Supporting Information

Polymeric dimethylytterbium and the terminal methyl complex (Tp^{tBu,Me})Yb(CH₃)(thf)

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Experimental Section

General considerations

If not otherwise specified all reactions were carried out under inert atmosphere (Argon) in a glovebox (MBraun MB200B < 0,1 ppm O₂, < 0,1 ppm H₂O). The syntheses of the organic ligands were carried out under standard Schlenk techniques in oven-dried glassware. The solvents were purified using Grubbs-type columns (MBraun SPS solvent purification system). Tetrahydrofuran was stored over activated molecular sieves (3Å). Deuterated solvents were purchased from Aldrich or Eurisotop and were stored over Na/K alloy in a glovebox. Potassium bis(trimethylsilyl)amide K[N(SiMe₃)₂] (95%, Sigma Aldrich) was sublimed before use and stored in a glovebox. The chloride content of MeLi (~1.6 M in Et₂O, Aldrich) was determined via potentiometric titration as described previously.¹ The newly synthesized complexes are stored at ambient temperature or at -40 °C under inert atmospheres, respectively. The proligand hydrotris(3-tert-butyl-5-methylpyrazolyl)borate (HTptBu,Me)2 and the ytterbium(II) precursors Yb(CH₂Ph)₂ (1)³ and Yb(Tp^{tBu,Me})₂⁴ were synthesized according to slight modifications of the literature procedures. The NMR spectra of air- and moisture-sensitive compounds were recorded by using J. Young valve NMR tubes on a BRUKER AVIII+300 (1H: 300.13 MHz, 11B: 96.29 MHz, 13C: 59.63 MHz), a BRUKER AVII+400 instrument (¹H: 400.13 MHz, ¹³C: 100.61 MHz) or a Bruker AVII+500 (¹H: 500.13 MHz, ¹³C: 125.76 MHz, ¹⁷¹Yb: 87.52 MHz). The residual solvent signals are referenced to TMS.⁵ Solid-state NMR spectra were recorded on a Bruker ASX 300 instrument (13C: 75.47 MHz, 171Yb: 52.52 MHz) equipped with MAS (magic angle spinning) hardware and using a ZrO₂ rotor with an outer diameter of 4 mm. Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a DRIFT cell (KBr window), and the samples were prepared in a glovebox and mixed with KBr powder. UV/Vis measurements were carried out in tetrahydrofuran or n-hexane on a PG Instruments T60 UV-Vis spectrophotometer. Elemental analysis (C, H, N) were performed with an Elementar Vario Micro Cube.

Synthesis Procedures

[Yb{N(SiMe_3)_2}_2]_2 (2): To a suspension of $[Yb(CH_2Ph)_2]_n$ (1, 514 mg, 1.4 mmol) in Et₂O (8 mL) a solution of HN(SiMe_3)_2 (467 mg, 2.8 mmol, 0.6 mL in Et₂O (2 mL) was slowly added and stirred overnight at ambient temperature. After filtration, the solvent was removed under reduced pressure. Recrystallization from *n*-hexane gave $[Yb{N(SiMe_3)_2}_2]_2$ (2) as red crystals. Crystalline yield: 411 mg, 58 %. ¹H NMR (400 MHz, [D₆]benzene, 26°C): δ 0.35 ppm. Elemental analysis calcd. (%) for C₁₂H₃₆N₂Si₄Yb (987.66 g/mol): C 29.19, H 7.35, N 5.67; found C 29.64, H 7.44, N 5.73. ICP-OES (%): found: I 0.04. This compound was synthesized previously from Ybl₂ and Na[N(SiMe_3)_2] in diethyl ether at 0 °C and subsequent desolvation of pre-isolated Yb[N(SiMe_3)_2]_2(OEt_2)_2 in toluene at 80 °C.⁶

