



AN ORGANOMETALLIC APPROACH TO THE SYNTHESIS OF CATIONIC YTTRIUM BIS(ALKOXIDE) COMPLEXES

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I. A. Gogolev,^a A. A. Kissel,^a Yu. V. Nelyubina,^a
A. A. Tyutyunov,^a and A. A. Trifonov*^{a,b}

^a Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
ul. Vavilova 28, str. 1, Moscow, 119334 Russia

^b Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
ul. Tropinina 49, Nizhny Novgorod, 603950 Russia

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Abstract

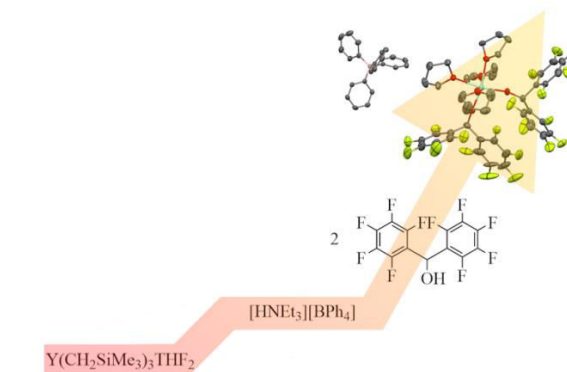
The synthesis and structure of a cationic bis(alkoxide) yttrium complex $\{[(C_6F_5)_2CHO]_2Y(THF)_4\}^+\{BPh_4\}^-$ that represents a separated ion pair with octahedral coordination environment of the Y^{3+} ion and angular mutual arrangement of the alkoxide ligands are reported. The formation of the related yttrium complexes containing $\{Ph(Me)(CF_3)CO\}^-$ and $\{(C_6F_5)Me_2CO\}^-$ ligands is evidenced by multinuclear NMR spectroscopy.

Key words: yttrium, alkoxide complexes, synthesis, structure.

Introduction

The molecular design of the coordination environment of rare-earth ions represents an important fundamental and applied problem in terms of fine-tuning the chemical and physical properties of the complexes [1, 2]. This is of particular importance for the elaboration of new materials for application in electronics. At a certain geometry of the ligand environment, the complexes of some lanthanide metals (Dy, Tb, Er) exhibit slow relaxation of magnetization, which is due to bistability at the molecular level [3, 4]. Such single-ion magnet (SIM) properties make lanthanide complexes promising candidates for the creation of innovative methods of information storage and development of quantum computers [5, 6].

A significant limitation that negatively affects the dynamics of magnetization relaxation in the zero magnetic field is quantum tunneling of magnetization, as well as Raman and direct relaxations [7, 8]. Recently, mononuclear cationic bis(alkoxide) Dy^{3+} complexes featuring an axial arrangement of ligands, which provides stabilization of an electron shell of the lanthanide ion and minimizes the effect of quantum tunneling, were shown to be the most promising high-performance SIMs [9–12]. However, such complexes are still characterized by blocking temperatures, which are inferior compared to those typical for metallocene type SIMs. Probably this may be related to the Raman relaxation pathway [10, 11]. A contribution of the Raman relaxation can be attenuated by reducing the ligand molecular C–H vibrations using fluorinated ligands [13, 14]. The application of fluorinated ligands can also have a positive impact on the magnetic properties due to non-valent Ln–F interactions, leading to a decrease in the number of equatorial ligands [15–17]. The elaboration of new synthetic approaches

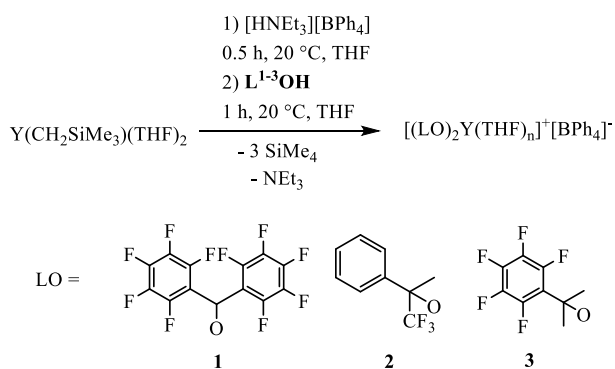


allowing for the design of low-coordinate Ln^{3+} cationic bis(alkoxide) complexes featuring axial symmetry remains a challenge for coordination chemistry. The diamagnetic Y^{3+} ion that has an ionic radius close to that of Dy^{3+} [18] seems to be an ideal candidate for the development of the synthetic methods as well for the investigation of the complex behavior in solution.

