Supporting Information: Synthesis and Reactivity of Magnesium Complexes Supported by Tris(2-dimethylaminoethyl)amine (Me_6tren)

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X-Ray Crystallography

*X-Ray Data for [(Me$_6$tren)MgBr]Br (**1**)*

Table S1. Crystal data and structure refinement for **1**

Empirical formula	$C_{12}H_{30}Br_2MgN_4$
Formula weight	414.53
Temperature/K	223
Crystal system	cubic
Space group	$P2_13$
a/Å	12.193(17)
b/Å	12.193(17)
c/Å	12.193(17)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	1813(4)
Z	4
ρ_{calc}mg/mm^3	1.519
m/mm^{-1}	4.502
F(000)	848.0
Crystal size/mm^3	0.08 × 0.08 × 0.03
2Θ range for data collection	6.68 to 50.48°
Index ranges	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-14 \leq l \leq 14$
Reflections collected	15533
Independent reflections	1108[R(int) = 0.0666]
Data/restraints/parameters	1108/0/60
Goodness-of-fit on F^2	0.876
Final R indexes [I>=2σ (I)]	R_1 = 0.0366, wR_2 = 0.1054
Final R indexes [all data]	R_1 = 0.0407, wR_2 = 0.1091
Largest diff. peak/hole / e Å^{-3}	0.50/-0.28
Flack parameter	0.03(2)

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **1**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	6397.8(4)	6397.8(4)	6397.8(4)	36.0(3)
Br2	4329.8(5)	5670.2(5)	670.2(5)	46.7(3)
Mg1	5212.7(13)	5212.7(13)	5212.7(13)	25.3(6)
N1	4174(3)	4174(3)	4174(3)	29.1(15)
N2	6455(3)	4732(3)	4005(3)	33.6(9)
C3	7549(5)	4498(5)	4483(5)	45.7(13)
C2	6026(4)	3713(4)	3492(4)	36.3(11)

C4	6582(5)	5608(5)	3177(5)	45.7(14)
C1	4814(4)	3853(4)	3199(4)	34.6(11)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	36.0(3)	36.0(3)	36.0(3)	-5.2(2)	-5.2(2)	-5.2(2)
Br2	46.7(3)	46.7(3)	46.7(3)	5.2(3)	-5.2(3)	-5.2(3)
Mg1	25.3(6)	25.3(6)	25.3(6)	1.5(6)	1.5(6)	1.5(6)
N1	29.1(15)	29.1(15)	29.1(15)	-0.2(17)	-0.2(17)	-0.2(17)
N2	29(2)	31(2)	41(2)	-10.1(17)	10.8(19)	6.5(18)
C3	34(3)	50(3)	52(3)	-10(3)	9(2)	12(2)
C2	40(3)	35(3)	33(3)	-8(2)	9(2)	4(2)
C4	41(3)	48(3)	48(3)	-3(3)	12(3)	-4(3)
C1	43(3)	31(3)	30(2)	-4.9(19)	-3(2)	-1(2)

Table S4. Bond Lengths for **1**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Mg1	2.503(4)	N1	C1[2]	1.475(6)
Mg1	N1	2.193(8)	N1	C1	1.475(6)
Mg1	N2	2.193(5)	N2	C3	1.483(7)
Mg1	N2[1]	2.193(5)	N2	C2	1.485(7)
Mg1	N2[2]	2.193(5)	N2	C4	1.478(8)
N1	C1[1]	1.475(6)	C2	C1	1.531(8)

[1]+Y,+Z,+X; [2]+Z,+X,+Y

Table S5. Bond Angles for **1**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Mg1	Br1	180.00(11)	C1[1]	N1	Mg1	108.3(3)
N2[1]	Mg1	Br1	98.25(12)	C1	N1	C1[2]	110.7(3)
N2[2]	Mg1	Br1	98.25(12)	C1	N1	C1[1]	110.7(3)
N2	Mg1	Br1	98.25(12)	C1[2]	N1	C1[1]	110.7(3)
N2[1]	Mg1	N1	81.75(12)	C3	N2	Mg1	114.1(3)
N2	Mg1	N1	81.75(12)	C3	N2	C2	108.7(4)
N2[2]	Mg1	N1	81.75(12)	C2	N2	Mg1	105.2(3)
N2[1]	Mg1	N2[2]	117.98(6)	C4	N2	Mg1	109.7(3)
N2[1]	Mg1	N2	117.98(6)	C4	N2	C3	108.2(4)
N2[2]	Mg1	N2	117.98(6)	C4	N2	C2	110.8(4)
C1	N1	Mg1	108.3(3)	N2	C2	C1	110.2(4)
C1[2]	N1	Mg1	108.3(3)	N1	C1	C2	110.6(4)

[1]+Y,+Z,+X; [2]+Z,+X,+Y

Experimental

Single crystals of $C_{12}H_{30}Br_2MgN_4$ were grown from acetonitrile/toluene at -30 ºC. A suitable crystal was selected and data collected on a Rigaku Mercury275R CCD (SCX mini)diffractometer. The crystal was kept at 223 K during data collection. Using Olex2,[1] the structure was solved with the XS[2] structure solution program using Direct Methods and refined with the XL[2] refinement package using Least Squares minimisation.

Crystal Data for $C_{12}H_{30}Br_2MgN_4$ (*M* =414.53): cubic, space group $P2_13$ (no. 198), *a* = 12.193(17) Å, *V* = 1813(4) Å^3, *Z* = 4, *T* = 223 K, μ(MoKα) = 4.502 mm^{-1}, *Dcalc* = 1.519 g/mm^3, 15533 reflections measured (6.68 ≤ 2Θ ≤ 50.48), 1108 unique (R_{int} = 0.0666) which were used in all calculations. The final R_1 was 0.0366 (>2sigma(I)) and wR_2 was 0.1091 (all data).

*X-Ray Data for [(Me$_6$tren)MgBr]$_2$[MgBr$_4$] (**4**)*

One molecule of tolulene was present in the crystal structure which was located on an inversion centre and refined in a negative part number to suppress bonds to symmetry related atoms.

Table S6. Crystal data and structure refinement for **4**

Empirical formula	$C_{55}H_{128}Br_{12}Mg_6N_{16}$
Formula weight	2118.51
Temperature/K	93
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.1927(3)
b/Å	19.9755(4)
c/Å	15.9698(11)
α/°	90.00
β/°	113.437(8)
γ/°	90.00
Volume/Å^3	4446.7(3)
Z	2
ρ_{calc}mg/mm^3	1.582
m/mm^{-1}	7.154
F(000)	2124.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
2Θ range for data collection	6.34 to 131.72°
Index ranges	-17 ≤ h ≤ 17, -23 ≤ k ≤ 21, -18 ≤ l ≤ 18
Reflections collected	72247
Independent reflections	7629[R(int) = 0.0364]
Data/restraints/parameters	7629/63/446
Goodness-of-fit on F^2	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0280, wR_2 = 0.0699
Final R indexes [all data]	R_1 = 0.0290, wR_2 = 0.0705

Largest diff. peak/hole / e Å^{-3} 1.16/-0.96

Table S7. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	8902.7(2)	7371.21(17)	6978.1(2)	36.82(9)
Br2	265.0(2)	8930.03(16)	-187.4(2)	31.92(8)
Br3	5132.2(2)	1783.44(17)	1918.4(2)	35.44(9)
Br4	6772.9(2)	1304.85(15)	4538.0(2)	32.72(9)
Br5	4484.8(2)	178.21(15)	3149.29(19)	26.52(8)
Br6	6697.7(2)	62.71(16)	2392.0(2)	33.58(9)
Mg2	2003.1(6)	8891.6(4)	146.2(6)	20.92(19)
Mg1	7718.4(6)	8109.4(4)	5806.4(6)	20.75(19)
Mg3	5806.4(6)	838.4(4)	2999.1(6)	22.29(19)
N1	8087.9(17)	7860.1(12)	4645.3(16)	25.5(5)
N2	8188.9(16)	9076.4(12)	6460.4(15)	23.9(5)
N3	6419.8(16)	7684.3(11)	5861.5(15)	22.5(5)
N4	6658.6(16)	8745.8(11)	4770.1(15)	21.6(5)
N5	2481.7(17)	8455.8(12)	1531.1(15)	24.5(5)
N6	2279.5(18)	9955.0(12)	9.8(15)	26.1(5)
N7	1959.8(17)	8241.2(12)	-978.0(16)	26.2(5)
N8	3555.4(16)	8838.1(12)	475.7(15)	22.7(5)
C1	7721(2)	7174.8(14)	4360(2)	31.2(7)
C2	9124(2)	7851.1(17)	4834(2)	37.4(7)
C3	9102(2)	9212.8(16)	6359(2)	32.4(7)
C4	8394(2)	9109.3(17)	7448.5(19)	35.7(7)
C5	6377(2)	7931.3(16)	6720(2)	32.1(7)
C6	6411(2)	6943.5(14)	5879(2)	28.7(6)
C7	7591(2)	8351.6(15)	3907.9(19)	28.4(6)
C8	6594(2)	8519.9(14)	3858.5(18)	27.1(6)
C9	7456(2)	9589.5(14)	5968.8(19)	25.6(6)
C10	6994(2)	9452.0(13)	4946.1(18)	24.6(6)
C11	5576.3(19)	7938.0(14)	5066.1(19)	25.0(6)
C12	5721(2)	8662.7(14)	4854.2(19)	25.2(6)
C13	2189(2)	7743.9(15)	1392(2)	33.2(7)
C14	2074(2)	8756.9(16)	2147(2)	34.0(7)
C15	2232(2)	10264.8(15)	839.0(19)	30.1(6)
C16	1580(3)	10309.6(16)	-803(2)	35.8(7)
C17	1599(2)	8661.3(17)	-1815(2)	35.0(7)
C18	1328(2)	7646.0(16)	-1142(2)	35.3(7)
C19	3544(2)	8509.9(15)	1967.2(18)	26.4(6)
C20	3996(2)	8392.5(15)	1282.5(18)	26.9(6)

