Supporting Information

Rare-Earth Metal Bis(allyl) Complexes Supported by the [2-(*N*,*N*-Dimethylamino)ethyl]tetramethylcyclopentadienyl Ligand: Structural Characterization, Reactivity, and Isoprene Polymerization

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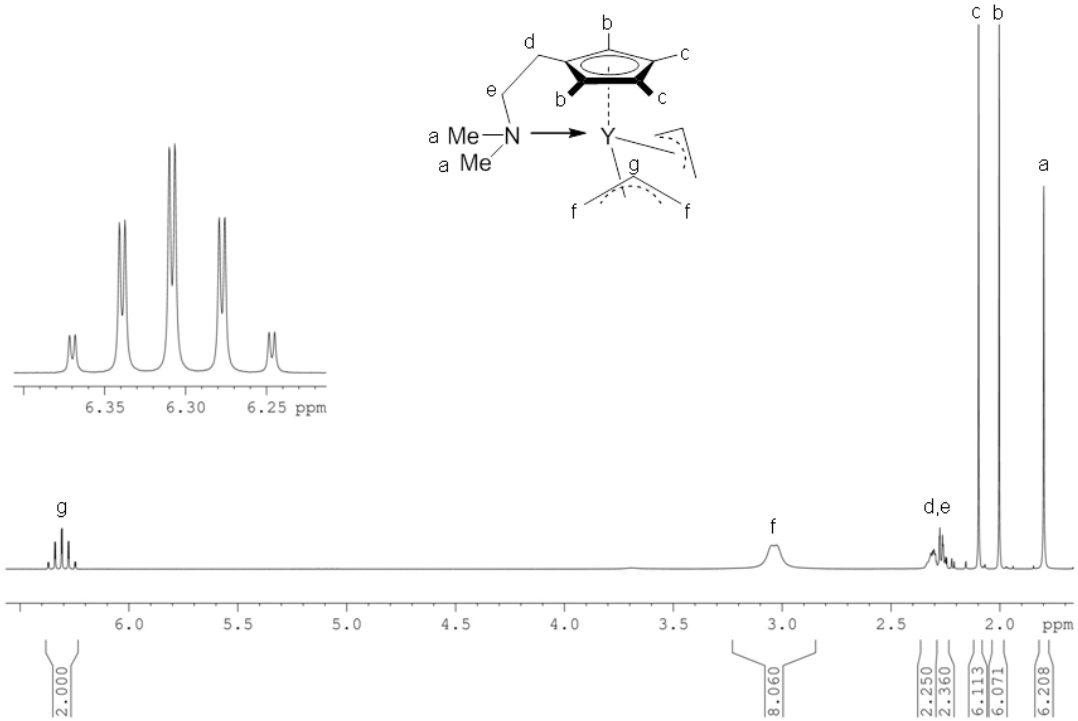

Figure S1. ^{1}H NMR spectrum (C_6D_6, 25 °C) of complex **1a**.

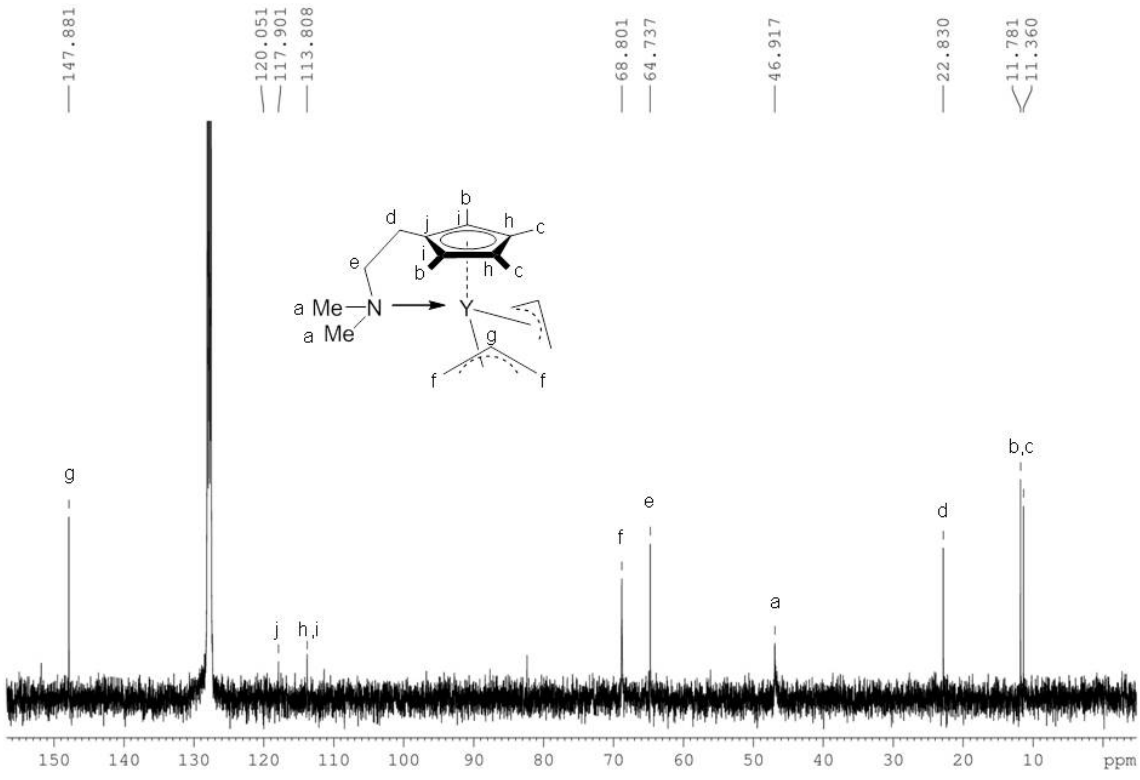

Figure S2. ^{13}C NMR spectrum (C_6D_6, 25 °C) of complex **1a**.

