Synthesis and Structures of the First Cationic Perfluoroaryllanthanoid(II) Complexes

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Abstract: Tetraphenylborate salts of solvated pentafluorophenyllanthanoid(II) cations $[Ln(C_6F_5)(thf)_n]^+$ (Ln = Eu, $n=6$ (**1**); Ln = Yb, $n=5$ (**2**)) were readily synthesized in high yield by reactions of ytterbium or europium with $HgPh(C_6F_5)$ and Me_3NHBPh_4 in THF. The structures of **1**·THF and **2** confirmed the existence of well-separated ions and both **1** and **2** show notable thermal stability at room temperature. The cation in **2** was also observed in the remarkable mixed-valent complex $[Yb^{II}(C_6F_5)(thf)_5][Yb^{III}(C_6F_5)_2\{N(SiMe_3)_2\}_2]$ (**3**), fortuitously isolated in low yield from a reaction of ytterbium metal, $HgPh(C_6F_5)$, and $HN(SiMe_3)_2$ in THF, and which additionally has an unusual bis(pentafluorophenyl)bis{bis(trimethylsilyl)amido)}ytterbate(III) anion. ^{171}Yb–^{19}F coupling has been observed in the low-temperature ^{171}Yb NMR spectra of **2** and $[Yb(C_6F_5)_2(thf)_4]$.

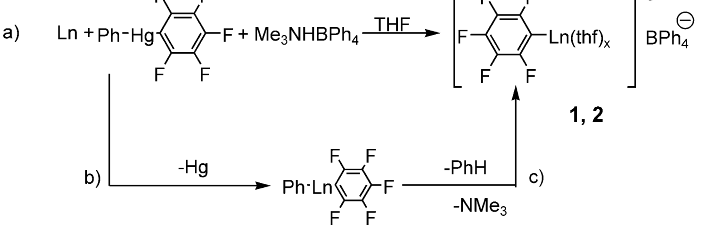
Keywords: borates · cations · fluorinated ligands · lanthanoids · organometallic compounds

Introduction

The phenomenal reactivity of zirconocene alkyl cations $[Cp_2ZrR]^+$ and their significance in industrial catalyst technology[1] has inspired general interest in the properties of d^0 organometallic complexes bearing a formal positive charge. The isolation and characterization of related Group 3 or lanthanoid (d^0/f^n) derivatives having a Ln–C σ bond, for example, $[Ln^{III}R_2]^+$ or $[Ln^{III}(L)R]^+$ (R = alkyl or aryl), has proven challenging.[2–10] Recent studies have yielded tetraorganoborate salts of novel scandium(III)-, yttrium(III)-, lanthanum(III)-, and lanthanoid(III)–alkyl cations that are highly reactive, for example, in ethylene polymerization (and in one instance, unexpected ring opening of a furyl group was observed[8]). To our knowledge, there are no similar cations with a lanthanoid in the *divalent* oxidation state and a residual Ln–C σ bond for example, $[Ln^{II}R]^+$, R = alkyl, aryl.[11] Even cyclopentadienyllanthanoid(II) cations are scarce and unstable.[12,13] We now demonstrate simple syntheses of surprisingly stable tetraphenylborate salts of the perfluoroaryllanthanoid(II) cations $[Ln(C_6F_5)(thf)_n]^+$ (Ln = Eu, $n=6$ (**1**); Ln = Yb, $n=5$ (**2**)) and their crystal structures. In addition, the structure of $[Yb^{II}(C_6F_5)(thf)_5][Yb^{III}(C_6F_5)_2\{N(SiMe_3)_2\}_2]$ (**3**), a remarkable mixed-valent ionic complex having a solvated pentafluorophenylytterbium(II) cation (analogous to **2**) and an unusual bis(pentafluorophenyl)bis{bis(trimethylsilyl)amido}ytterbate(III) anion is reported. Complex **3** is the first crystallographically charcaterized lanthanoid(III) fluorocarbon complex.

Results and Discussion

The synthesis of organolanthanoid(III) cations has been achieved by alkyl group abstraction from a pre-prepared metal–dialkyl by utilizing Lewis acidic BAr_3 or by protonolysis with $R_3NH{\cdot}BAr_4$.[2–10] However, for the lanthanoid(II) derivatives we have devised a straightforward one-pot synthesis that utilizes simple reagents and which avoids the nontrivial isolation of a suitable diorganolanthanoid(II) precursor. Thus redox transmetalation/ligand exchange reactions of ytterbium or europium metal, $HgPh(C_6F_5)$, and Me_3NHBPh_4, successfully gave the tetraphenylborate salts $[Ln(C_6F_5)(thf)_n]BPh_4$ (Ln = Eu, $n=6$ (**1**); Ln = Yb, $n=5$ (**2**)) in good yield (Scheme 1a). Presumably, these reactions pro-



Scheme 1. Synthesis of **1** and **2**.