[YbMe₂]_{*n*} **(3/3^{thf}):** Method a. According to a slightly modified procedure, previously described for synthesis of $[CaMe_2]_{n}$.¹ To a solution of Yb[N(SiMe_3)_2]_2(thf)_2 (490 mg, 768 mmol) in 8 ml Et₂O a solution of chloride-free methyl lithium (3.23 ml, 0.45 M, 1.46 mol) was slowly added under vigorous stirring. After adding approximately 2/3 of the MeLi solution, the product precipitated as an orange powder. The solvent was removed via filter cannula and the orange powder was washed with Et₂O (3 x 2 ml) and dried under vacuum. The product was obtained in quantitative yields as orange amorphous powder, denoted **3^{thf}**. Elemental analysis calcd. (%) for C₂H₆Yb (203.12g/mol): C 11.83, H 2.98, N 0; found C 11.03, H 3.01, N 0.23. ICP-OES (%): found: I 2.03.

Method b. Following the procedure described in method a, THF-free [Yb{N(SiMe₃)₂}₂]₂ (400 mg, 0.42 mmol) in 8 ml Et₂O and methyllithium in Et₂O (5.2 ml, 0.31 M 1.6 mmol) afforded [YbMe₂]_n as orange powder in quantitative yields. The powder was dried at high vacuum for 3 h. ¹³C CP-MAS NMR (75 MHz, 26 °C): δ_{iso} 24.9 (s, br, Yb–CH₃) ppm. ¹⁷¹Yb CP-MAS NMR (52 MHz, 26 °C): δ_{iso} 947.3 (s, br, Yb–CH₃) ppm. Elemental analysis calcd. (%) for C₂H₆Yb (203.12 g/mol): C 11.83, H 2.98, N 0; found C 11.85, H 2.95, N 0. ICP-OES (%): found: I 0.39.

(C_5Me_5)₂Yb(Et₂O) (5): To a suspension of [YbMe₂]_n (15 mg, 0.07 mmol) in 1 ml Et₂O a solution of HC₅Me₅ (20 mg, 0.15 mmol) in 3 ml Et₂O was slowly added under vigorous stirring. After stirring for 18 h at 40 °C the mixture was filtered and the bright green solution was reduced to 1 ml and stored at -40 °C. Crystalline yield: 23 mg, 60 %. ¹H NMR (400 MHz, [D₆]benzene, 26 °C): δ 2.90 (q, 4 H, O(CH₂CH₃)), 2.07 (s, 30 H, (CH₃)₅-Cp), 0.85 (t, 6 H, O(CH₂CH₃)). Elemental analysis calcd. (%) for C₂₄H₄₀OYb (517.60 g/mol): C 55.69, H 7.79, N 0; found C 55.13, H 6.81, N 0.1. This compound was synthesized previously from Ybl₂ and Na[C₅Me₅] 20 °C in diethyl ether at 20 °C, but not analyzed by XRD.⁷