C21	3262(2)	10028.0(15)	37(2)	30.0(6)
C22	3955(2)	9527.4(15)	683(2)	28.4(6)
C23	2957(2)	8013.0(15)	-777.8(19)	26.4(6)
C24	3674(2)	8568.2(15)	-339.9(18)	26.3(6)
C7S	-372(8)	3966(5)	1057(8)	78(3)
C1S	-91(10)	4484(8)	617(7)	47(2)
C2S	-745(10)	4626(7)	-241(8)	46(2)
C3S	-566(12)	5154(9)	-721(8)	46(2)
C4S	308(9)	5538(7)	-292(7)	43(2)
C5S	928(9)	5327(7)	573(7)	42(2)
C6S	714(12)	4810(9)	984(9)	46(2)

Table S8. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	29.47(17)	35.19(18)	31.88(17)	7.39(13)	-2.53(13)	2.56(13)
Br2	21.43(16)	37.74(18)	34.78(17)	-1.07(13)	9.26(13)	5.61(12)
Br3	41.76(19)	37.70(19)	29.83(16)	15.82(13)	17.37(14)	17.19(14)
Br4	35.08(18)	22.77(16)	29.18(16)	-0.45(12)	0.99(13)	-5.85(12)
Br5	23.79(15)	28.46(16)	26.47(15)	-6.02(11)	9.12(12)	-5.25(11)
Br6	39.28(19)	34.80(18)	33.35(17)	9.65(13)	21.54(14)	11.84(13)
Mg2	20.3(4)	21.1(5)	20.0(4)	0.0(3)	6.6(4)	3.7(3)
Mg1	20.5(4)	20.9(5)	17.4(4)	0.0(3)	3.9(3)	-1.0(3)
Mg3	22.5(5)	21.6(5)	20.6(4)	3.6(3)	6.4(4)	1.5(4)
N1	29.9(13)	20.2(12)	28.0(12)	-3.5(10)	13.2(10)	-2.7(10)
N2	23.1(12)	27.9(13)	17.6(11)	-3.8(9)	5.0(9)	-4.4(10)
N3	26.0(12)	20.5(12)	19.7(11)	-0.5(9)	7.7(9)	-2.1(9)
N4	24.8(12)	18.7(11)	19.6(11)	-2.0(9)	7.0(9)	-2.9(9)
N5	27.4(12)	22.8(12)	24.0(12)	1.3(9)	10.9(10)	3.3(10)
N6	34.0(14)	23.8(12)	20.8(11)	1.8(9)	11.2(10)	5.5(10)
N7	22.9(12)	27.9(13)	23.0(12)	-3.6(10)	3.8(10)	4.4(10)
N8	24.4(12)	24.6(12)	18.3(11)	-2.5(9)	7.7(9)	0.7(9)
C1	40.8(18)	21.2(15)	30.8(15)	-4.1(12)	13.4(13)	-4.2(13)
C2	33.5(17)	34.8(18)	49.3(19)	-6.1(15)	22.1(15)	-0.9(14)
C3	24.9(15)	37.7(18)	32.1(16)	-6.2(13)	8.6(13)	-8.2(13)
C4	42.9(19)	41.4(18)	18.5(14)	-7.0(13)	7.5(13)	-10.1(15)
C5	41.2(18)	32.9(17)	26.0(15)	-4.8(13)	17.2(13)	-4.9(14)
C6	31.1(16)	21.6(15)	31.9(15)	3.7(12)	11.2(13)	-4.0(12)
C7	42.0(17)	22.7(15)	23.6(14)	0.1(11)	16.4(13)	-4.1(13)
C8	34.6(16)	22.5(14)	18.8(13)	-1.2(11)	5.0(12)	-3.2(12)
C9	28.4(15)	21.4(14)	25.6(14)	-5.6(11)	9.4(12)	-3.0(11)
C10	26.9(14)	18.8(14)	23.8(14)	-1.3(11)	5.5(11)	-2.4(11)

C11	20.2(14)	25.6(15)	25.2(14)	-2.5(11)	4.9(11)	-2.8(11)
C12	20.9(14)	24.9(15)	25.9(14)	-1.2(11)	5.0(11)	0.2(11)
C13	41.1(18)	25.4(16)	31.5(16)	2.0(12)	12.8(14)	-2.5(13)
C14	45.7(19)	33.7(17)	29.2(15)	3.8(13)	21.7(14)	7.9(14)
C15	42.6(18)	23.8(15)	24.9(14)	0.7(12)	14.5(13)	7.9(13)
C16	52(2)	27.9(16)	24.2(15)	6.7(12)	11.0(14)	11.9(14)
C17	33.6(17)	42.4(19)	22.7(14)	-1.5(13)	4.3(13)	11.4(14)
C18	31.1(16)	34.1(17)	34.3(16)	-11.5(13)	6.2(13)	-1.2(13)
C19	28.2(15)	25.9(15)	20.3(13)	1.4(11)	4.6(11)	2.8(12)
C20	22.7(14)	30.9(16)	21.8(14)	0.9(12)	3.4(11)	6.6(12)
C21	38.4(17)	24.2(15)	31.3(15)	-0.8(12)	17.9(14)	-3.9(12)
C22	26.6(15)	31.0(16)	28.0(14)	-5.6(12)	11.3(12)	-6.9(12)
C23	24.4(15)	29.3(15)	22.8(13)	-4.6(12)	6.4(11)	6.5(12)
C24	25.5(14)	31.9(16)	20.5(13)	-3.2(11)	8.0(11)	5.2(12)
C7S	91(6)	56(5)	101(7)	19(5)	53(6)	23(4)
C1S	50(5)	50(4)	44(6)	1(4)	20(4)	18(3)
C2S	29(5)	65(5)	43(6)	-17(5)	12(4)	6(4)
C3S	32(5)	71(5)	25(6)	-1(4)	-1(4)	29(4)
C4S	44(6)	51(4)	38(6)	1(5)	21(5)	19(4)
C5S	27(5)	52(4)	39(5)	-16(4)	4(4)	13(3)
C6S	35(5)	61(4)	32(6)	3(4)	2(5)	30(3)

Table S9. Bond Lengths for **4**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Mg1	2.4970(9)	N5	C13	1.480(4)
Br2	Mg2	2.4787(9)	N5	C14	1.482(4)
Br3	Mg3	2.4870(9)	N5	C19	1.485(4)
Br4	Mg3	2.4887(9)	N6	C15	1.489(4)
Br5	Mg3	2.4923(9)	N6	C16	1.490(4)
Br6	Mg3	2.4937(9)	N6	C21	1.483(4)
Mg2	N5	2.213(2)	N7	C17	1.486(4)
Mg2	N6	2.193(3)	N7	C18	1.485(4)
Mg2	N7	2.196(2)	N7	C23	1.490(4)
Mg2	N8	2.205(2)	N8	C20	1.488(3)
Mg1	N1	2.197(2)	N8	C22	1.488(4)
Mg1	N2	2.177(2)	N8	C24	1.485(3)
Mg1	N3	2.182(2)	C7	C8	1.523(4)
Mg1	N4	2.197(2)	C9	C10	1.524(4)
N1	C1	1.480(4)	C11	C12	1.522(4)
N1	C2	1.481(4)	C19	C20	1.523(4)
N1	C7	1.488(4)	C21	C22	1.520(4)
N2	C3	1.485(4)	C23	C24	1.516(4)

N2	C4	1.484(3)	C7S	C1S	1.410(17)
N2	C9	1.487(4)	C1S	C2S	1.365(11)
N3	C5	1.483(4)	C1S	C6S	1.302(13)
N3	C6	1.480(4)	C2S	C3S	1.393(11)
N3	C11	1.489(3)	C3S	C4S	1.449(12)
N4	C8	1.490(3)	C4S	C5S	1.393(11)
N4	C10	1.488(3)	C5S	C6S	1.331(11)
N4	C12	1.492(4)			

Table S10. Bond Angles for **4**

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N5	Mg2	Br2	97.20(7)	C10	N4	C8	110.9(2)
N6	Mg2	Br2	100.28(7)	C10	N4	C12	110.8(2)
N6	Mg2	N5	118.72(9)	C12	N4	Mg1	107.91(16)
N6	Mg2	N7	115.89(10)	C13	N5	Mg2	105.56(17)
N6	Mg2	N8	80.90(9)	C13	N5	C14	108.1(2)
N7	Mg2	Br2	99.19(7)	C13	N5	C19	110.2(2)
N7	Mg2	N5	118.38(10)	C14	N5	Mg2	116.45(18)
N7	Mg2	N8	81.25(9)	C14	N5	C19	108.8(2)
N8	Mg2	Br2	178.37(7)	C19	N5	Mg2	107.68(17)
N8	Mg2	N5	81.22(9)	C15	N6	Mg2	103.60(17)
N1	Mg1	Br1	98.55(7)	C15	N6	C16	107.9(2)
N2	Mg1	Br1	99.39(7)	C16	N6	Mg2	116.65(19)
N2	Mg1	N1	117.42(9)	C21	N6	Mg2	108.81(17)
N2	Mg1	N3	117.11(9)	C21	N6	C15	109.7(2)
N2	Mg1	N4	81.40(9)	C21	N6	C16	109.9(2)
N3	Mg1	Br1	97.68(7)	C17	N7	Mg2	106.36(18)
N3	Mg1	N1	118.98(9)	C17	N7	C23	110.2(2)
N3	Mg1	N4	81.49(9)	C18	N7	Mg2	115.16(19)
N4	Mg1	Br1	179.06(7)	C18	N7	C17	108.2(2)
N4	Mg1	N1	81.50(9)	C18	N7	C23	108.9(2)
Br3	Mg3	Br4	108.63(4)	C23	N7	Mg2	107.96(16)
Br3	Mg3	Br5	110.07(4)	C20	N8	Mg2	107.80(17)
Br3	Mg3	Br6	109.84(3)	C22	N8	Mg2	108.12(17)
Br4	Mg3	Br5	106.53(3)	C22	N8	C20	110.9(2)
Br4	Mg3	Br6	114.72(4)	C24	N8	Mg2	107.41(16)
Br5	Mg3	Br6	106.95(4)	C24	N8	C20	111.9(2)
C1	N1	Mg1	106.14(18)	C24	N8	C22	110.5(2)
C1	N1	C2	107.0(2)	N1	C7	C8	111.6(2)
C1	N1	C7	110.9(2)	N4	C8	C7	109.8(2)
C2	N1	Mg1	116.01(19)	N2	C9	C10	111.7(2)
C2	N1	C7	109.4(2)	N4	C10	C9	110.5(2)

