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Salt metathesis reactions of $LnCl_3$ (Sc, Y *vs.* Sm, Yb) with potassium diphenylmethanide {[2,2′-(4-$MeC_6H_3NMe_2$)$_2$CH]K(THF)}$_2$

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Tables and Figures

Experimental section

All air- and moisture-sensitive reactions were performed under inert atmosphere using standard Schlenk-type techniques or in a glove-box filled with nitrogen. Tetrahydrofuran (THF) was purified by distillation from sodium/benzophenone ketyl, after drying over KOH. Benzene, *n*-hexane, and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. Benzene-d_6 were dried over sodium/benzophenone ketyl, condensed *in vacuo* over activated 4Å molecular sieves and degassed by several freeze-pump-thaw cycles prior to use. {[2,2'-(4-$MeC_6H_3NMe_2)_2CH$]K(THF)}$_2$ (**1**) was prepared according to literature procedure.[1] All other reagents and solvents were used as purchased from commercial suppliers. ^{1}H and ^{13}C{^{1}H} spectra were recorded on either a Bruker Avance-III (400.13 and 100.62 MHz for ^{1}H and ^{13}C, respectively) or a Bruker DPX 200 MHz instrument (200.13 and 50.31 MHz for ^{1}H and ^{13}C, respectively). Chemical shifts are reported in ppm (δ) relative to TMS, referenced to the chemical shifts of residual solvent resonances (^{1}H and ^{13}C{^{1}H}). IR spectra were recorded as Nujol mulls on a Bruker-Vertex 70 spectrophotometer. Lanthanide metal analyses were carried out by complexometric titration.[2] The C, H, and N elemental analyses were performed in the microanalytical laboratory of the G. A. Razuvaev Institute of Organometallic Chemistry.

Synthesis of {[2,2'-(4-$MeC_6H_3NMe_2)_2CH]_2Sc(\mu$-Cl)}$_2$ (2). Anhydrous $ScCl_3$ (0.250 g, 1.65 mmol) was slurried in THF (15 mL) and stirred at 60 °C for 2 h. To the resulting suspension was added dropwise a solution of **1** (1.295 g, 1.65 mmol) in 15 mL of THF at ambient temperature. The mixture was stirred for 6 h to give light yellow solution. Then the solvent was removed in vacuum. The residue was dissolved in 15mL of toluene and separated from KCl by centrifugation. Toluene was removed in vacuum and the solid residue was dissolved in 15 mL of THF/Hexane mixture (1:4). Cooling the concentrated solution at −30 °C overnight resulted in the formation of **2** as yellow crystals. The mother liquor was decanted and the crystals were washed with cold hexane and dried in vacuum for 15 min. Complex **2** was isolated in 75% yield (0.795 g; 0.62 mmol). Elemental analysis calculated for $C_{76}H_{100}Cl_2N_8Sc_2$ (1286.48 g/mol): C, 70.95; H, 7.83; N, 8.71; Sc, 6.99. Found: C, 71.12; H, 8.01; N, 8.55; Sc, 6.80. ^{1}H NMR (400 MHz, C_6D_6, 293 K): 2.04 (br s, 24H, $C_6H_3CH_3$), 2.57 (br s, 48H, NMe_2), 3.60 (br

[1] D. O. Khristolyubov, D. M. Lyubov, A. V. Cherkasov, G. K. Fukin, A. S. Shavyrin and A. A. Trifonov, *Organometallics*, 2018, **37**, 1627.
[2] S. J. Lyle and M. M. Rahman, *Talanta*, 1963, **10**, 1177.

s, 4H, ScC*H*), 6.69 (br d, 8H, $^{3}J_{HH}$ = 6.9 Hz, 8H, CH Ar), 6.77 (m, 8H, CH Ar), 6.87 (m, 8H, H^{6}) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6, 293 K): 21.2 (s, $C_6H_3CH_3$), 43.7 (s, $C_6H_3N(CH_3)_2$), 70.4 (br, Sc*C*H), 118.9 (s, C*H* Ar), 121.2 (s, C*H* Ar), 123.4 (s, C*H* Ar), 134.9 (s, *C* Ar), 139.3 (s, *C* Ar), 146.9 (br s, *C* Ar) ppm. IR (Nujol, KBr) ν/cm^{-1}: 2810 (s), 2780 (s), 1995 (w), 1885 (w), 1615 (m), 1560 (m), 1510 (s), 1415 (w), 1300 (s), 1260 (s), 1220 (w), 1195 (s), 1165 (s), 1045 (m), 1025 (m), 960 (s), 810 (s), 680 (m), 575 (s).