Herein, we report on the application of the organometallic approach to the cationic bis(alkoxy) Ln^{3+} complexes through alkane elimination reactions involving $Y(CH_2SiMe_3)_3(THF)_2$, $[NEt_3H][BPh_4]$, and a fluorinated alcohol. This method allowed for the synthesis and structural characterization of complex $\{[(C_6F_5)_2CHO]_2Y(THF)_4\}^+[BPh_4]^-$ (**1**) ($(C_6F_5)_2CHOH = L^1OH$). Additionally, the formation of the related complexes $[RO_2Y(THF)_4][BPh_4]$ ($RO = (C_6H_5)(CF_3)(Me)CO$, $(C_6F_5)Me_2CO$) was evidenced by the NMR scale reactions of 1,1,1-trifluoro-2-phenylpropan-2-ol (L^2OH) and 2-(perfluorophenyl)propan-2-ol (L^3OH).

Results and discussion

The alkane elimination reaction was used to develop a methodology for the synthesis of cationic bis(alkoxide) complexes. The interaction of $Y(CH_2SiMe_3)_3(THF)_2$ in $THF-d_8$ with one equivalent of $[HNEt_3][BPh_4]$ followed by the treatment with two equivalents of L^1OH resulted in the formation of yttrium complex $\{[(C_6F_5)_2CHO]_2Y(THF)_4\}^+[BPh_4]^-$ (**1**) (Scheme 1). The 1H NMR spectrum of the reaction mixture evidenced the formation of three equivalents of $SiMe_4$ and one equivalent of Et_3N (a quadruplet at 2.11 and a triplet at 1.05 ppm), while the signal characteristic of the hydroxyl group of L^1OH disappeared.



Scheme 1. Synthesis of bis(alkoxide) yttrium complexes **1–3**.

In order to isolate complex **1**, a preparative scale reaction of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ with 1 eq. of $[\text{HNEt}_3][\text{BPh}_4]$ in THF was carried out at room temperature (Scheme 1). The reaction mixture was stirred for 30 min, then a solution of 2 eq. of L^1OH in THF was added. An important condition for the successful isolation and crystallization of cationic complexes is the evaporation of the volatiles and drying of the solid residue for 40–50 min under vacuum to remove Et_3N . A similar procedure should be performed after the addition of the alcohol to the cationic bis(alkyl) complex to remove SiMe_4 . The recrystallization of the solid residue from a THF/hexane (3/1) afforded white crystals of complex **1** in 77% yield.

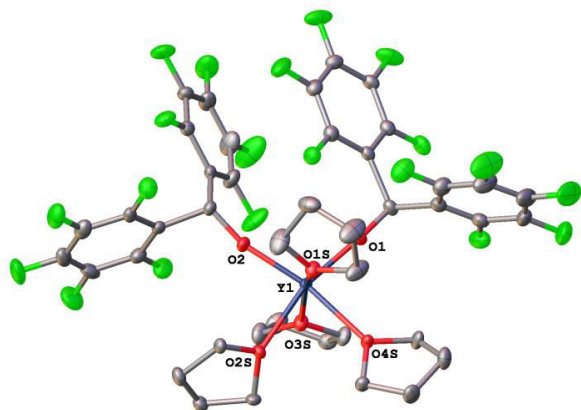


Figure 1. General view of the complex cation in **1** in representation of atoms *via* thermal ellipsoids at 30% probability level. Hydrogen atoms and the minor component of the disordered perfluorophenyl group are omitted for clarity. The labels are given only for the metal ion and oxygen atoms it coordinates. Selected bond lengths (Å) and angles (°): Y–O1 2.061(3), Y–O2 2.070(3), Y–O1S 2.345(3), Y–O2S 2.369(2), Y–O3S 2.344(3), Y–O4S 2.392(2), O1–Y–O2 105.44(11).