C7	N1	Mg1	107.40(17)	N3	C11	C12	111.2(2)
C3	N2	Mg1	104.66(17)	N4	C12	C11	110.7(2)
C3	N2	C9	110.6(2)	N5	C19	C20	111.6(2)
C4	N2	Mg1	116.08(19)	N8	C20	C19	110.7(2)
C4	N2	C3	107.4(2)	N6	C21	C22	111.9(2)
C4	N2	C9	109.1(2)	N8	C22	C21	110.3(2)
C9	N2	Mg1	108.92(16)	N7	C23	C24	111.0(2)
C5	N3	Mg1	106.31(17)	N8	C24	C23	110.8(2)
C5	N3	C11	109.6(2)	C2S	C1S	C7S	114.1(10)
C6	N3	Mg1	113.88(18)	C6S	C1S	C7S	124.0(9)
C6	N3	C5	108.1(2)	C6S	C1S	C2S	121.8(10)
C6	N3	C11	110.2(2)	C1S	C2S	C3S	119.1(8)
C11	N3	Mg1	108.56(16)	C2S	C3S	C4S	119.0(7)
C8	N4	Mg1	107.73(17)	C5S	C4S	C3S	116.0(9)
C8	N4	C12	111.1(2)	C6S	C5S	C4S	121.6(8)
C10	N4	Mg1	108.24(16)	C1S	C6S	C5S	122.4(8)

Experimental

Single crystals of $C_{55}H_{128}Br_{12}Mg_6N_{16}$ were grown from acetonitrile/toluene at -30 ºC. A suitable crystal was selected and data collected on a Rigaku MicroMax-007HF diffractometer. The crystal was kept at 93 K during data collection. Using Olex2,[1] the structure was solved with the XS[2] structure solution program using Direct Methods and refined with the XL[2] refinement package using Least Squares minimisation.

Crystal Data for $C_{55}H_{128}Br_{12}Mg_6N_{16}$ (M =2118.51): monoclinic, space group $P2_1/c$ (no. 14), a = 15.1927(3) Å, b = 19.9755(4) Å, c = 15.9698(11) Å, β = 113.437(8)°, V = 4446.7(3) Å^3, Z = 2, T = 93 K, μ(CuKα) = 7.154 mm^{-1}, *Dcalc* = 1.582 g/mm^3, 72247 reflections measured (6.34 ≤ 2Θ ≤ 131.72), 7629 unique (R_{int} = 0.0364) which were used in all calculations. The final R_1 was 0.0280 (>2sigma(I)) and wR_2 was 0.0705 (all data).

*X-Ray Data for (Me_6tren)$MgMe_2$ (**5**)*

The uncoordinated arm of the tren ligand was disordered over two positions. The ratio was refined freely and converged at 0.690.

Table S11. Crystal data and structure refinement for **5**

Empirical formula	$MgN_4C_{14}H_{30}$
Formula weight	278.73
Temperature/K	93
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.3141(3)
b/Å	11.5776(5)

c/Å	19.5193(14)
α/°	90.00
β/°	99.555(7)
γ/°	90.00
Volume/Å^3	1852.80(16)
Z	4
ρ_{calc}mg/mm^3	0.999
m/mm^{-1}	0.091
F(000)	616.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
2Θ range for data collection	6.08 to 56.56°
Index ranges	$-10 \leq h \leq 11$, $-15 \leq k \leq 15$, $-26 \leq l \leq 26$
Reflections collected	36292
Independent reflections	4566[R(int) = 0.0643]
Data/restraints/parameters	4566/170/227
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0458, wR_2 = 0.1004
Final R indexes [all data]	R_1 = 0.0622, wR_2 = 0.1081
Largest diff. peak/hole / e Å^{-3}	0.26/-0.20

Table S12. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Mg1	9669.9(5)	4540.1(3)	6806.5(2)	21.25(12)
N1	11231.6(12)	3297.8(9)	7575.1(5)	23.6(2)
N3	7099.3(13)	4361.0(9)	6170.5(6)	25.4(2)
C1	8901.1(18)	5601.9(12)	7632.0(7)	33.3(3)
C2	11113.5(16)	5499.9(11)	6170.1(7)	26.7(3)
C3	7949.3(15)	2406.4(11)	5871.4(7)	26.6(3)
C4	7079.3(16)	3510.4(12)	5605.5(7)	28.6(3)
C5	5926.6(17)	4029.7(14)	6625.0(8)	37.2(3)
C6	6643.2(19)	5504.1(12)	5870.9(8)	38.1(4)
C7	10289.9(17)	1785.7(11)	6715.2(7)	31.0(3)
C8	11719.4(16)	2264.0(11)	7219.6(7)	29.8(3)
C9	12696.9(17)	3930.7(12)	7900.4(8)	33.9(3)
C10	10303.9(19)	2960.9(14)	8123.8(8)	39.4(4)
N2	9646.0(12)	2657.7(9)	6197.1(5)	22.2(2)
C11A	10952(13)	2726(10)	5765(5)	21.3(18)
C12A	11634(5)	1570(3)	5566(2)	25.8(8)
N4A	12600(12)	1756(12)	5007(5)	23.0(15)
C13A	13842(6)	859(4)	5026(3)	36.7(11)
C14A	11554(7)	1740(5)	4329(3)	36.4(11)

C11B	10618(6)	2846(4)	5630(2)	22.8(9)
C12B	10647(2)	1869.4(16)	5101(1)	26.4(4)
N4B	12221(6)	1796(6)	4872(2)	31.2(9)
C13B	12078(4)	1247(3)	4190.8(13)	49.4(7)
C14B	13403(3)	1187(2)	5375.4(15)	44.0(6)

Table S13. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **5**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Mg1	22.5(2)	19.5(2)	22.3(2)	0.54(16)	5.40(17)	1.53(16)
N1	25.4(5)	20.8(5)	24.9(5)	2.0(4)	5.3(4)	-1.5(4)
N3	23.2(5)	24.4(6)	28.8(6)	2.0(4)	5.2(5)	3.3(4)
C1	35.5(8)	33.5(8)	31.9(8)	-4.6(6)	8.3(6)	7.3(6)
C2	29.6(7)	22.6(6)	28.1(7)	1.2(5)	5.4(5)	-1.8(5)
C3	25.3(7)	23.2(6)	30.2(7)	-1.9(5)	1.0(5)	-2.6(5)
C4	29.4(7)	28.0(7)	26.3(7)	0.9(5)	-1.7(5)	0.7(5)
C5	23.6(7)	46.6(9)	43.1(9)	0.5(7)	10.9(6)	-0.7(6)
C6	40.6(8)	28.4(7)	41.9(9)	5.3(6)	-2.9(7)	10.5(6)
C7	33.1(7)	17.7(6)	38.8(8)	1.6(5)	-3.3(6)	1.4(5)
C8	28.2(7)	22.6(6)	36.9(8)	-0.3(6)	0.2(6)	5.1(5)
C9	34.4(8)	30.6(7)	33.7(8)	-1.7(6)	-3.0(6)	-5.4(6)
C10	41.0(8)	41.8(9)	38.1(8)	14.6(7)	14.6(7)	3.2(7)
N2	21.7(5)	19.5(5)	25.8(5)	1.2(4)	5.3(4)	0.1(4)
C11A	21(4)	20(3)	23(4)	0(3)	5(3)	5(2)
C12A	29(2)	19.4(18)	31(2)	-0.7(16)	9.5(17)	3.1(15)
N4A	20(3)	25(2)	26(3)	-3(3)	8(2)	3(3)
C13A	31(2)	34(3)	48(3)	-7(2)	14(2)	8.1(19)
C14A	48(3)	34(3)	29(2)	-2(2)	10(2)	1(2)
C11B	23(2)	20.5(14)	25.5(18)	-1.2(12)	5.4(15)	-1.6(12)
C12B	28.7(10)	25.1(9)	26.4(10)	-2.6(7)	7.7(8)	-2.2(7)
N4B	33(2)	29.7(15)	33.4(18)	-7.7(14)	12.8(14)	-6.4(16)
C13B	60.0(18)	51.6(17)	43.9(14)	-19.3(13)	30.2(13)	-15.4(13)
C14B	33.0(12)	41.1(14)	59.6(16)	-7.3(13)	12.6(12)	4.6(10)

Table S14. Bond Lengths for **5**

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Mg1	N1	2.3148(11)	C7	C8	1.5166(19)
Mg1	N3	2.2959(12)	C7	N2	1.4658(16)
Mg1	C1	2.2042(14)	N2	C11A	1.484(11)
Mg1	C2	2.1710(13)	N2	C11B	1.490(5)
Mg1	N2	2.4814(11)	C11A	C12A	1.529(10)
N1	C8	1.4738(16)	C12A	N4A	1.473(11)

N1	C9	1.4722(17)	N4A	C13A	1.461(10)
N1	C10	1.4726(17)	N4A	C14A	1.459(8)
N3	C4	1.4766(17)	C11B	C12B	1.535(5)
N3	C5	1.4738(17)	C12B	N4B	1.454(5)
N3	C6	1.4709(17)	N4B	C13B	1.461(5)
C3	C4	1.5171(18)	N4B	C14B	1.452(4)
C3	N2	1.4768(16)			