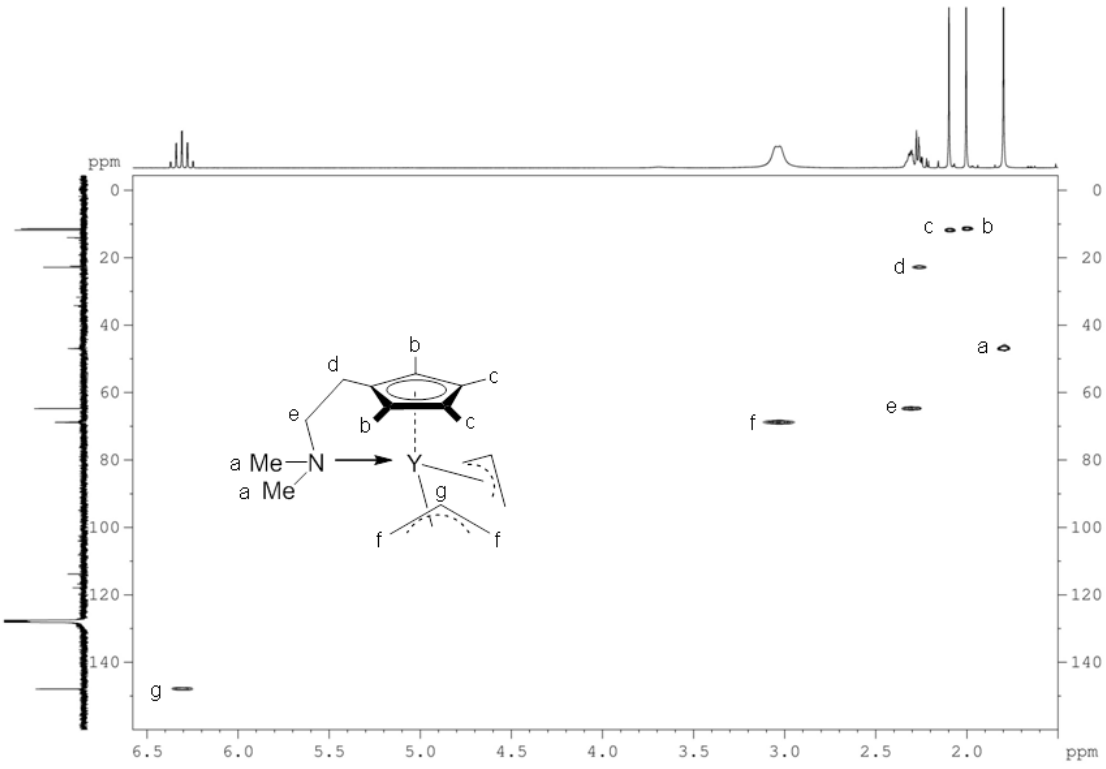

Figure S3. 2D ^{1}H-^{13}C HSQC NMR spectrum (C_6D_6, 25 °C) of complex **1a**.

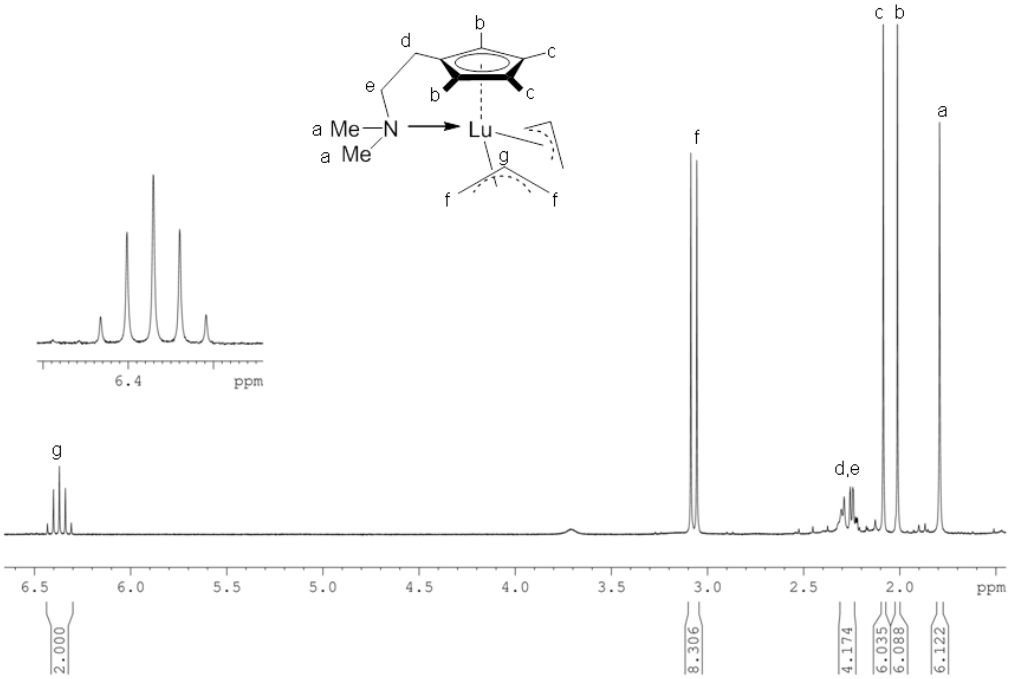

Figure S4. ^{1}H NMR spectrum (C_6D_6, 25 °C) of complex **1c**.