(**Tp**^{fBu,Me})**Yb**(**CH**₃)(**thf**) (**6**): In a micro-scaled reaction, hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate HTp^{fBu,Me} (10.5 mg, 0.025 mmol) in 2ml tetrahydrofuran was added dropwise to a suspension of [YbMe₂]_{*n*} (10 mg, 0.05 mmol) in tetrahydrofuran (1 ml). The mixture was stirred for 20 minutes at ambient temperature until a clear red solution formed. The solution was filtered, and the volume was reduced in vacuo. Single crystals of **6** suitable for XRD analysis could be obtained from a saturated THF solution at -40° C. Alternatively, Yb(Tp^{*fBu,Me*})₂ (60 mg, 0.06 mmol) in 0.4 ml THF was slowly added to a stirred suspension of [YbMe₂]_{*n*} (12 mg, 0.06 mmol) in 0.2 ml THF. After 15 minutes a clear red solution was obtained. The solvent was evaporated under reduced pressure, yielding 67 mg of a red solid (84% of **6**). According to NMR-scale experiments, complex **6** was produced immediately in the Yb(Tp^{*rBu,Me*})₂/[YbMe₂]_{*n*} reaction, indicating that the heteroleptic complex is the preferred species in donor solvents. The red color of solid **6** turned dark (decomposition) at ambient temperatures. ¹H NMR (500 MHz, [D8] thf, 26 °C): δ 5.80 (s, 3 H, pz-CH), 2.35 (s, 9 H, pz-CH₃). 1.35 (s, 27 H, pz-C(CH₃)₃), -1.29 (s, 3 H, Yb-CH₃) ppm. ¹¹B{¹H} NMR (160 MHz, [D₈]thf, 26 °C): δ -8.4 (s, br) ppm. ¹³C{¹H} NMR (125 MHz, [D₈]thf, 26 °C): δ 162.8 (3-pz-C), 145.2 (5-pz-C), 102.5 (4-pz-C), 32.6 (pz-C(CH₃)₃), 31.2 (pz-C(CH₃)₃), 13.4 (pz-CH₃, Yb-CH₃) ppm. ¹⁷Yb from ¹H-¹⁷¹Yb HSCQ (500.13 MHz, 87.52 MHz, [D₈]thf, 26 °C): 1140 ppm. Elemental analysis calcd. (%) for C₂₉H₅₁BN₆OYb (683.63 g/mol): C 50.95, H 7.52, N 12.29; found C 50.63, H 7.56, N 10.97.

Micro-scale reaction Yb[N(SiMe₃)₂]₂(thf)₂: In a J. Young NMR tube bis(trimethylsilyl)amine (8.3 mg, 0.052 mmol) in 0.5 ml deuterated tetrahydrofuran was added to $[YbMe_2]_n$ (5 mg, 0.025 mmol). Slow formation of methane was observed. The solvent was removed under reduced pressure. The residual crude product was dissolved in 1 ml *n*-hexane and the solution was filtrated. The volume was reduced under reduced pressure and stored at -40 °C. Crystalline yield: 95 %, 15 mg. ¹H NMR (400 MHz, [D8] thf, 26 °C): δ 0.18 (CH₄), 0.02 (N{SiCH₃}₂) ppm. ¹⁷¹Yb from ¹H-¹⁷¹Yb HSCQ (500.13 MHz, 87.52 MHz, [D8]thf, 26 °C): 671 ppm.

Crystal Structures and Crystallographic Data



Figure S1. Crystal structure of $[Yb\{N(SiMe_3)_2\}_2]_2$ (2). All atoms are represented by atomic displacement ellipsoids set at 50 % probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Yb1-N1 2.3222(18), Yb1-N3 2.4885(17), Yb1-N4 2.5728(18), Yb2-N2 2.3039(19), Yb2-N3 2.4471(18), Yb2-N4 2.4908(18), Yb1-N3-Yb2 89.18(6), Yb1-N4-Yb2 86.35(6), N1-Yb1-N3 129.44(6), N1-Yb1-N4 139.54(6), N3-Yb1-N4 90.76(6), N2-Yb2-N3 123.53(6), N2-Yb2-N4 127.72(7), N3-Yb2-N4 93.71(6). The crystal structure of complex **2** was previously reported in a PhD thesis.⁶



Figure S2. Crystal structure of [Yb(II)₆Yb(III)₂(CH₃)₁₄O₂(thf)₆] **(4) (A)** and its asymmetric unit **(B)**. All atoms except thf carbon atoms are represented by atomic displacement ellipsoids set at 50 % probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Yb1-C1 2.645(10), Yb1-C2 2.753(9), Yb1-C3 2.616(10), Yb1-C4 2.598(8), Yb1-O4 2.467(4), Yb2-C1 2.575(9), Yb2-C2 2.676(9), Yb2-O4 2.416(5), Yb3-C2 2.676(9), Yb3-C3 2.652(9), Yb3-O4 2.386(5), Yb4-C4 2.495(8), Yb4-C5 2.500(8), Yb4-C6 2.643(8), Yb4-C7 2.524(8), Yb4-O4 2.152(4). Yb1-C1-Yb2 76.6(3), Yb1-C3-Yb3 76.8(3), Yb1-C4-Yb4 84.4(3), Yb1-O4-Yb4 95.36(17), Yb2-C2-Yb3 80.3(2), Yb2-O4-Yb4 135.0(2), O4-Yb4-C4 94.9(2), O4-Yb4-C5 100.9(3), O4-Yb4-C6 166.9(2), O4-Yb4-C7 97.3(2),C4-Yb4-C5 91.4(3), C4-Yb4-C6 98.2(3), C4-Yb4-C7 93.1(3), C5-Yb4-C6 78.8(3), C5-Yb4-C7 160.8(3), C6-Yb4-C7 82.1(3)



