Organolanthanoids, 24[‡]
Organoamido- and Aryloxo-Lanthanoids, 21[‡]

Syntheses and Structures of Bis(aryloxo)fluoroytterbium(III) Complexes, $[Yb(OAr)_2F(THF)]_2$ (OAr = OC_6H_2-2,6-*t*Bu_2-4-R; R = H, Me, *t*Bu), and Bis(cyclopentadienyl)fluoroytterbium(III) Complexes, $[YbCp_2F]_3$, $[Yb(MeCp)_2F]_4$, $[YbCp_2F(OPPh_3)]_2$, and $[Yb(MeCp)_2F(THF)]_2$

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Dedicated to Prof. Dr. Othmar Stelzer on the occasion of his 60th birthday

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Reaction of $[Yb(OAr)_2(THF)_3]$ (OAr = OC_6H_2-2,6-*t*Bu_2-4-R; R = H, Me, *t*Bu) with perfluorodecalin in THF at room temperature results in C–F activation and formation of the first heteroleptic aryloxofluorolanthanoid complexes, $[Yb(OAr)_2F(THF)]_2$. Oxidation of bis(cyclopentadienyl)ytterbium(II) with perfluoro(methylcyclohexane) or perfluorodecalin in DME surprisingly gives unsolvated $[YbCp_2F]_3$. The analogous reaction of bis(methylcyclopentadienyl)ytterbium(II) yields unsolvated $[Yb(MeCp)_2F]_4$, whilst in THF, the oxidation provides $[Yb(MeCp)_2F(THF)]_2$. Treatment of $[YbCp_2F(THF)]_2$ with triphenylphosphane oxide gives $[YbCp_2F(OPPh_3)]_2$. X-ray structure determinations revealed $[Yb(OAr)_2F(THF)]_2$ (R = H or *t*Bu) to be centrosymmetric fluoride-bridged dimers with five-coordination for ytterbium. Examination of the structures of the cyclopentadienyl complexes showed that $[YbCp_2F]_3$ is trimeric with formal eight-coordination for ytterbium and a planar $(YbF)_3$ ring, whereas $[Yb(MeCp)_2F]_4$ is an eight-coordinate tetramer having a puckered $(YbF)_4$ ring with F–Yb–F angles of ca. 90° and Yb–F–Yb angles close to 180° [178.9(4), 168.4(3)°]. Both $[Yb(MeCp)_2F(THF)]_2$ and $[YbCp_2F(OPPh_3)]_2$ are nine-coordinate fluoride-bridged dimers.

Introduction

Heteroleptic lanthanoid fluorides $[LnF_nL_{3-n}]$ [L = cyclopentadienyl (Cp), OAr, OR, NR_2 etc.] provide a synthetic challenge since the high stability of lanthanoid fluorides[3] may favour rearrangement into LnF_3 and LnL_3. {A tendency in this direction is shown by the isolation of the fluoride-rich, multiple-fluoride-bridged cage $[Yb_5(C_5Me_5)_6F_9]$ from the reaction of $[Yb(C_5Me_5)_2(OEt_2)]$ with C_9F_{18} in toluene.[3]} They are also of interest as potential olefin polymerisation catalysts, especially in view of the success of cyclopentadienylzirconium fluorides[4] in this role.[5] Complexes of this type are extremely rare,[6–14] there being no reported aryloxofluorolanthanoid complexes[9–12] and few examples of cyclopentadienylfluorolanthanoids.[3,6–8,12–21] We now report the syntheses and structures of the first aryloxofluorolanthanoid complexes, $[Yb(OAr)_2F(THF)]_2$ (OAr = OC_6H_2-2,6-*t*Bu_2-4-R; R = H, Me, *t*Bu), and some new bis(cyclopentadienyl)fluorolanthanoid(III) complexes, $[YbCp_2F]_3$, $[Yb(MeCp)_2F]_4$, and $[YbCp_2F(OPPh_3)]_2$, as well as a new synthesis and the structure of the previously reported,[3] but structurally uncharacterized, $[Yb(MeCp)_2F(THF)]_2$.