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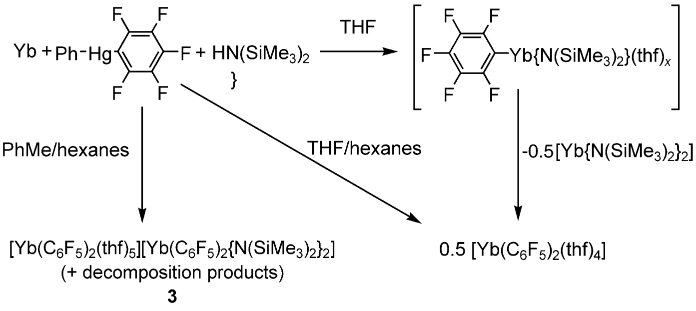
ceed by protolysis of the more basic Ln–Ph site of intermediate $\mathrm{LnPh(C_6F_5)}$[14] species (Scheme 1 b) by the trimethylammonium ion (Scheme 1 c). The successful isolation of **1** and **2** is remarkable since attempts to synthesize tetraphenylborate salts of related $[\mathrm{Ln^{II}Cp(thf)}_x]^+$ cations (Ln = Sm, Yb; Cp = $\mathrm{C_5Me_5}$, $\mathrm{C_9H_7}$) invariably gave crystals of $[\mathrm{Ln(thf)}_n][\mathrm{BPh_4}]_2$ complexes presumably by disproportionation.[13] Arguably, the $[\mathrm{LnCp(thf)}_x]^+$ cations, would be expected to be more stable than the current cations, having a polyhapto π-bound Cp ligand rather than the σ-bonded $\mathrm{C_6F_5}$ group, and indeed [LnCp“([18]crown-6)]$^+$ (Ln = Sm, Yb; Cp” = 1,3-$\mathrm{(Me_3Si)_2C_5H_3}$) species are known,[12] presumably stabilized by the bulk of the Cp“ ligand. The ubiquity of $[\mathrm{Ln(C_6F_5)(thf)}_n]^+$ was also apparent through the observation of the same ytterbium cation in $[\mathrm{Yb^{II}(C_6F_5)(thf)_5}][\mathrm{Yb^{III}(C_6F_5)_2\{N(SiMe_3)_2\}_2}]$ (**3**), a unique mixed-valent species fortuitously isolated in low yield from an attempted synthesis of a $[\mathrm{Yb^{II}\{N(SiMe_3)_2\}(C_6F_5)}]$ complex (Scheme 2). Thus, reaction of Yb metal, $\mathrm{HgPh(C_6F_5)}$, and $\mathrm{HN(SiMe_3)_2}$ in THF (a synthetic route analogous to that successfully used to prepare **1** and **2** and $[\mathrm{Yb(C_5Me_5)(C_6F_5)(thf)_3}]$[14]) and low temperature crystallization of the filtered and evaporated solution in PhMe/hexane gave a large amount of a dark colored intractable oil (most likely decomposition products) and a small amount of bright yellow **3**. An alternative workup procedure by addition of hexanes to the concentrated THF solution gave crystals of $[\mathrm{Yb(C_6F_5)_2(thf)_4}]$[14,15] in moderate yield, rather than the expected mixed ligand $[\mathrm{Yb^{II}\{N(SiMe_3)_2\}(C_6F_5)(thf)}_n]$ species (Scheme 2), a fact which clearly indicates that the mixed $\mathrm{C_6F_5/N(SiMe_3)_2}$ ligand set readily disproportionates. Whilst the origin of **3** is at this stage unclear, the compound presumably has been assembled from the various ytterbium-containing fragments present in solution. In any case, the persistence of the $[\mathrm{Yb^{II}(C_6F_5)(thf)_5}]^+$ ion under unfavorable conditions (as indicated by the oxidized and rearranged anion) attests to the unusual stability of this fragment (vide infra).



Scheme 2. The fortuitous formation of **3**.

All three complexes were characterized by IR spectroscopy. Comparison with the IR data for $[\mathrm{Ln(C_6F_5)_2(thf)}_n]$,[15] $[\mathrm{Yb\{N(SiMe_3)_2\}_2(thf)_2}]$,[16] and $[\mathrm{Yb(thf)_6}][\mathrm{BPh_4}]_2$[13] enables features associated with each functionality to be distinguished. For the $\mathrm{C_6F_5}$ group, ν(C–F) absorptions are evident at 922 (**1**) and 928 cm^{-1} (**2**) similar to those of $[\mathrm{Ln(C_6F_5)_2(thf)}_n]$.[15] However, the mixed oxidation state complex **3** has a further intense band at 956 cm^{-1}, not observed for the $\mathrm{Yb^{II}}$ complexes, and this can be assigned to the ν(C–F) absorption of the $\mathrm{Yb^{III}}$ anion. Similarly, a pair of bands attributable to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ of the two different fluorocarbon rings is observed near 1500 cm^{-1} in the spectrum of **3**. For $\mathrm{BPh_4}^-$, there are characteristic γ(C–H) and ring modes at 734 and 704 cm^{-1} in the spectra of **1** and **2**, whilst the $\mathrm{N(SiMe_3)_2}$ group of **3** gives features at 1247, 1072, and 760 cm^{-1}. Prominent ring stretching modes of coordinated THF at 1040–1020 and 867 cm^{-1} (the former coincident with a higher frequency ν(C–F) absorption) were seen for all complexes.

Diamagnetic **2** was also characterized by NMR spectroscopy (**1** gave only broad and featureless spectra) in THF solution. Room-temperature data exhibited ^{1}H and ^{19}F spectra typical of a $\mathrm{Yb^{II}}$–$\mathrm{BPh_4}$[13,17] and a $\mathrm{Yb^{II}}$–$\mathrm{C_6F_5}$[14,15] species, respectively, the ^{19}F resonances being only marginally shifted from those of $[\mathrm{Yb(C_6F_5)_2(thf)_4}]$[15] and $[\mathrm{Yb(C_5Me_5)(C_6F_5)(thf)_3}]$.[14] Significantly, the ^{171}Yb resonance of monocationic **2** ($\delta(^{171}\mathrm{Yb}) = 304$ ppm) lies between those of neutral $[\mathrm{Yb(C_6F_5)_2(thf)_4}]$ ($\delta(^{171}\mathrm{Yb}) = 463$ ppm)[14] and di-cationic $[\mathrm{Yb(thf)_6}]^{2+}$ ($\delta(^{171}\mathrm{Yb}) = 256$ ppm).[18] When cooled to $-30\,^{\circ}$C, the ^{171}Yb spectrum of **2** did not shift markedly but resolved into a slightly asymmetric multiplet (Figure 1 a). We interpret these data as the splitting of the ^{171}Yb resonance by the *o*-F and *m*-F of the $\mathrm{C_6F_5}$ group giving an overlapping triplet of triplets with $^3J_{\mathrm{Yb,F}}$ ~48 Hz and $^4J_{\mathrm{Yb,F}}$ ~33 Hz. Coupling from the *p*-F is not completely resolved, but from the splitting of the outer lines into doublets a tentative value for $^5J_{\mathrm{Yb,F}}$ ~8 Hz can be obtained. This is the first reported observation of ^{171}Yb–^{19}F coupling and prompted us to examine the ^{171}Yb NMR spectrum of $[\mathrm{Yb(C_6F_5)_2(thf)_4}]$[14] also at lower temperatures. In this case, the single broad room-temperature resonance resolves at $-40\,^{\circ}$C into a 17-line spectrum (Figure 1 b) comprising a pentet of pentets from the four *o*-F and four *m*-F, respectively, yielding $^3J_{\mathrm{Yb,F}}$ ~39 Hz and $^4J_{\mathrm{Yb,F}}$ ~13 Hz. These coupling constants are smaller than for **2**; thus, it is reasonable then that coupling to the *para*-fluorines is not resolved in this case.

