Yttrium complexes derived from 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-dimethoxycalix[4]arene (LH_2). Synthesis, properties, and structures of the $[LY(thf)(\mu\text{-}Cl)]_2$ and $[LY(thf)_3]^+[L_2Y]^-$ complexes*

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5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-dimethoxycalix[4]arene (**1**, LH_2) was deprotonated with two equivalents of potassium naphthalenide in THF at room temperature. The reaction of a dipotassium derivative of **1** prepared *in situ* with anhydrous YCl_3 in a THF medium afforded the corresponding yttrium alkoxychloride $[LY(thf)(\mu\text{-}Cl)]_2 \cdot 4thf$ (**2**·4thf) in 71% yield. According to the X-ray diffraction data, complex **2** has a dimeric structure. The reaction of equimolar amounts of $[(Me_3Si)_2N]_3Y$ and compound **1** in a THF—toluene mixture at 60 °C was accompanied by the complete replacement of the bis(trimethylsilyl)amide ligands to form the homoligand ionic complex $[LY(thf)_3]^+[L_2Y]^-$ (**3**). The structure of the latter was established by X-ray diffraction analysis.

Key words: rare-earth elements, yttrium, complexes, 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-dimethoxycalix[4]arene, X-ray diffraction analysis, molecular structure.

Complexes of early d-transition metals with polyfunctional fused aryloxide ligands, some of which exhibit high catalytic activity in polymerization of olefins,[1] have attracted recent attention. The nonrigid calix[4]arene ligand containing four O atoms around the periphery of the cavity readily coordinates to transition metal atoms. The total charge of the ligand, its steric parameters, and coordination properties can be substantially varied by alkylation or silylation of the hydroxy groups.[2,3] In addition, the acidity of the hydroxy groups of the ligand can be modified by introducing various substituents at the *para* position of the phenyl rings.[4]

A series of rare-earth metal complexes with calixarene ligands of different sizes were synthesized by the reactions of salts of these metals with calixarenes in the presence of Lewis bases.[5] Amide derivatives of scandium and lutetium coordinated by 25,27-*O*-benzylated calix[4]arene were prepared[6] by elimination of amine in the reactions of calixarene with trisamides $[(Me_2HSi)_2N]_3Ln$. Study of the reaction of $TmI_2(DME)_3$ with 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-26,28-dimethoxycalix[4]arene (**1**, LH_2) in THF demonstrated[7] that it was accompanied by oxidation of the metal atom to form a mixture of trivalent thulium derivatives, *viz.*, $[LTmI(Et_2O)]$ and $TmI_3(thf)_{3.5}$.

The aim of the present study was to prepare mixed-ligand yttrium derivatives, which could serve as the starting compounds for the synthesis of the corresponding alkyl derivatives stabilized by calixarene ligands. Since it is known that the chloride and amide anions serve as convenient leaving groups, which are most often used for the replacement by different hydrocarbon groups,[8] attempts were made to synthesize the yttrium chloride and amide complexes LYX (X = Cl or $(Me_3Si)_2N$).

Results and Discussion

One of procedures most commonly used for the synthesis of rare-earth metal complexes involves the exchange reactions of anhydrous halides with alkali metal derivatives. However, this method is of limited application because of the difficulties associated with purification of the target products from alkali metal halide that formed.[8]

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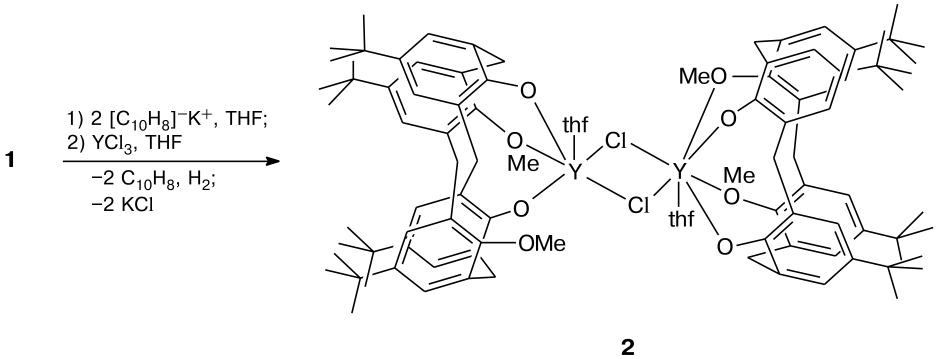
Scheme 1