Table S15. Bond Angles for **5**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Mg1	N2	73.98(4)	N3	C4	C3	111.15(11)
N3	Mg1	N1	131.76(4)	N2	C7	C8	110.71(11)
N3	Mg1	N2	74.27(4)	N1	C8	C7	110.79(11)
C1	Mg1	N1	94.14(5)	C3	N2	Mg1	108.09(7)
C1	Mg1	N3	95.09(5)	C3	N2	C11B	107.8(2)
C1	Mg1	N2	149.33(5)	C7	N2	Mg1	107.53(8)
C2	Mg1	N1	112.64(5)	C7	N2	C3	112.00(10)
C2	Mg1	N3	106.87(5)	C7	N2	C11A	102.2(4)
C2	Mg1	C1	112.82(6)	C7	N2	C11B	115.60(18)
C2	Mg1	N2	97.84(4)	C11A	N2	Mg1	106.1(5)
C8	N1	Mg1	111.60(8)	C11A	N2	C3	120.2(5)
C9	N1	Mg1	107.77(8)	C11A	N2	C11B	14.5(5)
C9	N1	C8	109.55(10)	C11B	N2	Mg1	105.4(2)
C10	N1	Mg1	109.32(8)	N2	C11A	C12A	115.8(8)
C10	N1	C8	110.22(11)	N4A	C12A	C11A	109.3(7)
C10	N1	C9	108.30(11)	C12A	N4A	C14A	110.7(7)
C4	N3	Mg1	110.99(8)	C13A	N4A	C12A	110.3(8)
C5	N3	Mg1	110.33(8)	C13A	N4A	C14A	109.0(8)
C5	N3	C4	110.45(11)	N2	C11B	C12B	117.6(4)
C6	N3	Mg1	106.81(8)	N4B	C12B	C11B	111.4(3)
C6	N3	C4	109.45(11)	C12B	N4B	C14B	111.3(4)
C6	N3	C5	108.72(11)	C13B	N4B	C12B	111.3(4)
N2	C3	C4	110.39(10)	C13B	N4B	C14B	110.4(4)

Experimental

Single crystals of $MgN_4C_{14}H_{30}$ were grown from ether/pentane at -30ºC. A suitable crystal was selected and data collected on a Rigaku R-AXIS RAPID imaging plate diffractometer. The crystal was kept at 93 K during data collection. Using Olex2,[1] the structure was solved with the XS[2] structure solution program using Direct Methods and refined with the XL[2] refinement package using Least Squares minimisation.

Crystal Data for $MgN_4C_{14}H_{30}$ (*M* =278.73): monoclinic, space group $P2_1/n$ (no. 14), *a* = 8.3141(3) Å, *b* = 11.5776(5) Å, *c* = 19.5193(14) Å, *β* = 99.555(7)°, *V* = 1852.80(16) Å^3, *Z* = 4, *T* = 93 K, μ(MoKα) = 0.091 mm^{-1}, *Dcalc* = 0.999 g/mm^3, 36292 reflections measured (6.08 ≤ 2Θ ≤ 56.56), 4566 unique (R_{int} = 0.0643) which were used in all calculations. The final R_1 was 0.0458 (>2sigma(I)) and wR_2 was 0.1081 (all data).

X-Ray Data for [(Me$_6$tren)MgBr]$_2$[Br$_2$Mg(μ-Cl$_2$)MgBr$_2$]

Table S16. Crystal data and structure refinement for [(Me$_6$tren)MgBr]$_2$[Br$_2$Mg(μ-Cl$_2$)MgBr$_2$]

Empirical formula	$C_{12}H_{30}Br_3ClMg_2N_4$
Formula weight	554.20
Temperature/K	223
Crystal system	triclinic
Space group	P-1
a/Å	7.945(7)
b/Å	9.961(8)
c/Å	14.237(12)
α/°	104.590(14)
β/°	95.656(16)
γ/°	92.374(17)
Volume/Å^3	1082.4(16)
Z	2
ρ_{calc}mg/mm^3	1.700
m/mm^{-1}	5.773
F(000)	552.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
2Θ range for data collection	6.24 to 49.42°
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 11, -16 ≤ l ≤ 16
Reflections collected	8439
Independent reflections	3682[R(int) = 0.0463]
Data/restraints/parameters	3682/0/205
Goodness-of-fit on F^2	1.109
Final R indexes [I>=2σ (I)]	R_1 = 0.0408, wR_2 = 0.0952
Final R indexes [all data]	R_1 = 0.0651, wR_2 = 0.1271
Largest diff. peak/hole / e Å^{-3}	0.65/-0.61

Table S17. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for [(Me$_6$tren)MgBr]$_2$[Br$_2$Mg(μ-Cl$_2$)MgBr$_2$]. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br2	4113.9(10)	1756.5(8)	7332.9(5)	67.1(3)
Br1	11332.3(7)	2946.3(7)	405.1(4)	46.5(2)

Br3	4024.1(8)	3178.2(6)	4913.3(5)	52.1(2)
Mg1	9596(2)	3142.5(18)	1762.7(12)	30.7(4)
Cl1	7458(2)	668.0(17)	5404.8(12)	59.9(5)
Mg2	4482(3)	1249(2)	5617.1(14)	43.5(5)
N2	10343(5)	1300(5)	2213(3)	34.4(11)
N3	7087(6)	3003(5)	988(3)	44.7(12)
N1	8132(5)	3322(5)	2983(3)	35.6(11)
N4	10562(6)	5204(4)	2613(3)	36.8(11)
C1	8128(8)	2009(7)	3274(4)	46.7(16)
C4	12165(8)	1054(7)	2234(5)	52.9(17)
C9	8923(8)	4455(6)	3773(4)	48.8(16)
C5	6397(7)	3584(7)	2666(5)	50.3(16)
C2	9824(8)	1444(7)	3198(4)	45.6(15)
C3	9434(8)	103(6)	1524(5)	51.7(16)
C6	5882(7)	2760(8)	1654(5)	55.0(18)
C12	12276(7)	5021(7)	3023(5)	54.8(17)
C10	9483(8)	5643(6)	3388(5)	50.3(16)
C7	6833(9)	4358(7)	786(6)	67(2)
C11	10724(9)	6290(6)	2097(5)	58.7(19)
C8	6780(9)	1921(8)	70(5)	69(2)

Table S18. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for $[(Me_6tren)MgBr]_2[Br_2Mg(\mu\text{-}Cl_2)MgBr_2]$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br2	87.6(6)	73.0(5)	41.9(4)	14.8(4)	13.7(4)	2.9(4)
Br1	47.4(4)	59.5(4)	33.5(3)	12.4(3)	10.8(3)	-2.6(3)
Br3	68.6(5)	41.9(4)	49.6(4)	18.0(3)	5.5(3)	10.3(3)
Mg1	29.7(9)	37.5(10)	24.7(9)	8.1(8)	2.4(7)	2.0(8)
Cl1	75.1(12)	52.4(10)	54.3(10)	18.8(8)	2.2(9)	8.2(9)
Mg2	49.7(12)	43.7(12)	39.0(11)	14.9(9)	3.2(9)	1.9(10)
N2	39(3)	34(3)	32(3)	10(2)	9(2)	2(2)
N3	38(3)	61(3)	36(3)	18(3)	-4(2)	0(3)
N1	34(2)	47(3)	29(2)	13(2)	11(2)	8(2)
N4	42(3)	31(3)	38(3)	12(2)	-1(2)	1(2)
C1	52(4)	61(4)	37(3)	26(3)	17(3)	4(3)
C4	48(4)	58(4)	61(4)	27(4)	9(3)	16(3)
C9	57(4)	57(4)	28(3)	0(3)	12(3)	13(3)
C5	36(3)	69(4)	57(4)	32(4)	14(3)	14(3)
C2	50(4)	57(4)	40(3)	30(3)	9(3)	8(3)
C3	63(4)	38(4)	52(4)	8(3)	4(3)	2(3)
C6	27(3)	87(5)	58(4)	34(4)	2(3)	0(3)

C12	43(4)	61(4)	54(4)	10(3)	-11(3)	2(3)
C10	53(4)	45(4)	47(4)	0(3)	5(3)	7(3)
C7	62(4)	73(5)	75(5)	41(4)	-13(4)	6(4)
C11	81(5)	29(3)	68(5)	19(3)	1(4)	-4(3)
C8	54(4)	97(6)	47(4)	7(4)	-13(3)	-7(4)

Table S19. Bond Lengths for $[(Me_6tren)MgBr]_2[Br_2Mg(\mu\text{-}Cl_2)MgBr_2]$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br2	Mg2	2.416(3)	N2	C3	1.450(7)
Br1	Mg1	2.456(2)	N3	C6	1.466(7)
Br3	Mg2	2.405(3)	N3	C7	1.466(8)
Mg1	N2	2.177(5)	N3	C8	1.460(8)
Mg1	N3	2.163(5)	N1	C1	1.467(7)
Mg1	N1	2.159(5)	N1	C9	1.448(7)
Mg1	N4	2.169(5)	N1	C5	1.463(7)
Cl1	Mg2	2.487(3)	N4	C12	1.464(7)
Cl1	Mg2[1]	2.460(3)	N4	C10	1.455(7)
Mg2	Cl1[1]	2.460(3)	N4	C11	1.461(7)
Mg2	Mg2[1]	2.865(4)	C1	C2	1.485(8)
N2	C4	1.477(7)	C9	C10	1.494(9)
N2	C2	1.475(7)	C5	C6	1.476(9)

[1]1-X,-Y,1-Z

Table S20. Bond Angles for $[(Me_6tren)MgBr]_2[Br_2Mg(\mu\text{-}Cl_2)MgBr_2]$

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	Mg1	Br1	98.46(13)	C3	N2	C2	110.5(5)
N3	Mg1	Br1	100.30(15)	C6	N3	Mg1	106.8(3)
N3	Mg1	N2	116.2(2)	C6	N3	C7	109.1(5)
N3	Mg1	N4	115.8(2)	C7	N3	Mg1	107.0(4)
N1	Mg1	Br1	178.43(14)	C8	N3	Mg1	115.4(4)
N1	Mg1	N2	80.83(17)	C8	N3	C6	109.4(5)
N1	Mg1	N3	81.28(19)	C8	N3	C7	108.9(5)
N1	Mg1	N4	81.09(19)	C1	N1	Mg1	108.9(3)
N4	Mg1	Br1	98.13(14)	C9	N1	Mg1	107.7(3)
N4	Mg1	N2	120.83(18)	C9	N1	C1	110.7(5)
Mg2[1]	Cl1	Mg2	70.79(10)	C9	N1	C5	111.8(5)
Br2	Mg2	Cl1[1]	113.50(10)	C5	N1	Mg1	108.0(3)
Br2	Mg2	Cl1	109.05(9)	C5	N1	C1	109.5(5)
Br2	Mg2	Mg2[1]	128.72(11)	C12	N4	Mg1	104.8(3)
Br3	Mg2	Br2	113.70(9)	C10	N4	Mg1	107.5(4)
Br3	Mg2	Cl1	105.94(9)	C10	N4	C12	110.6(5)
Br3	Mg2	Cl1[1]	105.09(10)	C10	N4	C11	109.4(5)