Synthesis of {[2,2'-(4-MeC$_6$H$_3$NMe$_2$)$_2$CH]$_2$Y(μ-Cl)}$_2$ (3). Complex **3** was prepared similarly for **2** starting from YCl_3 (0.200 g, 1.02 mmol) and {[2,2'-(4-$MeC_6H_3NMe_2)_2CH]K(THF)\}_2$ (0.803 g, 1.02 mmol). Complex **3** was isolated in 88% yield (0.650 g, 0.45 mmol). Elemental analysis calculated for $C_{76}H_{100}Cl_2N_8Y_2\cdot(C_4H_8O)$ (1446.48 g/mol): C, 66.43; H, 7.53; N, 7.75; Y, 12.29. Found C, 66.63; H, 7.77; N, 7.61; Y, 12.15. ^{1}H NMR (400 MHz, C_6D_6, 293 K): 2.13 (s, 24H, $C_6H_3CH_3$), 2.54 (s, 48H, NMe_2), 3.36 (br s, 4H, YC*H*), 6.63 (br d, $^{3}J_{HH}$ = 7.6 Hz, 8H, C*H* Ar), 6.83 (d, $^{3}J_{HH}$ = 7.8 Hz, 8H, C*H* Ar), 7.11 (br s, overlaps with C_6D_6, 8H, C*H* Ar) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6, 293 K): 21.0 (s, $C_6H_3CH_3$), 46.0 (br s, NMe_2), 63.9 (br s, Y*CH*), 119.7 (s, *C*H Ar), 121.5 (br s, *C*H Ar), 126.5 (s, *C*H Ar, overlaps with C_6D_6, 135.2 (s, *C* Ar), 139.8 (s, *C* Ar), 141.4 (br s, *C* Ar) ppm. IR (Nujol, KBr) ν/cm^{-1}: 2820 (s), 2770 (s), 1990 (w), 1880 (w), 1610 (m), 1590 (m), 1565 (m), 1500 (s), 1405 (w), 1300 (s), 1260 (s), 1230 (w), 1190 (s), 1160 (s), 1095 (s), 1045 (s), 1020 (m), 950 (s), 880 (m), 820 (s), 690 (m), 570 (s).

Reactions of YbCl$_3$ with 1, formation of [2,2'-(4-MeC$_6$H$_3$NMe$_2$)$_2$CH]$_2$Yb (4) and [2,2'-(4-MeC$_6$H$_3$NMe$_2$)$_2$CH]$_2$ (6). To a suspension of $YbCl_3$ (0.235 g, 0.84 mmol) in THF (15 mL) was added a solution of **1** (0.660 g, 0.84 mmol) in THF (15 mL). The reaction mixture was stirred at ambient temperature for 6 h. THF was removed in vacuum and the dark brown residue was extracted with toluene (20 mL). Than all volatiles were again removed in vacuum and hexane (5 mL) was added to give dark brown oil which transforms into black crystals of **4** in 30 min. Complex **4** was isolated in 28% yield (0.170 g, 0.236 mmol). Mother liquid was decanted, additionally diluted with hexane (15 mL) and hydrolyzed with water. The resulted hexane solution was separated from water, dried over $MgSO_4$ and concentrated till ¼ of its volume. Storing of the concentrated solution at −30 °C for 12 h resulted in formation of colorless crystals of **6**, which was isolated in 30% yield (0.146 g, 0.26 mmol). **Characterization of 6**: Elemental analysis calculated for $C_{38}H_{50}N_4$ (562.83 g/mol): C, 81.10; H, 8.95; N, 9.95.

Found: C, 81.04; H, 9.08; N, 9.88. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): 2.23 (s, 12H, $C_6H_3CH_3$), 2.30 (br s, 24H, NMe_2), 6.11 (s, 2H, C*H*−C*H*), 6.81 (d, $^{3}J_{HH}$ = 7.8 Hz, 4H, C*H* Ar), 6.90 (d, $^{3}J_{HH}$ = 7.8 Hz, 4H, C*H* Ar), 7.33 (br s, 4H, C*H* Ar) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 293 K): 21.4 (s, $C_6H_3CH_3$), 43.0 (br s, *C*H−*C*H), 45.8 (s, NMe_2), 120.8 (br s, *C*H Ar), 126.6 (br s, *C*H Ar), 132.4 (br s, *C*H Ar), 132.6 (br s, *C* Ar), 141.1 (br s, *C* Ar), 150.9 (br s, *C* Ar) ppm. IR (Nujol, KBr) ν/cm^{-1}: 2820 (s), 2780 (s), 2490 (w), 1990 (w), 1885 (m), 1745 (m), 1685 b(s), 1605 (s), 1575 (w), 1500 (s), 1400 (w), 1295 (s), 1260 (s), 1230 (w), 1185 (s), 1160 (s), 1090 (s), 1040 (s), 950 (s), 920 (m), 880 (m), 815 (s), 740 (m), 720 (m), 700 (s), 635 (m), 565 (s), 530 (s). GC-MS: $[MH]^+$ 563.56 m/z.