2

Compound **1** was deprotonated with a solution of potassium naphthalenide in THF in a molar ratio of 1 : 2. The reaction proceeded at room temperature (~20 °C) at a rate at which the reagents were mixed, as evidenced by the disappearance of the dark-green color characteristic of the naphthalene radical anion, the absence of the signal of $C_{10}H_8^-$ in the ESR spectrum of the reaction mixture, and elimination of hydrogen. The reaction of a dipotassium derivative of **1** prepared *in situ* with 1 equiv. of YCl_3 in THF was carried out at room temperature (~20 °C) for 24 h. The $[LY(thf)(\mu\text{-}Cl)]_2$ complex (**2**) (Scheme 1) was isolated in 71% yield.

Compound **2** is poorly soluble in THF-d_8 and pyridine-d_5, which hinders the use of NMR spectroscopy for studying its behavior in solution. Slow cooling of a hot tetrahydrofuran solution of **2** afforded its colorless crystals sensitive to atmospheric oxygen and moisture. Crystals of **2** were studied by X-ray diffraction analysis. The quality of the experimental data is not sufficiently high due to disorder of the THF molecules of crystallization and one of the *tert*-butyl groups. Hence, it is unreasonable to discuss the bond lengths and bond angles in molecule **2**. However, the results of X-ray diffraction analysis provide unambiguous information on the geometry of the molecule and the arrangement of the bonds between its atoms. According to the X-ray diffraction data, complex **2** in the crystalline state has a dimeric structure (Fig. 1). The crystals contain four THF molecules of crystallization per dimeric molecule. In complex **2**, the Y atom has a coordination number of 7 and is coordinated by four O atoms of the calixarene fragment, the O atom of the THF molecule, and two Cl atoms. The Cl atoms serve as bridges between two Y atoms giving rise to a dimer.

With the aim of preparing an yttrium complex containing simultaneously the calixarene and bis(trimethylsilyl)amide ligands, we studied the reaction of equimolar amounts of yttrium trisamide $[(Me_3Si)_2N]_3Y$ and compound **1** in a THF—toluene mixture at 60 °C. The reaction was accompanied by elimination of hexamethyldisilazane, which allowed us to follow its course by GLC. In spite of prolonged heating (72 h), we failed to obtain hexamethyldisilazane in quantitative yield (the yield of the latter was no higher than 70%). After removal of volatile compounds and extraction of the solid residue with hot hexane, the starting yttrium trisamide was detected in a small amount (12%). Recrystallization of the product from a THF—cyclohexane mixture at room temperature (~20 °C) afforded the calixarene complex $[LY(thf)_3]^+[L_2Y]^-$ (**3**) (Scheme 2) as colorless crystals in 53% yield.

Contrary to the expectations, the reaction of $[(Me_3Si)_2N]_3Y$ with compound **1** did not give the alkoxyamide complex; instead, the bis(trimethylsilyl)amide ligands in the coordination sphere of the Y atom were completely replaced. Earlier,[6] it has been reported that the reactions of rare-earth metal amides containing the less bulky $[(Me_2HSi)_2N]_3Ln$ fragments (Ln = Sc or Lu) with calix[4]arenes (LH_2) proceeded readily at room temperature to give the $LLn[N(SiHMe_2)_2]$ complexes in good yields, whereas the reactions of the bis(trimethylsilyl)amide analogs $[(Me_3Si)_2N]_3Ln$ (Ln = Sc or Lu) were more complicated and gave unidentifiable products. Apparently, even in the case of yttrium having a larger ionic radius,[9] the rare-earth atom of the $[(Me_3Si)_2N]M$ fragment cannot coordinate the calix[4]arene dianion due to steric hindrances. This fact is responsible for the formation of complex **3**.