Results and Discussion

Syntheses

Reaction of the ytterbium(II) aryloxides $[Yb(OAr)_2(THF)_3]$ (OAr = OC_6H_2-2,6-*t*Bu_2-4-R; R = H, Me, *t*Bu) with perfluorodecalin gives the corresponding heteroleptic bis(aryloxo)fluorolanthanoid(III) complexes, shown (below) to be the dimers $[Yb(OAr)_2F(THF)]_2$.

$$2\,[Yb(OAr)_2(THF)_3] + C_{10}F_{18} \rightarrow [Yb(OAr)_2F(THF)]_2 + \text{unsaturated fluorocarbons} \quad (1)$$

Pefluorodecalin was recently introduced as an oxidant in lanthanoid chemistry in the synthesis of $[YbCp_2F(THF)]_2$.[21] This provided the first example of C–F activation of a saturated fluorocarbon by a lanthanoid complex. The compound has also been used to give Group 4 organometallic fluorides.[22]

The versatility of perfluorocycloalkanes in the preparation of heteroleptic lanthanoid fluorides is also illustrated

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by syntheses of new bis(cyclopentadienyl)fluoroytterbium(III) complexes. Thus, reaction of [$YbCp_2(DME)$] with perfluorodecalin or perfluoro(methylcyclohexane) in 1,2-dimethoxyethane surprisingly yields *unsolvated* bis(cyclopentadienyl)fluoroytterbium(III), shown to be trimeric (Equation 2).

$$3\,[YbCp_2(DME)] + C_{10}F_{18}\ (C_7F_{14}) \rightarrow [YbCp_2F]_3 + \text{unsaturated fluorocarbons} \quad (2)$$

This contrasts isolation of the solvated complex [$YbCp_2F(THF)]_2$ from the synthesis in tetrahydrofuran.[21] A similar reaction of [Yb(MeCp)$_2$(THF)] with perfluorodecalin in DME also gives an *unsolvated* complex, revealed to be the novel and unexpected tetramer, [Yb(MeCp)$_2$F]$_4$, by X-ray crystallography.

$$4\,[Yb(MeCp)_2(THF)] + C_{10}F_{18} \rightarrow [Yb(MeCp)_2F]_4 + \text{unsaturated fluorocarbons} \quad (3)$$

The use of THF as a solvent for this reaction provides Yb(MeCp)$_2$F(THF), which has been previously prepared by C–F activation of the more reactive perfluoro-2,3-dimethylpent-2-ene in THF.[3] These syntheses (1)–(3) establish oxidation of ytterbium(II) compounds by perfluorodecalin to be a general route to heteroleptic ytterbium(III) fluorides. However, perfluoro(methylcyclohexane) was an unsatisfactory oxidant for [Yb(MeCp)$_2$(THF)] in THF [cf. $YbCp_2(DME)$[21]] and hence is a less widely applicable reagent. The low-moderate yields are probably due to incomplete deposition of the products, which have appreciable solubility in the reaction media, rather than competing reactions. Any LnF_3 formed by rearrangement (see Introduction) would have coprecipitated with the heteroleptic fluoro complexes, precluding the observed satisfactory analyses (below). In the present syntheses, the reduction products were not examined, but it has been shown that the oxidation of [$YbCp_2(DME)$] by perfluoro(methylcyclohexane) yields perfluorotoluene and *p*-, *m*-, and *o*-$HC_6F_4CF_3$,[21] and that reduction of perfluorodecalin by low oxidation state group 4 metallocenes gives perfluoronaphthalene and specific hydropolyfluoronaphthalenes.[23]

The first complex of a bis(cyclopentadienyl)fluorolanthanoid with a ligand other than an ether has been obtained by displacement of coordinated THF by triphenylphosphane oxide.

$$[YbCp_2F(THF)]_2 + 2\,Ph_3PO \rightarrow [YbCp_2F(OPPh_3)]_2 + 2\,THF \quad (4)$$

It is of interest that this could be achieved without incurring rearrangement into the strongly-bonded phosphane oxide complex [$YbCp_3(OPPh_3)$][1] and the highly stable[3] YbF_3.