Reactions of $SmCl_3$ with 1, formation of $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Sm$ (5) and $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2$ (6). The reaction and isolation were done similarly for Yb starting from $SmCl_3$ (0.286 g, 1.11 mmol) and **1** (0.803 g, 1.02 mmol). Complex **5** was isolated as black crystals in 25% yield (0.197 g, 0.28 mmol). Compound **6** was isolated in 35% yield (0.218 g, 0.39 mmol).

Table S1. Crystal data and structure refinement details for complexes **2**, **3** and **6**.

	2	**3**	**6**
Empirical formula	$C_{76}H_{100}Cl_2N_8Sc_2$	$C_{76}H_{100}Cl_2N_8Y_2$, C_4H_8O	$C_{38}H_{50}N_4$
Formula weight	1286.48	1446.46	562.82
T, K	100	100	298
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	*C2/c*	*Pn*	*P-1*
Unit cell dimensions	*a* = 13.8079(6) Å *b* = 24.4696(12) Å *c* = 21.6657(9) Å *α* = 90° *β* = 92.397(4)° *γ* = 90°	*a* = 16.5565(8) Å b = 12.9744(6) Å c = 17.9722(8) Å α = 90° β = 100.3570(10)° γ = 90°	*a* = 9.7599(5) Å b = 9.8086(5) Å c = 19.7235(10) Å α = 99.649(2)° β = 96.827(2)° γ = 107.339(2)°
V, Å^3	7155.0(6)	3797.7(3)	1748.02(16)
Z	4	2	2
d_{calc}, g/cm^3	1.194	1.265	1.069
μ, mm^{-1}	0.311	1.640	0.063
F_{000}	2752	1528	612
Crystal dimentions, mm	0.26 × 0.21 × 0.14	0.40 × 0.20 × 0.15	0.16 × 0.14 × 0.05
θ Range for data collection, °	2.92–25.03	1.54–28.70	2.22–25.11
HKL indices	$-16 \le h \le 16$ $-29 \le k \le 29$ $-25 \le l \le 25$	$-22 \le h \le 22$ $-17 \le k \le 17$ $-24 \le l \le 24$	$-11 \le h \le 11$ $-11 \le k \le 11$ $-23 \le l \le 23$
Reflns collected	49325	39798	20099
Independent reflns (R_{int})	6318 (0.0818)	19206 (0.0397)	5871 (0.0533)
Parameters (restraints)	451 (20)	879 (8)	392 (333)
Completeness to θ, %	99.8	100.0	94.2
$S(F^2)$	1.022	1.027	1.084
Flack parameter		0.468(6)	
Final *R* indices ($I > 2\sigma(I)$)	R_1 = 0.0620 wR_2 = 0.1397	R_1 = 0.0527 wR_2 = 0.1129	R_1 = 0.0846 wR_2 = 0.1410
R indices (all data)	R_1 = 0.0984 wR_2 = 0.1593	R_1 = 0.0728 wR_2 = 0.1224	R_1 = 0.1487 wR_2 = 0.1617
Largest diff. peak and hole, e/Å^3	0.61 / –0.80	1.18 / –0.34	0.17 / –0.16