Bis(alkoxide) complex **1** is moisture- and air-sensitive. It is well soluble in THF and pyridine, but sparingly soluble in toluene and hexane. It can be stored under an inert atmosphere at room temperature for several months without any sign of decomposition.

The ^1H NMR spectrum of complex **1** shows a broadened singlet at 6.45 ppm which corresponds to the proton of the methanide group of the ligand. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the carbon of methanide group gives rise to a singlet at 60.9 ppm. The signals at 7.28, 6.86, and 6.72 ppm in the ^1H NMR spectrum are attributed to the phenyl protons of the BPh_4^- anion.

The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum shows a singlet at -4.7 ppm which corresponds to the boron atom of the BPh_4^- anion. Three characteristic signals are observed for the fluorine nuclei in the ^{19}F spectrum: a doublet at -143.4 ppm ($^3J_{\text{FF}} = 16.0$ Hz) can be assigned to the *ortho*-F nucleus, a triplet at -152.9 ppm ($^3J_{\text{FF}} = 23.0$ Hz) corresponds to the *meta*-F nucleus, and a triplet at -160.9 ppm ($^3J_{\text{FF}} = 21.2$ Hz) can be attributed to the *para*-F nucleus.

Single crystals suitable for X-ray diffraction analysis were obtained by slow concentration of a solution of **1** in a THF/hexane (3/1) mixture at room temperature. Complex **1** crystallizes in the monoclinic space group $\text{P}2_1/c$ as a separated ion pair consisting of the complex cation, yttrium bis(alkoxide) $\{[(\text{C}_6\text{F}_5)_2\text{CHO}]_2\text{Y}(\text{THF})_4\}^+$, and the anion $[\text{BPh}_4]^-$. The coordination environment of the Y^{3+} ion is formed by two oxygen atoms of the two alkoxide ligands L^1O and four oxygen atoms of the THF molecules. The Y^{3+} ion has a coordination number of six and adopts a geometry of a slightly distorted octahedron, as quantified by "continuous shape measures" (the crystal data and structure refinement parameters are given in Table S1 in the Electronic Supplementary Information (ESI), the SHAPE analysis is given in Table S2) [19]. Surprisingly, in contrast to the previously reported related cationic Dy^{3+} complexes with fluorinated ligands featuring linear arrangement of the alkoxide ligands [14], the alkoxy ligands in **1** are in *cis*-positions with the O–Y–O angle of $105.44(11)^\circ$. The dihedral angles between the planes of the perfluorophenyl fragments in these ligands are $84.15(15)^\circ$ and $77.6(2)^\circ$ ($80.7(3)^\circ$ with the minor component of the disordered perfluorophenyl group). The bond distances between Y^{3+} and the oxygen atoms of the alkoxide ligands are nearly identical (2.070(3) and 2.061(3) Å), while the Y–O(THF) bond lengths range from 2.344(3) to 2.392(2) Å. The Y–O_{RO} bonds in **1** appeared to be shorter than in six-coordinate yttrium phenoxides but comparable to the Y–O^tBu bonds. For example, in the six-coordinate yttrium complex $\text{NH}\{\text{C}_2\text{H}_4\text{N}=\text{PPh}_2(2,4\text{-}^t\text{Bu}_2\text{-}1\text{-C}_6\text{H}_4\text{O})\}_2\text{Y}(\text{O}^t\text{Bu})$ coordinated by an iminophosphorane "salen" ligand, the Y–O^tPh bonds are as long as 2.223(5) Å and 2.161(6) Å, but the Y–O^tBu bond length is only 2.069(6) Å [20]. In complex $\{3,5\text{-}^t\text{Bu}_2\text{-}1\text{-OC}_6\text{H}_4\text{CH}=\text{N}(\text{trans-}1,2\text{-cyclo-C}_6\text{H}_{10})\text{N}=\text{C}(\text{Me})\text{CH}_2\text{C}(\text{CF}_3)_2\text{O}\}\text{Y}(\text{N}(\text{SiHMe}_2)_2)(\text{THF})$, the Y–O^tPh bond length is 2.1530(18) Å, while Y–O(Alkoxide) and Y–O(THF) bond lengths are 2.1358(17) and 2.4240(18) Å, respectively [21, 22]. The bond lengths of 2.094(10), 2.074(12), and 2.123(11) Å were found in the neutral complex $\text{Y}\{\text{OCMe}(\text{CF}_3)_2\}_3(\text{THF})_3$ [23]. In this complex, the Y–O(THF) bonds (2.413(12)–2.453(10) Å) are noticeably longer than those in **1**.