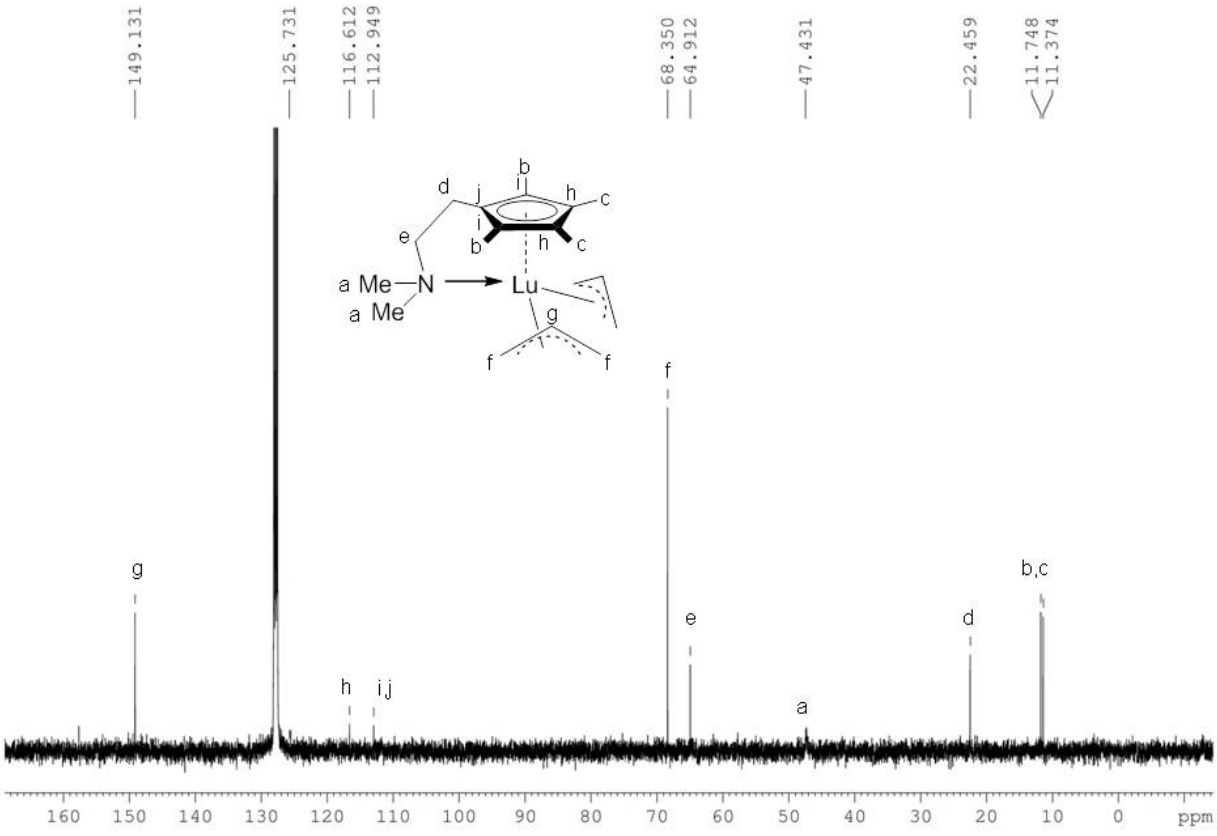

Figure S5. ^{13}C NMR spectrum (C_6D_6, 25 °C) of complex **1c**.

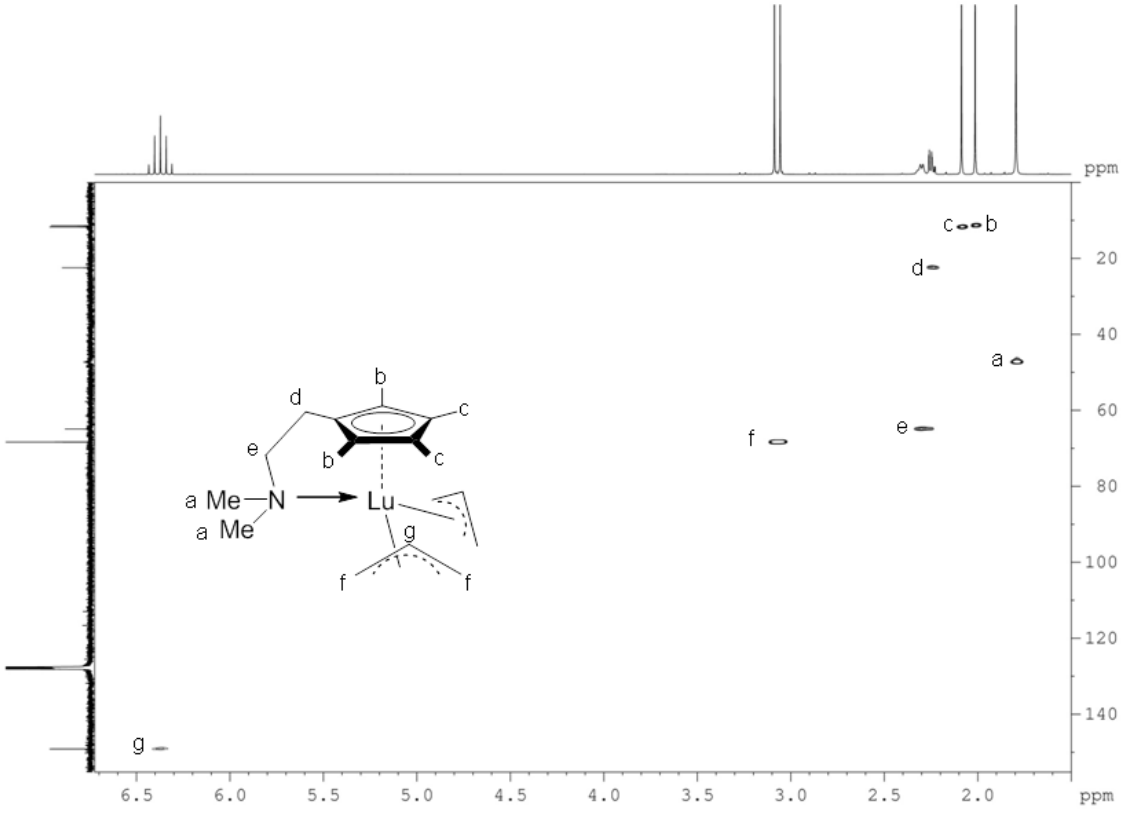

Figure S6. 2D ^{1}H-^{13}C HSQC NMR spectrum (C_6D_6, 25 °C) of complex **1c**.

