Neutral ligand induced methane elimination from rare-earth metal tetramethylaluminates up to the six-coordinate carbide state

Ajay Venugopal, Ina Kamps, Daniel Bojer, Raphael J. F. Berger, Andreas Mix, Alexander Willner, Beate Neumann, Hans-Georg-Stammler and Norbert W. Mitzel*

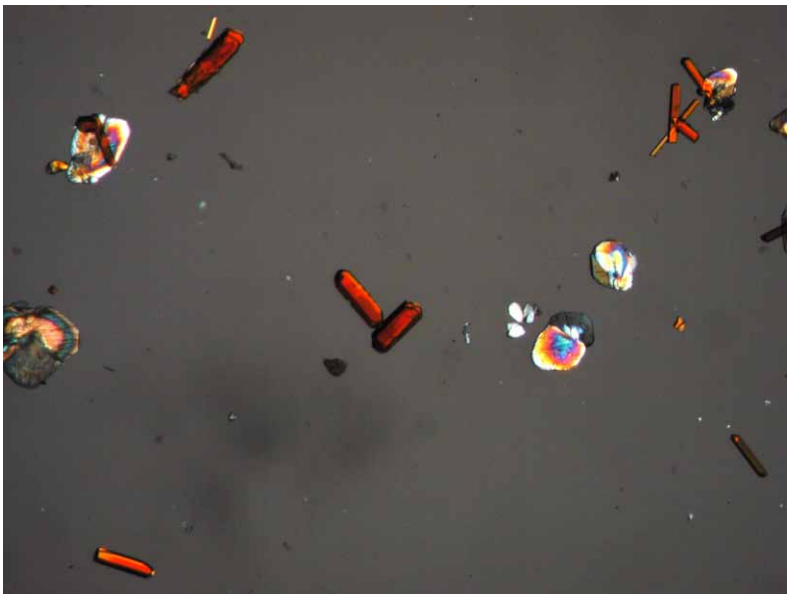

Figure S1: Compound **4** (red crystals) and compound **5** (pale yellow crystals)