In compound **1**, the O–Y–O angle between the axial ligands (the THF molecule and one of the alkoxide ligands) is $166.06(9)^\circ$. The same angles between the equatorial ligands range from $81.72(9)$ to $99.92(10)^\circ$. No close contacts between the yttrium center and the fluorine atoms were found; the shortest Y...F distance is 3.513(3) Å.

Similarly to the synthesis of **1**, the reactions of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ with one equivalent of $[\text{HNEt}_3][\text{BPh}_4]$ and two equivalents of L^2OH or L^3OH were carried out in THF-*d*₈ and monitored by ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$, and ^{19}F NMR spectroscopy. The formation of complexes **2** and **3** was detected in solution: the signals of the hydroxyl protons of alcohols

L^2OH in the 1H spectra disappeared (3.20 for L^2OH and 2.61 for L^3OH), and the signals typical of $SiMe_4$ and Et_3N (2.63, 0.99 ppm for **2**; 2.48, 0.93 ppm for **3**) appeared. No formation of C–F bond activation products was observed in any case. The 1H NMR spectra of the complexes **2** and **3** contain three distinct low-field signals (7.27, 6.86, and 6.72 ppm for **2**; 7.21, 6.88, and 6.74 ppm for **3**) which correspond to the phenyl protons of the BPh_4^- anion. In the 1H NMR spectrum of complex **2**, the broadened multiplets observed at 7.62, 7.29, and 7.03 ppm can be attributed to the aromatic protons of the L^2O ligand. Additionally, a multiplet at 1.58 ppm can be assigned to the protons of the methyl group (split, presumably, due to its proximity to the CF_3 -group). In the $^{13}C\{^1H\}$ NMR spectrum, the methyl group of the ligand is represented by a signal at 26.4 ppm, while the aromatic carbons of the ligands give rise to the singlets at 128.6 and 127.8 ppm. The $^{11}B\{^1H\}$ NMR spectrum displays a singlet at –6.6 ppm referring to the boron atom of the anion. Finally, a multiplet in the range from –80.2 to –80.5 ppm in the ^{19}F spectrum can be attributed to the fluorine nuclei of the ligand.

For the product formed in the reaction of L^3OH , the singlet observed at 1.60 ppm in the 1H NMR spectrum corresponds to the methyl groups of the alkoxide ligand. In the $^{13}C\{^1H\}$ NMR spectrum, this group gives rise to a singlet at 26.3 ppm. The $^{11}B\{^1H\}$ spectrum displays one singlet of the boron nucleus at –4.8 ppm. The ^{19}F spectrum contains three signals attributed to the fluorine nuclei of the ligands: a doublet at –138.2 ppm (*ortho*-F) and two triplets at –159.1 (*meta*-F) and –163.3 (*para*-F) ppm.

In general, the signals of quaternary carbon nuclei are of low intensity; in the case of complexes **2** and **3**, they were not observed.

