2 Crystallographic data

2.1 $Yb[CH(SiMe_3)_2]_3$

The $Yb[CH(SiMe_3)_2]_3$ complex was characterized by the tools of solid-state X-ray crystallography (Figure S2). All the crystallographic parameters are summarized in Table S1 Figure S1 shows a view of the molecule. The structure contains 0.5 solvent molecules per complex molecule which are highly disordered along the c-axis. The disordered solvent is described by partially occupied $(Me_3Si)_2CH_2$ with all isotropic displacement parameters set equal and using distance restraints. All hydrogen atoms, with exception of the ones belonging to the solvent molecules, were found in the difference Fourier map and refined freely. Table S1 provides also the comparison between selected distances and angles of the paramagnetic $Yb[CH(SiMe_3)_2]_3$ complex and its diamagnetic analogue $Lu[CH(SiMe_3)_2]_3$.[29]

Table 1 Crystal data and structure refinement for $Yb[CH(SiMe_3)_2]_3$.

Empirical formula	$C_{24.5}H_{67}Si_7Yb$
Formula weight	731.45
Temperature/K	100.00
Crystal system	trigonal
Space group	*P*31*c*
a/Å	16.1800(8)
b/Å	16.1800(8)
c/Å	8.5692(4)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	1942.8(2)
Z	2
ρ_{calc}g/cm^3	1.250
μ/mm^{-1}	2.635
F(000)	764.0
Crystal size/mm^3	0.1 × 0.08 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.906 to 61.044
Index ranges	$-23 \le h \le 23$, $-22 \le k \le 22$, $-12 \le l \le 12$
Reflections collected	29458
Independent reflections	3935 [R_{int} = 0.0373, R_{sigma} = 0.0312]
Data/restraints/parameters	3935/69/189
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0175, wR_2 = 0.0351
Final R indexes [all data]	R_1 = 0.0197, wR_2 = 0.0359
Largest diff. peak/hole / e Å^{-3}	0.85/-0.58
Flack parameter	0.003(4)