In the solid state, crystals of **1**·THF obtained from THF solution, have well-separated $[\mathrm{Eu(C_6F_5)(thf)_6}]^+$ ions and $\mathrm{BPh_4}^-$ ions (closest contact ~3.6 Å) and one unbound THF in the lattice. The europium atom in **1**·THF is seven-coordinate, bound to the *ipso*-carbon atom of the $\mathrm{C_6F_5}$ group and six oxygen atoms of coordinated THF ligands in a distorted pentagonal bipyramidal array (Figure 2). Two of the equatorial THF ligands are pushed out of the plane by their proximity to an *o*-F atom of the $\mathrm{C_6F_5}$ groups as shown by C(1)-Eu(1)-O angles > 100 ° (Table 1). The coordination geometry closely resembles that of the neutral analogue $[\mathrm{Eu(C_6F_5)_2(thf)_5}]$,[19] with a THF ligand replacing one of the $\mathrm{C_6F_5}^-$ groups. However, the Eu–C bond of **1**·THF (2.735(2) Å) is shorter (0.087 Å) than that in the neutral complex (2.822(2) Å)[19] emphasizing the bond lengthening caused by the *trans* disposition of the two $\mathrm{C_6F_5}^-$ groups in the latter. From the Yb–C distance (2.649(3) Å) in seven-coordinate $[\mathrm{Yb(C_5Me_5)(C_6F_5)(thf)_3}]$ (ignoring a weak Yb–*o*-F interaction) which lacks a *trans* anionic group, $\mathrm{Eu^{II}}$–$\mathrm{C_6F_5}$ for seven coordination is estimated to be 2.77 Å after account-

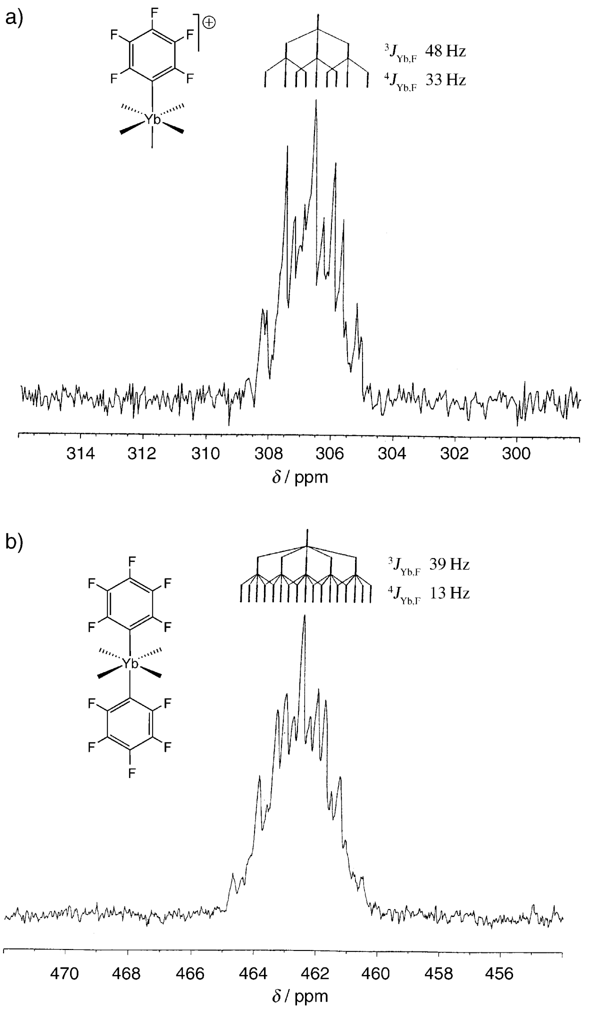


Figure 1. Low-temperature ^{171}Yb NMR spectra of **2** (a) and [Yb(C_6F_5)$_2$(thf)$_4$] (b) in THF solution at 243 K and 233 K, respectively, showing Yb–F coupling.

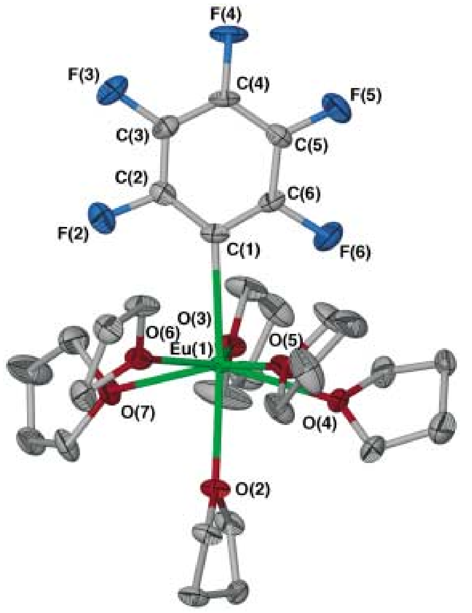


Figure 2. Structure of the [Eu(C_6F_5)(thf)$_6$]$^+$ ion in **1**·THF (50 % thermal ellipsoids; hydrogen atoms removed for clarity).

Table 1. Selected bond lengths [Å] and angles [°] for **1**·THF.