Experimental section

General remarks

All the reactions and manipulations were carried out under an argon atmosphere using Schlenk techniques or in a nitrogen atmosphere glovebox. After drying over NaOH, THF was purified by distillation from sodium/benzophenone ketyl. Hexane was dried over sodium and then distilled. THF- d_8 was purified by distillation from sodium/benzophenone ketyl and stored in a glovebox. Fluorinated carbinols, bis(2,3,4,5,6-pentafluorophenyl)methanol (L^1OH), 1,1,1-trifluoro-2-phenylpropan-2-ol (L^2OH), and 2-(perfluorophenyl)propan-2-ol (L^3OH), were purchased from SIA P&M-Invest Ltd, kept in an inert atmosphere over CaH_2 for several days, condensed under vacuum, and stored in a glovebox. $[Y(CH_2SiMe_3)_3THF_2]$ [24] and $[HNEt_3][BPh_4]$ [25] were synthesized according to the published procedures. Rare-earth analysis was carried out by complexometric titration [26]. Elemental analysis was performed in the Laboratory of Microanalysis of INEOS RAS.

Syntheses

NMR reaction of $Y(CH_2SiMe_3)_3THF_2$ with $[HNEt_3][BPh_4]$ and L^1OH (1). In a glovebox, a solution of $[HNEt_3][BPh_4]$ (0.045 g, 0.107 mmol) in 0.2 mL of THF- d_8 was added to a solution of $Y(CH_2SiMe_3)_3THF_2$ (0.053 g, 0.107 mmol) in 0.2 mL of THF- d_8 . The reaction mixture was stirred at

ambient temperature for 20 min, then a solution of L^1OH (0.078 g, 0.215 mmol) in 0.3 mL of THF- d_8 was added. The resulting mixture was transferred to an NMR tube. 1H NMR (400 MHz, THF- d_8 , 293 K): 7.29 (m, 8H, *o*-CH, BPh_4), 6.87 (t, $^3J_{HH} = 6.6$ Hz, 8H, *m*-CH, BPh_4), 6.73 (t, $^3J_{HH} = 6.7$ Hz, 4H, *p*-CH, BPh_4), 6.46 (br. s, 2H, Ar_2CH), 3.57 (m, α - CH_2 , THF, together with THF- d_8), 2.66 (q, $^3J_{HH} = 7.5$ Hz, 6H, CH_2 , Et_3N), 1.72 (m, β - CH_2 , THF, together with THF- d_8), 0.99 (br. t, $^3J_{HH} = 7.6$ Hz, 9H, CH_3 , Et_3N), 0.07 (s, 36H, $Si(CH_3)_4$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, THF- d_8 , 293 K): 143.3 (s, ArC), 139.8 (s, ArC), 126.8 (s, ArC), 124.5 (s, ArC), 124.3 (s, ArC), 123.9 (s, ArC), 122.3 (s, ArC), 120.1 (s, ArC), 112.9 (s, ArC), 67.7 (m, α - CH_2 , together with THF- d_8), 61.2 (s, Ar_2CH), 45.7 (s, CH_2 , Et_3N), 25.8 (m, β - CH_2 , together with THF- d_8), 12.3 (s, CH_3 , Et_3N), 0.9 (s, $Si(CH_3)_4$) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, THF- d_8 , 293 K): –4.7 (s, BPh_4) ppm. ^{19}F NMR (376 MHz, THF- d_8 , 293 K): –144.1 (d, $^3J_{FF} = 16.0$ Hz, *o*-F), –152.3 (t, $^3J_{FF} = 23.0$ Hz, *m*-F), –161.1 (t, $^3J_{FF} = 21.2$ Hz, *p*-F) ppm.

