Supporting Information

Synthesis and Solid State Structure of a Metalloid Tin Cluster $[Sn_{10}(trip_8)]$

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Content

Experimental Section

General Procedures. All manipulations were performed in an atmosphere of purified argon using standard Schlenk and glove-box techniques. Toluene and *n*-pentane were dried using mBraun Solvent Purification System. Deuterated solvents were dried over activated molecular sieves (4 Å) and degassed prior to use. The anhydrous nature of the solvents was verified by Karl Fischer titration. $Trip_4Sn_2$[1] as well as $(LMg)_2$ and $(L'Mg)_2$ (L = $HC[C(Me)N(dipp)]_2$; dipp = 2,6-*i*-Pr_2-C_6H_3; L' = $HC[C(Me)N(mes)]_2$, mes = 2,4,6-Me_3-C_6H_2)[2] were prepared by literature method. ^{1}H (300 MHz), $^{13}C\{^1H\}$ (75.5 MHz) and ^{119}Sn (111.9 MHz) NMR (δ in ppm) spectra were recorded using a Bruker Avance DPX-300 spectrometer and the spectra were referenced to the trace of respective protonated solvent impurities present in the deuterated solvents. The ^{119}Sn spectra are referenced to external Me_4Sn. IR spectra were measured in an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. The spectrometer was placed in a glovebox to allow measurement in inert gas atmosphere.

Synthesis of $Sn_{10}(trip)_8$ (1) and RMg(trip) (2)

95 mg (181 mmol) $Trip_4Sn_2$ and 96 mg (109 mmol) $(LMg)_2$ were dissolved in 8 mL of toluene, resulting in an orange-red solution, which was heated to 95 °C for 24 h whereupon the color intensified and finally turned dark red to purple. All volatiles were removed in vacuum and the resulting red-purple residue, which was re-dissolved in *n*-pentane and stored at −30 °C for 12 h. **2** was formed as colorless crystals and isolated by filtration. All volatiles were removed from the remaining solution, yielding **1** as red-purple crystalline solid. Single crystals of **1** were obtained from a solution of **1** in *n*-hexane upon storage at -30 °C for 6 d.

1: ^{1}H NMR (Tol-d_8, 300 MHz): δ 1.10 (m, 18H, *o*-$CH(CH_3)_2$), 1.14 (d, $^3J_{HH}$ = 6.8 Hz, 18H, *o*-$CH(CH_3)_2$), 1.17 (d, $^3J_{HH}$ = 6.8 Hz, 18H, *o*-$CH(CH_3)_2$), 1.19 (d, $^3J_{HH}$ = 6.9 Hz, 18H, *o*-$CH(CH_3)_2$), 1.21 (d, $^3J_{HH}$ = 6.9 Hz, 18H, *o*-$CH(CH_3)_2$), 1.10-1.21 (d, 6H, *o*-$CH(CH_3)_2$, covered by other signals), 1.23 (d, $^3J_{HH}$ = 6.9 Hz, 48 H, *p*-$CH(CH_3)_2$), 2.59 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, -$CH(CH_3)_2$), 2.79 (sept, $^3J_{HH}$ = 6.9 Hz, 8H, -$CH(CH_3)_2$), 2.94 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, -$CH(CH_3)_2$), 3.26 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, -$CH(CH_3)_2$), 3.34 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, -$CH(CH_3)_2$), 2.59-3.34 (sept, 4H, -$CH(CH_3)_2$), 6.94 (s, 8 H, C_6H_2), 6.95-7.12 (s, 8 H, C_6H_2, covered by solvent peaks); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 24.7 (-$CH(CH_3)_2$), 24.8 (-$CH(CH_3)_2$), 24.9 (-$CH(CH_3)_2$), 25.0 (-$CH(CH_3)_2$), 26.9 (-$CH(CH_3)_2$) , 29.4 (-$CH(CH_3)_2$), 35.1 (-$CH(CH_3)_2$), 35.2 (-$CH(CH_3)_2$), 43.1 (-$CH(CH_3)_2$) , 96.3 , 120.0 (-C_6H_3), 122.8 (-C_6H_3), 124.9 (-C_6H_3), 126.2 (-C_6H_3), 142.7 (-C_6H_3), 145.3 (*o*-C_6H_3), 147.4 (*o*-C_6H_3), 149.5 (*o*-C_6H_3), 157.9 (*o*-C_6H_3), 162.9 (*ipso*-C_6H_3), 170.8 (*ipso*-C_6H_3); ^{119}Sn (C_6D_6, 111.9 MHz): 134.7, 236.7, 358.9. IR (neat): ν 2958 (s), 2925 (m), 2867 (m), 1660 (w), 1622 (w), 1593 (w), 1551 (m), 1520 (s), 1469 (m), 1459 (m), 1435 (m), 1406 (m), 1381 (m), 1361 (m), 1314 (m), 1259 (m), 1174 (m), 1098 (m), 1055 (m), 1020 (m), 934 (w), 874 (w), 849 (w), 793 (m), 757 (m), 714 (w), 700 (w), 467 (w), 439 (w) cm^{-1}.

2: ^1H NMR (Tol-d_8, 300 MHz): δ 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 12H, trip-*o*-CH(CH_3)$_2$), 1.13 (d, $^3J_{HH}$ = 6.8 Hz, 12H, dipp-*o*-CH(CH_3)$_2$), 1.21 (d, $^3J_{HH}$ = 6.8 Hz, 12H, dipp-*o*-CH(CH_3)$_2$), 1.29 (d, $^3J_{HH}$ = 6.9 Hz, 6H, trip-*p*-CH(CH_3)$_2$), 1.70 (s, 6H, backbone-CH_3), 2.35 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, trip-*o*-C*H*(CH_3)$_2$), 2.84 (sept, $^3J_{HH}$ = 6.9 Hz, 1 H, trip-*p*-C*H*(CH_3)$_2$), 3.27 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, dipp-*o*-C*H*(CH_3)$_2$), 4.95 (s, 1 H, backbone-C*H*), 6.90 (s, 2 H, C_6H_2), 7.02 (s, 2 H, *p*-C_6H_3), 7.14-7.15 (s, 4 H, *m*-C_6H_3), covered by solvent peak).

Reaction of Sn_2trip_4 and $(R'Mg)_2$

50 mg (152 mmol) $Trip_4Sn_2$ and 80 mg (152 mmol) $(L'Mg)_2$ were dissolved in 5 mL of toluene, resulting in an orange-red solution, which was stirred over 24 h at rt, whereupon it turned into an orange-brown solution with a black precipitate. All volatiles were removed under reduced pressure, the resulting solid was suspended in *n*-hexane and all insoluble precipitates (elemental Sn) was filtered off. Single crystals of **3** were obtained after storage of the *n*-hexane solution at -30 °C for 1 d.