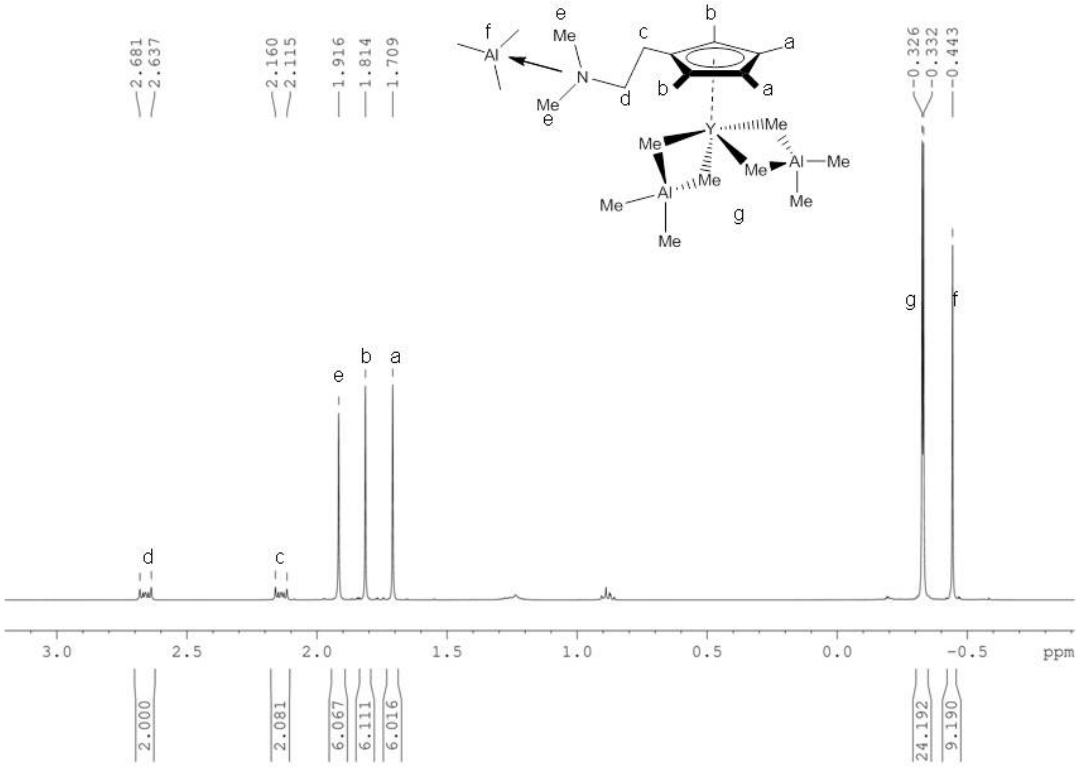

Figure S7. ^{1}H NMR spectrum (C_6D_6, 25 °C) of complex **4**.