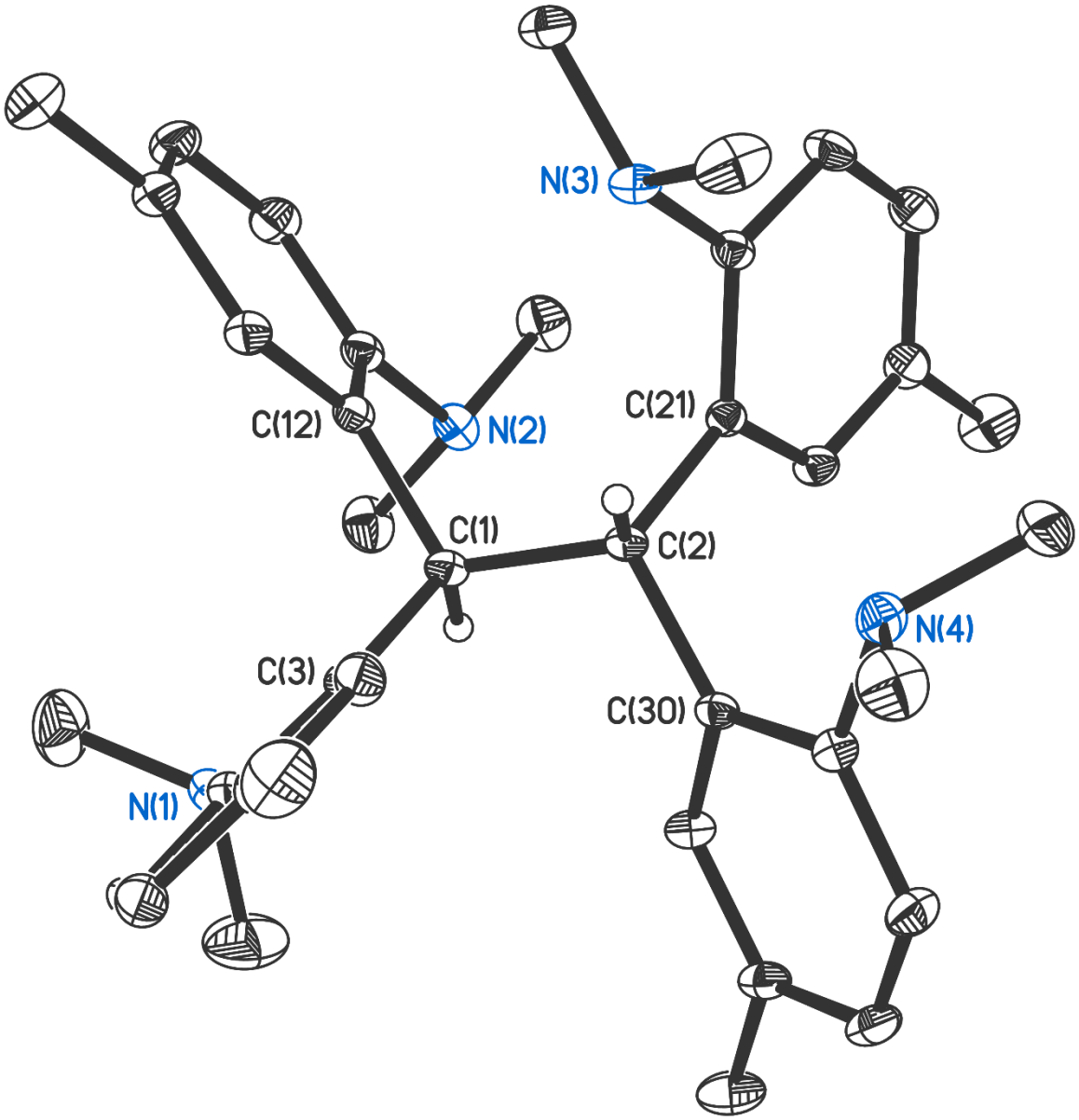

Figure S1. Molecular structure of $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2$ (**6**). Thermal ellipsoids are given with 10 % probability. Hydrogen atoms except diphenylmethanido CH are omitted for clarity. Selected bond distances (Å) and angles (°): C(1)−C(2) 1.561(3); C(1)−C(12) 1.525(3), C(1)−C(3) 1.530(4), C(2)−C(21) 1.526(3), C(2)−C(30) 1.529(3); C(3)−C(1)−C(12) 111.0(2), C(2)−C(1)−C(12) 115.5(2), C(21)−C(2)−C(30) 111.6(2), C(1)−C(2)−C(21) 115.5(2), C(1)−C(2)−C(30) 110.4(2), C(2)-C(1)-C(3) 109.9(2).