Figure S3. Crystal structure of $(C_5Me_5)_2$ Yb(Et₂O) (5). All atoms are represented by atomic displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.

	$(C_5Me_5)_2Yb(Et_2O)$ (5)	$(C_5Me_5)_2$ Yb(thf)
Yb1-O1	2.454(4)	2.412(5)
Yb1-Cp*1 (ring centroid)	2.4171(9)	-
Yb1-Cp [*] 2 (ring centroid)	2.4079(8)	-
Yb1-C(Cp*1), range	2.678(6)-2.702(5)	2.654(7)-2.694(8)
Yb1-C(Cp*1), av.	2.691	2.672
Yb1-C(Cp*2), range	2.674(5)-2.728(5)	2.643(7)-2.664(7)
Yb1-C(Cp*2), av.	2.701	2.654
Cp [*] 1-Yb1-Cp [*] 2	140.25	143.5(3)
Cp*1-Yb1-O1	111.45	108.8(3)
Cp [*] 2-Yb1-O1	108.19	107.7(3)

Table S1. Selected structural parameters [Å, °] for complex 5 and $(C_5Me_5)_2Yb(thf)^8$



Figure S4. Crystal structure of $(Tp^{HBu,Me})Yb(CH_3)(thf)$ (6). All atoms are represented by atomic displacement ellipsoids set at 50 % probability. Hydrogen atoms expect B-H and disorder in the solvent thf are omitted for clarity.

	ma	olecule 1	mole	ecule 2	
	Yb1-C25	2.521(4)	Yb2-C54	2.503(4)	
	Yb1-B1	3.371(4)	Yb2-B2	3.366(4)	
Yb1-N 2.467(3)-2.491(3)		Yb2-N	2.469(3)-2.474(3)		
	Yb1-O1	2.441(2)	Yb2-O2	2.440(3)	
	C25-Yb1-N2	128.32(12)	C54-Yb2-N8	136.20(12)	
	C25-Yb1-N4	139.39(12)	C54-Yb2-N10	129.87(12)	
	C25-Yb1-N6	117.48(12)	C54-Yb2-N12	117.34(13)	
C25-Yb1-O1 89.79(12		89.79(12)	C54-Yb2-O2	93.25(12)	
	B1-Yb1-C25	165.48(13)	B2-Yb2-C54	166.27(14)	

Table S2. Selected structural parameters [Å, °] for complex 6

Table S3. Selected structural parameters [Å, °] for complex (Tp^{tBu,Me})Ca(CH₃)(thf)¹

	molecule 1	molecule 2		
Ca1-C29 2.4822(16)		Ca2-C58	2.4772(16)	
Ca1-B1	3.3616(16)	Ca2-B2	3.3515(17)	
Ca1-N 2.4461(12)-2.4777(12)		Ca2-N	2.4494(12)-2.4608(13)	
Ca1-O1	2.4026(10)	Ca2-O2	2.4006(11)	
C29-Ca1-N2	128.32(5)	C58-Ca2-N8	129.42(5)	
C29-Ca1-N4	116.46(5)	C58-Ca2-N10	116.30(5)	
C29-Ca1-N6	139.52(5)	C58-Ca2-N12	136.82(5)	
C29-Ca1-O1	89.36(5)	C58-Ca2-O2	92.62(5)	
B1-Ca1-C29	164.81(5)	B2-Ca2- C58	165.58(5)	

X-ray Crystallography and Crystal Structure Determinations.

