Synthesis, Structure, and Lanthanide Derivatives of an Unusual Hexameric Alcohol: [2,4,6-(CF₃)₃C₆H₂CH₂OH]₆

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Dedicated to Professor Konrad Seppelt on the Occasion of his 60th Birthday

Abstract. Hitherto unknown 2,4,6-tris(trifluoromethyl)benzyl alcohol (3) was synthesized in 41 % yield by treatment of freshly prepared R_FLi (2) with paraformaldehyde (R_F = 2,4,6-tris(trifluoromethyl)phenyl). According to an X-ray diffraction study the crystal structure of **3** consists of S₆ symmetric cyclic hexamers [2,4,6-(CF₃)₃C₆H₂CH₂OH]₆. Deprotonation of **3** with NaN(SiMe₃)₂ in toluene afforded the unsolvated sodium alkoxide derivative R_FCH₂ONa (4). Homoleptic lanthanide alkoxides of the type Ln(OCH₂R_F)₃ (Ln = Nd (5), Sm (6), Yb (7)) were made by treatment of $Ln(C_5H_5)_3$ with three equivalents of **3**. Similar reactions in a 1:1 molar ratio afforded the bis(cyclopentadienyl)lanthanide alkoxide derivatives $(C_5H_5)_2Ln(OCH_2R_F)$ (Ln = Nd (8), Sm (9), Yb (10)).

Keywords: methanol hexamer; fluorine; 2,4,6-tris(trifluoromethyl)phenyl substituent; lanthanides; cyclopentadienyl lanthanide complexes; X-ray structure

Synthese, Struktur und Lanthanoidderivative eines ungewöhnlichen hexameren Alkohols: [2,4,6-(CF₃)₃C₆H₂CH₂OH]₆

Inhaltsübersicht. Der bislang unbekannte 2,4,6-Tris(trifluoromethyl)benzylalkohol (**3**) wurde in 41 % Ausbeute durch Umsetzung von frisch hergestelltem R_FLi (**2**) mit Paraformaldehyd synthetisiert (R_F = 2,4,6-Tris(trifluoromethyl)phenyl). Nach der Röntgenstrukturanalyse enthält die Kristallstruktur von **3** S₆-symmetrische, cyclische Hexamere [2,4,6-(CF₃)₃C₆H₂CH₂OH]₆. Deprotonierung von **3** mit NaN(SiMe₃)₂ in Toluol lieferte das unsolvatisierte Natriumalkoxid R_FCH_2ONa (4). Homoleptische Lanthanoidalkoxide des Typs $Ln(OCH_2R_F)_3$ (Ln = Nd (5), Sm (6), Yb (7)) wurden durch Umsetzung von $Ln(C_5H_5)_3$ mit drei Äquivalenten 3 erhalten. Die gleichen Reaktionen im Molverhältnis 1:1 lieferten die Bis(cyclopentadienyl)lanthanoidalkoxide ($C_5H_5)_2Ln(OCH_2R_F$) (Ln = Nd (8), Sm (9), Yb (10)).

Introduction

The structure of methanol in different physical states has been the subject of detailed investigations for decades. In the crystal at -110 °C, solid methanol forms infinite zigzag chains *via* hydrogen bonds [1]. The C-O distance is 1.42 Å, and the O···O distance is 2.66 Å. Above the melting point these infinite chains break up, and shorter chains and/or cyclic oligomers of the type (MeOH)_n with n = 3-20 are formed [2–4]. In his famous book "*The Nature of the Chemical Bond*" *Pauling* has already illustrated the structure of solid and liquid methanol, including the cyclic hexamer (MeOH)₆ [5]. It has later been demonstrated that this hexamer is the predominant cluster species present in liquid methanol at room temperature [6–8]. The two energetically

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lowest lying isomers of this cluster are those adopting either S_6 or C_2 symmetry (Scheme 1).



Scheme 1 S_6 and C_2 symmetric forms of hexameric methanol clusters (MeOH)₆.