3: ^1H NMR (Tol-d_8, 300 MHz): δ 1.15 (d, $^3J_{HH}$ = 6.8 Hz, 6H, trip-*p*-CH(CH_3)$_2$), 1.21 (d, $^3J_{HH}$ = 6.8 Hz, 12H, trip-*o*-CH(CH_3)$_2$), 1.66 (s, 6H, backbone-CH_3), 2.07 (s, 6H, mes-*p*-CH_3), 2.10-2.16 (sept, 2H, covered by solvent peak), 2.18 (s, 12H, mes-*o*-CH_3), 2.73 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, trip-*p*-C*H*(CH_3)$_2$), 5.01 (s, 1 H, backbone-C*H*), 6.67 (s, 4 H, mes-C_6H_2), 6.87 (s, 2 H, trip-C_6H_2).

Fig. S1. ^{1}H-NMR of **1** in Tol-d_8 at rt

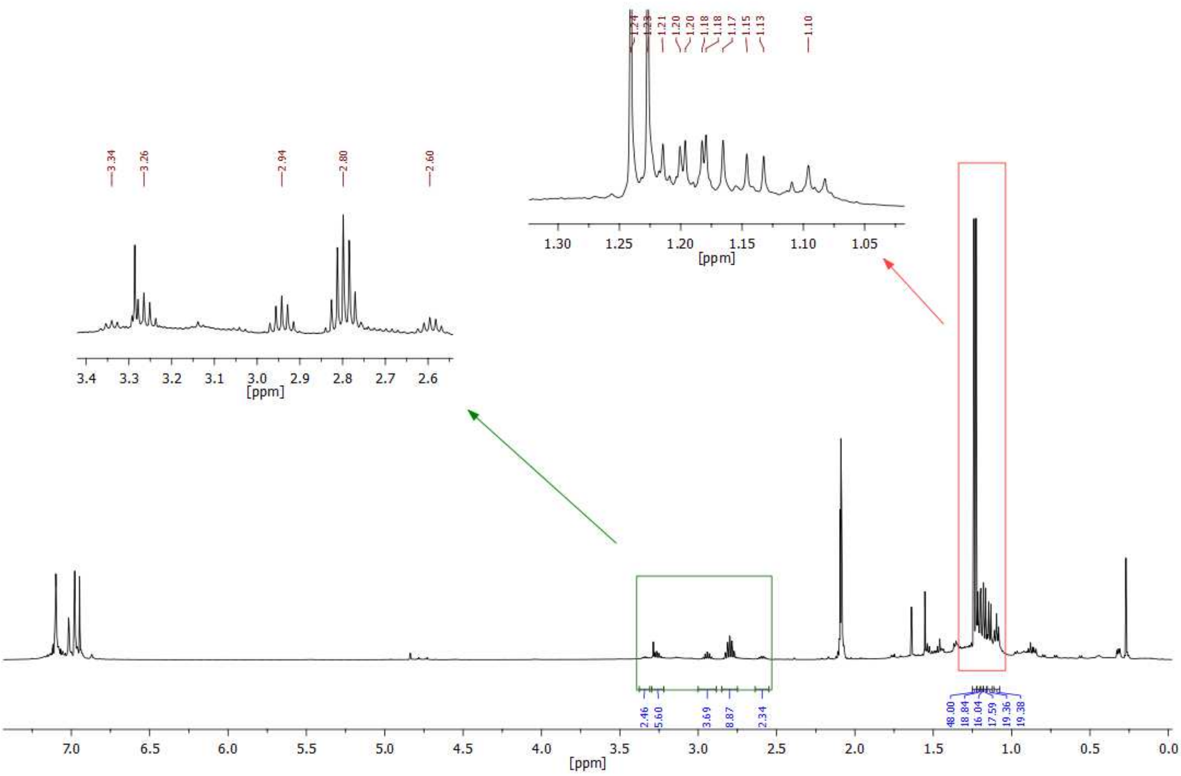


Fig. S2. ^{13}C-NMR of **1** in C_6D_6 at rt

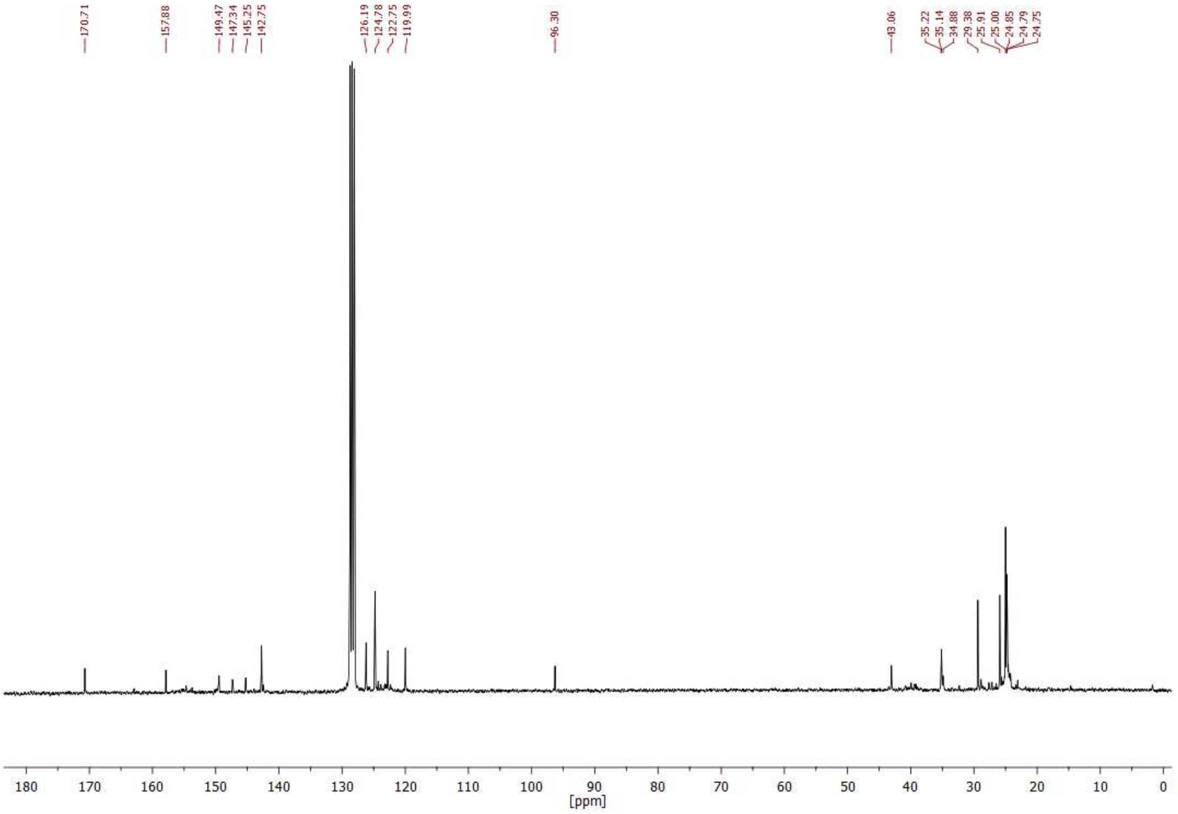


Fig. S3. ^{119}Sn-NMR of **1** in Tol-d_8 at rt

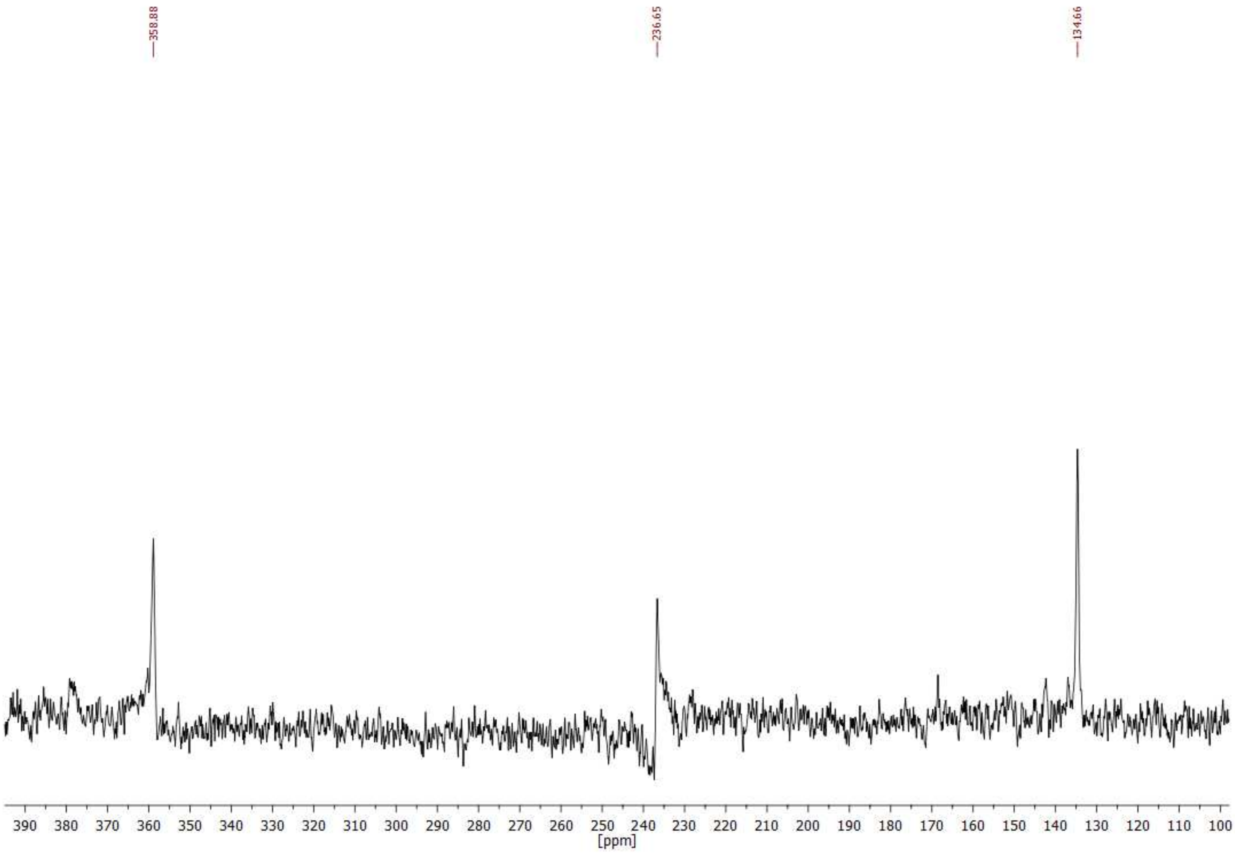


Fig. S4. IR spectrum of **1**

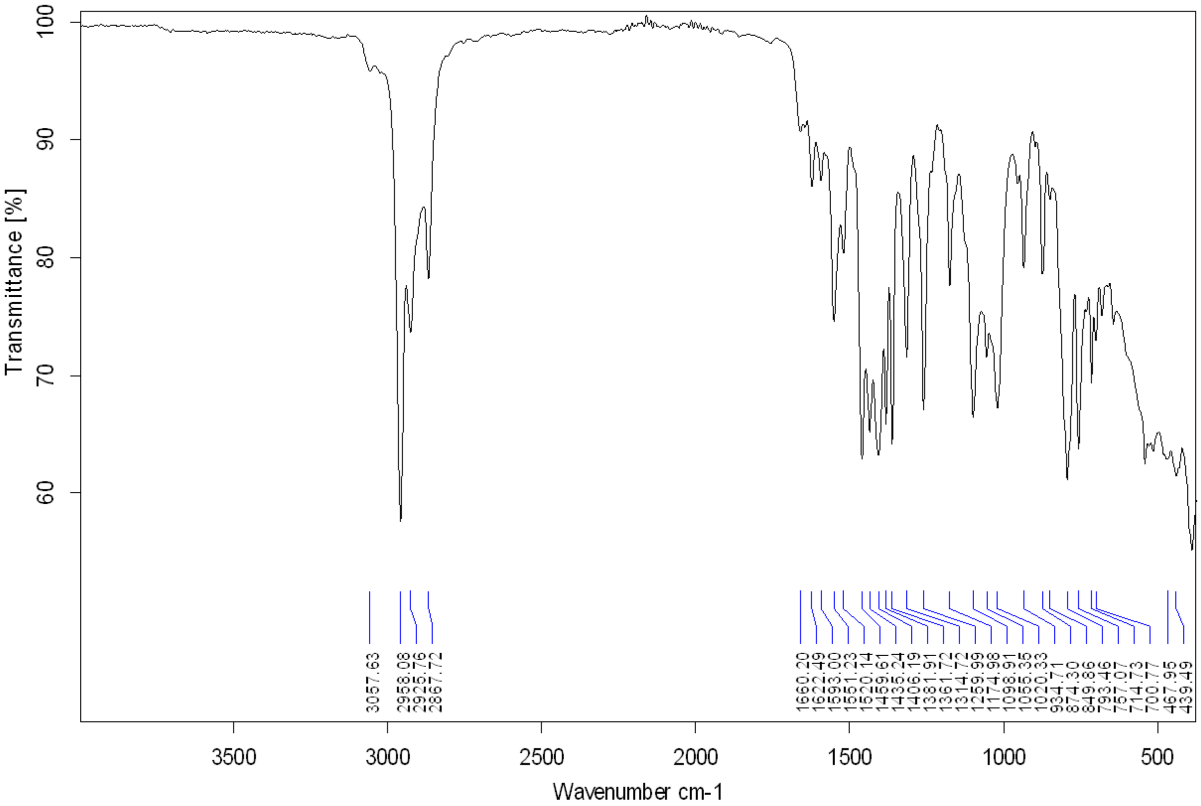


Fig. S5. In situ ^{1}H-NMR of the reaction of $(LMg)_2$ and Sn_2trip_4 in Tol-d_8 after 6h at 95 °C.