Br3	Mg2	Mg2[1]	117.51(12)	C11	N4	Mg1	117.7(4)
Cl1[1]	Mg2	Cl1	109.21(10)	C11	N4	C12	106.6(5)
Cl1	Mg2	Mg2[1]	54.17(8)	N1	C1	C2	109.5(5)
Cl1[1]	Mg2	Mg2[1]	55.04(9)	N1	C9	C10	110.4(5)
C4	N2	Mg1	115.9(3)	N1	C5	C6	110.2(5)
C2	N2	Mg1	106.7(3)	N2	C2	C1	111.3(4)
C2	N2	C4	109.2(4)	N3	C6	C5	111.8(5)
C3	N2	Mg1	107.5(3)	N4	C10	C9	111.5(5)
C3	N2	C4	107.0(5)				

[1]1-X,-Y,1-Z

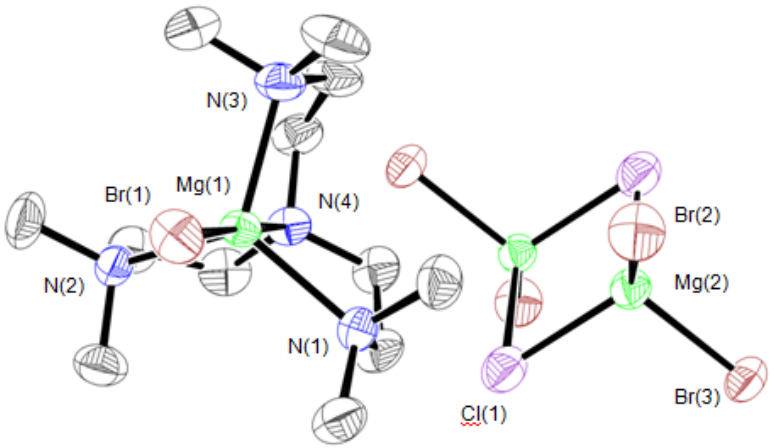
Experimental

Single crystals of $C_{12}H_{30}Br_3ClMg_2N_4$ were grown from dicholormethane/pentane at -30 ºC. A suitable crystal was selected and data collected on a Rigaku Mercury275R CCD (SCX mini)diffractometer. The crystal was kept at 223 K during data collection. Using Olex2,[1] the structure was solved with the XS[2] structure solution program using Direct Methods and refined with the XL[2] refinement package using Least Squares minimisation.

Crystal Data for $C_{12}H_{30}Br_3ClMg_2N_4$ (*M* =554.20): triclinic, space group P-1 (no. 2), a = 7.945(7) Å, b = 9.961(8) Å, c = 14.237(12) Å, α = 104.590(14)°, β = 95.656(16)°, γ = 92.374(17)°, V = 1082.4(16) Å^3,Z = 2, T = 223 K, μ(MoKα) = 5.773 mm^{-1}, *Dcalc* = 1.700 g/mm^3, 8439 reflections measured ($6.24 \leq 2\Theta \leq 49.42$), 3682 unique ($R_{int}$ = 0.0463) which were used in all calculations. The final R_1 was 0.0408 (>2sigma(I)) and wR_2 was 0.1271 (all data).

Preparation of *[(Me$_6$tren)MgBr]$_2$[Br$_2$Mg(μ-Cl)MgBr$_2$]*

This compound was prepared using the same route as for **4**, though the crude material was crystallized by layering toluene and dichloromethane at -30ºC.



^{1}H NMR spectra

Figure S1: ^{1}H NMR spectrum of [(Me$_6$tren)MgBr]Br (**1**)

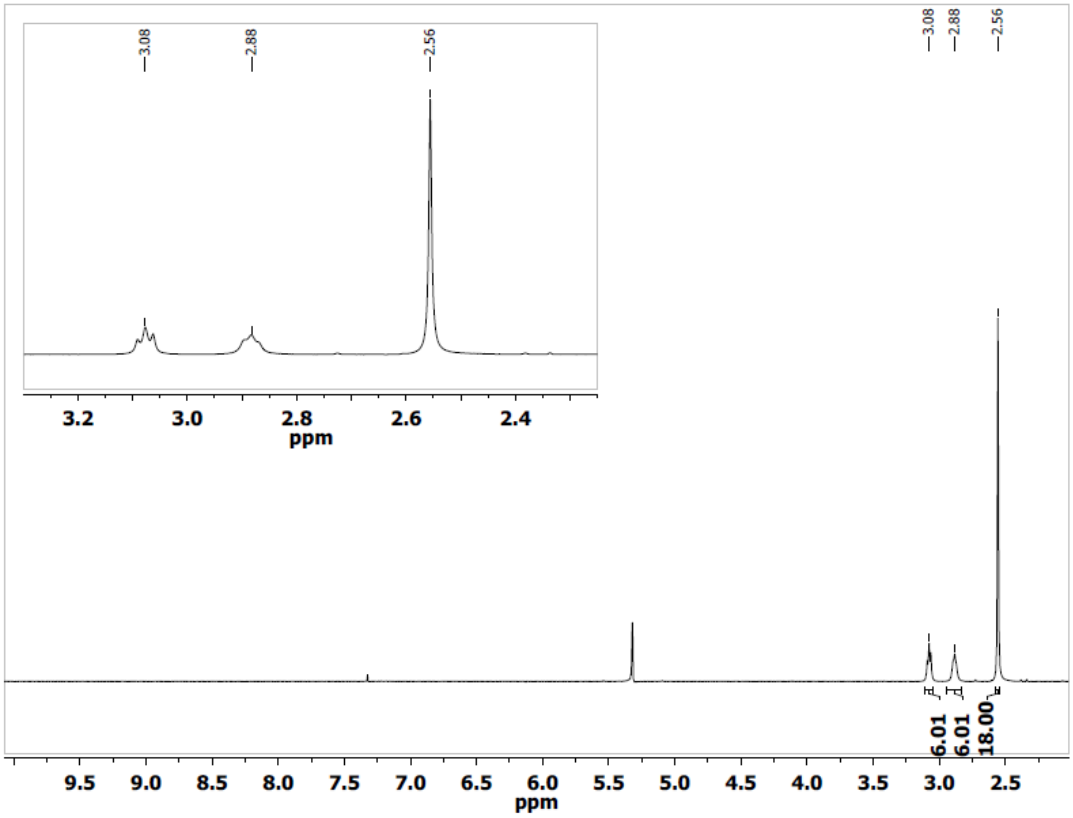


Figure S2: ^{13}C{^{1}H} NMR spectrum of [(Me$_6$tren)MgBr]Br (**1**)

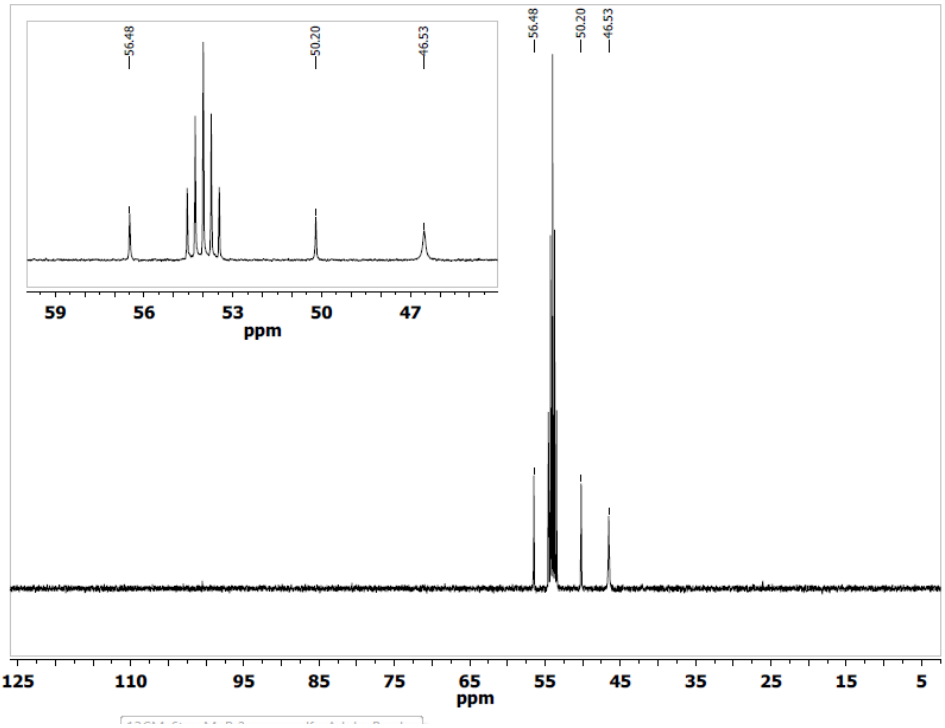


Figure S3: ^{1}H NMR spectrum of [(Me$_6$tren)MgCl]Cl (**2**)