Characterization

The composition of the complexes was established by lanthanoid metal and fluorine analyses. The latter were very valuable, particularly for the highly hydrolytically labile [Yb(OAr)$_2$F(THF)]$_2$ complexes, in view of the similarity in molecular weights between the fluoro and the corresponding hydroxo complexes. Further, the presence of fluorine in single crystals of [Yb(OC_6H_2-2,4,6-*t*Bu$_3$)$_2$F(THF)]$_2$ · 3 THF was established by EDAX-measurements. The THF of solvation was lost on drying under vacuum in isolation of the bulk product. By contrast, for OAr = OC_6H_3-2,6-*t*Bu$_2$, both bulk product and single crystals have the same composition. The extreme sensitivity of [Yb(OAr)$_2$F(THF)]$_2$ compounds to hydrolysis was illustrated by the invariable observation of weak bands at ca. 3600 cm^{-1} in their infrared spectra, near to reported ν(OH) absorptions [3685, 3651m(sp)] of [Yb(OC_6H_2-2,4,6-*t*Bu$_3$)$_2$(OH)(THF)]$_2$,[24] and these bands intensified rapidly on brief deliberate exposure of the mulls/disk to the atmosphere. (The plate protected Nujol mulls or the KBr disks were briefly in air on transfer to the chamber of the IR spectrometer). Extreme sensitivity is not observed for the cyclopentadienylfluoroytterbium(III) complexes, which showed no analogous absorption in similarly recorded spectra. When solutions of the complexes were stored for several days to grow single crystals (see Experimental Section), there was no evidence of decomposition into LnF_3.

For the tetrahydrofuran complexes, absorption bands at 1050–1020 cm^{-1} and 880–860 cm^{-1} can be attributed to ring stretching modes of coordinated THF, shifted from the free ligand values (1070, 912 cm^{-1}) as expected on coordination[25] {e.g. compare [Yb(MeCp)$_2$F(THF)]$_2$ and [Yb(MeCp)$_2$F]$_4$; Experimental Section}, though phenolate absorption also occurs in the latter region.[26] By contrast the spectra of [$YbCp_2F$]$_3$ and [Yb(MeCp)$_2$F]$_4$, isolated from DME, do not show any absorption at 900–840 cm^{-1} corresponding to the intense absorption of free DME at 858 cm^{-1},[27] expected at higher energy on coordination.[28] In the spectrum of [$YbCp_2F(OPPh_3)$]$_2$, ν(PO) is observed at 1179 cm^{-1}, lowered from the free ligand value (1195 cm^{-1}) as expected on coordination.[29] The relatively small shift is consistent with observations for other Ln($OPPh_3$) complexes, which show a decrease in the shift of ν(PO) from La to Lu.[1,30]

Comparison of the far infrared spectra of [Yb(OAr)$_2$F(THF)]$_2$ and [Yb(OAr)$_2$(THF)$_3$] complexes (Experimental section) suggests an intense ν(YbF) absorption is located at 390–375 cm^{-1} (Table 1) with the possibility of a second absorption (expected for a halogen-bridged dimeric structure[31]) near 300 cm^{-1} at least for OAr = OC_6H_2-2,6-*t*Bu$_2$-4-R, R = Me, or *t*Bu. The former are at higher frequencies than reported ν(YbF) values (330–298 cm^{-1})[3,21] for formally eight and nine-coordinate bis(cyclopentadienyl)fluorolanthanoid(III) complexes (Table 1), consistent with the lower coordination number, and are expectedly lower than ν(YbF) (569, 546 cm^{-1}) of matrix isolated, three-coordinate YbF_3.[32] No infrared absorption band was observed for [$YbCp_2F$]$_3$ at 350–275 cm^{-1}, where ν(YbF) is expected, but the Raman spectrum showed a ν(YbF) line at 336 cm^{-1}. Thus, ν(YbF) for the highly symmetrical structure (see below), is infrared inactive. For the less symmetrical $[Yb(MeCp)_2F]_4$, ν(YbF) was observed in the infrared spectrum, and the assignment for $[Yb(MeCp)_2F(THF)]_2$ is in agreement with that reported[3] (Table 1). There is some uncertainty over ν(YbF) of $[YbCp_2F(OPPh_3)]_2$ as Ph_3PO has weak absorption in the relevant region,[33] but the higher frequency band of two near 300 cm^{-1} seems the more likely. Overall, it is not possible to distinguish between eight- and nine-coordinate bis(cyclopentadienyl)fluorolanthanoid(III) complexes on the basis of ν(YbF) frequencies (Table 1).