Compound **3** is sensitive to atmospheric moisture and oxygen, soluble in THF and Py, moderately soluble in toluene, and insoluble in hexane. Slow vacuum concentration of a saturated solution of compound **3** in a THF—cyclohexane mixture at room temperature (~20 °C) afforded colorless crystals of **3** suitable for X-ray diffraction analysis. Under these conditions, compound **3** crystallized as a solvate containing eight THF molecules of crystallization and one cyclohexane molecule per two molecules of the complex. Upon storage of the solvate of complex **3** in dynamic vacuum at room temperature (~20 °C) for 3 h, the solvent molecules of crystallization were completely removed. According to the results of

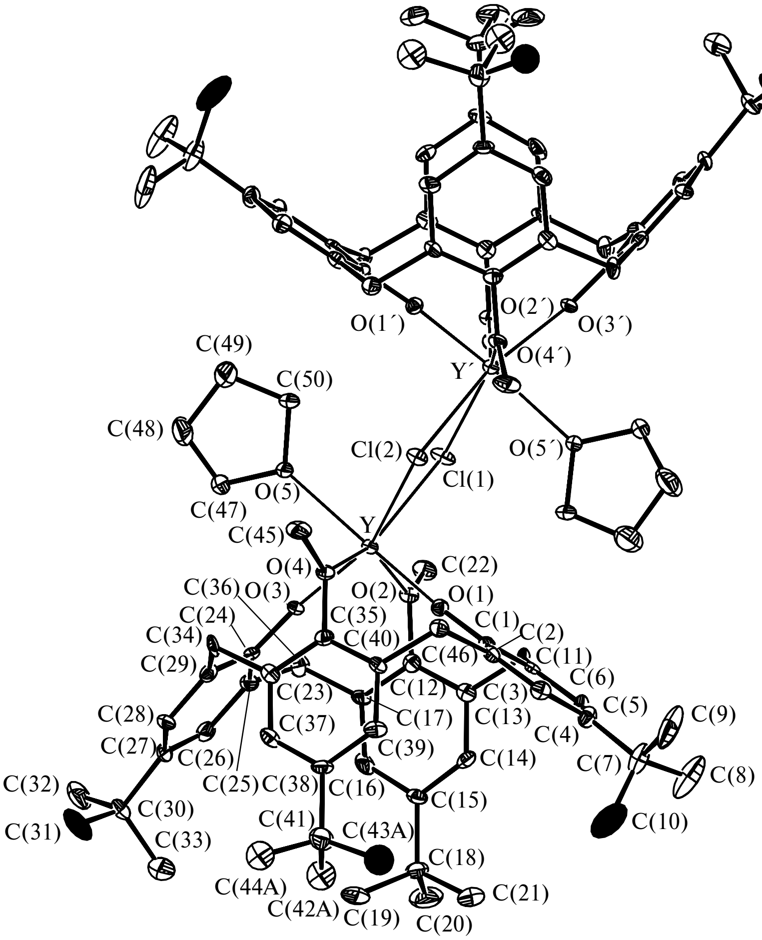
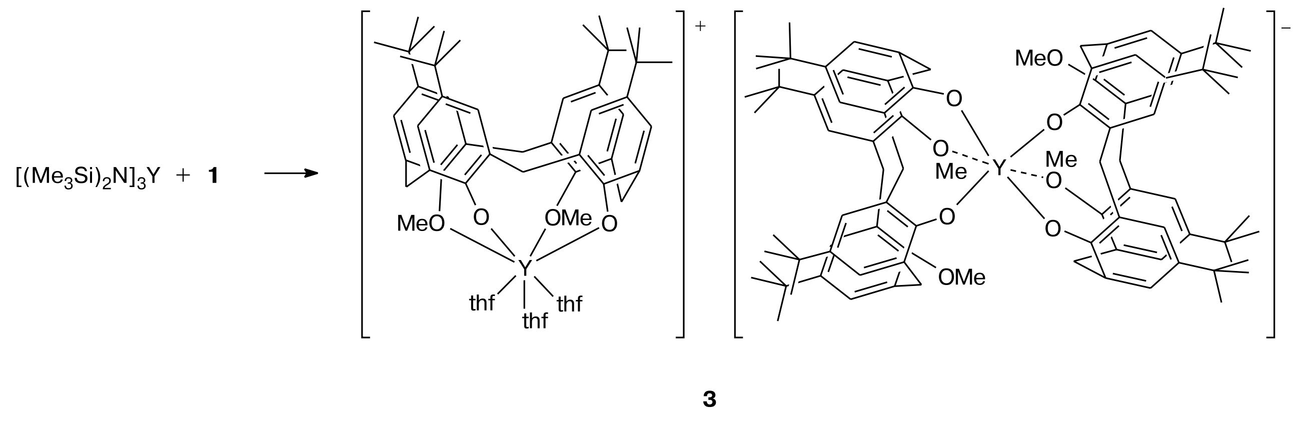