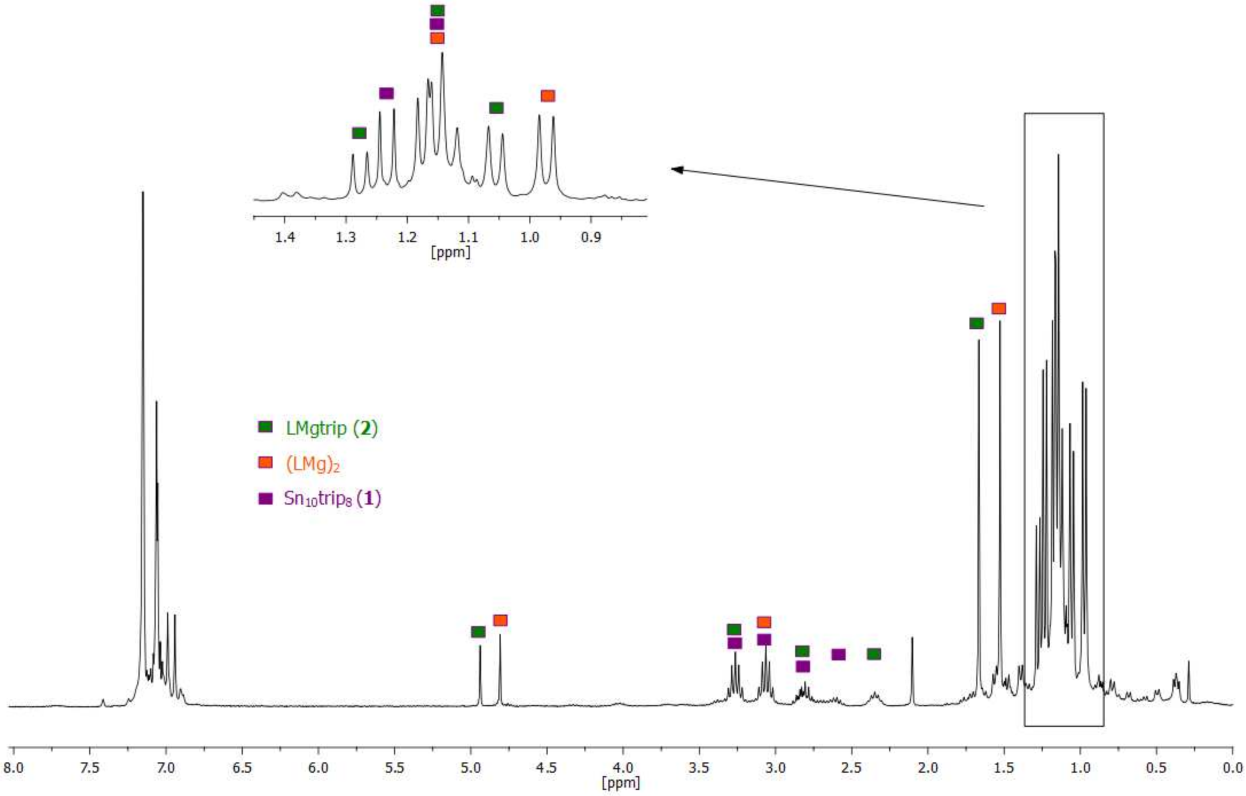


Fig. S6. In situ ^{1}H-NMR of the reaction of $(LMg)_2$ and Sn_2trip_4 in Tol-d_8 after 24h at 95 °C.

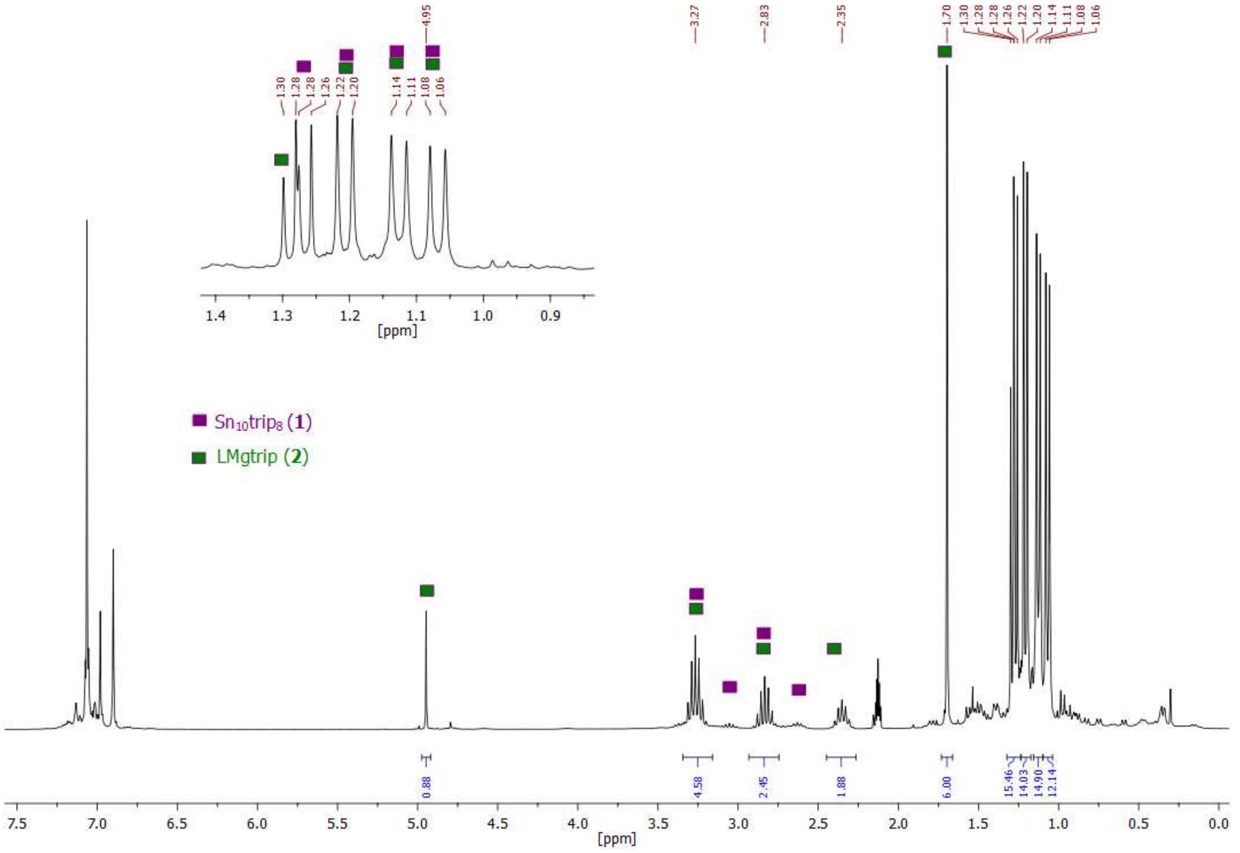


Fig. S7. Temperature-dependant ^{1}H-NMR spectra of **1** in Tol-d$_8$ (11 (10 °C), 22 (25 °C), 33 (60 °C), 44 (80 °C), 55 (110 °C))