Both isomers have been size selected by momentum transfer in collisions with He, and identified by their IR spectra [9]. The predominant species present in gaseous methanol has been shown to be the cyclic tetramer (MeOH)₄ [10]. More recently, *Wieghardt* et al. described the assembly of (MeOH)₆ in a hydrophobic ligand cavity. X-ray crystallography revealed the presence of the cyclic S_6 symmetric methanol hexamer in crystals of [GaLF₃]-(MeOH)_{6/2}·(MeOH)₃·CH₂Cl₂ where L represents the

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Scheme 2 Preparation of 2,4,6-tris(trifluoromethyl)benzyl alcohol (3).

macrocyclic ligand 1,4,7-tris(2-amino-3,5-di-*t*-butylbenzyl)-1,4,7-triazacyclononane [11]. In the present contribution we report the synthesis and structural characterization of an unusual methanol derivative, 2,4,6-tris(trifluoromethyl)benzyl alcohol (**3**), which was found to adopt the cyclic S_6 symmetric hexamer form in the solid state.

Since 1987 the chemistry of the 2,4,6-tris(trifluoromethyl)phenyl substituent ("nonafluoromesityl", abbreviated as $R_{\rm F}$) has been intensively investigated [12–14]. The combination of steric bulk and electronic stabilization makes this ligand an ideal choice for the stabilization of low-coordinated main-group derivatives [12]. More recently, the nonafluoromesityl ligand has also been successfully employed in transition metal chemistry [15-17]. However, due to severe steric hindrance, certain purely organic R_F derivatives have been found to be inaccessible. For example, the carboxylic acid $R_FC(=O)OH$ fails to undergo normal esterification with ethanol [18], and various attempts to prepare 2,4,6-tris(trifluoromethyl)acetophenone have been unsuccessful [18]. This prompted us to investigate the synthesis of the hitherto unknown 2,4,6-tris(trifluoromethyl)benzyl alcohol, R_FCH₂OH.

Results and Discussion

It was found that 2,4,6-tris(trifluoromethyl)benzyl alcohol (3) can be obtained by treatment of freshly prepared R_FLi (2) with a slight excess of paraformaldehyde (Scheme 2). R_FLi (2) is readily accessible by direct metalation of the parent fluorocarbon using *n*-butyllithium. Addition of $(CH_2O)_n$ to a solution of 2 in diethylether/hexane caused a vigorous reaction to occur after an induction period of *ca.* 10 min. In the course of this reaction complete dissolution of the suspended paraformaldehyde was observed. Standard work-up afforded 3 in 41 % yield as a waxy, low-melting, crystalline solid exhibiting a pleasant aromatic odor.

Analytical and spectroscopic characterization of **3** was straightforward and unambiguous. In the ¹⁹F NMR spectrum the *ortho*- and *para*-CF₃ groups give rise to resonances at δ -59.1 and -63.9, respectively, in an intensity ratio of 2:1. The most remarkable finding is the presence of a hexameric structure of **3** in the crystal. Slow cooling of a saturated solution of **3** in diethyl ether to -20 °C afforded large,

Table 1 Crystal data for compound 3

formula	C ₁₀ H ₅ F ₉ O
M _r	312.14
Crystal size /mm	0.40 x 0.30 x 0.30
Space group	PĪ
a /Å	11.481(5)
b /Å	12.753(5)
c /Å	13.698(6)
$\alpha /^{\circ}$	70.00(1)
βl°	81.18(2)
y /°	66.29(2)
V/Å ³	1725.3(1)
Ζ	6
μ / mm^{-1}	0.214
ϑ range /°	4.04-22.52
independent reflections	4000
data / restraints / parameters	3999 / 1305 / 554
goodness-of-fit on F^2	1.033
final R indices $[I > 2 \text{sigma}(I)]$	R1 = 0.0459, w $R2 = 0.1037$
R indices (all data)	R1 = 0.0553, wR2 = 0.118

Table 2 Selected bond lengths /Å and angles /° of 3.