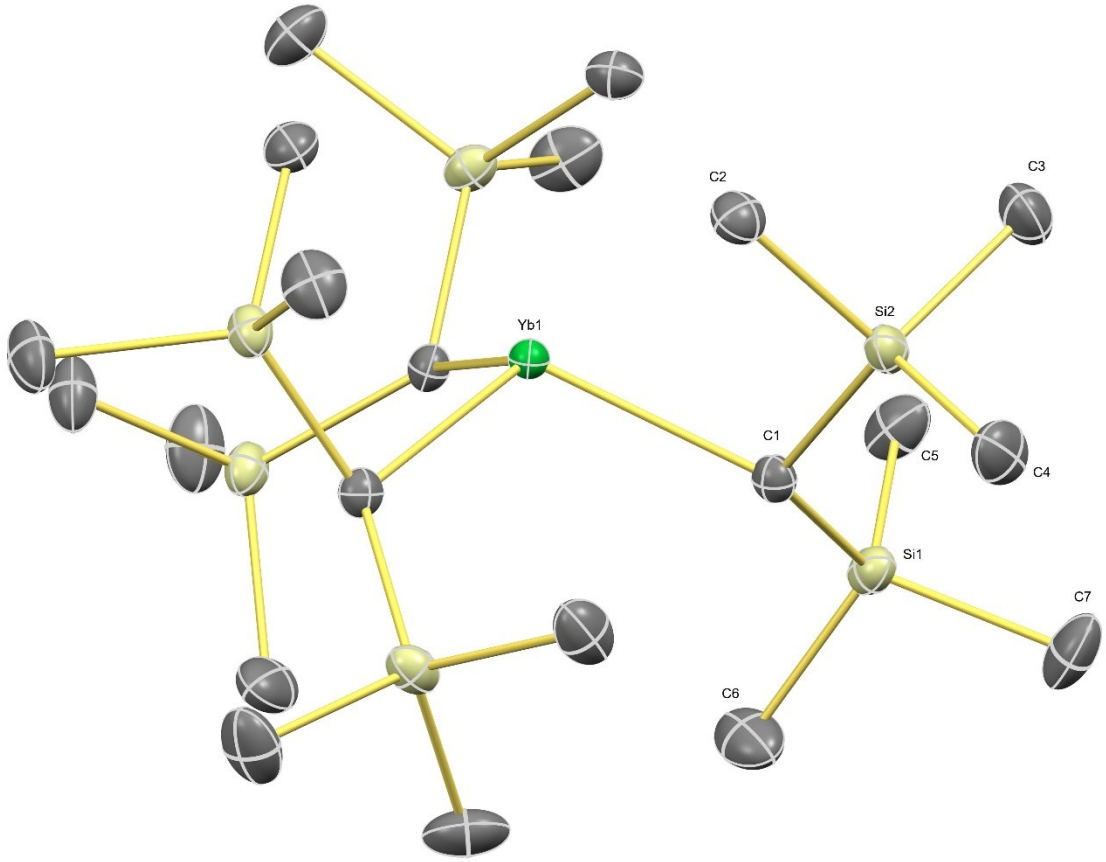

Figure S1: Thermal ellipsoid plot at 50% probability of Yb[CH(SiMe3)2]3. Hydrogen atoms have been omitted for clarity.

Table S2: Comparison of selected bond lengths and angles for $Yb[CH(SiMe_3)_2]_3$ and $Lu[CH(SiMe_3)_2]_3$. The C(1)–Yb–C(1') angle is equal to 109.25(7)°

	Distance \Å								
Atoms	M-C1	M-C2	M-Si1	M-Si2	Si2-C1	Si2-C2	Si2-C3	Si1-C1	Si1-C5
Yb	2.324(3)	2.963(3)	3.7096(8)	3.2596(8)	1.843(3)	1.905(3)	1.869(3)	1.846(3)	1.870(4)
Lu	2.319(3)	2.937(3)	3.677	3.242(1)	1.837(3)	1.907(3)	1.876(7)	1.844(3)	1.872(5)
	Angle \°								
Atoms	M-C1-Si1	M-C1-Si2	M-C2-Si2	M-C1-C2	C1-Si2-C2				
Yb	125.25(14)	102.32(13)	80.91(11)	66.07(9)	106.80(14)				
Lu	125.7(1)	101.9(1)	81.0(1)	68.6(1)	106.7(1)				

2.2 $Yb[CH(SiMe_3)2]_{3-n}[O-2,6-tBu_2-C_6H_3]_n$ with n = 1 and 2

Table S3: Crystal data and structure refinement for $Yb[CH(SiMe_3)_2]_2[O-2,6-tBu_2-C_6H_3]$.*

Empirical formula	$C_{28}H_{59}OSi_4Yb$
Formula weight	697.15
Temperature/K	100
Crystal system	triclinic
Space group	*P*-1
a/Å	12.7256(7)
b/Å	13.6737(7)
c/Å	20.4896(11)
α/°	89.3522(8)
β/°	89.6376(8)
γ/°	89.7839(8)
Volume/Å^3	3565.0(3)
Z	4
ρ_{calc}g/cm^3	1.299
μ/mm^{-1}	2.775
F(000)	1444.0
Crystal size/mm^3	0.1 × 0.09 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.988 to 63.136
Index ranges	$-17 \leq h \leq 18$, $-20 \leq k \leq 20$, $-28 \leq l \leq 28$
Reflections collected	56510
Independent reflections	21831 [R_{int} = 0.0367, R_{sigma} = 0.0508]
Data/restraints/parameters	21831/6/743
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.0747
Final R indexes [all data]	R_1 = 0.0678, wR_2 = 0.0862
Largest diff. peak/hole / e Å^{-3}	1.96/-1.58

* All hydrogen atoms were found in the difference Fourier map. Hydrogen atoms of methyl groups with large distances to the metal atom were placed at calculated positions and refined according to the riding model. Hydrogen atoms close to the metal center were refined freely with exception of the hydrogen atoms at C8B and C8AB. The hydrogen atom at the carbon atom C8AB with an occupancy of about 30 percent cannot be located from the difference density map and has therefore been placed at a calculated position and refined using the riding model. One SiMe3-group in each of the two crystallographically independent molecules is disordered over two sites and has been described by split positions.