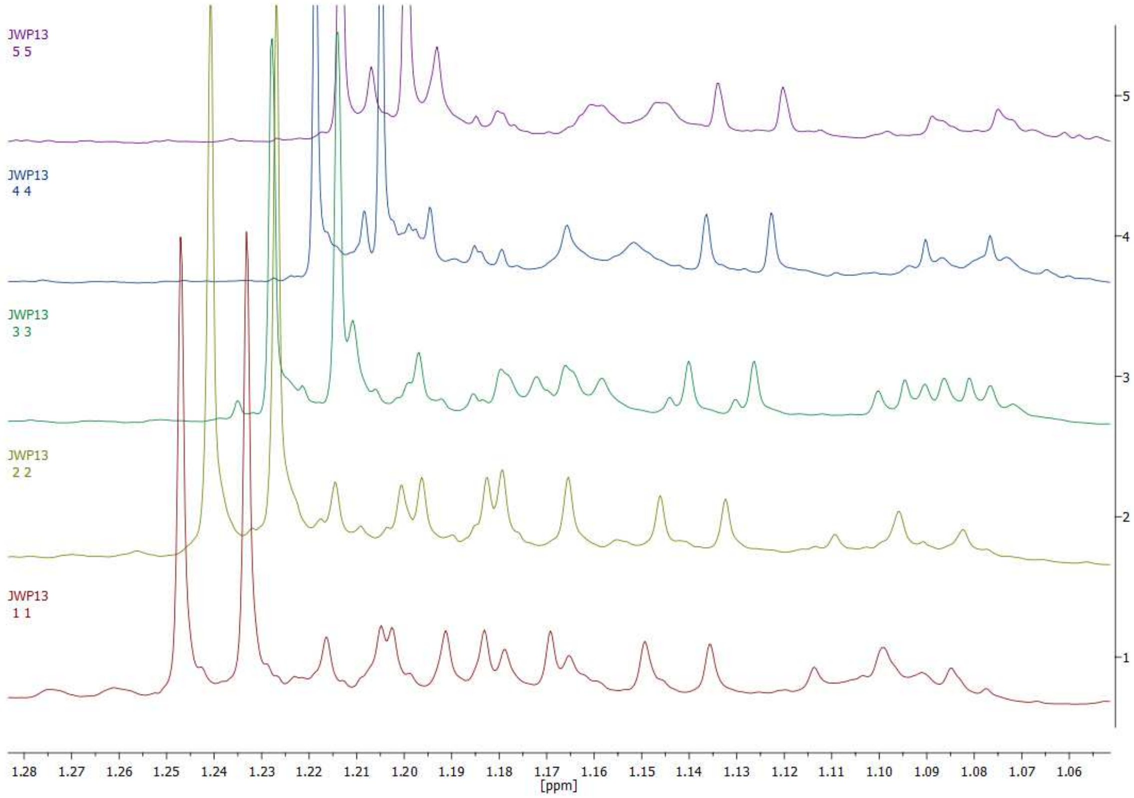


Fig. S8. Temperature-dependant ^{1}H-NMR spectra of **1** in Tol-d$_8$ (11 (− 80 °C), 22 (− 60 °C), 33 (− 40 °C), 44 (− 10 °C), 55 (0 °C))