Crystals of **2**, **4**, **5** and **6** were grown by standard techniques from saturated solutions using *n*-hexane (**2**), diethyl ether (**5**), thf (**4**) and a mixture of d8-thf and *n*-hexane for **6** at -40 °C. Suitable crystals for X-ray structure analyses were selected in a glovebox and coated with Parabar 10312 (previously known as Paratone N, Hampton Research) and fixed on a nylon loop/glass fiber.

X-ray data for above mentioned compounds were collected on a Bruker APEX II DUO instrument, equipped with an IµS microfocus sealed tube and QUAZAR optics for MoK α (λ = 0.71073 Å) radiation. The data collection strategy was determined using COSMO⁹ employing ω -scans. Raw data were processed using APEX¹⁰ and SAINT,¹¹ corrections for absorption effects were applied using SADABS.¹² The structures were solved by direct methods and refined against all data by full-matrix least-squares methods on F² using SHELXTL¹³ and SHELXLE.¹⁴ All graphics were produced employing MERCURY¹⁵ and POV-Ray.¹⁶ Disorder models for THF are calculated using DSR,¹⁷ a program included in ShelXle, for refining disorder.

Further details of the refinement and crystallographic data are listed in Table S3, and in the CIF files. CCDC depositions 2039518-2039521 contain all the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/structures/</u>.

Crystallographic data

Table S4. Crystallographic data

Compound ^[a]	[Yb{N(SiMe ₃) ₂ } ₂] ₂ (2)	Yb ₈ (CH ₃) ₁₄ O ₂ (thf) ₆ (4)	(C ₅ Me ₅) ₂ Yb(Et ₂ O) (5)	(Tp ^{rBu,Me})Yb(CH ₃)(thf) (6)
Molecular formula	$C_{24}H_{72}N_4Si_8Yb_2$	C ₃₈ H ₉₀ O ₈ Yb ₈	$C_{24}H_{40}OYb$	$C_{31}H_{55}BN_6O_{1.5}Yb$
CCDC	2039521	2039518	2039519	2039520
M [g/mol]	987.65	2059.41	517.60	719.66
Temperature [K]	100	100	150	100
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal dimensions [mm]	0.106x0.132x0.409	0.90x0.020x0.018	0.224x0.176x0.105	0.108x0.079x0.064
Crystal description	Orange needle	Orange needle	Green plate	Orange needle
Crystal system	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group	PĪ	PĪ	P212121	PĪ
a [Å]	8.8586(4)	11.0309(12)	8.521(3)	11.6943(12)
b [Å]	12.4947(6)	12.0062(13)	15.070(4)	15.8997(16)
c [Å]	21.8119(9)	12.2428(14)	18.244(5)	19.6227(19)
α [°]	73.7690(10)	109.5700(10)	90	79.970(3)
β [°]	86.7190(10)	111.8730(10)	90	80.792(3)
Y [°]	71.3230(10)	97.5130(10)	90	81.066(3)
V [³]	2194.58(17)	1355.9(3)	2343.9(4)	3515.9(3)
Z	2	1	4	4
ρ [mg/m³]	1.495	2.522	1.467	1.380
μ [mm ⁻¹]	4.473	13.685	4.001	2.692
F (000)	992	942	1048	1480
θ range [°]	0.973 to 30.546	2.701 to 28.782	1.753 to 32.046	1.811 to 28.696
Indices	-12 ≤ h ≤ 12	-14 ≤ h ≤ 14	-11 ≤ h ≤ 11	-15 ≤ h ≤ 15
	-17 ≤ k ≤ 17	-16 ≤ k ≤ 16	-22 ≤ k ≤ 22	-21 ≤ k ≤ 21
	-31 ≤ I ≤ 31	-16 ≤ I ≤ 16	-27 ≤ I ≤ 27	-26 ≤ I ≤ 26
Number of reflexes	108603	36789	35504	169173
Unique reflexes	13408	7010	8160	18045
R₁/wR₂ (I>2σ)[a]	0.0225/0.0472	0.0383/0.0812	0.0294/0.0553	0.0356/0.0719
R ₁ /wR ₂ (all data) ^[b]	0.0294/0.0501	0.0599/0.0910	0.0437/0.0605	0.0664/0.0837
GOF (in F ²) ^[c]	1.028	1.022	1.034	1.038