Eu(1)–C(1)	2.735(2)	Eu(1)–O(5)	2.586(2)
Eu(1)–O(2)	2.593(2)	Eu(1)–O(6)	2.601(2)
Eu(1)–O(3)	2.597(2)	Eu(1)–O(7)	2.580(2)
Eu(1)–O(4)	2.632(2)		
C(1)-Eu(1)-O(2)	173.50(6)	O(3)-Eu(1)-O(4)	75.06(6)
C(1)-Eu(1)-O(3)	81.84(7)	O(3)-Eu(1)-O(5)	143.08(6)
C(1)-Eu(1)-O(4)	108.54(7)	O(3)-Eu(1)-O(6)	143.20(6)
C(1)-Eu(1)-O(5)	91.69(7)	O(3)-Eu(1)-O(7)	72.71(6)
C(1)-Eu(1)-O(6)	85.52(6)	O(4)-Eu(1)-O(5)	72.71(6)
C(1)-Eu(1)-O(7)	100.55(7)	O(4)-Eu(1)-O(6)	141.67(6)
O(2)-Eu(1)-O(3)	103.58(5)	O(4)-Eu(1)-O(7)	132.37(6)
O(2)-Eu(1)-O(4)	76.62(5)	O(5)-Eu(1)-O(6)	71.37(6)
O(2)-Eu(1)-O(5)	86.07(5)	O(5)-Eu(1)-O(7)	143.95(6)
O(2)-Eu(1)-O(6)	87.99(5)	O(6)-Eu(1)-O(7)	75.91(6)
O(2)-Eu(1)-O(7)	77.98(6)		

ing for the difference in ionic radii.[20] The current value is also in agreement with an earlier derived Eu^{II}–C(Ph) bond length of 2.74 Å[19] (based on Ln^{III}–C bond lengths of [LnPh$_3$(thf)$_3$], Ln = Er, Tm). The only other known europium(II) aryl [Eu(dpp)$_2$(thf)$_2$] (dpp = 2,6-diphenylphenyl) has a considerably more bulky aryl ligand but shorter Eu–C bond lengths (2.606(4), 2.623(4) Å)[21] than in **1**·THF. If this complex is viewed as four-coordinate (ignoring the two *ipso*-C(Ar)–Eu interactions[21]), then the difference is consistent with the difference in coordination numbers. The current M–C_6F_5 bonding is also comparable with that of [Al(C_6F_5)$_3$(thf)], for which the Al–C distances (av 1.995(3) Å) were considered normal,[22] after accounting for the 0.76 Å difference in ionic radii.[20] The Eu–O distances of **1**·THF correspond closely to average values of seven-coordinate [Eu(C_6F_5)$_2$(thf)$_5$] (<2.607> Å),[19] [EuI$_2$(thf)$_5$] (<2.587> Å),[21] and [{Eu(C_5Me_5)(CCPh)(thf)$_2$}$_2$] (<2.62> Å).[23] Perhaps surprisingly there is no lengthening of Eu(1)–O(2) which is *trans* (173.58(8)°) to the C_6F_5 group given recent observations[24–27] of *trans* influences of anionic groups opposite neutral donors in lanthanoid chemistry (including bond lengthening of up to 0.2 Å of an Y–O(THF) bond *trans* to a bulky aryl in [Y(dmp)Cl$_2$(thf)$_3$], dmp = 2,6-dimesitylphenyl[25]). The longest (significantly) Eu–O distance in **1**·THF is for an equatorial ligand and this must arise from local crowding. Considerable steric stress in the related series **1**·THF, [Eu(C_6F_5)$_2$(thf)$_5$], and [EuI$_2$(thf)$_5$] is indicated by the respective sums of the steric coordination numbers[28] of the ligands (assuming C_6F_5 ~Ph), namely 8.5, 8.6, and 8.3, respectively.

The structure of **2** reveals three similar ion pairs in the asymmetric unit, each having a [Yb(C_6F_5)(thf)$_5$]$^+$ ion and BPh$_4^-$ ion. The major distinctions between the crystallographically independent units are derived from relative rotations of the THF and phenyl ring planes as well as some variation in the constituent bond lengths (of greater than 3σ in the extremes). The structure of **3** displays the same divalent ytterbium cation (Figure 3) as in **2**, but without the complications of the latter, and a ytterbium(III) complex anion [Yb(C_6F_5)$_2${N(SiMe$_3$)$_2$}$_2$]$^-$ (vide infra). The Yb^{II}–C and Yb^{II}–O distances in **3** are comparable with average values in **2** (Table 2). The Yb atom in the cations of **2** and **3** is bound to five THF ligands and one C_6F_5 group in an octahedral

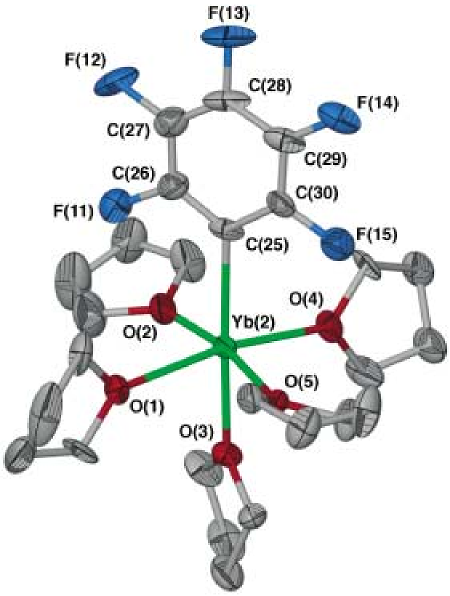


Figure 3. Structure of the $[Yb(C_6F_5)(thf)_5]^+$ ion in **3** (50 % thermal ellipsoids; hydrogen atoms removed for clarity).

Table 2. Selected bond lengths [Å] and angles [°] for the $[Yb(C_6F_5)(thf)_5]^+$ ions in **2** (average values for the three crystallographically independent cations) and **3**.