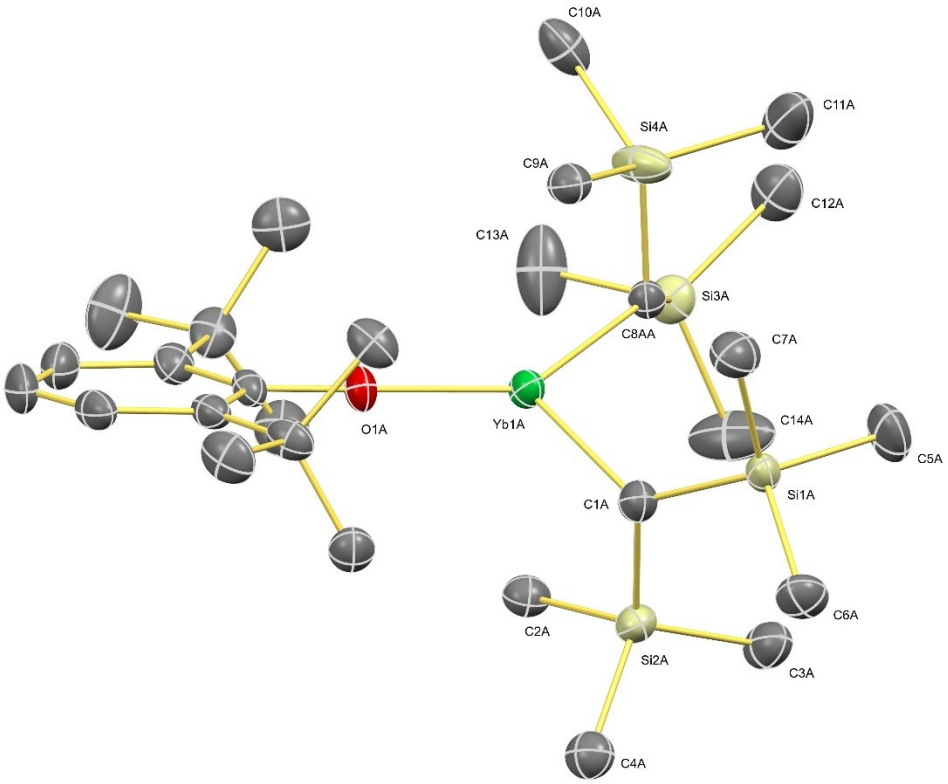

Figure S2: Thermal ellipsoid plot at 50% probability of $Yb[CH(SiMe_3)_2]_2[O-2,6-tBu-C_6H_3]$. Hydrogen atoms as well as the minority orientation of two disordered $SiMe_3$-groups have been omitted for clarity.

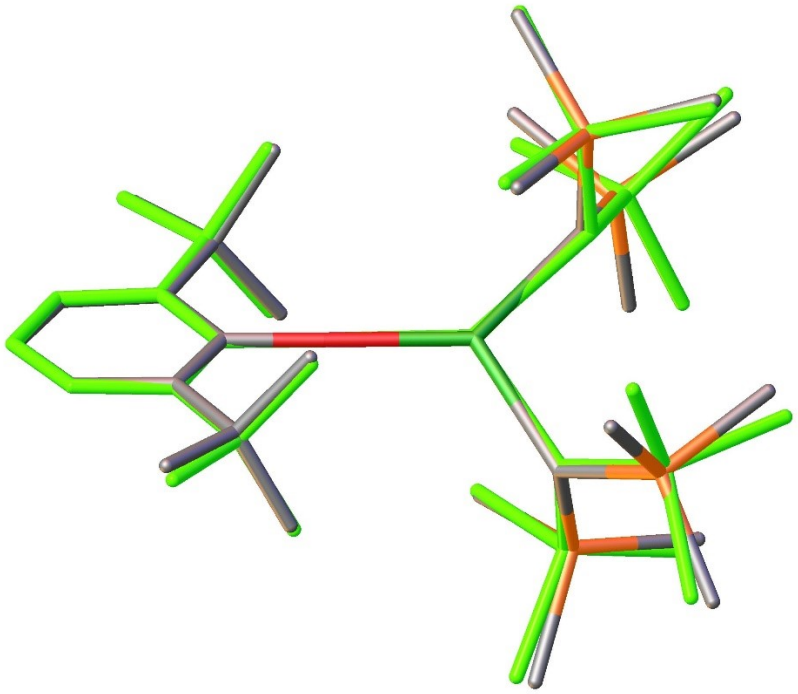

Figure S3: Overlay of both crystallographically independent molecules of $Yb[CH(SiMe_3)_2]_2[O-2,6-tBu-C_6H_3]$ in the asymmetric unit. In molecules one of the $SiMe_3$-groups is disordered over two sites. Only the orientation with the larger occupancy factor is shown.