Intramolecular (one d	of three independ	lent molecules in the asymm	netric unit)
C(1)-C(6)	1.403(6)	C(1)-C(10)	1.520(7)
C(3)-C(4)	1.379(6)	C(3)-C(2)	1.388(6)
C(5)-C(4)	1.374(6)	C(5)-C(6)	1.391(6)
C(10)-O(1)	140.8(6)		
C(2)-C(1)-C(6)	117.2(4)	C(2)-C(1)-C(10)	121.1(5)
C(6)-C(1)-C(10)	121.7(4)	C(4)-C(3)-C(2)	120.2(4)
C(4)-C(5)-C(6)	120.8(4)	C(3)-C(2)-C(1)	121.3(4)
C(5)-C(4)-C(3)	119.6(4)	C(5)-C(6)-C(1)	120.8(4)
O(1)-C(10)-C(1)	108.8(4)		
Intermolecular			
O…O (ave.)		2.647	
O2b···O1a···O3a, O2a···O1b···O3b		111.5	
O1b…O2a…O3a, O1a…O2b…O3b		118.3	
O2a…O3a…O1a, O2b…O3b…O1b		119.1	

colorless X-ray quality single-crystals (cubes). The compound crystallizes in the triclinic space group P1(-). The structure of an isolated molecule of **3** is depicted in Figure 1, and Figure 2 shows the structure of a hexameric unit. Crystal data and selected bond lengths and angles are listed in Tables 1 and 2, respectively.

Bond lengths and angles in an isolated R_FCH₂OH molecule are all within the normal range. The most striking structural feature of the crystal structure of 3 is the presence of hexameric aggregates [2,4,6-(CF₃)₃C₆H₂CH₂OH]₆. Six R_FCH_2OH molecules form a cyclic structure through six O-H…O hydrogen bonding interactions. The average O…O distance is 2.647 Å. This value compares favorably with that reported by Wieghardt for the methanol hexamer found in $[GaLF_3](MeOH)_{6/2} \cdot (MeOH)_3 \cdot CH_2Cl_2 \quad (O \cdots O \quad 2.62(1) \text{ A})$ [11]. In both hexamers the cyclic structures adopt S_6 symmetry as shown in Scheme 1. Already in 1979 Saenger pointed out the general importance of circularly arranged hydrogen bonds [19]. Three types of such circular hydrogen bonds can be distinguished: Those pointing all in the same direction are called *homodromic*, while those pointing regularly in opposite directions are called antidromic. Heterodromic hydrogen bonds are not ordered. In the case of 3 a



Figure 1 Structure of one molecule of 3.

difference electron density map of the crystal structure clearly showed a homodromic arrangement of the hydrogen bonds within the twelve-membered ring system of hexameric $[2,4,6-(CF_3)_3C_6H_2CH_2OH]_6$.

We also report here an initial study of the derivative chemistry of **3**, thereby focussing on its function as an ancillary ligand in (organo)lanthanide chemistry. An unsolvated sodium alkoxide derivative is readily prepared according to Scheme 3 by the reaction of **3** with NaN(SiMe₃)₂ in toluene solution. Under these conditions R_FCH_2ONa (4) can be isolated as a white, moisture-sensitive powder in 72 % yield.

The product is soluble in hot toluene, while coordinating solvents like THF or acetonitrile lead to rapid decomposition (formation of red or brown solutions). Analytical and spectroscopic data of **4** are in agreement with the presence of an unsolvated sodium alkoxide of presumably polymeric or oligomeric structure. As for the parent alcohol, the ¹⁹F NMR spectrum of **4** displays two singlets at δ –60.5 and –63.3 ppm, which can be assigned to the *ortho*- and *para*-CF₃ groups, respectively (intensity ratio 2:1).

A possible synthetic route to lanthanide alkoxides involves salt-elimination reactions between anhydrous lanthanide trichlorides and alkali metal alkoxides in an appropriate organic solvent. However, a characteristic feature of this type of preparations is the formation of so-called "ate-complexes" in which the resulting alkali metal halides are partially retained and incorporated in the molecular structures [20]. In order to circumvent this possible complication, we chose a salt-free synthetic route to prepare homoleptic lanthanide alkoxides derived from **3**. The method involves protonation of all three cyclopentadienyl ligands in $Ln(C_5H_5)_3$ (Ln = Nd, Sm, Yb) by three equivalents of **3** in toluene solution according to Scheme 4.

Rapid reactions were observed in boiling toluene. After *ca.* 30 min the color of the lanthanide starting material had disappeared in all three cases. Recrystallization of the crude



Figure 2 Molecular structure of the cyclic hexamer [2,4,6-(CF₃)₃C₆H₂CH₂OH]₆.



Scheme 3 Preparation of R_FCH₂ONa (4).