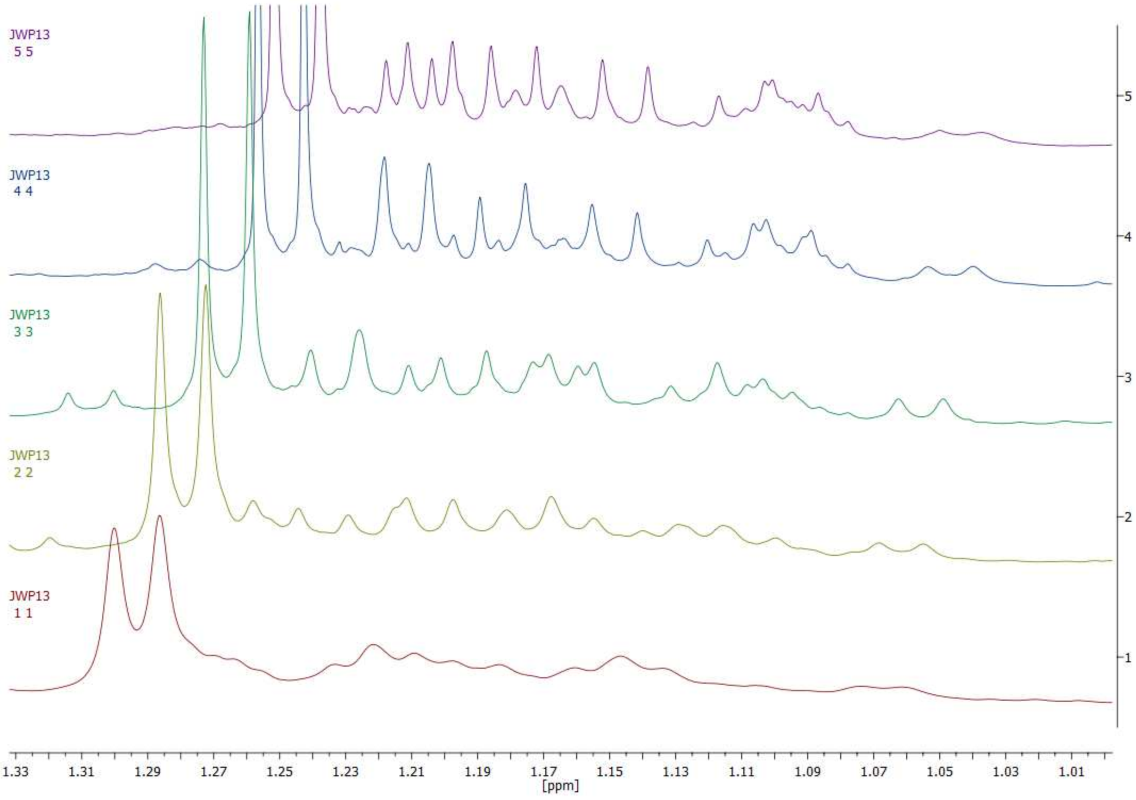


Fig. S9. UV/Vis spectrum of **1**

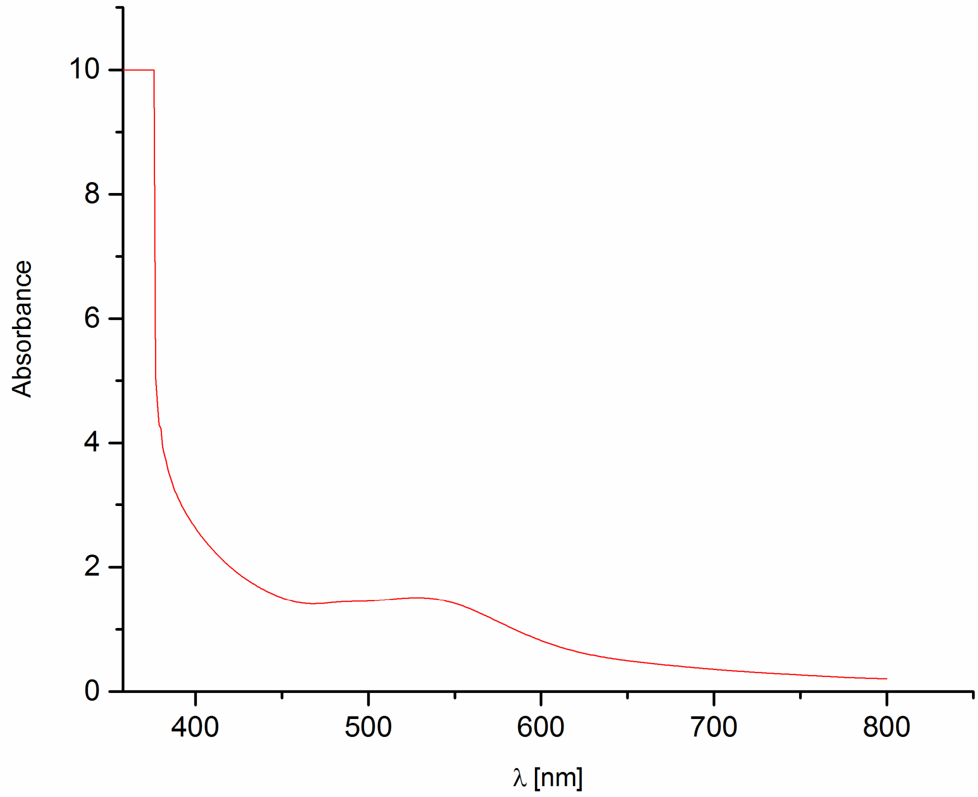


Fig. S10. ^{1}H-NMR of LMgtrip (**2**) in Tol-d$_8$

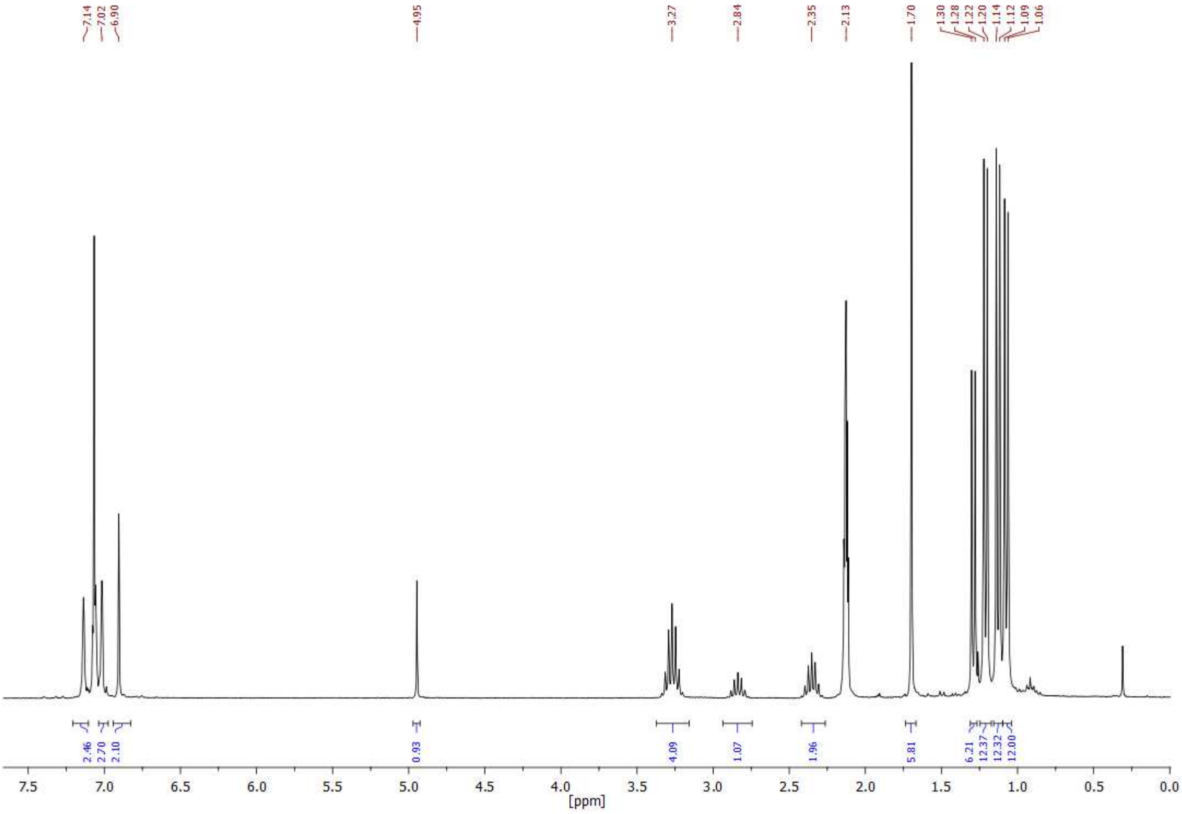


Fig. S11. In situ ^{1}H-NMR of the reaction of $(L'Mg)_2$ and Sn_2trip_4 in Tol-d_8 after 24h at rt.