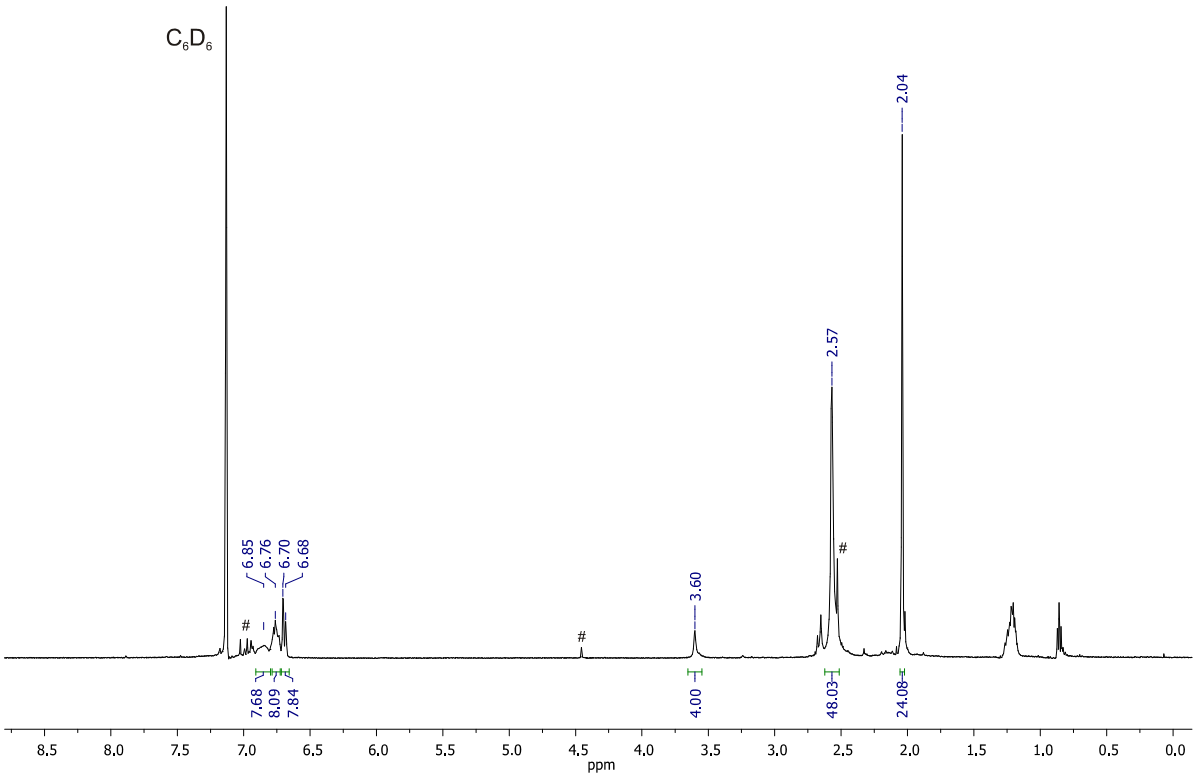

Figure S2. ^{1}H NMR spectrum of {[2,2'-(4-Me$C_6H_3NMe_2$)$_2$CH]$_2$Sc(μ-Cl)}$_2$ (**2**) (400 MHz, C_6D_6, 293 K). # – traces of starting diphenylmethane 2,2'-(4-Me$C_6H_3NMe_2$)$_2$$CH_2$.