Fig. 1. Structure of complex **2**.

X-ray diffraction analysis, compound **3** is a ionic complex. The Y atom in the $[LY(thf)_3]^+$ cation is coordinated by the doubly deprotonated calixarene ligand and three THF molecules (Fig. 2). The single-charged $[L_2Y]^-$ anion, in turn, also contains the Y atom coordinated by two calixarene ligands (Fig. 3). In the $[LY(thf)_3]^+$ cation, the Y atom forms two covalent bonds with the O atoms of the phenol fragments and two coordination bonds with the O atoms of the methoxy groups. The Y—O covalent bonds (2.069(2) and 2.075(2) Å; Table 1) are somewhat longer than the analogous bonds in monomeric phenoxide $Y(OC_6H_3Bu^t{}_2\text{-}2,6)_3$ **10** and are comparable in lengths to

Scheme 2



3

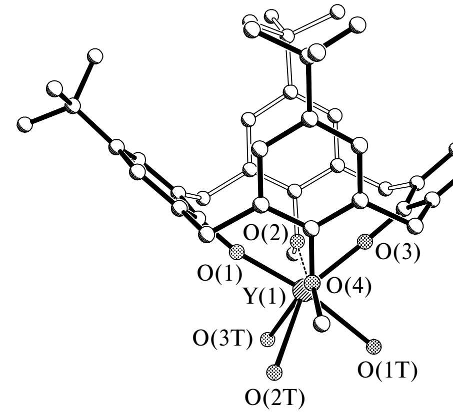


Fig. 2. Structure of the cation in complex **3**.

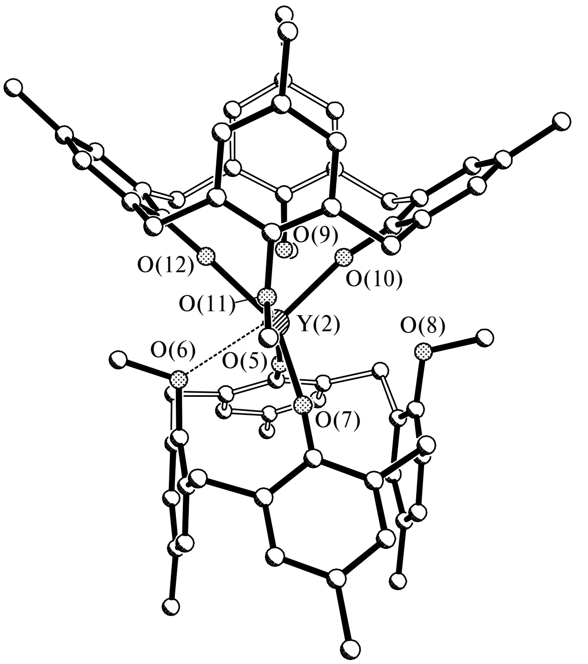


Fig. 3. Structure of the anion in complex **3**. The methyl groups of the *tert*-butyl fragments are omitted.