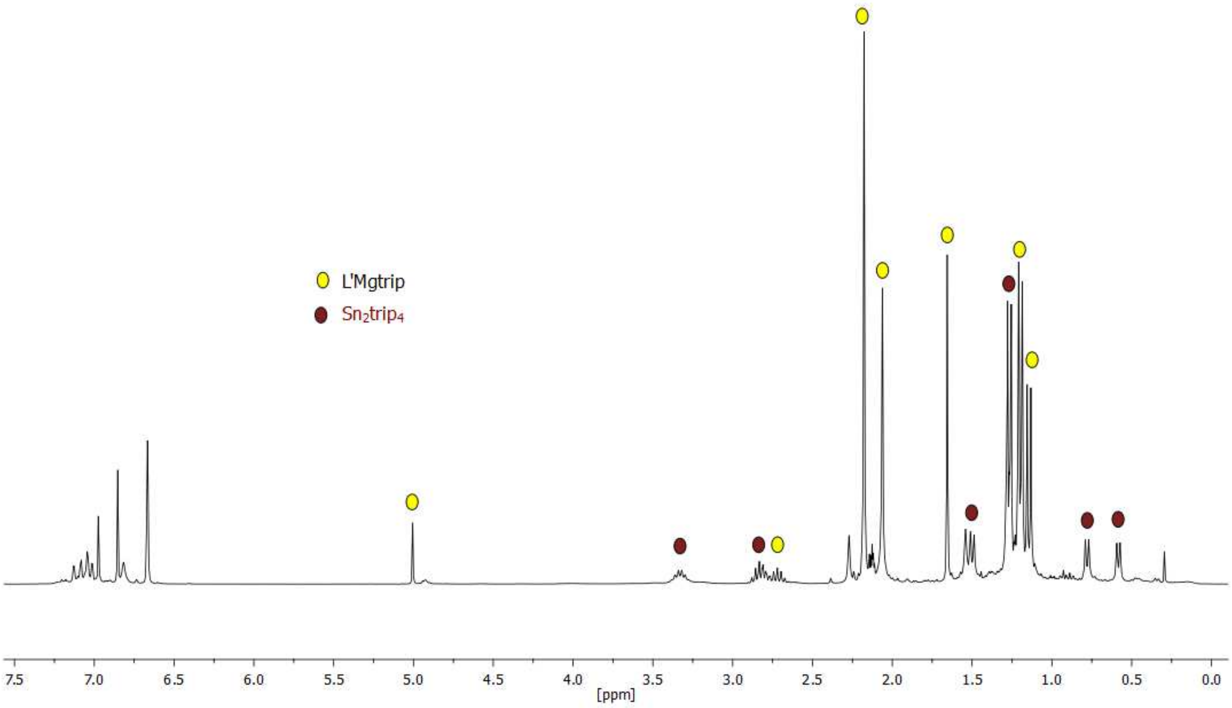
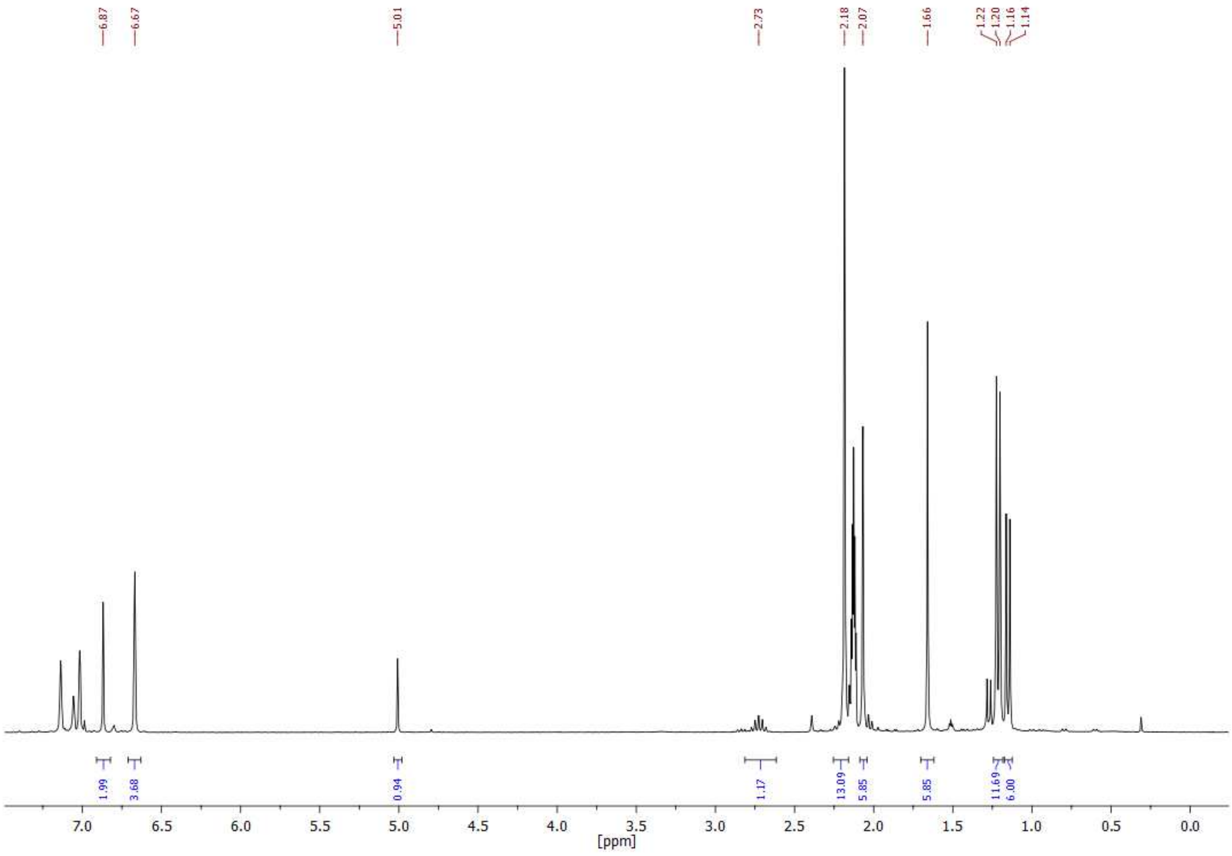


Fig. S12. ^{1}H-NMR L'Mgtrip (**3**) in Tol-d_8 at rt.



Single-crystal X-ray analysis.

The crystals of **1**, **2**, and **3** were mounted on nylon loops in inert oil. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated Mo$_{K\alpha}$ radiation, λ = 0.71073 Å) at 100 K. The structures were solved by Direct Methods (SHELXS-97)[3] and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-2014 and shelXle).[4] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined rigid methyl groups. The absolute structures of **2** and **3** could be determined reliably. Parsons quotient method was used to determine the absolute structure parameter x.[5] CCDC 1480548 (**1**), 1499559 (**2**) and 1489510 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S1: Crystal structure data of **1** and **3**

Identification code	**1**	**2**	**3**
Empirical formula	$C_{144}H_{232}Sn_{10}$	$C_{44}H_{64}Mg\,N_2$	$C_{38}H_{52}Mg\,N_2$
Formula weight	3150.18	645.28	561.12
Density (calculated)	1.506 g·cm^{-1}	1.080 g · cm^{-3}	1.100 g · cm^{-3}
$F(000)$	1596	1416	1224
Temperature	100(1) K	100(2) K	104(2) K
Crystal size [mm]	0.210 × 0.150 × 0.110	0.358 × 0.218 × 0.194	0.224 × 0.125 × 0.073
Crystal colour	dark red	colourless	colourless
Crystal description	block	block	tablet
Crystal system	triclinic	orthorhombic	orthorhombic
Space group	P -1	$P2_12_12_1$	$P2_12_12_1$
a [Å]	14.287(2)	9.0942(5)	11.2579(2)
b [Å]	15.400(2)	20.5821(11)	16.4458(3)
c [Å]	16.699(2)	21.2116(12)	18.2926(3)
α [°]	102.618(8)	90	90
β [°]	97.963(8)	90	90
γ [°]	99.865(8)	90	90
Volume	3472.6(9) Å^3	3970.3(4) Å^3	3386.79(10) Å^3
Z	1	4	4
Cell measurement reflect. used	9838	9071	9899
θ range for data collection	2.100°- 30.694°	1.920°- 33.250°	2.124°- 30.525°
Index ranges	$-19 \le h \le 18$	$-12 \le h \le 13$	$-16 \le h \le 13$
	$-21 \le k \le 22$	$-31 \le k \le 31$	$-22 \le k \le 21$
	$-23 \le l \le 23$	$-32 \le l \le 31$	$-24 \le l \le 25$
Absorption coefficient	1.811 mm^{-1}	0.076 mm^{-1}	0.080 mm^{-1}
Max./min. Transmission	0.75/0.62	0.75/0.67	0.75/0.66
R_{merg} before/after correction	0.0641/0.0484	0.0531/0.0407	0.0493/0.0449
Reflections collected	67514	62564	38334
Independent reflections	19130	14450	9070
R_{int}	0.0436	0.0293	0.0327
Reflections with $I > 2\sigma(I)$	11772	11590	7951
Restraints / Parameters	13 / 720	3 / 470	0 / 384
GooF	1.111	1.035	1.028
Weighting details	$w = 1/[\sigma^2(F_{obs}^2) + (0.0498P)^2 + 65.4214P]$ where $P = (F_{obs}^2 + 2F_{calc}^2)/3$		
R_1 [$I > 2\sigma(I)$]	0.0628	0.0459	0.0370
wR_2 [$I > 2\sigma(I)$]	0.1378	0.1084	0.0848
R_1 [all data]	0.1357	0.0680	0.0468
wR_2 [all data]	0.1927	0.1226	0.0898
Absolute struct. parameter	–	-0.07(4)	-0.11(6)
Largest diff. peak and hole	3.481/-2.376	0.601/-0.306	0.288/-0.211