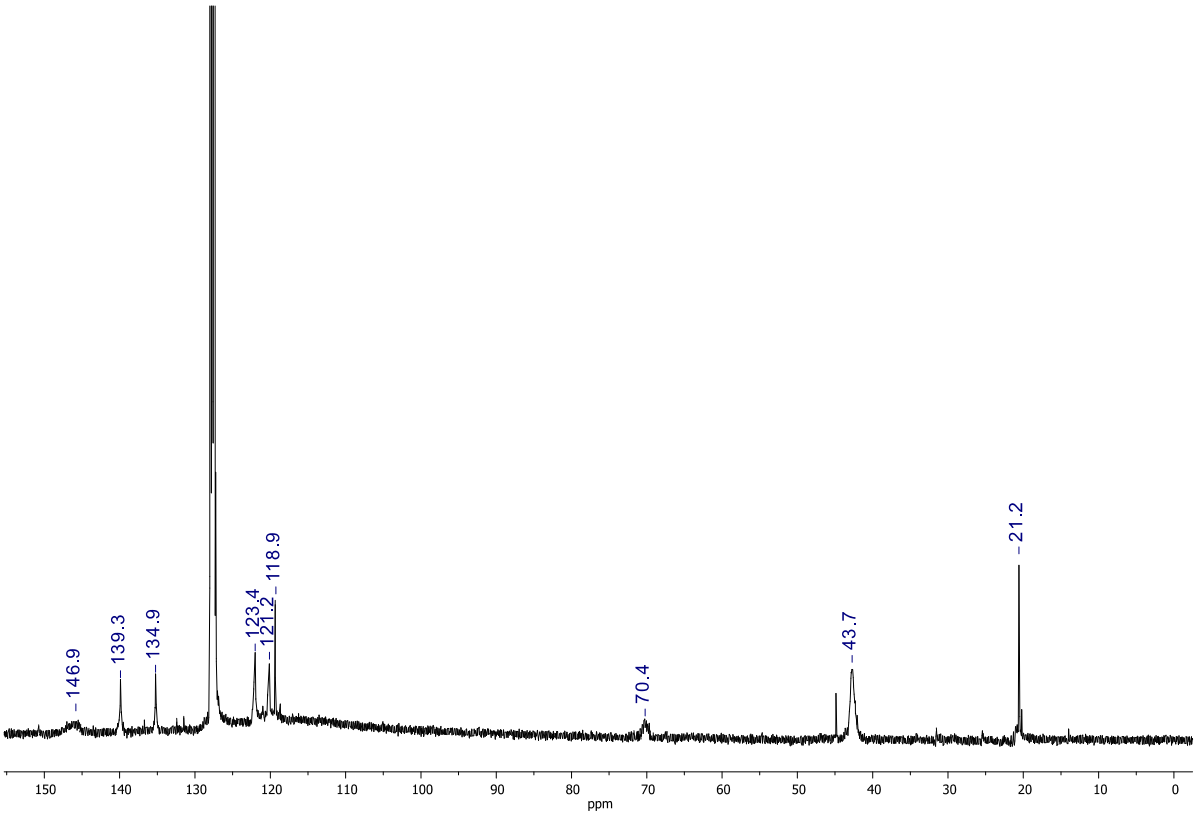

Figure S3. ^{13}C{^{1}H} NMR spectra of {[2,2'-(4-Me$C_6H_3NMe_2$)$_2$CH]$_2$Sc(μ-Cl)}$_2$ (**2**) (100 MHz, C_6D_6, 293 K).

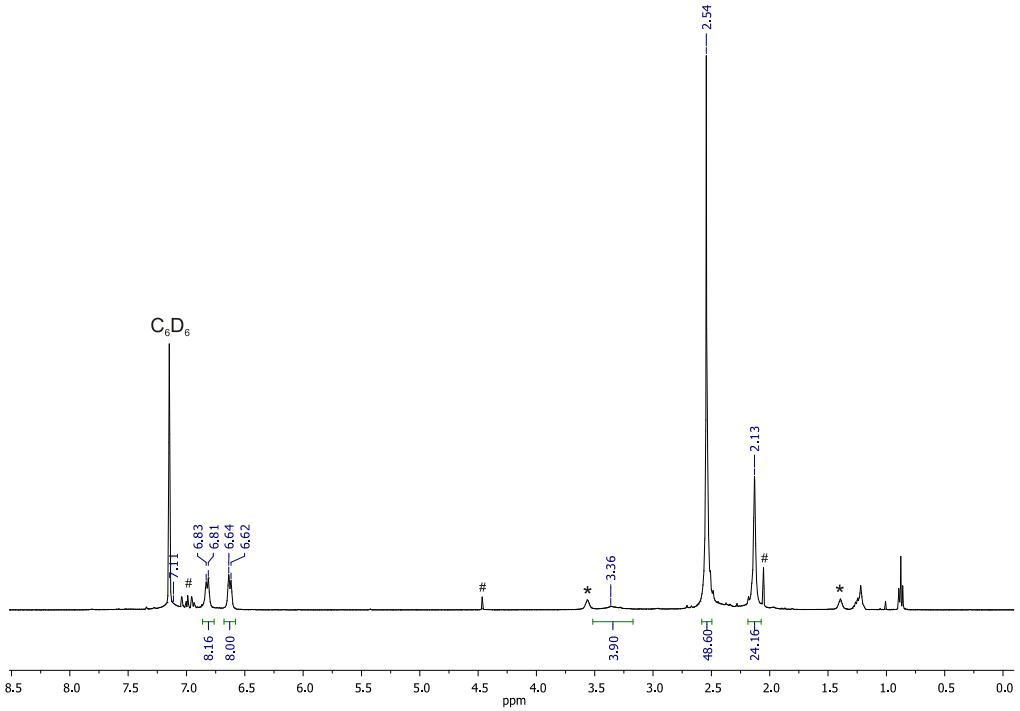

Figure S4. ^{1}H NMR spectra of {[2,2'-(4-Me$C_6H_3NMe_2$)$_2$CH]$_2$Y(μ-Cl)}$_2$ (**3**) (400 MHz, C_6D_6, 293 K). * – signals of solvated THF; # – traces of starting diphenylmethane 2,2'-(4-Me$C_6H_3NMe_2$)$_2$$CH_2$.