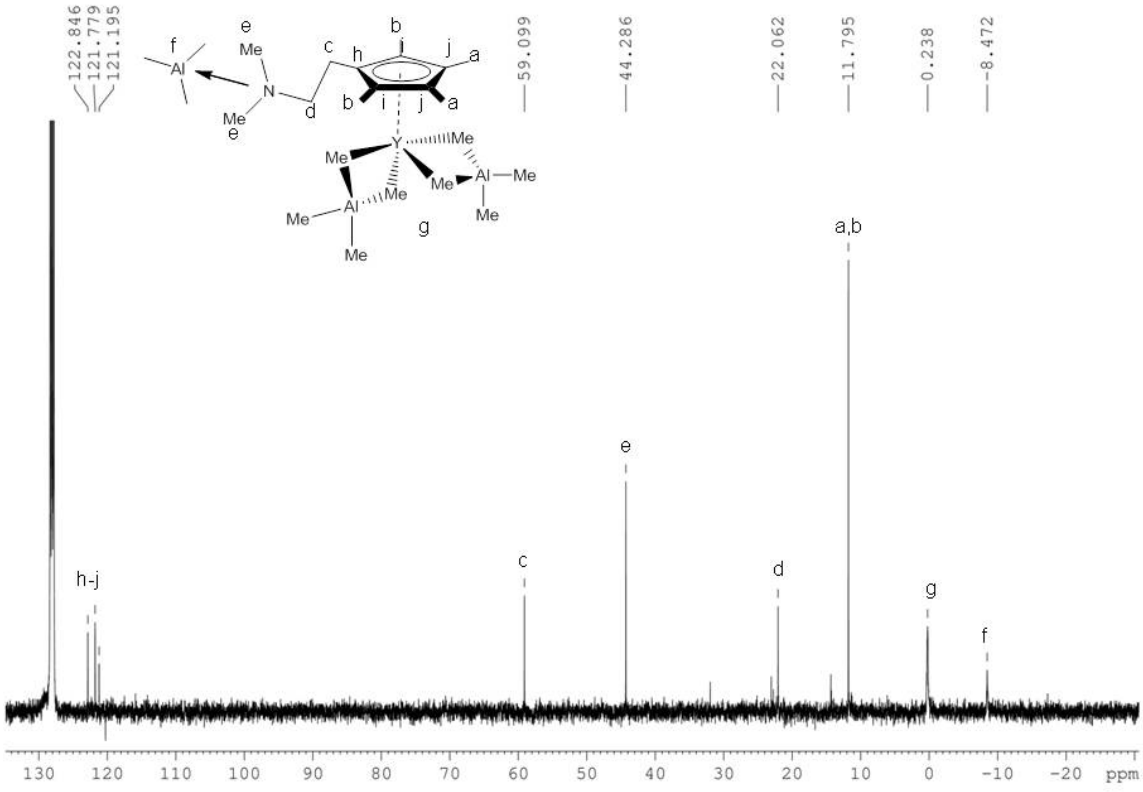

Figure S8. ^{13}C NMR spectrum (C_6D_6, 25 °C) of complex **4**.

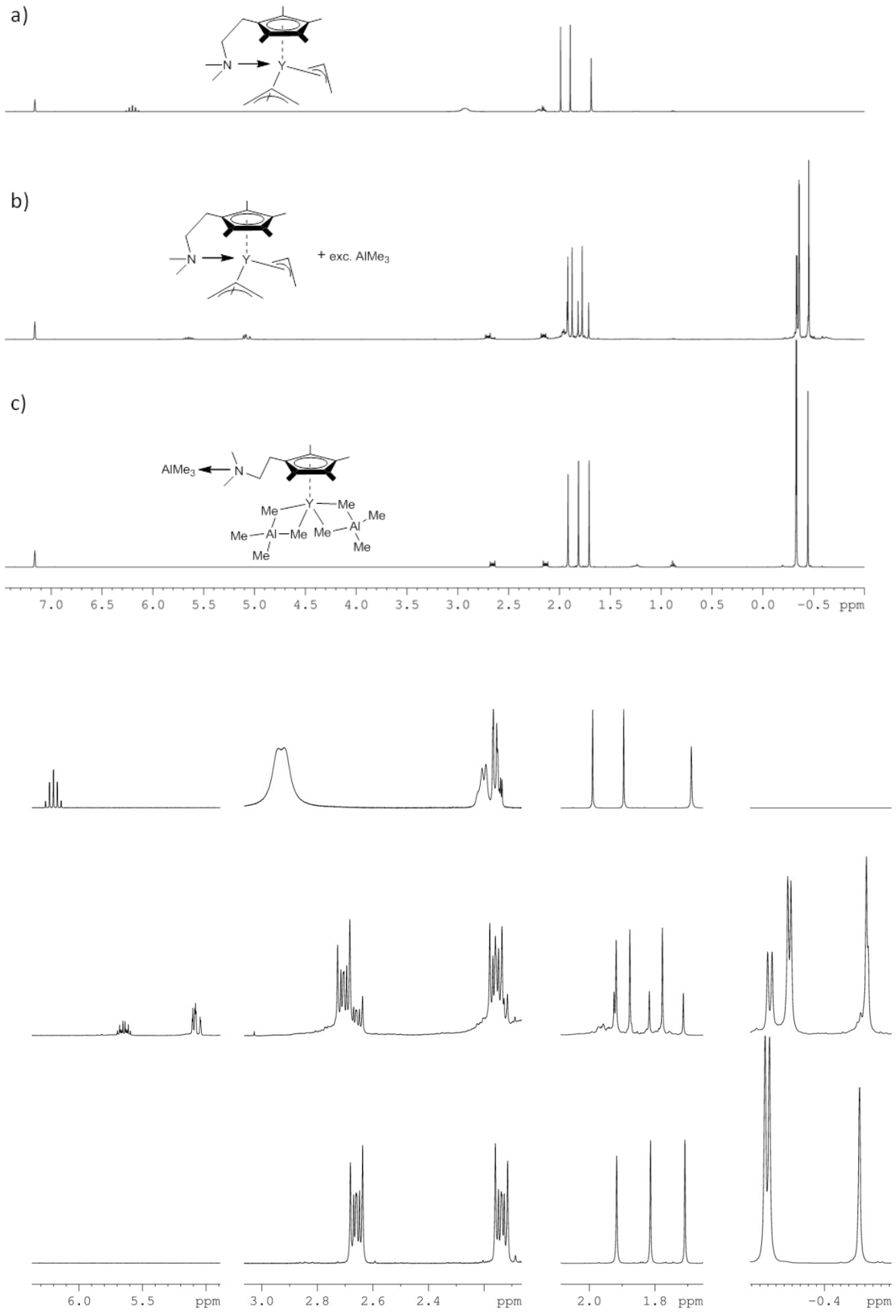

Figure S9. Top) ^{1}H NMR spectra (400 MHz, 25 °C, C_6D_6) of a) pure [$Cp^{NMe2}Y(\eta^3\text{-}C_3H_5)_2$] (**1a**); b) reaction product of [$Cp^{NMe2}Y(\eta^3\text{-}C_3H_5)_2$] with 10 eq. $AlMe_3$ after evaporation of volatiles; c) [$Cp^{NMe2AlMe3}Y(AlMe_4)_2$] (**4**). Bottom) selected regions.