5-7: Ln = Nd, Sm, Yb

Scheme 4 Synthesis of the lanthanide(III) aryloxides 4-6.

products from *n*-hexane afforded the unsolvated lanthanide alkoxides **4-6** in low to moderate yields (22-50 %). ¹H NMR spectra showed only signals attributable to the $R_FCH_2O^$ ligands, thus confirming the complete elimination of all three cyclopentadienyl ligands and formation of homoleptic alkoxides. Although Scheme 4 depicts these compounds as monomeric species, a dimeric or even higher oligomeric structure cannot be ruled out, as no X-ray quality crystals could be grown thus far and conventional molecular weight determinations were precluded due to the high air-sensitivity of **4-6**. However, the mass spectra did not exhibit any peaks corresponding to dimers, oligomers or fragments thereof, so that the monomeric tricoordinate structure appears plausible.

*Organo*lanthanide derivatives containing the new alkoxide ligand have also been found to be readily accessible *via* the same synthetic route with the starting materials being employed in a 1:1 molar ratio (Scheme 5).

The reactions depicted in Scheme 5 were carried out in THF solution at room temperature in order to ensure elimination of only one cyclopentadienyl ligand and formation of the monoalkoxide complexes 8-10. These were isolated in moderate yields (30-65 %) as blue (8) or orange (9, 10) air-sensitive crystals, which are soluble in THF and toluene, but poorly soluble in *n*-hexane. The composition of the compounds as shown in Scheme 5 was proven by elemental analyses and spectroscopic data. In the case of 8 and 9 resonances due to coordinated THF are clearly seen in the ¹H



8-10: Ln = Nd, Sm, Yb

Scheme 5 Preparation of the complexes $(C_5H_5)_2Ln(OCH_2R_F)$ (8–10).

NMR spectra. All signals are paramagnetically shifted under the influence of the central lanthanide ions. For example, the cyclopentadienyl resonances are observed as singlets at $\delta = 3.17$ (8), 12.54 (9) and -33.59 (10).

Conclusion

In summarizing these results we have developed a straightforward, one-pot synthetic route leading to the hitherto unknown fluorinated alcohol 2,4,6-tris(trifluoromethyl)benzyl alcohol (3). In the crystal, 3 forms an S_6 symmetric cyclic hexamer of the type [2,4,6-(CF₃)₃C₆H₂CH₂OH]₆. Initial studies on the derivative chemistry of 3 have demonstrated that this compound is a valuable precursor for the synthesis of novel alkali metal and lanthanide alkoxides. It can easily be anticipated that it will be a versatile ligand for other main group and transition metals as well.

Experimental Section

General Procedures. The reactions were carried out in an atmosphere of dry nitrogen with the use of standard Schlenk techniques. Solvents were dried over Na/benzophenone and freshly distilled under nitrogen prior to use. IR spectra were recorded on a Perkin Elmer FT-IR Spectrometer System 2000. NMR spectra were recorded on a Bruker DPX 400 NMR spectrometer (1H 400.13 MHz, ¹³C 101.62 MHz, ²⁹Si 79.49 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonances (¹H, ¹³C) or an internal standard (¹H, ²⁹Si: TMS = 0 ppm). Elemental analyses were performed at the Chemistry Department of the Otto-von-Guericke-Universität using a Leco CHNS 932 apparatus. Melting and decomposition points were measured on a Electrothermal IA 9100 apparatus. X-ray data collection and structure refinement: The measurement on 3 was performed on a Siemens SMART CCD system with MoK_{α} radiation ($\lambda = 0.71073$ Å) and graphite monochromator. Selected crystals of 3 were mounted on a glass fiber and transferred to the cold nitrogen stream (Siemens LT-2 attachment). Full hemispheres of the reciprocal space were scanned by ω in three sets of frames of 0.3°. The SADABS routine was applied

as an absorption correction. For structure solution and refinement the programs SHELXS86 and SHELXL97 were used [21, 22]. The compounds 1,3,5-(CF₃)₃C₆H₃ [14], R_FLi [13, 14], NaN(SiMe₃)₂ [23], and Ln(C₅H₅)₃ (Ln = Nd, Sm, Yb) [24] were prepared according to literature procedures.