Selected interatomic distances for Yb[CH(SiMe$_3$)$_2$]$_2$[O−2,6−tBu−C$_6$H$_3$]

Atom1	Atom2	Distances in molecule A /Å	Distances in molecule B /Å
Yb1	Si2	3.1076(10)	3.1291(10)
Yb1	Si4	3.1029(11)	3.1266(10)
Yb1	O1	2.035(2)	2.033(2)
Yb1	C1	2.333(4)	2.329(3)
Yb1	C2	2.712(4)	2.761(4)
Yb1	C9	2.698(4)	2.706(4)
Yb1	C8A	2.340(5)	2.329(3)

Table S4: Crystal data and structure refinement for Yb[CH(SiMe$_3$)$_2$][O−2,6−tBu$_2$−C$_6$H$_3$]$_2$.*

Empirical formula	$C_{35}H_{61}O_2Si_2Yb$
Formula weight	743.05
Temperature/K	100.6(8)
Crystal system	triclinic
Space group	*P*-1
a/Å	12.6794(3)
b/Å	14.3880(3)
c/Å	22.0967(5)
α/°	106.804(2)
β/°	102.021(2)
γ/°	90.361(2)
Volume/Å^3	3764.84(15)
Z	4
ρ_{calc}g/cm^3	1.311
μ/mm^{-1}	2.574
F(000)	1540.0
Crystal size/mm^3	0.25 × 0.2 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.034 to 56.564
Index ranges	-16 ≤ h ≤ 16, -19 ≤ k ≤ 19, -29 ≤ l ≤ 29
Reflections collected	79448
Independent reflections	18685 [R_{int} = 0.0711, R_{sigma} = 0.0621]
Data/restraints/parameters	18685/88/766
Goodness-of-fit on F^2	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0584, wR_2 = 0.1398
Final R indexes [all data]	R_1 = 0.0762, wR_2 = 0.1508
Largest diff. peak/hole / e Å^{-3}	3.85/-2.26

*The crystal under investigation turned out to be twinned with twin matrix -1 0 0 0 1 0 0 -0.89 1 with a volume ratio of the individuals of 97:3. The twinning as well as some icing causes relatively large residual electron density peaks. The asymmetric unit contains two crystallographically independent molecules. The hydrogen atoms at C1A and C1B were refined freely, all other were placed at calculated positions and refined according to the riding model.