2		**3**	
<Yb(X)–C(1X)>	2.59(1)	Yb(2)–C(25)	2.569(9)
<Yb(X)–O(6X)>	2.46(1)	Yb(2)–O(3)	2.440(6)
<Yb(X)–O(2X)>	2.42(1)	Yb(2)–O(1)	2.430(5)
<Yb(X)–O(3X)>	2.41(1)	Yb(2)–O(2)	2.413(6)
<Yb(X)–O(4X)>	2.41(1)	Yb(2)–O(4)	2.420(5)
<Yb(X)–O(5X)>	2.42(1)	Yb(2)–O(5)	2.414(6)
<C(1X)-Yb(X)-O(6X)>	173.3(5)	C(25)-Yb(2)-O(3)	175.5(2)
<O(2X)-Yb(X)-O(4X)>	173.4(4)	O(1)-Yb(2)-O(4)	166.6(2)
<O(3X)-Yb(X)-O(5X)>	159.1(4)	O(2)-Yb(2)-O(5)	170.9(2)
<C(1X)-Yb(X)-O(2X)>	92.9(5)	C(25)-Yb(2)-O(1)	100.2(2)
<C(1X)-Yb(X)-O(3X)>	93.4(4)	C(25)-Yb(2)-O(2)	93.8(2)
<C(1X)-Yb(X)-O(4X)>	87.6(5)	C(25)-Yb(2)-O(4)	92.8(2)
<C(1X)-Yb(X)-O(5X)>	101.4(5)	C(25)-Yb(2)-O(5)	93.7(2)
<O(2X)-Yb(X)-O(3X)>	90.4(4)	O(1)-Yb(2)-O(2)	87.1(2)
<O(2X)-Yb(X)-O(5X)>	86.5(5)	O(1)-Yb(2)-O(3)	83.4(2)
<O(2X)-Yb(X)-O(6X)>	90.2(4)	O(1)-Yb(2)-O(5)	86.4(2)
<O(3X)-Yb(X)-O(4X)>	91.1(4)	O(2)-Yb(2)-O(3)	83.6(2)
<O(3X)-Yb(X)-O(6X)>	82.8(4)	O(2)-Yb(2)-O(4)	88.8(2)
<O(4X)-Yb(X)-O(5X)>	92.8(5)	O(3)-Yb(2)-O(4)	83.5(2)
<O(4X)-Yb(X)-O(6X)>	91.6(4)	O(3)-Yb(2)-O(5)	89.3(2)
<O(5X)-Yb(X)-O(6X)>	79.5(4)	O(4)-Yb(2)-O(5)	96.0(2)

array. The decrease in coordination number in the respective cations of **1**·THF and **2** or **3** is consistent with the larger ionic radius[20] of Eu$^{\text{II}}$ than Yb$^{\text{II}}$ and also with the observed structures of $[Yb(C_6F_5)_2(thf)_4]$[14] and $[Eu(C_6F_5)_2(thf)_5]$.[19] It is a response to the considerable crowding of the Eu analogues reducing the sum of the steric coordination number of the ligand set to a more normal 7.3. As with **1**·THF above, the geometry of the cations in **2** and **3** closely resembles that of the analogous neutral diorganoytterbium(II) complex $[Yb(C_6F_5)_2(thf)_4]$,[14] with one of the $C_6F_5^-$ groups replaced by a THF ligand. The Yb$^{\text{II}}$–C distance in **3** (Table 2) is comparable with that in $[Yb(C_5Me_5)(C_6F_5)(thf)_3]$ (2.597(5) Å).[14] In addition, the difference in Ln–C distances between **1**·THF and the cation of **3** corresponds closely to the difference (0.18 Å) between the ionic radii of seven-coordinate Eu^{2+} and six-coordinate Yb^{2+}. As with the Eu system above, the current Yb–C distances are shorter than the corresponding distance in $[Yb(C_6F_5)_2(thf)_4]$ (2.649(3) Å),[14] presumably as a result of the *trans* influence of the two C_6F_5 groups in the latter. Furthermore [Yb(dpp)(I)(thf)$_3$] and [Yb(dpp)$_2$(thf)$_2$] have Yb$^{\text{II}}$–C distances of 2.529(4) Å,[21] and 2.521(3), 2.518(3) Å,[29] respectively, somewhat shorter than the current value as expected for lower Yb$^{\text{II}}$ coordination numbers. The Yb$^{\text{II}}$–O(THF) bond lengths in **3** (Table 2) are similar to those of *trans*-$[Yb(C_6F_5)_2(thf)_4]$ (2.428(2), 2.440(2) Å),[14] although both are longer than in the completely solvated dication $[Yb^{II}(thf)_6]^{2+}$ (av 2.376(4),[13] av 2.378(5),[18] 2.390(7) Å[30]), perhaps reflecting the higher charge in the latter, as the crowding is quite comparable.

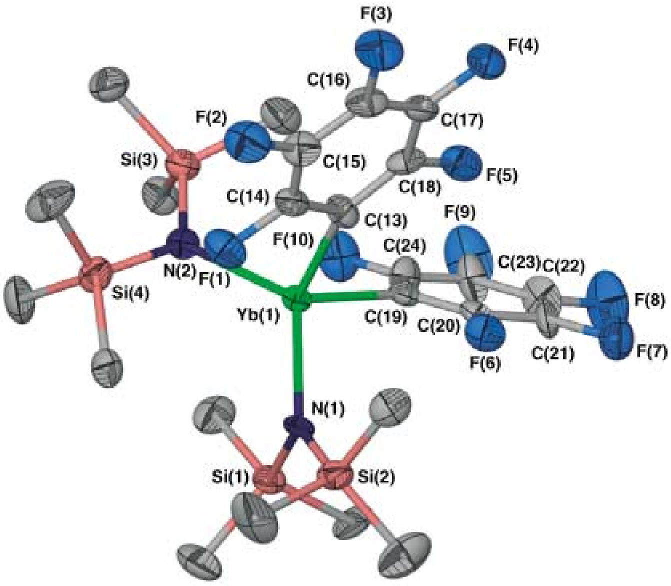


Figure 4. Structure of the $[Yb(C_6F_5)_2\{N(SiMe_3)_2\}_2]^-$ ion in **3** (50 % thermal ellipsoids; hydrogen atoms omitted for clarity).

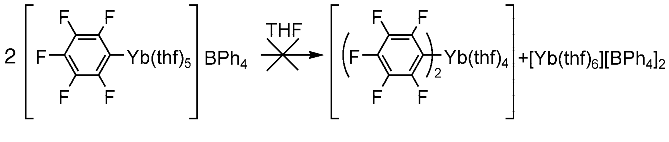
The anion of **3** consists of a trivalent ytterbium at the center of distorted tetrahedron (Figure 4) with the four-coordinate Yb atom bound to two $N(SiMe_3)_2$ ligands and two C_6F_5 groups. This is the first structurally characterized perfluoroorganolanthanoid(III) species.[11] The bulkiness of the $N(SiMe_3)_2$ groups leads to a large N-Yb-N angle and correspondingly narrow C-Yb-C angle (Table 3). The two C_6F_5 groups are asymmetrically bound to Yb, each having one of the *ortho*-fluorines tilted toward the metal (as evidenced by narrow C-C-Yb angles Table 3) although the Yb···F distances (3.25, 3.28 Å) are perhaps too long to be considered as interactions, though only 0.10–0.15 Å longer than the weak Yb···F intramolecular interaction of $[Yb(C_5Me_5)(C_6F_5)(thf)_3]$.[14] In $[Ce(SC_6F_5)_3(thf)_3]$, $[Ho(SC_6F_5)_3(thf)_3]$, and $[Sm(SC_6F_5)_3(py)_4]$ intramolecular Ln–F bonds are in the range 2.579(2)-2.749(2) Å,[31] well

Table 3. Selected bond lengths [Å] and angles [°] for the $[Yb(C_6F_5)_2\{N(SiMe_3)_2\}_2]^-$ ion in **3**.