 $[a] R_1 = \Sigma(||F_0| - |F_c||) / \Sigma|F_0|, F_0 > 4\sigma(F_0). [b] wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2 / \Sigma[w(F_0^2)^2]\}^{1/2}. [c]: GOF = \left[\frac{(\Sigma W(F_0^2 - F_c^2)^2)}{(no-np)}\right]^{0.5}$



Figure S5. ¹H NMR spectrum (400 MHz) of [Yb{N(SiMe₃)₂}]₂ in D₆[benzene] at 26 °C. Residual solvent signal is marked with *.



Figure S6. ¹H MAS NMR spectrum (300 MHz, spinning frequency 4000 Hz) of [YbMe₂]_n.



Figure S7. ¹⁷¹Yb CP/MAS NMR spectrum (52 MHz, spinning frequency 4000 Hz) of [YbMe₂]_n.



Figure S8. ¹³C CP/MAS NMR spectrum (75 MHz, spinning frequency 4000 Hz) of [YbMe₂]_n.



Figure S9. ¹H NMR spectra (400 MHz) of a micro-scale reaction of [YbMe₂]_{*n*} with bis(trimethylsilyl)amine, performed in a J. Young NMR tube in [D₈]thf at 26 °C. Both the comparison with the spectra of 2^{thf} and bis(trimethylsilyl)amine and the formation of CH₄ (marked with #) indicated a successful reaction.



Figure S10. ¹H NMR spectrum (500 MHz) of a micro-scale reaction of [YbMe₂]_n with hydro tris(3-tert-butyl-5-methylpyrazolyl)borate HTp^{fBu,Me}, performed in a J. Young NMR tube in [D₈]thf at 26 °C. Residual solvent signal is marked with *.



Figure S11. ¹³C{¹H} NMR spectrum (125 MHz) of a micro-scale reaction of [YbMe₂]_n with hydrotris(3-tert-butyl-5-methylpyrazolyl) borate HTp^{fBu,Me}, performed in a J. Young NMR tube in [D₈]thf at 26 °C. Residual solvent signal are marked with *.



Figure S12. ¹¹B NMR spectrum (160 MHz) of a micro-scale reaction of $[YbMe_2]_n$ with hydrotris(3-tert-butyl-5-methylpyrazolyl) borate HTp^{fBu,Me}, performed in a J. Young NMR tube in $[D_8]$ thf at 26 °C.



Figure S13. ¹H–¹³C HSQC NMR spectrum (500 MHz, 125 MHz) of a micro-scale reaction of [YbMe₂]_n with hydrotris(3-tertbutyl-5-methylpyrazolyl) borate HTp^{fBu,Me}, performed in a J. Young NMR tube in [D₈]thf at 26 °C.



Figure S14. ¹H–¹⁷¹Yb HSQC NMR spectrum (500 MHz, 87.52 MHz) of complex 6 in [D₈]thf at 26 °C.



Figure S15. ¹H NMR spectra (400 MHz) of a reaction of [YbMe₂]_n with hydrotris(3-tert-butyl-5-methylpyrazolyl)borate HTp^{rBu,Me} (bottom) and the dried solids (top) in [D₈]thf at 26 °C. Residual solvent signal is marked with *. The missing methyl signal at - 1.3 ppm in the spectrum of the dried and the resolved solids indicated decomposition.



Figure S16. ¹H NMR spectrum (400 MHz) of $(C_5Me_5)_2$ Yb(Et₂O) in D₆[benzene] at 26 °C. Residual solvent signal is marked with *.

