra for m/z 50 – 1000 were recorded, but it was checked that no ions of considerable signal intensity were present at higher m/z ratios. For gas-phase fragmentation experiments, ions of interest were mass-selected with isolation widths of 1 - 12 u (centered at the given m/z ratios), subjected to excitation voltages of amplitudes of V_{exc} , and allowed to collide with the helium gas. The given assignments are based on the observed m/z ratios, isotope patterns, and results of the gas-phase fragmentation experiments. For controlling the HCT instrument and the simulation of ion patterns, the Compass software package (Bruker Daltonik) was used.

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