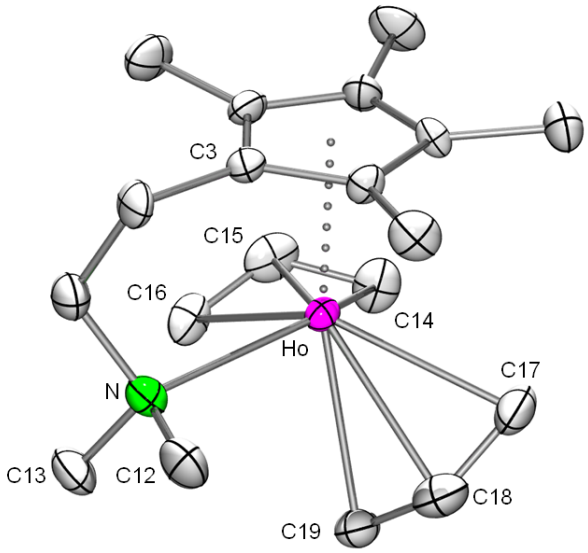

Figure S10. Molecular structure of $[Cp^{NMe2}Ho(C_3H_5)_2]$ (**1b**); atomic displacement parameters set at the 50% level; hydrogen atoms omitted for clarity.

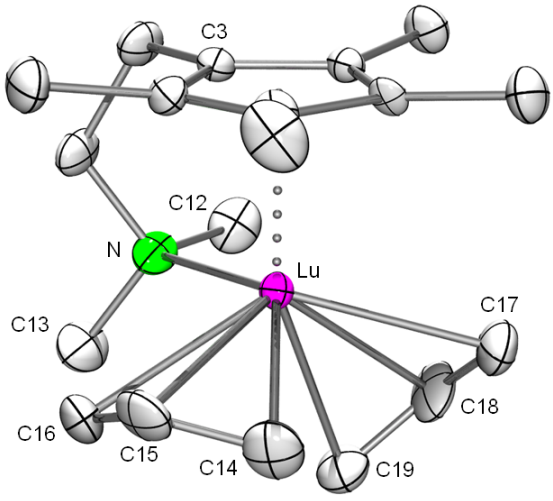

Figure S11. Molecular structure of $[Cp^{NMe2}Lu(C_3H_5)_2]$ (**1c**); atomic displacement parameters set at the 50% level; hydrogen atoms omitted for clarity.

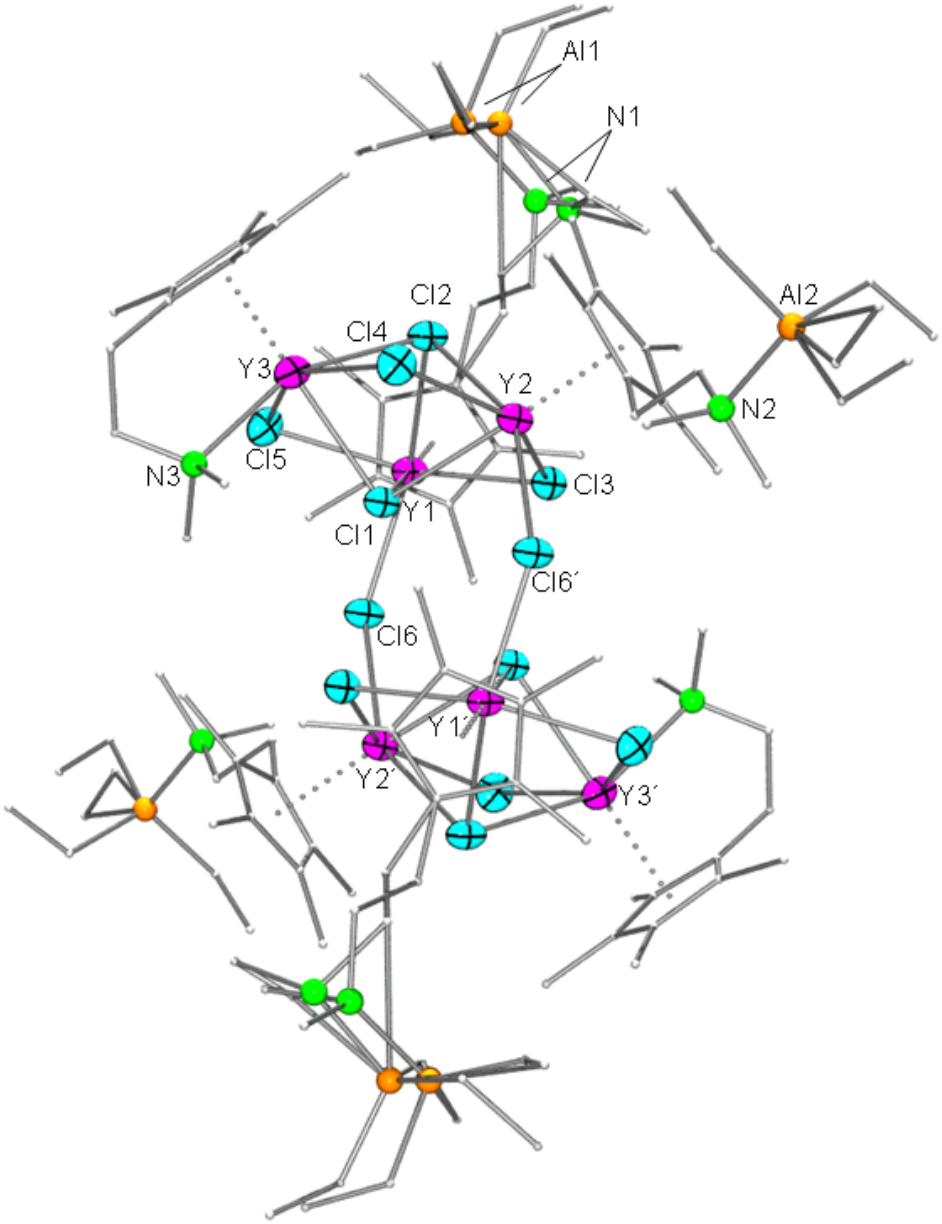

Figure S12. Molecular structure of $[\{(Cp^{NMe2AlEt3})_2(Cp^{NMe2})Y_3Cl_5\}(\mu\text{-}Cl)]_2$ (**3a**); atomic displacement parameters set at the 50% level; aluminum, carbon, and nitrogen atoms are shown as ball-stick representation; hydrogen atoms have for clarity. Disorders of the cyclopentadienyl sidearm and of the ethyl groups at the aluminum centers are shown.