2,4,6-Tris(trifluoromethyl)benzyl alcohol (3): In a 500 ml flask equipped with a reflux condenser, paraformaldehyde (6.60 g, 220 mmol) was added in one portion to a freshly prepared solution of R_FLi (**2**, 200 mmol) in diethylether/hexane (*ca.* 150 ml). After an induction period of *ca.* 10 min a vigorous reaction occurred, causing to reaction mixture to reflux. Stirring at reflux temperature was continued for 15 h. After cooling to room temperature 1M H_2SO_4 (120 ml) was added, the organic layer was separated and the aqueous layer was extracted with diethylether (4 x 70 ml). The combined extracts were dried over anhydrous MgSO₄. Diethylether and hexane were distilled off at atmospheric pressure and the crude product was purified by vacuum-distillation (83-87 °C / 13 torr) to afford 25.51 g (41 %) **3** in the form of a colorless, low-melting solid. M. p. 50 °C. Elemental analysis calcd (%) for $C_{10}H_5F_9O$ (312.13): C 38.5, H 1.6; found: C 38.6, H 1,8.

¹H NMR (25 °C, CDCl₃): $\delta = 8.13$ (s, 2H, C₆H₂), 4.96 (s, 2H, CH₂), 2.13 (br, 1H, $v_{1/2} = 35$ Hz, OH) ppm. ¹³C NMR (25 °C, CDCl₃): $\delta = 141.4$ (qqq, ³J₃(¹³C⁻¹⁹F) = 1.1 Hz, ³J₄(¹³C⁻¹⁹F) = 1.1 Hz, ⁵J₂(¹³C⁻¹⁹F) = 1.1 Hz, *ipso*-C₆H₂), 132.8 (q, ²J(¹³C⁻¹⁹F) = 31.5 Hz, *o*-C₆H₂), 131.5 (q, ²J(¹³C⁻¹⁹F) = 31.5 Hz, *p*-C₆H₂), 127.2 (qqq, ³J₁(¹³C⁻¹⁹F) = 3.7 Hz, ³J₂(¹³C⁻¹⁹F) = 2.3 Hz, ⁵J₁(¹³C⁻¹⁹F) = 1.0 Hz, m-C₆H₂), 123.0 (q, ¹J(¹³C⁻¹⁹F) = 102.2 Hz, *o*-CF₃), 122.5 (q, ¹J(¹³C⁻¹⁹F) = 102.2 Hz, *p*-CF₃), 56.8 (sept, ⁴J₁(¹³C⁻¹⁹F) = 2.5 Hz, CH₂) ppm. ¹⁹F(¹H) NMR (25 °C, CDCl₃): $\delta = -59.1$ (s, 6F, *o*-CF₃), -63.9 (s, 3F, *p*-CF₃) ppm. MS (EI, 70 eV): m/z 295 (M - OH, 10 %), 263 (M - F - CH₂OH, 23 %), 241 (R_F - 2HF, 100 %), 69 (CF₃, 8 %). IR (KBr): 3200 s, 1743 s, 1636 s, 1601 s, 1278 vs, 1295 vs, 1130 vs, 920 s, 686 s, cm⁻¹.

Sodium [2,4,6-tris(trifluoromethyl)phenyl]methoxide (4): R_FCH_2OH (1, 9.36 g, 30 mmol) was added as a solid to a solution of NaN-(SiMe₃)₂ (5.50 g, 30 mmol) in toluene (120 ml), and the mixture was stirred for 15 h at room temperature. Precipitation of white, microcrystalline 4 commenced after ca. 1 h. After removal of all volatile materials *in vacuo* the residue was washed with *n*-hexane (50 ml) and isolated by filtration. Drying under vacuum afforded 7.26 g (72 %) 4 as a moisture-sensitive, white solid, which decomposes at 130 °C. Elemental analysis calcd (%) for C₁₀H₄F₉ONa (334.12): C 36.0, H 1.2; found: C 35.2, H 1,6.