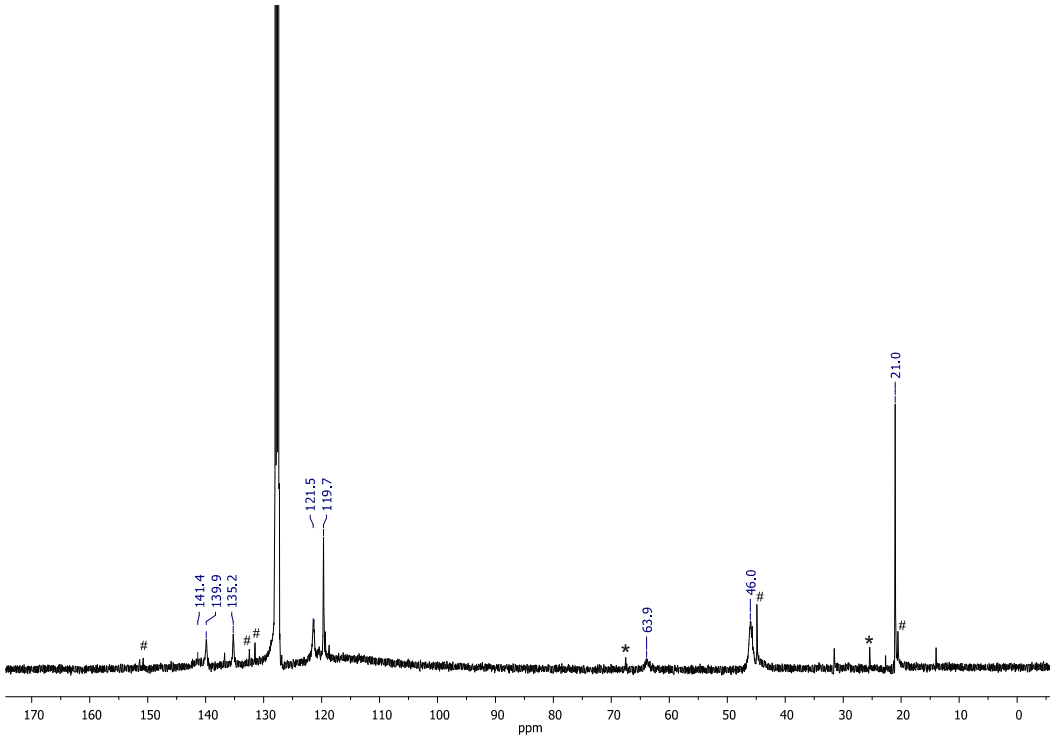

Figure S5. ^{13}C{^{1}H} NMR spectra of {[2,2'-(4-Me$C_6H_3NMe_2$)$_2$CH]$_2$YCl}$_2$ (**3**) in C_6D_6 (293K) * – signals of solvated THF; # - signal of traces of starting diphenylmethane 2,2'-(4-Me$C_6H_3NMe_2$)$_2$$CH_2$.