Yb(1)–N(1)	2.178(6)	Yb(1)–N(2)	2.175(7)
Yb(1)–C(13)	2.432(9)	Yb(1)–C(19)	2.449(8)
N(1)-Yb(1)-N(2)	117.9(2)	N(1)-Yb(1)-C(13)	119.6(3)
N(1)-Yb(1)-C(19)	96.5(2)	N(2)-Yb(1)-C(13)	99.2(3)
N(2)-Yb(1)-C(19)	121.1(3)	C(13)-Yb(1)-C(19)	103.0(3)
C(14)-C(13)-Yb(1)	115.8(6)	C(18)-C(13)-Yb(1)	130.8(7)
C(20)-C(19)-Yb(1)	114.7(5)	C(24)-C(19)-Yb(1)	131.4(7)

short of the current values. The Yb^{III}–*ipso*-C and Yb^{III}–$N(SiMe_3)_2$ bond lengths in **3** are comparable with those of the four-coordinate Yb^{III}–aryl complex $[Yb(dmp)\{N(SiMe_3)_2\}Cl_2Li(thf)_2]$ (2.403(4), 2.158(3) Å).[32] Arguably, the Yb–σ-aryl linkage in the latter is lengthened due to the bulky 2,6-mesityl substituents, and indeed this and the current Yb–C bond lengths are at the long end of the range for the terminal unsubstituted Ph groups of six-coordinate $[YbPh_3(thf)_3]$[14,33] and $[Yb^{III}Ph_2(thf)(\mu\text{-}Ph)_3Yb^{II}(thf)_3]$ (2.39(6)–2.46(4) Å)[34] despite the higher coordination numbers of the last two compounds. Longer Yb^{III}–$N(SiMe_3)_2$ bonds than in **3** were observed in four-coordinate $[Yb\{N(SiMe_3)_2\}_2(NPh_2)_2Na(thf)_2]$ (2.216(4) Å[35]), implying that the anion in **3** is not sterically overcrowded (sum of steric coordination numbers[28] of the ligand set is 6.9).

Satisfactory elemental analyses (C,H and/or Ln) were obtained for complexes **1** and **2**, both of which displayed remarkable thermal stability. The solid tetraphenylborate salts appear stable for several weeks at room temperature (C,H analyses for **2** were obtained after this period) and when a solid sample of **2** was heated in a sealed capillary, evidence of decomposition was observed only above 130 °C, with evolution of THF, and the sample at no stage went dark in color. In contrast, $[Yb(C_6F_5)_2(thf)_4]$ or $[Eu(C_6F_5)_2(thf)_5]$ show near complete decomposition to intractable, dark colored materials within 1–2 days storage at room temperature under nitrogen.[15] After heating a solution of **2** in [D$_8$]THF at 60 °C for 3 h, the ^{19}F NMR spectrum of the resulting mixture showed a forest of fluoroaromatic resonances in the region $\delta = -140$ to -170 ppm with no evidence of any polyfluoroarylytterbium(II) compound or C_6F_5H. Heating a solution of **2** in THF at 60 °C for 24 h gave an amorphous material mixed with a white crystalline solid which was shown to be $[Yb^{II}(thf)_6][BPh_4]_2$[13] by X-ray crystallography. Whilst this observation could be simply explained by disproportionation of **2** (Scheme 3), the absence of dark colored decomposition products argues against the concomitant formation of $[Yb(C_6F_5)_2(thf)_4]$. GC/MS analyses of the supernatant THF solution after exposure to air showed evidence of radical decomposition/coupling products such as the polyphenyls PhC_6F_4H, PhPh, and PhC_6H_4Ph. Clearly the thermal reactions of **2** (and presumably also **1**) are substantially different to those of other Ln–C_6F_5 species in which F^- abstraction and tetrafluorobenzyne formation are considered to be the key steps (similar to that proposed for $Li(C_6F_5)$[36]).[15] Radical-induced decomposition of BPh_4^- is known[37] and homolytic scission of the Yb–C bond would give $C_6F_5\cdot$ and a Yb^I (pseudo-radical) species, both of which could initiate radical breakdown of BPh_4^-. In addition, thermally induced group exchange between BPh_4^- and $[Yb(C_6F_5)(thf)_5]^+$, analogous to that between $[Tl(C_6F_5)_2Br]$ and BPh_4^- affording $TlPh_2Br$,[38] giving a $[YbPh(thf)_5]^+$ ion would provide a source of Ph$^\bullet$ leading to formation of (unfluorinated) polyphenyls, as observed. A further interesting feature of the hydrolysis products is evidence for a *p*-HC_6F_4OR species (^{19}F NMR: $\delta = -140.3$ (d, $J = 20$ Hz), -157.6 (d, $J = 19$ Hz), compare *p*-HC_6F_4OMe: $\delta = -141.0$ (dd, $^3J = 21$ Hz, $^4J = 9$ Hz), -158.4 ppm (dd, $^3J = 21$ Hz, $^4J = 9$ Hz)), which may relate to the $HC_6F_4OC_4H_7^+$ ion (plausibly derived from *p*-$HC_6F_4OCH_2CH{=}CHCH_3$ or *p*-$HC_6F_4OCH_2CH_2CH{=}CH_2$) in the mass spectrum. Lanthanoid-induced ring-opening of THF (and also of a furyl group[8]) by a highly Lewis acidic organolanthanoid(III) cation has recently been reported,[39] and a THF-derived ytterbium(III) *n*-buten-2-olate (Yb–$OCH_2CH{=}CHCH_3$) fragment has been observed.[40] A ytterbium alkoxide formed by opening of THF would be an effective nucleophile for C_6F_5H giving *p*-HC_6F_4X.[41]



Scheme 3.