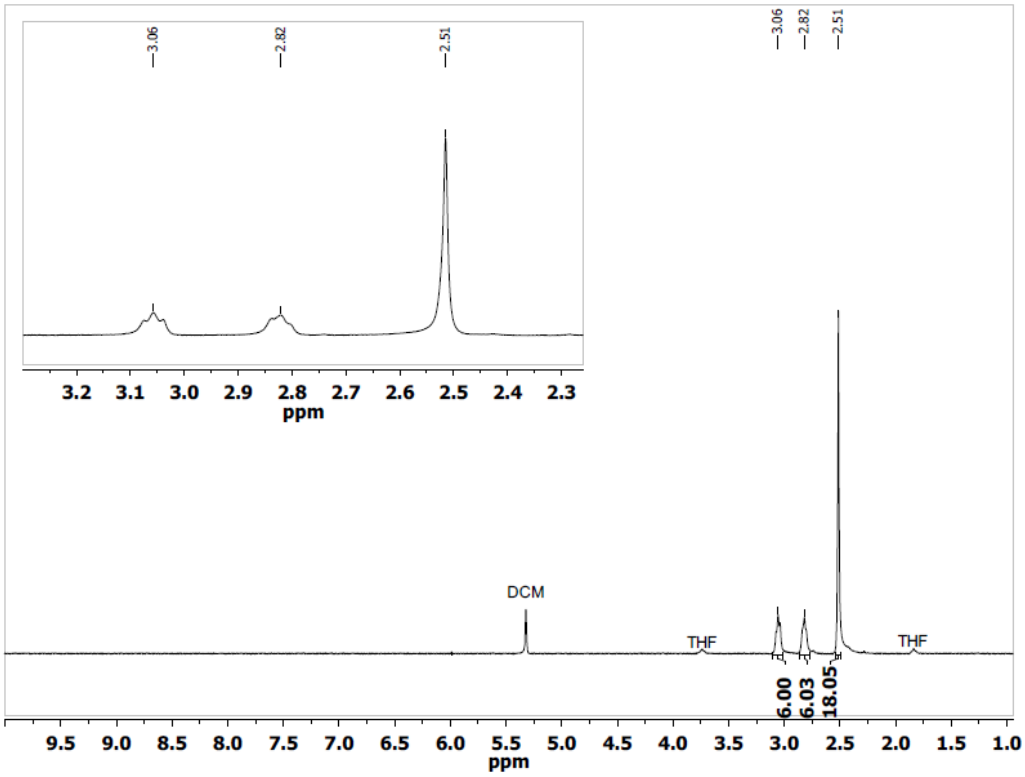


Figure S4: ^{13}C{^{1}H} NMR spectrum of [(Me$_6$tren)MgCl]Cl (**2**)

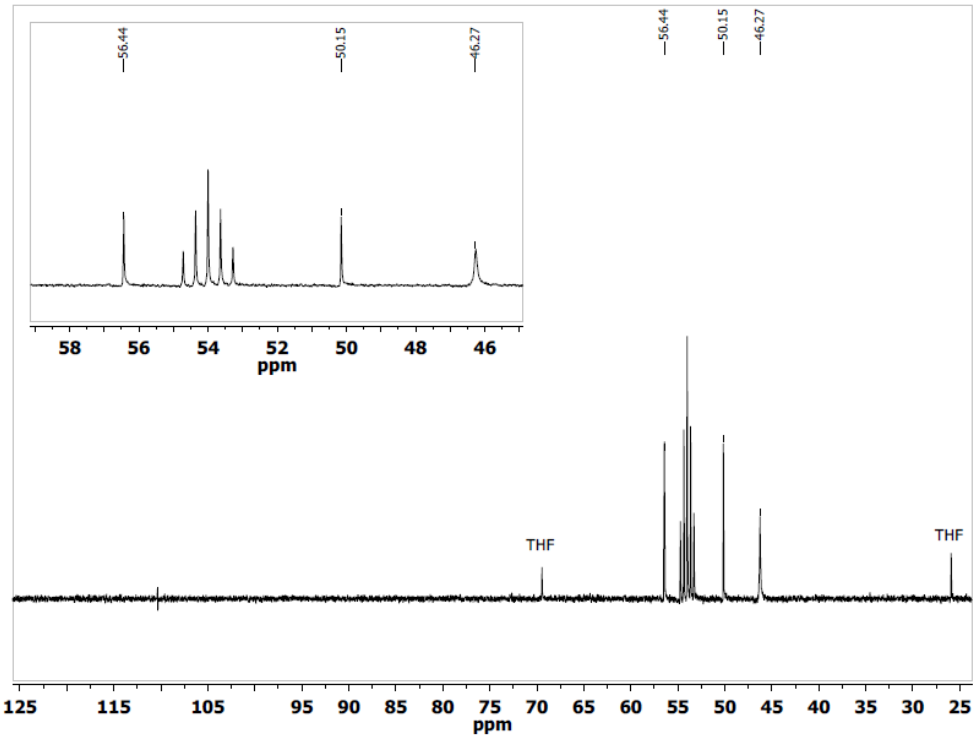


Figure S5: ^{1}H NMR spectrum of [(Me$_6$tren)MgMe]Br (**3**)

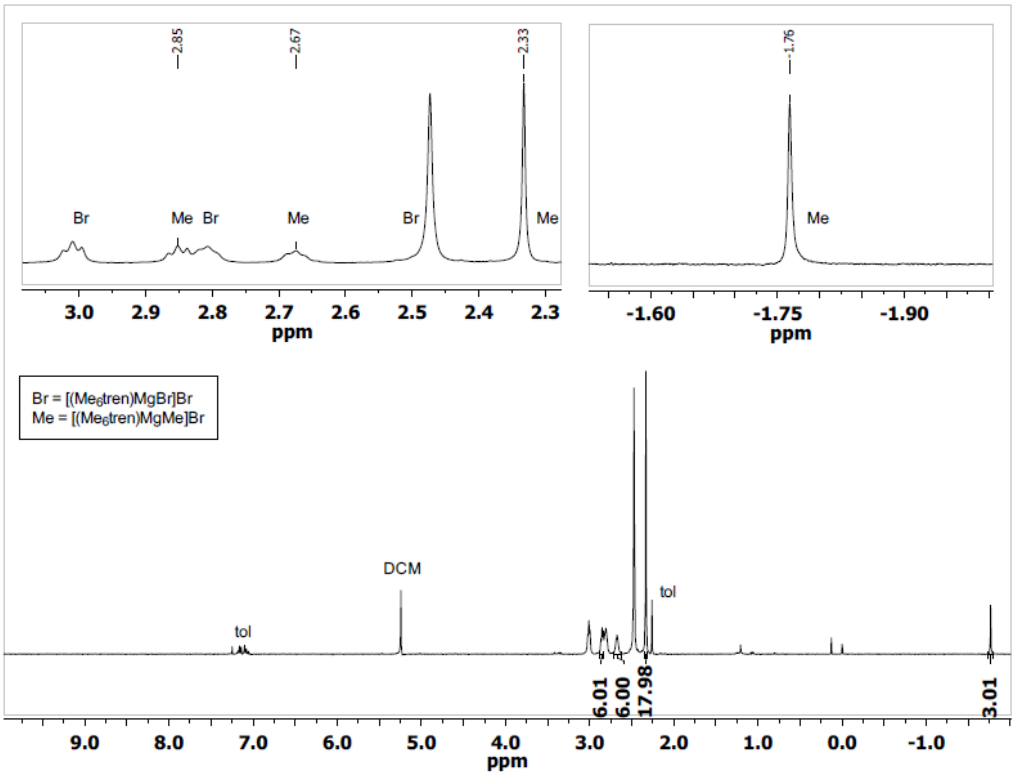


Figure S6: ^{13}C{^{1}H} NMR spectrum of [(Me$_6$tren)MgMe]Br (**3**)

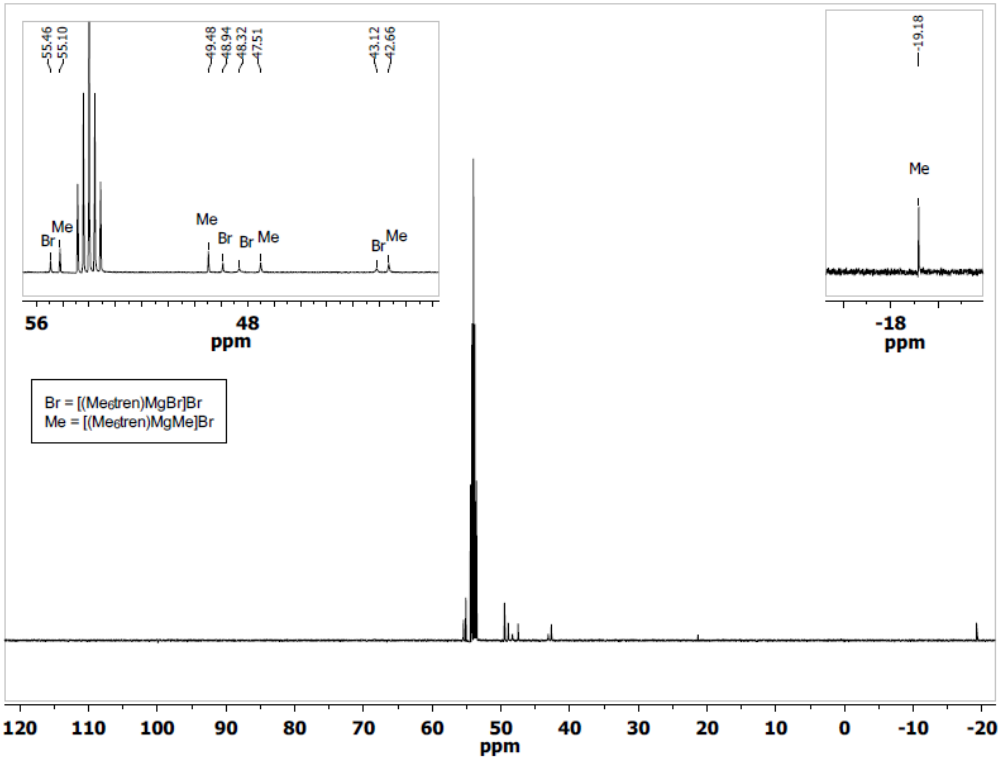


Figure S7: ^{1}H NMR spectrum of $[(Me_6tren)MgBr]_2[MgBr_4]$ (**4**)