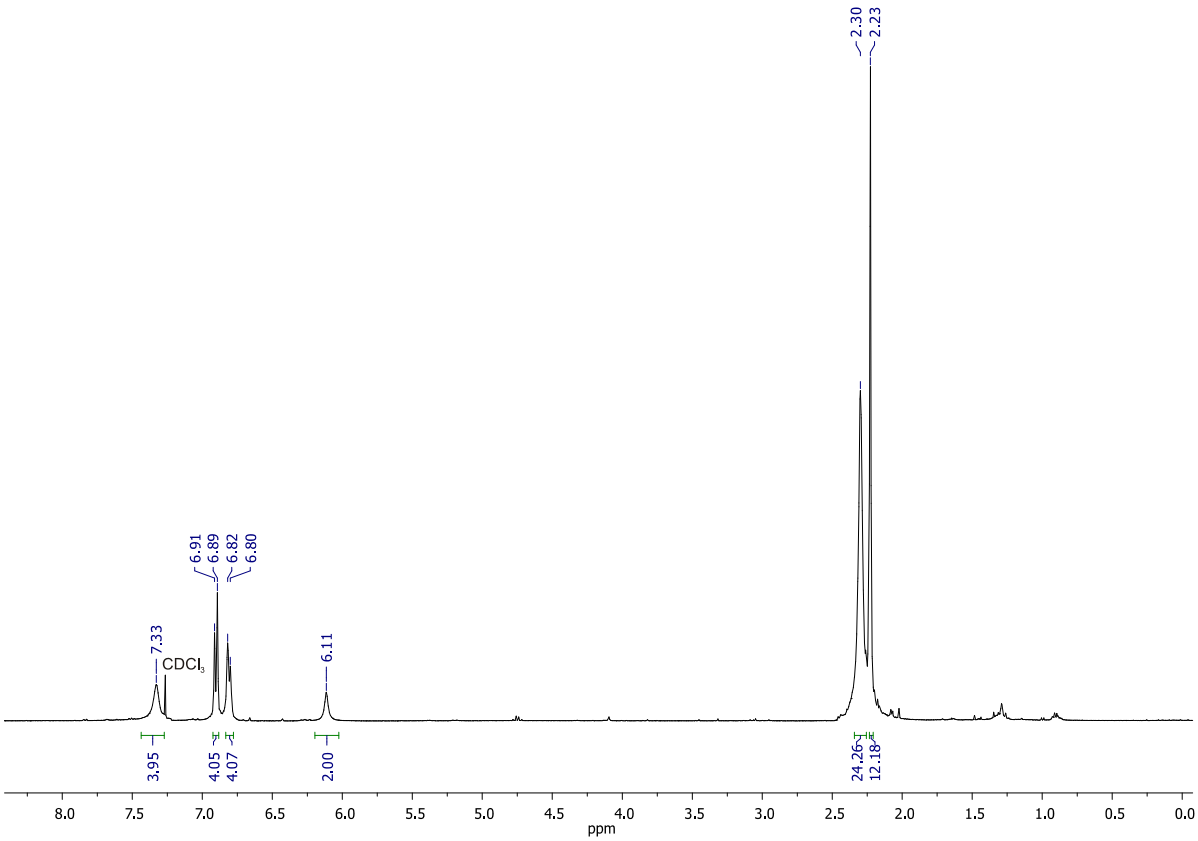

Figure S6. ^{1}H NMR spectrum of [2,2'-(4-MeC_6H_3NMe_2)$_2$CH]$_2$ (**6**) (400 MHz, $CDCl_3$, 293 K).

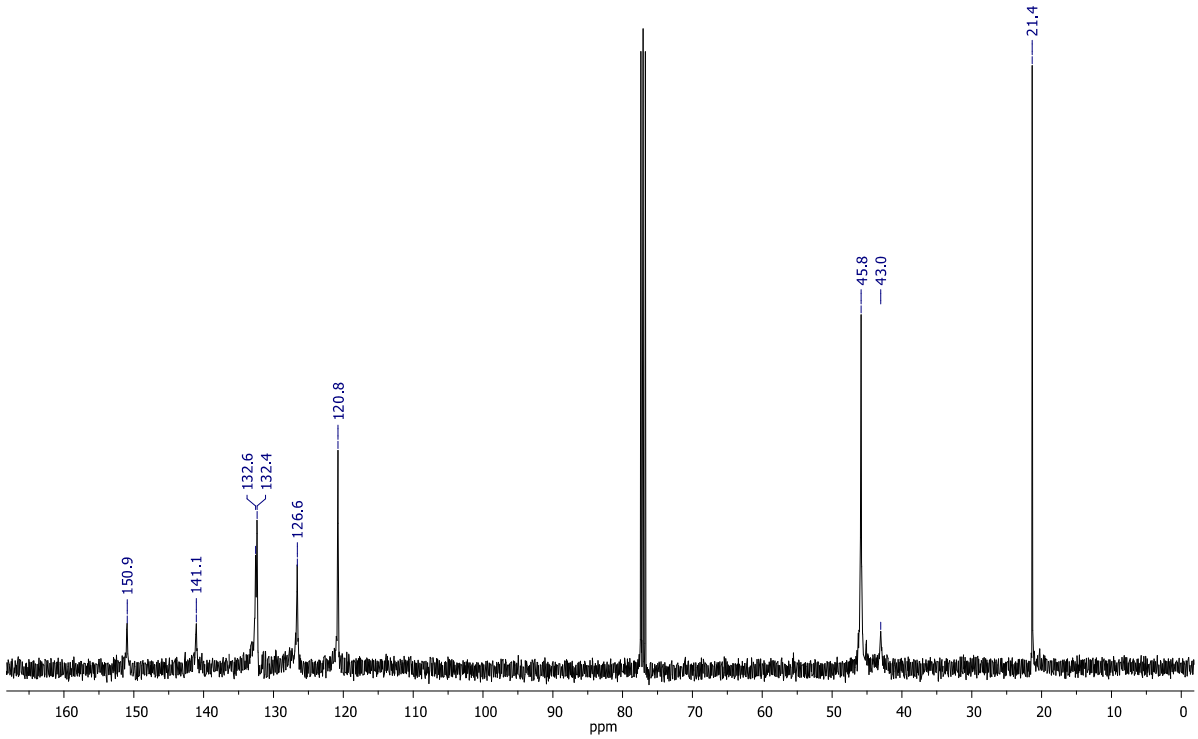

Figure S7. ^{13}C{^{1}H} NMR spectrum of [2,2'-(4-MeC_6H_3NMe_2)$_2$CH]$_2$ (**6**) (100 MHz, $CDCl_3$, 293 K).