Table 1. Selected bond lengths (d) and bond angles (ω) in complex **3**

Bond	d/Å	Angle	ω/deg
Y(1)—O(1)	2.0688(19)	O(1)—Y(1)—O(3)	110.55(8)
Y(1)—O(3)	2.0745(19)	O(1)—Y(1)—O(3T)	92.94(7)
Y(1)—O(4)	2.4950(19)	O(1)—Y(1)—O(4)	81.80(7)
Y(1)—O(2)	2.5652(19)	O(3)—Y(1)—O(4)	78.90(7)
Y(1)—O(3T)	2.451(2)	O(3T)—Y(1)—O(4)	142.37(7)
Y(1)—O(2T)	2.466(2)	O(3)—Y(1)—O(2)	78.19(7)
Y(1)—O(1T)	2.491(2)	O(10)—Y(2)—O(5)	109.46(7)
Y(2)—O(10)	2.1389(18)	O(10)—Y(2)—O(12)	92.39(7)
Y(2)—O(5)	2.1409(19)	O(5)—Y(2)—O(12)	110.95(7)
Y(2)—O(12)	2.1861(19)	O(10)—Y(2)—O(7)	110.45(7)
Y(2)—O(7)	2.2035(19)	O(5)—Y(2)—O(7)	93.40(7)
Y(2)—O(11)	2.5456(19)	O(12)—Y(2)—O(7)	139.04(7)
Y(2)—O(6)	2.5515(18)	O(10)—Y(2)—O(11)	81.10(7)

the terminal bonds in the $Y_2(OC_6H_3Me_2\text{-}2,6)_6(thf)_2$ [11] and $Y(OCBu^t{}_2CH_2PMe_2)_3$ [12] compounds. According to the general tendency, the terminal Y—O bonds in compound **3** are substantially shorter than the analogous bridging bonds in yttrium alkoxides.[13] The Y—O coordination bonds in the $[LY(thf)_3]^+$ cation (2.565(2) and 2.495(2) Å) are similar in length to the corresponding bonds in yttrium complexes with polydentate alcohols.[13c] The distances between the Y atom and the O atoms of the THF molecules (2.451(2), 2.466(2), and 2.491(2) Å) are slightly larger than the corresponding distances in the $Cp^*{}_2YCl(thf)$ complex.[14] In the $[L_2Y]^-$ anion, the Y—O covalent bonds (2.139(2), 2.186(2), 2.141(2), and 2.204(2) Å) are substantially longer than those in the $[LY(thf)_3]^+$ cation but they are shorter than the bridging bonds in yttrium alkoxide complexes studied earlier.[13] An elongation of the Y—O covalent bonds in anion **2** is accompanied by a substantial decrease in the O—Y—O bond angles (92.39(7) and 93.40(7)°) compared to that in the cation (110.55(8)°). These changes in the geometric parameters of the LY fragment are, most likely, attributable to the mutual repulsion between two bulky calixarene ligands in the $[L_2Y]^-$ anion. It should be noted that, in contrast to the cation, only one methoxy group of each ligand in the anion is coordinated to the Y atom (the Y—O bonds lengths are 2.495(2) and 2.565(2) Å), whereas there is no bond with the second methoxy group (the Y—O distances are 3.480(2) and 3.521(2) Å).

Therefore, the reaction of yttrium chloride with a dipotassium derivative of calix[4]arene afforded dimeric mixed-ligand calixarene chloride complex **2**. The large volume of the bis(trimethylsilyl)amide ligand, apparently, hinders the simultaneous coordination of calix[4]arene ligand **1** to the rare-earth atom, which does not allow one to use rare-earth metal derivatives of the bis(trimethylsilyl)amide series for the synthesis of calixarene amide complexes.