Conclusion

We have demonstrated that novel perfluoroaryllanthanoid(II) cations can be readily synthesized in one step from simple reagents. These solvated cations display lanthanoid(II) coordination geometries similar to the corresponding neutral $[Ln(C_6F_5)_2(thf)_n]$ derivatives but with significantly shortened metal–carbon bonds. Surprisingly these organolanthanoid(II) cations exhibited greater thermal stability than their neutral diorganolanthanoid(II) counterparts and indeed the $[Yb(C_6F_5)(thf)_5]^+$ fragment ultimately appears as the counterion for the oxidized anion $[Yb^{III}(C_6F_5)_2\{N(SiMe_3)_2\}_2]^-$, a 'decomposition product' of the $Yb^{II}/(C_6F_5)/\{N(SiMe_3)_2\}$ system. This serendipitous mixed-valent complex allowed the first structural characterization of a polyfluorphenyllanthanoid(III) species.

Experimental Section

General remarks: All reactions were carried out under dry nitrogen or argon using dry box and standard Schlenk techniques. Solvents were dried by distillation from sodium wire/benzophenone. Elemental analyses (C,H) were performed by the Campbell Microanalytical Service, University of Otago, New Zealand. Metal analyses of samples digested in concentrated HNO_3/H_2SO_4 were by complexometric titration with Na_2EDTA and xylenol orange indicator. IR data (4000–650 cm^{-1}) were recorded for Nujol mulls sandwiched between NaCl plates using a Perkin Elmer 1600 Fourier transform infrared spectrometer. NMR spectra were obtained on a Bruker AC300 MHz spectrometer; ^{19}F spectra were referenced to external $CFCl_3$ in [D$_6$]acetone; ^{171}Yb spectra were referenced to external 0.15 M $Yb(C_5Me_5)_2$ in THF/10% [D$_6$]benzene.[42] [D$_8$]THF was degassed and distilled from Na/K alloy prior to use. $HgPh(C_6F_5)$[43] and Me_3NHBPh_4[44] were prepared according to the literature procedures.

[Eu(C_6F_5)(thf)$_6$][BPh$_4$] (1): A Schlenk flask was charged with Eu pieces (1.06 g, 7.0 mmol), HgPh(C_6F_5) (1.78 g, 4.0 mmol), Me_3NHBPh_4 (1.52 g, 4.0 mmol), and THF (60 mL). The reaction mixture was stirred for three days at room temperature and then filtered and the yellow filtrate was concentrated and cooled to −20 °C. Large yellow crystals of **1**·THF formed, some of which were mounted for X-ray crystallography. The remaining crystals were collected by filtration and dried under vacuum at room temperature for 1 h to give **1** (yield: 2.50 g, 83 %). IR (Nujol): $\tilde{\nu}=$ 1624w, 1579 m, 1414vs, 1294m, 1266w, 1224w, 1177w, 1136w, 1072w, 1020vs, 922s, 867s, 734s, 705s, 612m cm^{-1}. ^{1}H NMR (300 MHz, [D$_8$]THF): a very broad feature centered at approximately $\delta=7.0$ ppm was observed; elemental analysis (%) calcd for $C_{54}H_{68}BEuF_5O_6$ (1070.88): C 60.57, H 6.40, Eu 14.19; found: C 59.37, H 6.04, Eu 14.40.

[Yb(C_6F_5)(thf)$_5$][BPh$_4$] (2): A Schlenk flask was charged with Yb powder (1.40 g, 8.0 mmol), HgPh(C_6F_5) (1.78 g, 4.0 mmol), Me_3NHBPh_4 (1.52 g, 4.0 mmol), and THF (60 mL). The reaction mixture was stirred for 6 h at room temperature and then filtered and the orange-yellow filtrate was concentrated and cooled to −20 °C. Orange-yellow crystals of **2** formed and were collected by filtration and dried under vacuum at room temperature for 1 h. A second crop was obtained from the filtrate by addition of hexanes and cooling (yield: 2.20 g, 54 %). M.p. 130 °C (decomp); IR (Nujol): $\tilde{\nu}=1624$w, 1579 m, 1415 s, 1300w, 1228w, 1175w, 1149w, 1137w, 1023vs, 928 s, 867 s, 839 m, 734vs, 704vs, 611m cm^{-1}; ^{1}H NMR (300 MHz, [D$_8$]THF): $\delta=6.69$ (t, $J=7.0$ Hz, 4H; *p-H*(Ph)), 6.83 (t, $J=7.2$ Hz, 8H; *m-H*(Ph)) 7.24 ppm (br s, 8H; *o-H*(Ph)); ^{19}F NMR (282.4 MHz, [D$_8$]THF): $\delta=-111.6$ (m, 2F; F2,6), −161.4 (m, 1F; F4), −161.8 ppm (m, 2F; F3,5); ^{171}Yb NMR (52.5 MHz, 0.1 M in THF, 303 K): $\delta=304$ ppm (br s; $\Delta\nu_{1/2}=500$ Hz); (243 K): $\delta=307$ ppm (tt $^3J_{Yb,F}=48$ Hz, $^4J_{Yb,F}$ 33 Hz); elemental analysis calcd (%) for $C_{50}H_{60}BF_5O_5Yb$ (1019.87): C 58.89, H 5.93, Yb 16.97; found: C 58.83, H 6.02, Yb 17.14.