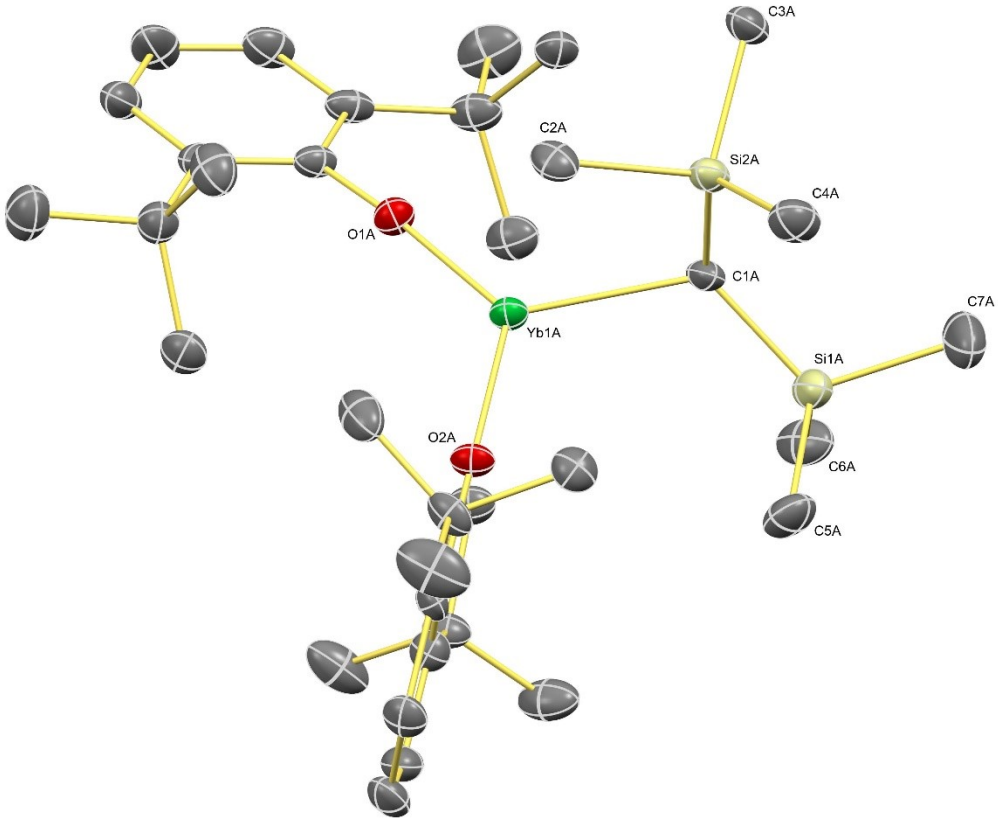

Figure S4: Thermal ellipsoid plot at 50% probability of Yb[CH(SiMe3)2][O−2,6−tBu−C6H3]$_2$. Hydrogen atoms have been omitted for clarity.

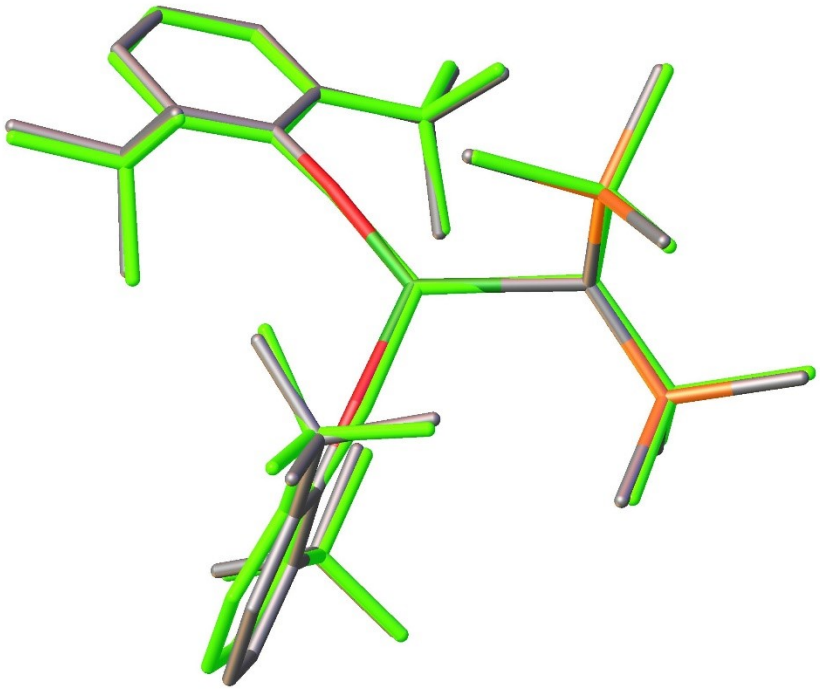

Figure S5: Overlay of both crystallographically independent molecules of Yb[CH(SiMe3)2][O−2,6−tBu−C6H3]$_2$in the asymmetric unit.

Selected interatomic distances for Yb[CH(SiMe$_3$)$_2$][O−2,6−tBu−C$_6$H$_3$]$_2$

Atom1	Atom2	Distances in molecule A /Å	Distances in molecule B /Å
Yb1	Si2	3.069(2)	3.083(2)
Yb1	O1	2.033(5)	2.033(5)
Yb1	O2	2.012(5)	2.020(5)
Yb1	C1	2.352(7)	2.341(7)