Experimental

The syntheses were carried out under conditions precluding exposure to atmospheric oxygen and moisture using the standard Schlenk technique. Hexane, toluene, and THF were dried over sodium benzophenone ketyl, thoroughly degassed, and condensed *in vacuo* into a reaction tube immediately before use. The IR spectra were recorded on a Specord M-80 instrument. The samples were prepared as Nujol mulls. The ^1H and ^{13}C NMR spectra of solutions in THF-d_8 were measured on a Bruker DPX 200 instrument (200 MHz for ^1H and 50 MHz for ^{13}C) at 20 °C. The chemical shifts are given in the δ scale with respect to the known chemical shifts of the residual protons and the C atoms

Table 2. Crystallographic parameters of complexes **2** and **3**

Parameter	**2**	**3**
Molecular formula	$C_{100}H_{132}Cl_2O_{10}Y_2 \cdot 4C_4H_8O$	$C_{169}H_{236}O_{19}Y_2$
Molecular weight	2031.19	2747.38
Space group	*C*2/*c*	*P*2(1)/*n*
a/Å	34.8258(4)	25.9470(17)
b/Å	16.8175(3)	21.0564(13)
c/Å	20.4730(4)	29.2086(19)
α/deg	90	90
β/deg	108.048(1)	98.7320(10)
γ/deg	90	90
V/Å^3	11400.7(3)	15773.2(18)
Z	4	4
ρ_{calc}/g cm^{-3}	1.183	1.157
μ/mm^{-1}	1.117	0.794
θ Scan range/deg	1.23—25.00	10.61—22.46
Number of meausured reflections	16386	59717
Number of reflections with $I > 2\sigma$	9856 (R_{int} = 0.1268)	18234 (R_{int} = 0.0822)
Number of parameters in refinement	605	1792
R_1 ($I > 2\sigma(I)$)	0.0920	0.0506
wR_2 ($I > 2\sigma(I)$)	0.1289	0.1170

of the deuterated solvent. Volatile organic products were analyzed on a Tsvet-530 instrument equipped with a katharometer as a detector and a 2 m×3-mm steel column (5% SE-30 Chromaton N-AW); helium was used as the carrier gas. Yttrium amide was prepared according to a known procedure.[15]

Bis[(5,11,17,23-tetra-*tert*-butyl-25,27-dioxo-26,28-dimethoxycalix[4]arene)(tetrahydrofuran)yttrium chloride], [LY(thf)(μ-Cl)]$_2$ (2). A solution of compound **1** (0.21 g, 0.31 mmol) in THF (10 mL) was slowly added with vigorous stirring to a solution of potassium naphthalenide, which was prepared by the reaction of $C_{10}H_8$ (0.080 g, 0.62 mmol) and potassium (0.026 g, 0.66 mmol) in THF (15 mL), at ~20 °C. In the course of the reaction, the dark-green reaction mixture turned colorless and hydrogen was eliminated. The solution was stirred for 30 min and then YCl_3 (0.061 g, 0.31 mmol) was added. The reaction mixture was stirred for 24 h and heated to 60 °C. The solid residue was filtered off and extracted repeatedly with hot THF. The combined extracts were concentrated and cooled to ~20 °C to form colorless crystals of **2** in a yield of 0.22 g (71%). Found (%): C, 67.89; H, 7.61. $C_{116}H_{164}Cl_2O_{14}Y_2$. Calculated (%): C, 68.59; H, 8.07. IR, ν/cm^{-1}: 1610, 1380, 1360, 1320, 1305, 1290, 1210, 1140, 110, 1050, 1000, 950, 860, 800, 780. ^{1}H NMR, δ: 0.78 and 1.41 (both s, 36 H each, Bu^t); 2.90 (br.s, 8 H, CH_2); 3.51 (s, 12 H, OMe); 4.22 (br.s, 8 H, CH_2); 6.67 and 6.99 (both s, 8 H each, Ar$\underline{H}$).