Thermal decomposition of 2: A solution of **2** in [D$_8$]THF was heated at 60 °C for 3 h then examined by NMR spetroscopy: ^{1}H NMR (300 MHz, [D$_8$]THF): broad aromatic resonances were observed at $\delta=6.9$, 7.0, 7.5, 7.7 ppm; ^{19}F NMR (282.4 MHz, [D$_8$]THF): broad resonances with little or no fine structure were observed at $\delta=-141.1$, −142.1 −148.8, −150.9, −153.0, −156.6*, −159.4, −165.0, −169.0*, −169.7*, −174.8 ppm (* major peaks rel. int. ~1:1:2, all other peaks <10 % of the largest peak). Crystals of **2** (0.23 g, 0.23 mmol) were dissolved in THF (3.0 mL). The resulting bright yellow solution was heated to 60 °C for 24 h giving a white precipitate containing colorless crystals of [Yb(thf)$_6$][BPh$_4$]$_2$ (unit cell at 123 K: $a=11.9712(2)$, $b=13.3394(2)$, $c=21.0812(4)$ Å, $\beta=94.552(1)$°, $V=3355.8(2)$ Å[13]). After standing for three days the pale yellow supernatant solution was exposed to air and examined by GC/MS: RT (min), rel. int. (%), 7.51, 100, *m/z* 94 (PhOH), 8.10, 31, *m/z* 101 ($C_5H_9O_2$), 9.03, 26, *m*/z 120 (PhCOMe), 10.01, 20, *m/z* 71, 10.43, 75, *m/z* 200 ($C_{10}H_4F_4$), 10.83, 22, *m/z* 182, 11.39, 29, *m/z* 220 ($HC_6F_4OC_4H_7$), 11.45, 38, *m/z* 218 ($HC_6F_4OC_4H_5$), 12.00, 32, *m/z* 200, 12.72, 27, *m/z* 272 (PhC_6F_4H), 13.80, 98, *m/z* 154 (PhPh), 14.29, 12, *m/z* 242 (BPh_3), 14.84, 56, *m/z* 200, 17.79, 40, *m/z* 170 (PhC_6H_4OH or PhOPh), 21.25, 14, *m/z* 356 ($PhC_6F_3HC_6F_4H$), 25.58, 25, *m/z* 230 (PhC_6H_4Ph).

[Yb(C_6F_5)(thf)$_5$][Yb(C_6F_5)$_2${N(SiMe$_3$)$_2$}$_2$] (3): A Schlenk flask was charged with Yb powder (1.74 g, 10.0 mmol), HgPh(C_6F_5) (2.22 g, 5.0 mmol), HN(SiMe$_3$)$_2$ (0.81 g, 5.0 mmol), and THF (60 mL). The reaction mixture was stirred for 6 h at room temperature and then filtered and the orange filtrate was evaporated. A 1:2 mixture of PhMe and hexane (60 mL) was added to the oily residue and the solution was cooled to −20 °C. After several weeks, some yellow crystals of **3** had formed, mixed with a large amount of a dark colored oil, and were hand picked for characterization by X-ray crystallography. IR (Nujol): $\tilde{\nu}=1629$w, 1600w, 1533m, 1511m, 1495m, 1413s, 1323m, 1247s, 1178m, 1072m, 1040s, 956s, 934s, 883 m, 866s, 834s, 780w, 758w, 669m cm^{-1}. From an identical reaction, the filtered reaction mixture was reduced to 15 mL and hexanes (25 mL) were added. Cooling to −20 °C overnight gave bright orange crystals of [Yb(C_6F_5)$_2$(thf)$_4$] that were collected by filtration and dried under vacuum (yield: 0.85 g, 52 %, based on available C_6F_5). The IR and ^{171}Yb NMR (THF solution) spectra were identical with those reported.[14,15] ^{171}Yb NMR (52.5 MHz, 0.15 M in THF, 233 K): $\delta=463$ ppm (pp, $^3J_{Yb,F}=39$ Hz, $^4J_{Yb,F}=13$ Hz); elemental analysis calcd (%) for $C_{28}H_{32}F_{10}O_4Yb$ (651.36): Yb 26.57; found: Yb 25.98.

X-ray crystallographic study: Crystals were mounted in an inert atmosphere under viscous oil onto a glass fiber. Low-temperature (123 K) data were collected on an Enraf–Nonius CCD area detector diffractometer (Mo$_{K\alpha}$ radiation, $\lambda=0.71073$ Å, frames comprised 1.0° increments in ϕ or ω yielding a sphere of data) with proprietary software (Nonius B.V., 1998). Each data set was empirically corrected for absorption by using SORTAV[45] then merged (R_{int} as quoted) to N unique reflections. The structures were solved by conventional methods and refined with anisotropic thermal parameter forms for the non-hydrogen atoms by full-matrix least-squares on all F^2 data using SHELX 97.[46] Hydrogen atoms were included in calculated positions and allowed to ride on the parent carbon atom.

Crystal cata: **1**·THF: $C_{58}H_{76}B_1Eu_1F_5O_7$ (1142.96), monoclinic, $P2_1/c$, $a=10.7264(1)$, $b=19.0589(1)$, $c=27.1660(2)$ Å, $\beta=97.292(1)$°, $V=5509(2)$ Å^3, ρ_{calcd} ($Z=4$) 1.378 g cm^{-3}, $\mu_{Mo}=1.21$ mm^{-1}, $F(000)$ 2372, $T_{min,max}$ *0.696, 0.743*, $N_{total}=65571$, $N=13466$ ($R_{int}=0.040$), $R=0.031$, $wR_2=0.073$ ($R=0.050$, $wR_2=0.079$ all data). **2**: $C_{50}H_{60}B_1F_5O_5Yb_1$ (1019.83), monoclinic, $P2_1/c$, $a=17.4016(1)$, $b=32.8938(3)$, $c=24.1992(2)$ Å, $\beta=96.0466(3)$°, $V=13774(5)$ Å^3, ρ_{calcd} ($Z=12$) 1.475 g cm^{-3}, $\mu_{Mo}=2.103$ mm^{-1}, $F(000)$ 6240, $T_{min,max}$ 0.538, 0.623, $N_{total}=125157$, $N=33566$ ($R_{int}=0.095$), $R=0.056$, $wR_2=0.114$ ($R=0.129$, $wR_2=0.136$ all data). **3**: $C_{50}H_{76}F_{15}N_2O_5Si_4Yb_2$ (1528.57), monoclinic, $P2_1/c$, $a=18.1981(3)$, $b=16.9262(3)$, $c=20.5077(4)$ Å, $\beta=96.872(1)$ °, $V=6271(2)$ Å^3, ρ_{calcd} ($Z=4$) 1.619 g.cm^{-3}, μ_{Mo} 3.13 mm^{-1}, $F(000)$ 3044, $T_{min,max}=0.610$, 0.811, N_{total} 75454, N 15382 ($R_{int}=0.229$), R 0.066, wR_2 0.101 (R 0.225, wR_2 0.137 all data).

CCDC-226006–CCDC-226008 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

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