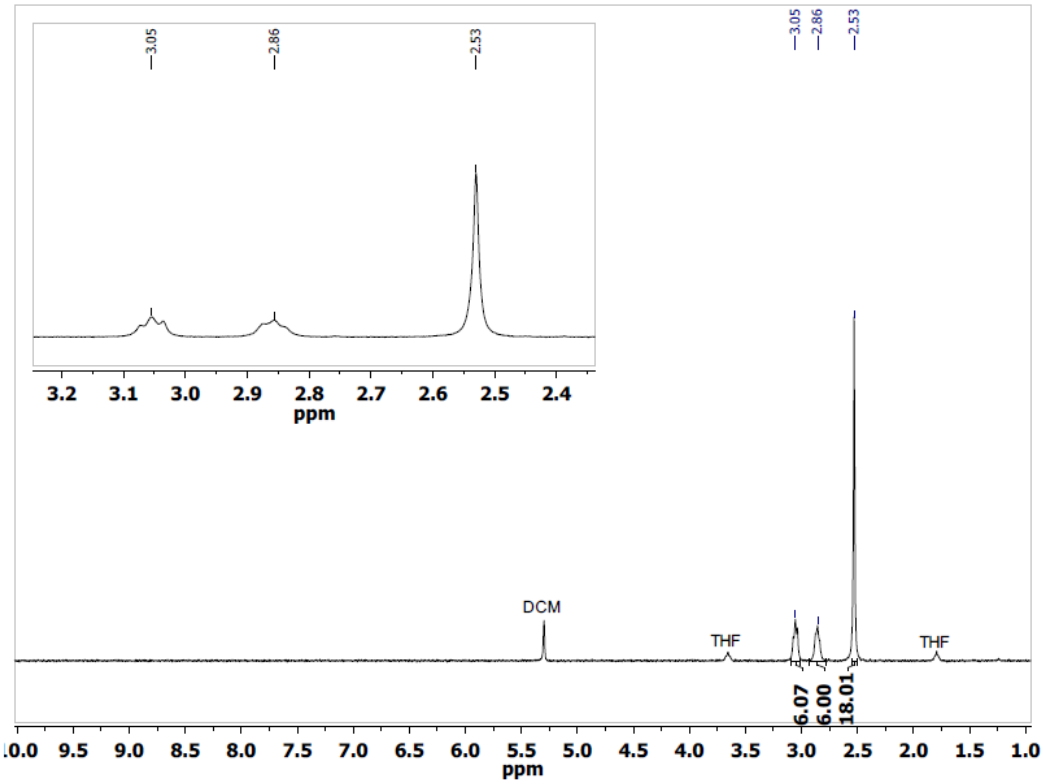


Figure S8: ^{13}C{^{1}H} NMR spectrum of $[(Me_6tren)MgBr]_2[MgBr_4]$ (**4**)

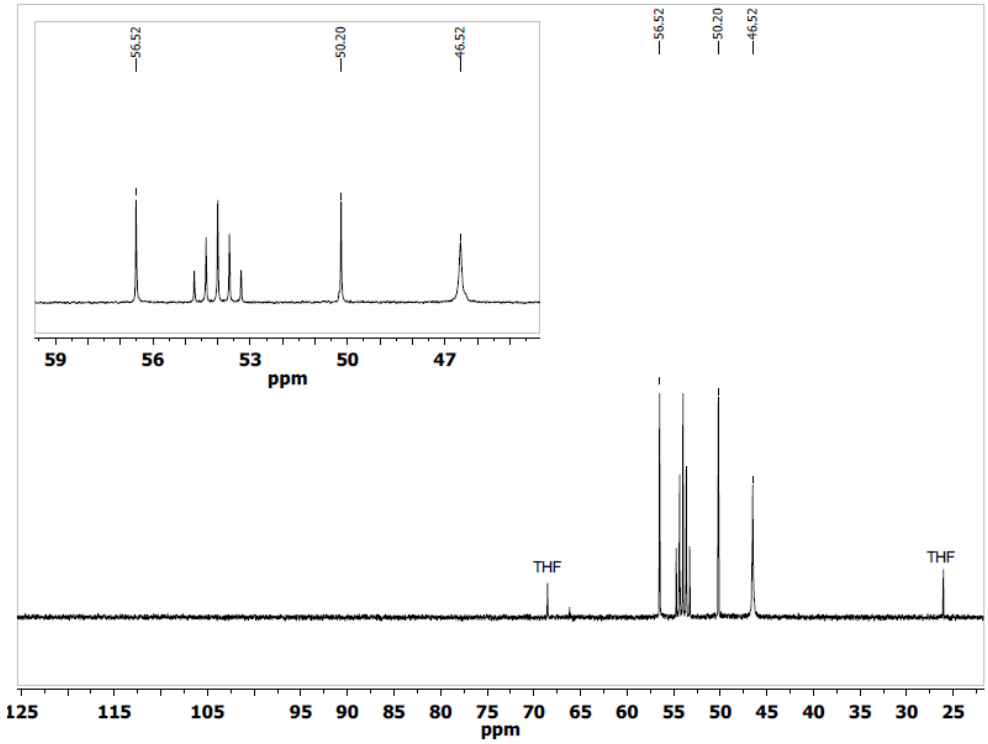


Figure S9: ^{1}H NMR spectrum of (Me_6tren)$MgMe_2$ (**5**)

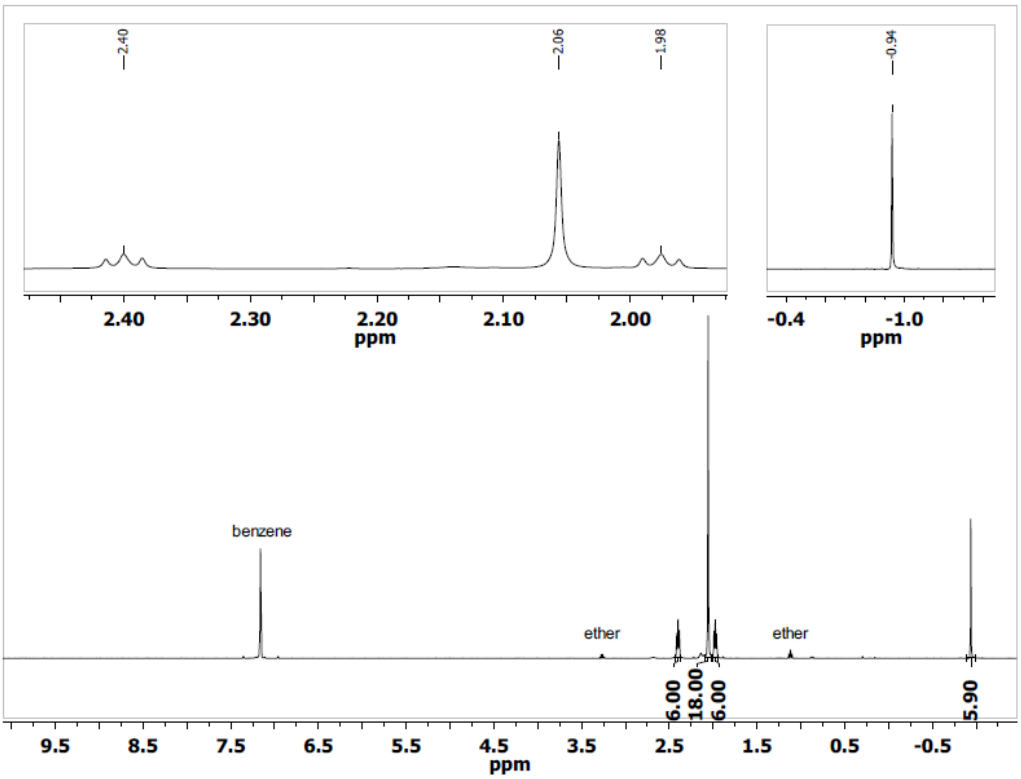


Figure S10: ^{13}C{^{1}H} NMR spectrum of (Me_6tren)$MgMe_2$ (**5**)

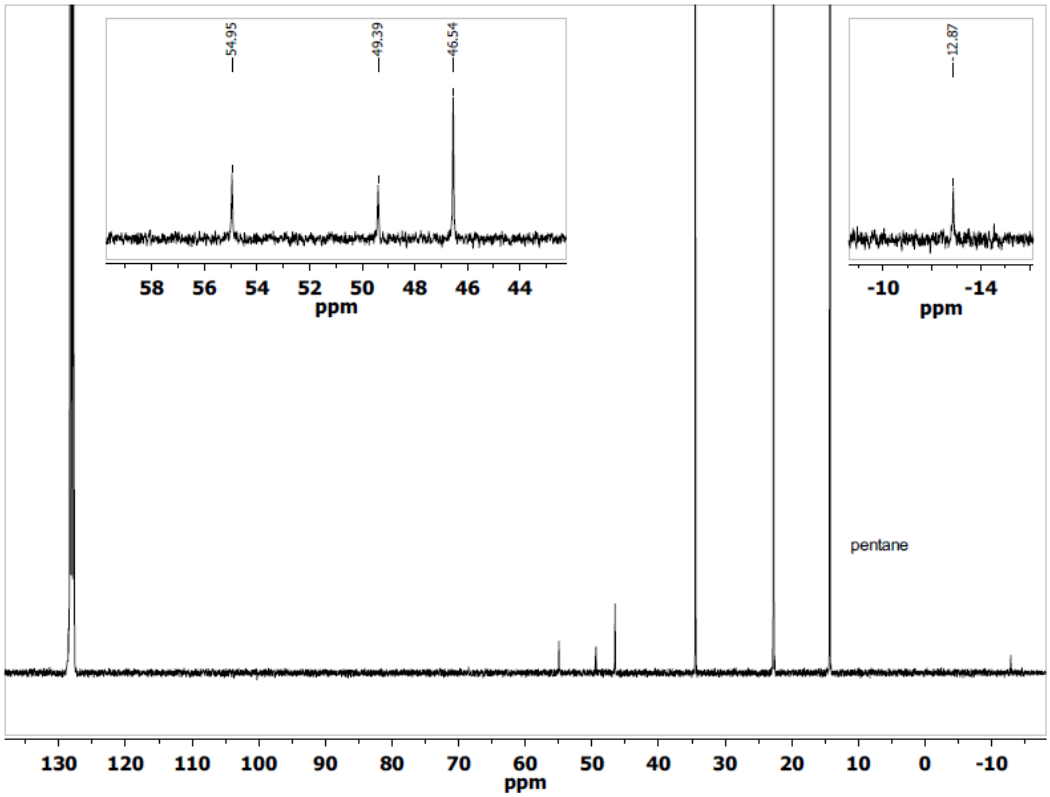


Figure S11: ^{1}H NMR spectrum of $(Me_6tren)Mg(CCPh)_2$ (**6**)