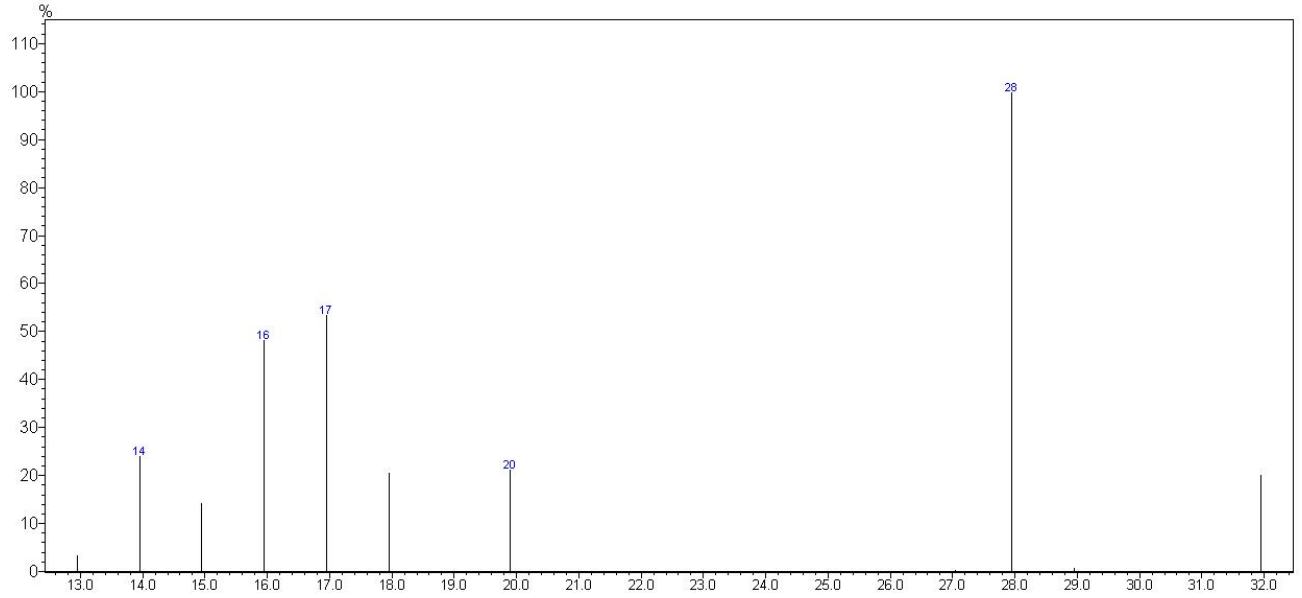

Figure S2: Mass spectrum (GC/MS) of the gas resulting from the deuterolysis of compound **5** with D_2O after drying over CaH_2. The formally anionic CH_3, CH_2 and C groups result in the formation of CH_3D (*m*/*z* = 17), CH_2D_2 (*m*/*z* = 18) and CD_4 (*m*/*z* = 20). The peaks at 28 and 32 are N_2 and O_2 from air.

Table S 1. Results of quantumchemical calculations at the RI-DFT(BP86)/def2-SV(P) + cosmo level for compound 3 and oxygen analogues (continuation of Table 1 in the manuscript). **6a** – **6d** are doubly deprotonated species. The deprotonated sites are also listed. All calculations show the close fit of the calculations and experimental structure for **3**, but serious misfit for the oxygen centred structures.

No			**3**	**6**	**6a**	**6b**	**6c**	**6d**
central atom			C	O	O	O	O	O
charge			neutral	2+	neutral	neutral	neutral	neutral
description					**6** – $2H^+$	**6** – $2H^+$	**6** – $2H^+$	**6** – $2H^+$
deprotonated positions					C12/C12a	C32/C32a	C11/C11a	C13/C13a
X33	M1		2.694	3.504	3.787	2.506	2.437	4.069
X33	M2		2.442	2.619	2.600	2.593	2.676	2.407
X33	Al1		2.072	2.037	2.019	1.983	2.041	2.097
X33	Al3		2.109	1.993	1.926	3.882	3.441	1.915
M1	C24		2.491	2.450	2.538	2.424	2.406	2.454
M1	C12		2.838	3.308	2.431	3.297	4.308	5.766
M1	N1		2.830	2.604	2.674	2.735	2.646	2.730
M1	N2		2.878	2.579	2.717	2.725	2.708	2.652
M2	C40		2.506	2.459	2.456	2.455	2.456	2.705
Al2	C24		2.102	2.154	2.100	2.085	2.089	2.134
M2	C24		2.398	2.378	2.383	2.527	2.539	2.423
M2	C13		2.602	2.517	2.513	2.580	2.518	2.321
M2	C23		2.645	2.476	2.541	2.572	2.602	2.700
M2	C32		2.687	2.696	2.718	2.436	2.470	3.016
Al1	X33	M1	86.3	89.3	74.3	104.2	124.8	123.9
Al3	X33	M1	167.7	155.5	154.3	149.8	159.0	123.3
M2	X33	M1	87.0	78.0	71.4	93.3	92.8	68.7
M2	X33	Al3	84.9	89.5	90.6	65.5	107.2	98.3
Al1	X33	Al3	102.1	110.6	123.0	95.6	66.2	110.5
Al1	X33	Al1s	98.9	100.7	98.0	101.7	96.4	115.0
M1	C24	M2	92.8	108.3	102.9	96.9	97.0	106.4
M2	C24	Al2	86.6	84.2	85.7	84.3	84.7	85.4
M1	C24	Al2	177.7	166.1	170.6	173.2	170.8	161.6
M2	C40	M2s	86.9	95.8	91.5	89.8	92.3	96.0
Al3	C32	M2	79.2	86.4	84.3	112.7	77.7	78.4
Al1	C12	M1	82.7	95.7	118.3	80.1	66.8	72.9
Al1	C13	M2	79.5	86.6	83.7	84.0	84.6	95.6
Al2	C23	M2	80.1	82.0	80.8	82.3	82.7	79.3