(5,11,17,23-Tetra-*tert*-butyl-25,27-dioxo-26,28-dimethoxycalix[4]arene)tris(tetrahydrofuran)yttrium bis(5,11,17,23-tetra-*tert*-butyl-25,27-dioxo-26,28-dimethoxycalix[4]arene)yttrate, [LY(thf)$_3$]$^+$[L$_2$Y]$^-$ (3). A solution of compound **1** (1.09 g, 1.61 mmol) in toluene (5 mL) was added to a solution of $[(Me_3Si)_2N]_3Y$ (0.92 g, 1.61 mmol) in a mixture of THF (15 mL) and toluene (15 mL). The reaction mixture was stirred at 60 °C for 72 h. All volatile products were evaporated *in vacuo* and $(Me_3Si)_2NH$ was detected in the condensate by gas chromatography in a yield of 0.54 g (70%). The solid residue was extracted with hot hexane (3×20 mL) and $[(Me_3Si)_2N]_3Y$ was isolated from the extract in a yield of 0.11 g (12%). A hexane-insoluble colorless powder was dissolved in a 1 : 1 THF—cyclohexane mixture (20 mL) on heating (60 °C). Slow concentration of the solution *in vacuo* at ~20 °C afforded a colorless crystalline precipitate. The mother liquor was separated by decantation and the crystals were dried in dynamic vacuum at ~20 °C (3 h). Complex **3** was obtained in a yield of 0.68 g (53%) as colorless crystals. Found (%): C, 73.82; H, 7.88. $C_{150}H_{198}O_{15}Y_2$. Calculated (%): C, 74.47; H, 8.24. IR, ν/cm^{-1}: 1600, 1390, 1360, 1320, 1300, 1290, 1210, 1180, 1140, 1110, 1050, 1000, 950, 920, 900, 860, 800, 780, 700. ^{1}H NMR, δ: 0.92 (s, 18 H, Bu^t); 0.93 (s, 36 H, Bu^t); 1.37 (s, 54 H, Bu^t); 2.99 (d, 8 H, CH_2, J = 11.8 Hz); 3.23 (d, 4 H, CH_2, J = 12.6 Hz); 3.55 (s, 12 H, OMe); 4.09 (s, 6 H, OMe); 4.23 (d, 4 H, CH_2, J = 12.2 Hz); 4.72 (d, 8 H, CH_2, J = 11.6 Hz); 6.62 (s, 8 H, Ar$\underline{H}$); 6.72 (s, 4 H, Ar$\underline{H}$); 6.99 (s, 8 H, Ar$\underline{H}$); 7.15 (s, 4 H, Ar$\underline{H}$). ^{13}C NMR, δ: 30.3 ($C(\underline{C}H_3)_3$); 30.5 (CH_2); 30.9 ($C(\underline{C}H_3)_3$); 31.3 ($C(\underline{C}H_3)_3$); 31.5 (CH_2); 31.7 ($C(\underline{C}H_3)_3$); 32.1 (CH_2); 32.7 (CH_2); 33.1 ($\underline{C}(CH_3)_3$); 33.36 ($\underline{C}(CH_3)_3$); 33.4 ($\underline{C}(CH_3)_3$); 33.5 ($\underline{C}(CH_3)_3$); 64.8 (OCH_3); 123.4, 123.6, 124.0, 124.8, 125.5, 129.9, 131.2, 131.6, 132.2, 138.6, 143.4, 147.5, 151.3, 154.7, 157.0, 162.0, (Ar$\underline{C}$).

X-ray diffraction study. The X-ray diffraction data for complexes **2** and **3** were collected on a Bruker SMART CCD diffractometer (λ-Mo-Kα radiation, graphite monochromator, 173 K, ω scan technique). The crystallographic data and principal details of structure refinement for compounds **2** and **3** are given in Table 2. The structures were solved by direct methods using the SHELXS-86 program package[16] and refined anisotropically by the least-squares method using the SHELXL-93 program package.[17] The H atoms were placed in geometrically calculated positions and refined using the riding model. The atomic coordinates of **2** and **3** were deposited with the Cambridge Structural Database.

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