NMR reaction of $Y(CH_2SiMe_3)_3THF_2$ with $[HNEt_3][BPh_4]$ and L^2OH (2). In a glovebox, a solution of $[HNEt_3][BPh_4]$ (0.045 g, 0.107 mmol) in 0.2 mL of THF- d_8 was added to a solution of $Y(CH_2SiMe_3)_3THF_2$ (0.053 g, 0.107 mmol) in 0.2 mL of THF- d_8 . The reaction mixture was stirred at ambient temperature for 20 min, then a solution of L^2OH (0.041 g, 0.215 mmol) in 0.3 mL of THF- d_8 was added. The resulting mixture was transferred to an NMR tube. 1H NMR (400 MHz, THF- d_8 , 293 K): 7.62 (m, 4H, *o*-CH, Ar, L^2O), 7.29 (m, 12H, *o*-CH, BPh_4 , together with *m*-CH, Ar, L^2O), 7.03 (m, 2H, *p*-CH, Ar, L^2O), 6.87 (t, $^3J_{HH} = 6.7$ Hz, 8H, *m*-CH, BPh_4), 6.73 (t, $^3J_{HH} = 6.4$ Hz, 4H, *p*-CH, BPh_4), 3.57 (m, α - CH_2 , THF, together with THF- d_8), 2.63 (q, $^3J_{HH} = 7.0$ Hz, 6H, CH_2 , Et_3N), 1.58 (m, CH_3 , L^2O , together with β - CH_2 of THF and THF- d_8), 0.99 (t, $^3J_{HH} = 7.0$ Hz, 9H, CH_3 , Et_3N), 0.00 (s, 36H, $Si(CH_3)_4$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, THF- d_8 , 293 K): 136.1 (s, *o*-CH, BPh_4), 127.5 (m, Ar, L^2O , together with CF_3), 124.8 (s, *m*-CH, BPh_4), 121.0 (s, *p*-CH, BPh_4), 66.5 (m, α - CH_2 THF, together with THF- d_8), 46.4 (s, CH_2 , Et_3N), 25.3 (s, CH_3 , L^2O), 24.3 (m, β - CH_2 , THF, together with THF- d_8), 10.4 (s, CH_3 , Et_3N), –1.0 (s, $Si(CH_3)_4$) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, THF- d_8 , 293 K): –6.6 (s, BPh_4) ppm. ^{19}F NMR (376 MHz, THF- d_8 , 293 K): –80.5 – –80.2 (m, CF_3) ppm.

NMR reaction of $Y(CH_2SiMe_3)_3THF_2$ with $[HNEt_3][BPh_4]$ and L^3OH (3). In a glovebox, a solution of $[HNEt_3][BPh_4]$ (0.045 g, 0.107 mmol) in 0.2 mL of THF- d_8 was added to a solution of $Y(CH_2SiMe_3)_3THF_2$ (0.053 g, 0.107 mmol) in 0.2 mL of THF- d_8 . The reaction mixture was stirred at ambient temperature for 20 min, then a solution of L^3OH (0.049 g, 0.215 mmol) in 0.3 mL of THF- d_8 was added. The resulting mixture was transferred to an NMR tube. 1H NMR (400 MHz, THF- d_8 , 293 K): 7.24 (m, 8H, *o*-CH, BPh_4), 6.83 (t, $^3J_{HH} = 7.0$ Hz, 8H, *m*-CH, BPh_4), 6.69 (t, $^3J_{HH} = 7.1$ Hz, 4H, *p*-CH, BPh_4), 3.55 (m, α - CH_2 , THF, together with THF- d_8), 2.42 (q, $^3J_{HH} = 7.1$ Hz, 6H, CH_2 , Et_3N), 1.69 (m, β - CH_2 , THF, together with THF- d_8), 1.57 (s, 12H, CH_3 , L^3O), 0.93 (t, $^3J_{HH} = 7.6$ Hz, 9H, CH_3 , Et_3N), –0.03 (s, 36H, $Si(CH_3)_4$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, THF- d_8 , 293 K): 137.2 (s, *o*-CH, BPh_4), 125.8 (s, *m*-CH, BPh_4), 122.0 (s, *p*-CH, BPh_4), 68.4 (s, α - CH_2), 47.4 (s, CH_2 , Et_3N), 34.8 (s, CH_3 , L^3O), 26.4 (s, β - CH_2), 13.6 (s, CH_3 , Et_3N), 0.1 (s, $Si(CH_3)_4$) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, THF- d_8 , 293 K): –4.8 (s, BPh_4) ppm. ^{19}F NMR (376 MHz, THF- d_8 , 293 K): –138.2 (d,

$^3J_{\text{FF}} = 26.4$ Hz, *o-F*), -159.1 (t, $^3J_{\text{FF}} = 22.9$ Hz, *m-F*), -163.3 (t, $^3J_{\text{FF}} = 21.9$ Hz, *p-F*) ppm.