Cell parameters (*P*-1): a = 13.9232, b = 17.0282, c = 18.0040 [Å]; α = 65.191, β = 67.445, γ = 89.805 [°].

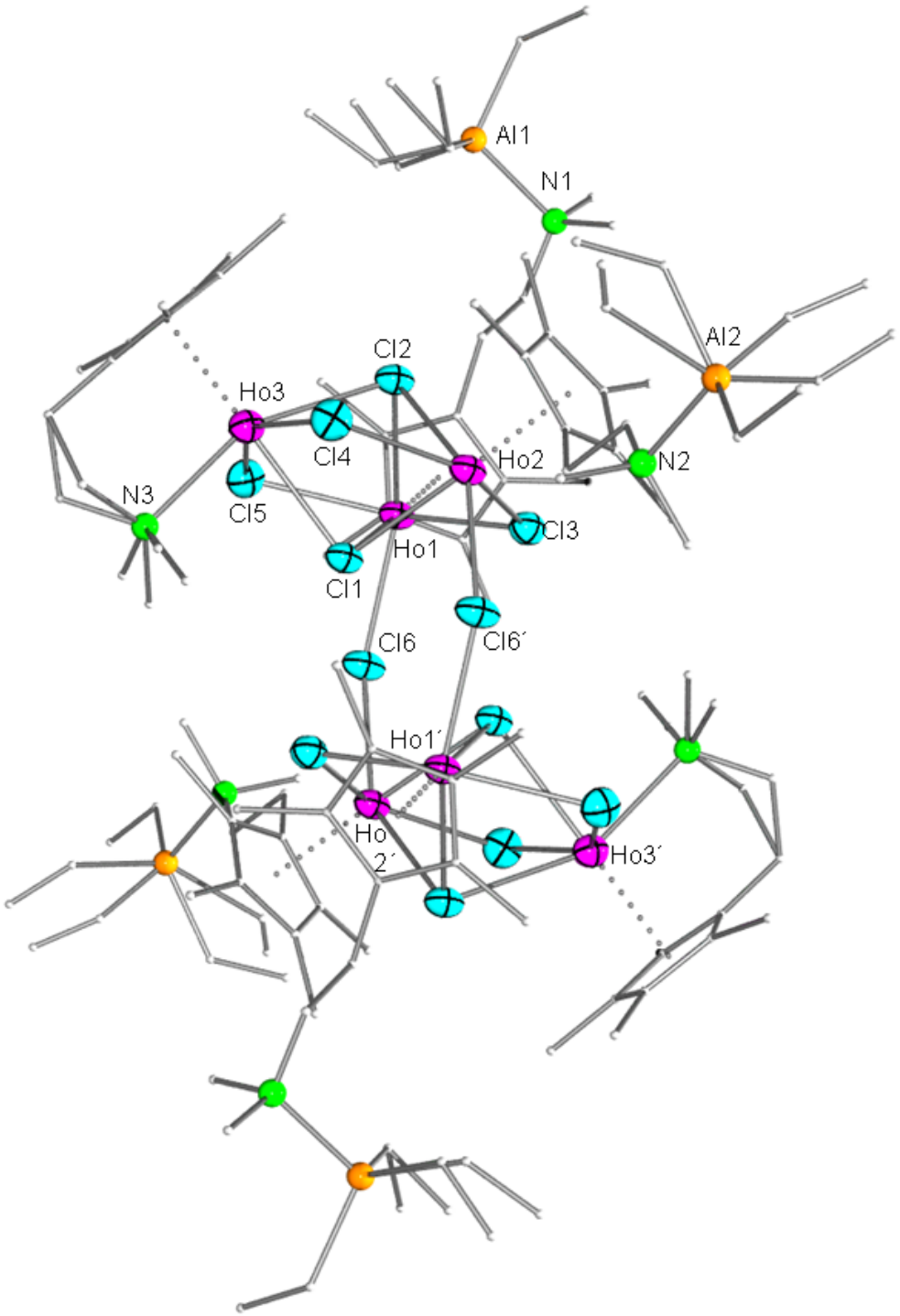

Figure S13. Molecular structure of $[\{(Cp^{NMe2AlEt3})_2(Cp^{NMe2})Ho_3Cl_5\}(\mu\text{-}Cl)\}]_2$ (**3b**); atomic displacement parameters set at the 50% level; aluminum, carbon, and nitrogen atoms are shown as ball-stick representation; hydrogen atoms omitted for clarity. Disorders of the cyclopentadienyl sidearm at N3 and of the ethyl groups at the aluminum centers are shown.