Fig. S13. Single crystal structure of **2** (Thermal ellipsoids at 50% probability levels, H atoms omitted for clarity)

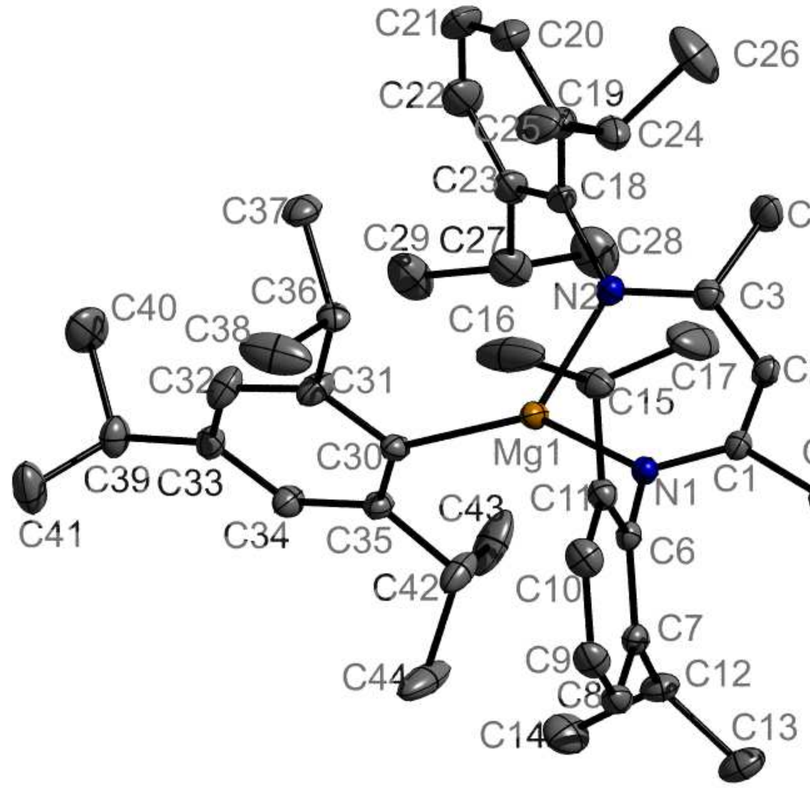
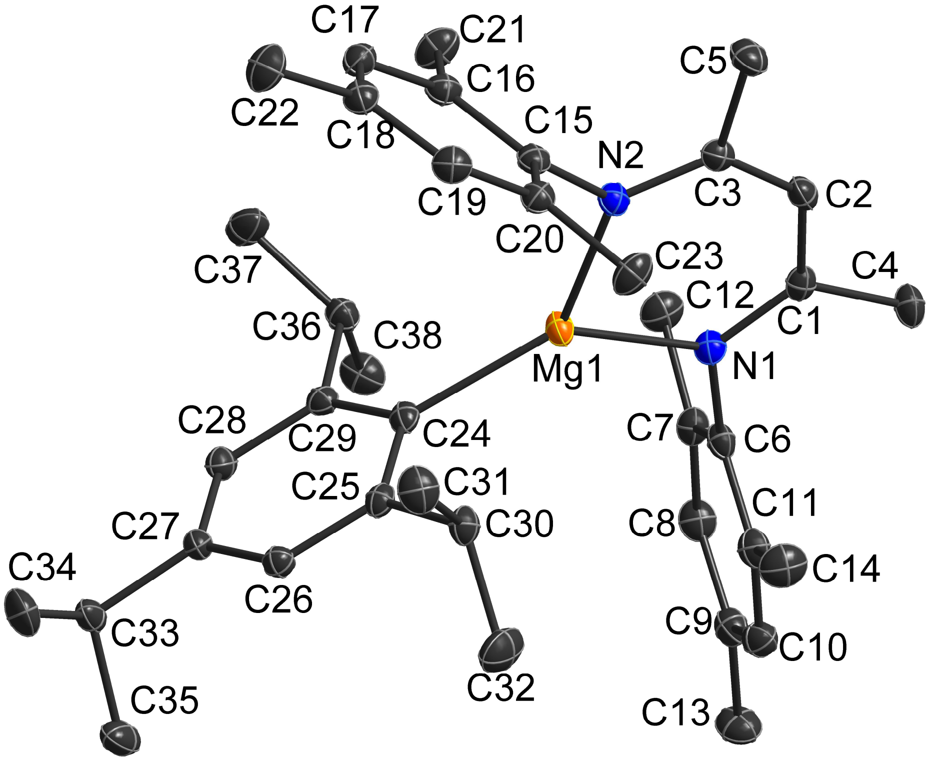


Fig. S14. Single crystal structure of **3** (Thermal ellipsoids at 50% probability levels, H atoms omitted for clarity)



References

[1] M. Weidenbruch, A. Schäfer, H. Kilian, S. Pohl, W. Saak, H. Marsmann, *Chem. Ber.*, 1992, **125**, 563-566.

[2] S.J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A.J. Edwards, G. J. McIntyre, *Chem. Eur. J.*, 2010, **16**, 938-955.

[3] G. M. Sheldrick, *Acta Cryst.* 1990, **A46**, 467-473.

[4] SHELXL-2014, G. M. Sheldrick, Acta Cryst. **2008**, *A64*, 112-122; shelXle, C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.* **2011**, *44*, 1281-1284.

[5] For more details see: S. Parsons, H. D. Flack, *Acta Cryst*. 2004, **A60**, s61; b) S. Parsons, H. D. Flack, T. Wagner, *Acta Cryst*. 2013, **B69**, 249-259.