Synthesis of $[\text{Y}(\text{L}^1\text{O})_2\text{THF}_4][\text{BPh}_4]$ (1**).** A solution of $[\text{HNEt}_3][\text{BPh}_4]$ (0.250 g, 0.593 mmol) in 5 mL of THF was added to a solution of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3\text{THF}_2$ (0.294 g, 0.593 mmol) in 5 mL of THF. The reaction mixture was stirred at room temperature for 30 min. The volatiles were removed under vacuum, and the residue obtained was dissolved in 5 mL of THF. Then a solution of L^1OH (0.432 g, 1.186 mmol) in 4 mL of THF was added, and the reaction mixture was stirred at room temperature for 1 h. THF was removed under vacuum, and the solid residue obtained was dissolved in a THF/hexane mixture (3/1, 7 mL). Concentrating the resulting solution at room temperature resulted in the formation of white crystals of **1**. The mother liquid was decanted, and the crystals were washed with cold hexane and dried under vacuum at ambient temperature for 10 min. Complex **1** was isolated in 77% yield (0.649 mg, 0.457 mmol). Anal. Calcd for $\text{C}_{66}\text{H}_{54}\text{BF}_{20}\text{O}_6\text{Y}$ (1422.84 g·mol⁻¹): C, 55.71; H, 3.83; Y, 6.25. Found: C, 55.74; H, 3.82; Y, 6.31%.

X-ray crystallography

X-ray diffraction data for **1** were collected at 120 K with a Bruker APEX2 CCD diffractometer, using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å, ω -scans). The structure was solved using Intrinsic Phasing with the ShelXT [27] structure solution program in Olex2 [28] and then refined with the XL [29] refinement package using Least-Squares minimization against F^2 in the anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. The disordered lattice molecules of THF were treated as diffuse contributions to the overall scattering without specific atom positions using the Solvent Mask routine implemented in OLEX2. The crystal data and structure refinement parameters are given in Table S1 in the ESI. CCDC 2283275 contains the supplementary crystallographic information for this paper.

Conclusions

Hence, we demonstrated the applicability of the organometallic approach to the synthesis of cationic yttrium bis(alkoxide) species containing fluorinated alkoxide ligands. The stepwise protonolysis of the Y–C bonds in the parent complex $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ with one equivalent of $[\text{HNEt}_3][\text{BPh}_4]$ and two equivalents of L^{1-3}OH allowed for the clear formation of the cationic bis(alkoxide) complexes in nearly quantitative yields. Complex **1** was isolated in the crystalline form in 77% yield. The X-ray diffraction study showed that **1** represents a separated ion pair. At present, the works on obtaining single-crystals of complexes **2** and **3** and establishing their structures are ongoing in our lab.

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Corresponding author

* E-mail: trif@iomc.ras.ru. Tel: +7(495)135-9202 (A. A. Trifonov)

Electronic supplementary information

The crystal data and structure refinement parameters for complex **1** (Table S1); the results of the SHAPE analysis for complex **1** (Tables S2); the NMR spectra of the reaction of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3\text{THF}_2$ with $[\text{HNEt}_3][\text{BPh}_4]$ and L^1OH (Figs. S1–S4); the NMR spectra of complex **1** (Figs. S5–S8); the NMR spectra of the reaction of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3\text{THF}_2$ with $[\text{HNEt}_3][\text{BPh}_4]$ and L^2OH or L^3OH (Figs. S9–S16). For ESI, see DOI: 10.32931/io2301a.

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