 ^{1}H NMR (25 °C, CDCl₃): δ = 7.93 (s, 2H, C_6H₂), 4.79 (s, 2H, CH₂) ppm. $^{19}\text{F}\{^{1}\text{H}\}$ NMR (25 °C, C_6D_6): δ = -60.5 (s, 6F, o-CF₃), -63.3 (s, 3F, p-CF₃) ppm. MS (EI, 70 eV): m/z 832 (2M + C_6H_3CF_2 + 0, 5 %), 565 (M + Na + F_3CC_6H_4CO_2, 35 %), 549 (M + Na + F_3CC_6H_4CO, 22 %), 295 (R_FCH_2, 100 %), 263 (R_F - F - CH_20, 37 %, 241 (R_F - 2HF, 40 %), 195 (R_F + H - CF_4, 10 %). IR (KBr): 1633 s, 1596 s, 1293 vs, 1279 vs, 1270 vs, 1202 vs, 1135 vs, 919 s, 687 s cm^{-1}.

Synthesis of tris[2,4,6-tris(trifluoromethyl)phenylmethoxy]lanthanides(III) (5-7)

(General Procedure)

Three equivalents of R_FCH_2OH (3) were added as a solid to a suspension of tris(cyclopentadienyl)lanthanide(III) in toluene (70 ml). The reaction mixture was heated to reflux and stirred for 30 min, whereby the lanthanide precursors dissolved completely. All volatiles were removed under vacuum, and the oily residue was extracted with boiling *n*-hexane (70 ml). The extract was filtered through a thin layer of Celite filter aid and concentrated to a total volume of *ca.* 35 ml. Standing at room temperature for 24 h afforded the crystalline product which was isolated by filtration and drying *in vacuo*.

71 °C. Elemental analysis calcd (%) for $C_{30}H_{12}F_{27}NdO_3$ (1078.55): C 35.0, H 1.2; found: C 33.7, H 1.7.

¹**H** NMR (25 °C, CD₃CN): δ = 8.74 (br, $v_{1/2}$ = 72 Hz, 12H, C₆H₂ + CH₂) ppm. ¹⁹**F**{¹**H**} NMR (25 °C, CD₃CN): δ = -61.8 (s, 9F, *p*-CF₃), -63.8 (br, $v_{1/2}$ = 140 Hz, 18F, *o*-CF₃) ppm. MS (EI, 70 eV): *m/z* 377 (NdOCH₂R_F - CF₃CO, 1 %), 291 (R_FCH₂O - F, 18 %), 263 (R_F - F, 100 %), 244 (R_F - 2F, 30 %), 195 (R_F + H - CF₄, 48 %). **IR** (KBr): 1635 s, 1598 s, 1304 vs, 1279 vs, 1261 vs, 1202 vs, 1127 vs, 917 s, 687 s cm⁻¹.

¹H NMR (25 °C, THF-*d*₈): δ = 7.49 - 7.60 (m, 4H, C₆H₂ + CH₂), 7.26 - 7.37 (m, 8H, C₆H₂ + CH₂) ppm. ¹⁹F{¹H} NMR (25 °C, CD₃CN): δ = -57.7 - -58.7 (m, 18F, *o*-CF₃), -62.5 - -64.8 (m, 9F, *p*-CF₃) ppm. MS (EI, 70 eV): *m/z* 295 (R_FCH₂, 14 %), 291 (R_FCH₂O - F, 17 %), 273 (R_FCH₂O - 2F, 100 %), 263 (R_F - F, 98 %), 244 (R_F - 2F, 38 %), 195 (R_F + H - CF₄, 68 %). IR (KBr): 1635 s, 1598 s, 1301 vs, 1278 vs, 1203 vs, 1135 vs, 917 s, 686 s, 526 m, 495 m, 463 m cm⁻¹.

¹**H** NMR (25 °C, CD₃CN): δ = 8.22 (br, $v_{1/2}$ = 42 Hz, 6H C₆H₂), 4.85 (br, 6H, CH₂) ppm. ¹⁹F{¹H} NMR (25 °C, CD₃CN): δ = -57.8 (br, $v_{1/2}$ = 30 Hz, 18F, *o*-CF₃), -62.4 (br, $v_{1/2}$ = 30 Hz, 9F, *p*-CF₃) ppm. MS (EI, 70 eV): *mlz* 295 (R_FCH₂, 12 %), 291 (R_FCH₂O - F, 27 %), 263 (R_F - F, 100 %), 244 (R_F - 2 F, 60 %). IR (KBr): 1634 s, 1295 vs, 1278 vs, 1204 vs, 1131 vs, 919 s, 687 s, 554 m, 533 m, 518 m, 494 m cm⁻¹.