DRIFT Spectra



Figure S17. DRIFT spectrum of [YbMe₂]_n via route I.



Figure S18. Overlain DRIFT spectra of [YbMe₂]_n (3^{thf}, red) and [CaMe₂]_n (blue).¹



Figure S19. DRIFT spectrum of [YbMe₂]_n via route II.



Figure S20. Overlain DRIFT spectra of [YbMe₂]_n (3, red) and [CaMe₂]_n (blue).¹



Figure S21. UV/Vis spectra of Ybl₂(THF)₂ and (Tp^{fBu,Me})Yb(CH₃)(THF) in tetrahydrofuran.



Figure S22. UV/Vis spectra of (C₅Me₅)₂Yb(Et₂O) and (Tp^{*t*Bu,Me})₂Yb in *n*-hexane.



Figure S23. UV/Vis spectra of $Yb[N(SiMe_3)_2]_2(THF)_2$ and $[Yb{N(SiMe_3)_2}_2]_2$ in *n*-hexane.

Potentiometric determination of iodine in different precursor complexes

Samples of $Yb[N(SiMe_3)_2]_2(THF)_2$ (21 mg) and $[Yb{N(SiMe_3)_2}_2]_2$ (16 mg) were quenched with methanol (2 ml) and deionized water (2 ml). The solvents were removed completely under reduced pressure. The residual solids where dissolved with diluted nitric acid and titrated with 0.001 M AgNO₃.



Figure S24. Potentiometric titrations of $Yb[N(SiMe_3)_2]_2(THF)_2$ (2 do) (orange and grey) and $[Yb{N(SiMe_3)_2}_2]_2$ (2) (blue and yellow) (3 aliquots) with 0.001 M AgNO₃.



Figure S25. Numerical derivation of the curves shown in Figure S10. For $[Yb{N(SiMe_3)_2}_2]_2$ (**2**) (blue and yellow) no definite minima is observable. For $Yb[N(SiMe_3)_2]_2(THF)_2$ (**2 do**) (orange and grey).

References

- 1. B. M. Wolf, C. Stuhl, C. Maichle-Mössmer and R. Anwander, J. Am. Chem. Soc., 2018, 140, 2373-2383.
- 2. S. Trofimenko, Chem. Rev., 1993, 93, 943-980
- 3. B. M. Wolf, C. Stuhl and R. Anwander, Chem. Commun., 2018, 54, 8826-8829.
- 4. X. Zhang, R. McDonald and J. Takats, New J. Chem., 1995, **19**, 573-585.
- 5. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.
- 6. J. M. Boncella, PhD Thesis, University of California, Berkeley, 1982.
- 7. T. D. Tilley, J. M. Boncella, D. J. Berg and R. A. Andersen, *Inorg. Synth.*, 1990, **27**, 165-150.

8.

- 9. COSMO v. 1.61, Bruker AXS Inc., Madison, WI, 2012.
- 10. APEX 3 V. 2017.3-0, Bruker AXS Inc., Madison, WI, 2017.
- 11. SAINT v. 8.38A, Bruker AXS Inc., Madison, WI, 2017.
- 12. SADABS, L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, J. Appl. Cryst., 2015, 48, 3-10.
- 13. SHELXT, Acta Cryst., 2015, A71, 3-8.
- 14. SHELXLE, C. B. Huebschle, G. M. Sheldrick, B. Dittrich, J. Appl. Crystallogr , 2011, 44, 1281-1284.
- Mercury CSD 2.0 New Features for the Visualization and Investigation of Cryst. Structures,
 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.*, 2008, **41**, 466-470.
- 16. v. 3.6, P. o. V. P. L., POV-Ray Williamstown, Victoria, Australia, 2004, <u>http://www.povray.org</u>.
- 17. D. Kratzert, J. J. Holstein and I.Krossing, DSR: enhanced modelling and refinement of disordered structures with SHELXL. *J. Appl. Cryst*, 2015, **48**, 933-938.