Table S1. Crystallographic data for complexes **1**, **2**, and **3**

	1a (Ln = Y)	**1b** (Ln = Ho)	**1c** (Ln = Lu)	**2** (Ln = Nd)	**3b** (Ln = Ho)·$(C_6H_6)_4$
Formular	$C_{19}H_{32}NY$	$C_{19}H_{32}NHo$	$C_{19}H_{32}NLu$	$C_{39}H_{62}Cl_2N_2Nd_2$	$C_{126}H_{216}Al_4Cl_{12}Ho_6N_6$
Fw	363.37	439.39	449.43	918.29	3337.94
temp (K)	173(2)	173(2)	173(2)	173(2)	173(2)
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1$	$P2_1$	$P2_1$	P-1	P-1
a (Å)	8.4644(4)	8.4569(8)	8.4482(9)	8.7736(9)	14.0630(11)
b (Å)	13.9975(5)	13.9798(13)	13.9076(10)	10.4931(15)	17.0674(12)
c (Å)	8.5546(4)	8.5604(8)	8.5517(9)	12.2435(15)	17.9374(14)
α (deg)	90.00	90.00	90.00	67.958(11)	66.845(6)
β (deg)	114.260(3)	114.331(7)	114.482(8)	81.853(9)	68.304(6)
γ (deg)	90.00	90.00	90.00	74.973(10)	88.529(6)
vol ($Å^3$)	924.05(7)	922.17(15)	914.44(15)	1007.8(2)	3641.8(5)
Z	2	2	2	1	1
ρ_{calcd} (mg/mm^3)	1.306	1.582	1.632	1.513	1.522
μ (mm^{-1})	3.151	4.285	5.393	2.707	3.508
R_1(all) [a]	0.0416	0.0304	0.0198	0.0430	0.0498
wR_2(all) [b]	0.0928	0.0677	0.0399	0.0919	0.1027
GOF (on F^2) [c]	1.154	1.052	1.051	1.223	1.100

[a] $R1 = \Sigma(||F_0|-|F_c||)/\Sigma|F_0|$; [b] $wR2 = \{\Sigma[w(F_0^2-F_c^2)^2/\Sigma[w(F_0^2)^2]\}^{1/2}$; [c] GOF = $\{\Sigma[w(F_0^2-F_c^2)^2]/(n-p)\}^{1/2}$.

Table S2. NMR data of *trans*-1,4- (**T**) and 3,4- (**V**) units of polyisoprene obtained from **2**/**B**/$AlMe_3$.

Position	^{13}C	^{1}H	Position	^{13}C	^{1}H
T_5	16.0	1.61	T_5^{I}	16.2	n.d.
T_4	26.7	2.08	T_4^{I}	32.1	2.04
T_1	39.7	2.00	T_1^{I}	37.4	1.89
T_3	124.2	5.13	T_3^{I}	123.0	5.09
T_2	134.9	–	T_2^{I}	135.3	–
V_5	18.6	1.63	T_5^{II}	n.d.	n.d.
V_4	31.3	1.43	T_4^{II}	n.d.	n.d.
V_3	47.2	2.03	T_1^{II}	39.8	n.d.
V_1	111.2	4.71	T_3^{II}	124.0	n.d.
V_2	147.6	–	T_2^{II}	135.1	–

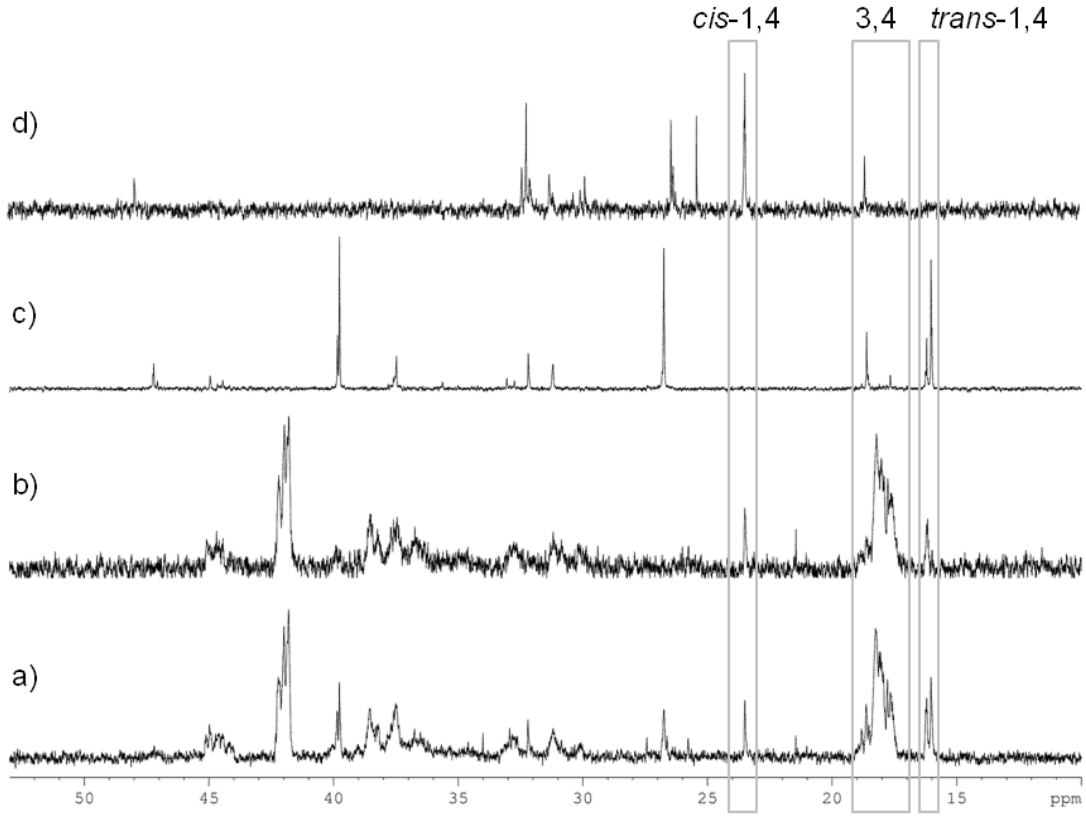

Figure S14. ^{13}C NMR ($CDCl_3$, 25 °C) spectra of polyisoprenes obtained from pre-catalyst **1a** activated with co-catalyst **A** (a), **B** (b), **B** with 10 equiv $AlMe_3$ (c) and **B** with 10 equiv Al*i*Bu_3 (d).