Bis(η^5 -cyclopentadienyl)(tetrahydrofuran)[2,4,6-tris(trifluoromethyl)phenylmethoxy]neodymium(III) (8): A solution of Nd(C₅H₅)₃ (1.230 g, 3.83 mmol) and 3 (1.195 g, 3.83 mmol) in THF (100 ml) was stirred at room temperature until the starting materials had completely dissolved (*ca.* 1 h). The reaction mixture was evaporated to dryness. Washing of the residue with n-hexane (70 ml) and drying *in vacuo* afforded 0.578 g (30 %) of 8 as a pale blue, microcrystalline solid. Elemental analysis calcd (%) for C₂₄H₂₂F₉NdO₂ (657.68): C 43.8, H 3.4; found: C 41.8, H 3.4.

¹**H** NMR (25 °C, CD₃CN): δ = 9.54 (br, $v_{1/2}$ = 44 Hz, 2H, C₆H₂), 3.61 (m, 4H, THF-OCH₂), 3.17 (br, $v_{1/2}$ = 33 Hz, 10H, C₅H₅), 1.79 (m, 4H, THF-CH₂), -2.62 (br, $v_{1/2}$ = 66 Hz, 2H, CH₂) ppm. ¹⁹**F**{¹**H**} NMR (25 °C, CD₃CN): δ = -55.2 (br, $v_{1/2}$ = 105 Hz, 6F, *o*-CF₃), -61.8 (s, 3F, *p*-CF₃) ppm. **IR** (KBr): 1653 s, 1633 s, 1596 s, 1311 vs, 1280 vs, 1271 vs, 1144 vs, 917 s, 861 w, 687 s cm⁻¹.

Bis(η^5 -cyclopentadienyl)(tetrahydrofuran)[2,4,6-tris(trifluoromethyl)phenylmethoxy]samarium(III) (9): A similar reaction of Sm(C₅H₅)₃ (0.567 g, 1.64 mmol) and 3 (0.512 g, 1.64 mmol) gave 0.709 g (65 %) 9 as orange crystals. Elemental analysis calcd (%) for C₂₄H₂₂F₉O₂Sm (663.80): C 43.4, H 3.3; found: C 44.0, H 3.7.

¹**H** NMR (25 °C, CD₃CN): δ = 12.54 (s, 10H, C₅H₅), 8.64 (s, 2H, C₆H₂), 8.53 (br, $v_{1/2} = 58$ Hz, 2H, CH₂), 3.64 (m, 4H, THF-OCH₂), 1.80 (m, 4H, THF-CH₂) ppm. ¹⁹F{¹H} NMR (25 °C, CD₃CN): δ = -56.4 (br, $v_{1/2} = 40$ Hz, 6F, *o*-CF₃), -62.1 (s, 3F, *p*-CF₃) ppm. IR (KBr): 1635 s, 1595 s, 1303 vs, 1279 vs, 1261 vs, 1201 vs, 917, 862 w, 686 s cm₋₁.

Bis(η^5 -cyclopentadienyl)(tetrahydrofuran)[2,4,6-tris(trifluoromethyl)phenylmethoxy]ytterbium(III) (10): Treatment of Yb(C₅H₅)₃ (0.608 g, 1.65 mmol) with 3 (0.518 g, 1.65 mmol) afforded 0.601 g (53 %) 10 in the form of orange crystals. Elemental analysis calcd (%) for C₂₄H₂₂F₉O₂Yb (686.46): C 42.0, H 3.2; found: C 40.3, H 3.2.

¹H NMR (25 °C, CD₃CN): δ = -0,54 (s, 2H, C₆H₂), -0,97 (br, 2H, CH₂), -33.59 (br, $v_{1/2}$ = 444 Hz, 10H, C₅H₅) ppm (THF signals not observed). ¹⁹F{¹H} NMR (25 °C, CD₃CN): δ = -63.7 (br, $v_{1/2}$ = 120 Hz, 6F, *o*-CF₃), -67.9 (s, 3F, $p{\rm -CF_3})$ ppm. IR (KBr): 1624 s, 1568 s, 1301 vs, 1280 vs, 1262 vs, 1191 vs, 1136 vs, 915 s, 860 m, 683 s, 522 s cm^{-1}.

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Supporting Information Available: Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 246643. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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