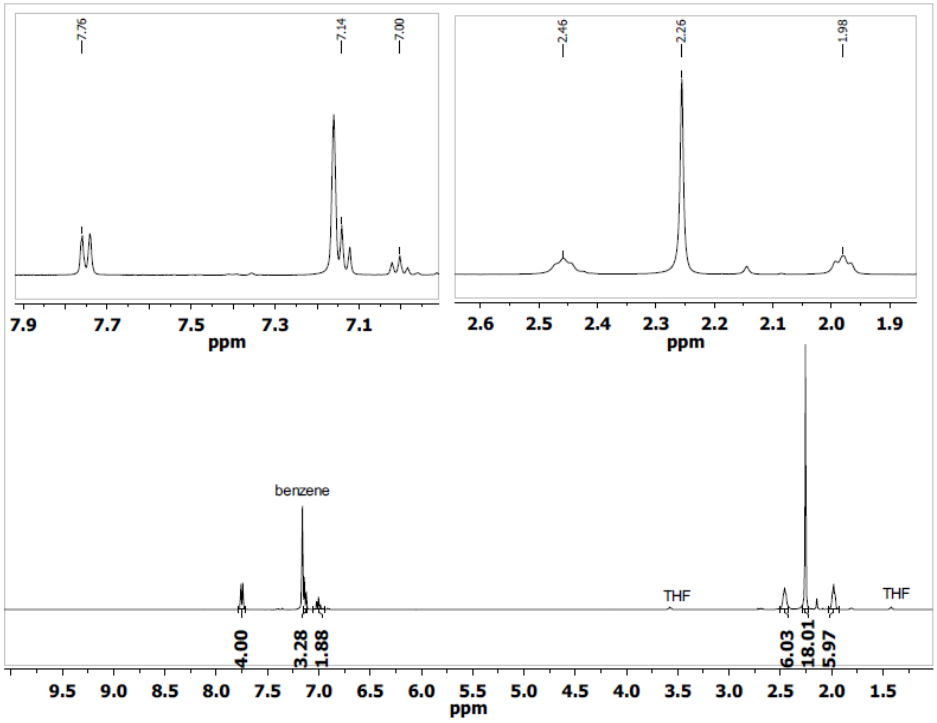


Figure S12: ^{13}C{^{1}H} NMR spectrum of $(Me_6tren)Mg(CCPh)_2$ (**6**)

(in order to achieve sufficient solubility to obtain a ^{13}C NMR spectrum, **6** was generated in situ. Peaks corresponding to excess phenyl acetylene have not been picked.)

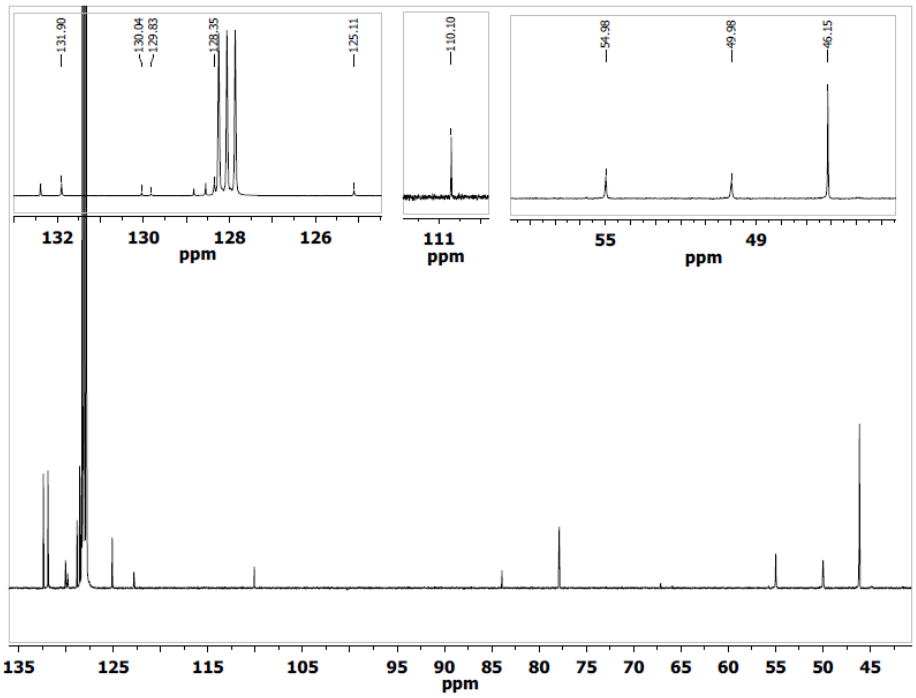


Figure S13: ^{1}H NMR spectrum of [(Me$_6$tren)MgMe]BAr^F (**7**)

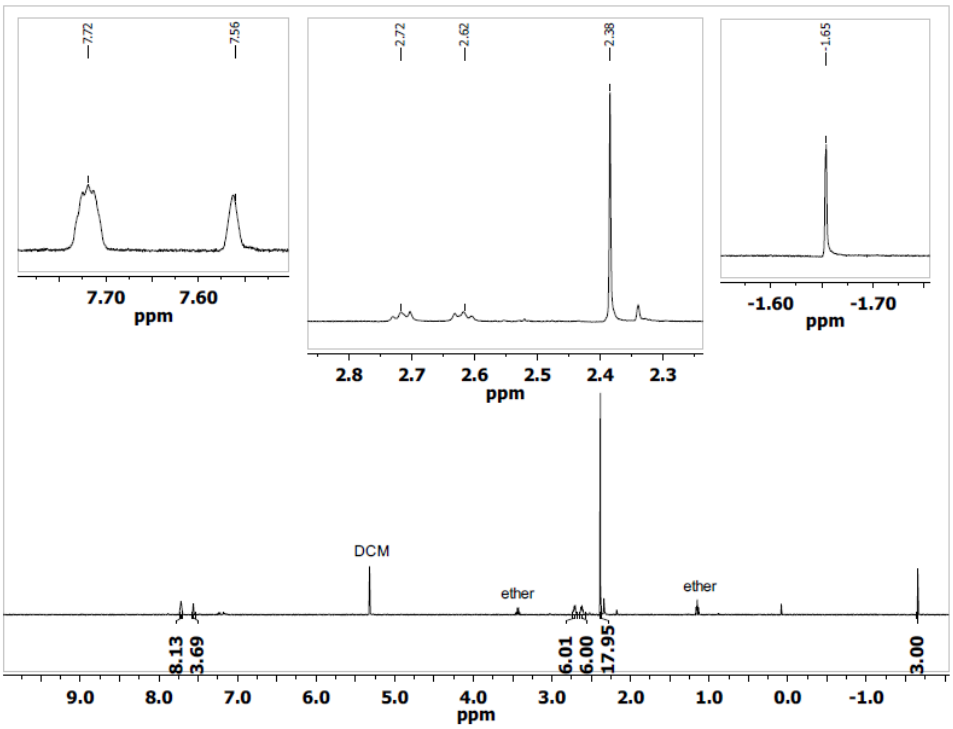
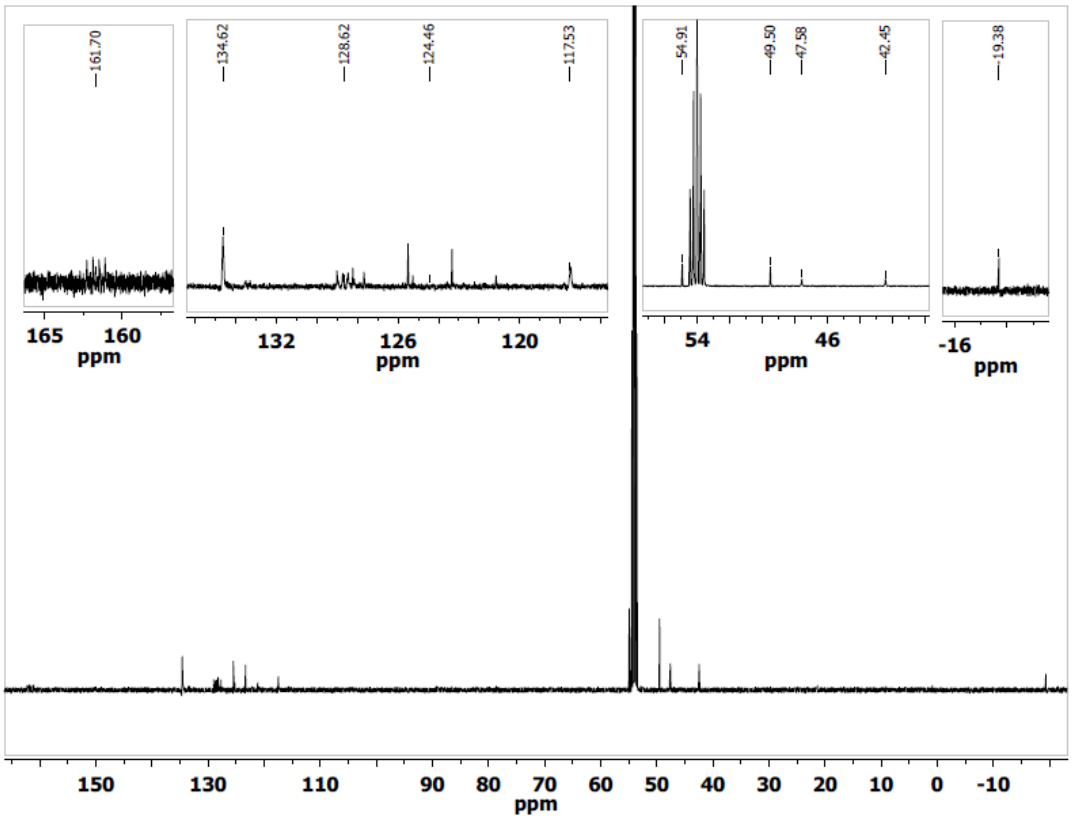


Figure S14: ^{13}C{^{1}H} NMR spectrum of [(Me$_6$tren)MgMe]BAr^F (**7**)



1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr*. **2009**, *42*, 339.
2. Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr*. **2008**, *A64*, 112.