Table 1. ν(Yb–F) frequencies of heteroleptic fluorolanthanoid(III) complexes

Compound	ν(Yb–F) [cm^{-1}][a]
$[Yb(OC_6H_3\text{-}2,6\text{-}t\mathrm{Bu}_2)_2F(THF)]_2$[b]	387, 304 (?)
$[Yb(OC_6H_2\text{-}2,6\text{-}t\mathrm{Bu}_2\text{–}4\text{-}Me)_2F(THF)]_2$[b]	381, 302
$[Yb(OC_6H_2\text{-}2,4,6\text{-}t\mathrm{Bu}_3)_2F(THF)]_2$[b]	375, 304
$[YbCp_2F]_3$[b]	336 (Raman)
$[Yb(MeCp)_2F]_4$[b]	328
$[YbCp_2F(OPPh_3)]_2$[b]	306 (?)
$[Yb(MeCp)_2F(THF)]_2$[b]	332 (326[3])
$[YbCp_2F(THF)]_2$[21]	298
$[Eu(Me_5C_5)_2F(OEt_2)]$[3]	311
$[Sm(Me_5C_5)_2F(OEt_2)]$[3]	304
$[Yb(Me_5C_5)_2F(OEt_2)]$[3]	303

[a] From far infrared spectra, except where indicated otherwise. – [b] This work.

No metal containing ions were observed in the mass spectra of $[Yb(OAr)_2F(THF)]_2$ complexes, but trinuclear and dinuclear ions were observed for $[YbCp_2F]_3$, $[Yb(MeCp)_2F]_4$, $[YbCp_2F(OPPh_3)]_2$ and $[Yb(MeCp)_2F(THF)]_2$. In each case the highest observed ion was $[Yb_3L_5F_3]^+$ (L = Cp or MeCp) or this ion ±H. (For the methylcyclopentadienyl complexes, this ion was close to the instrument limit, hence the possibility of formation of tetranuclear ions cannot be ruled out.) An analogous ion was the highest observed in the spectra of $[YbCp_2F(THF)]_2$,[21] $[ScCp_2F]_3$,[15] and $[Sm(t\mathrm{Bu}Cp)_2F]_3$.[20] Formation of trinuclear ions for the dimeric complexes $[YbCp_2F(OPPh_3)]_2$ and $[Yb(MeCp)_2F(THF)]_2$ evidently involves thermally induced dissociation of the neutral ligand and further association, as observed for $[YbCp_2F(THF)]_2$.[21] Because of such reactions, the mass spectra are an uncertain guide as to solid state structures. In general the fragmentation patterns of the Cp complexes were similar to those of $[YbCp_2F(THF)]_2$ [21] and $[ScCp_2F]_3$,[15] whilst those of the MeCp complexes showed features (loss of $MeCp^{\bullet}$, $Me^{\bullet}$, and, for the THF complex, $H^{\bullet}$) similar to those of $[Ln(MeCp)_3]$.[34] However there was no evidence of the electron impact-induced ring expansions shown by $[Ln(MeCp)_3]$.[34] For the phosphane oxide complex, no ions with coordinated Ph_3PO were observed, although such ions, notably $LnCp_2(OPPh_3)^+$, have been observed with low intensity in the mass spectra of some $[LnCp_3(OPR_3)]$ complexes.[1]

X-ray Crystal Structures

1. $[Yb(OC_6H_2\text{-}2,6\text{-}t\mathrm{Bu}_2\text{-}4\text{-}X)_2F(THF)]_2$ (X = H or *t*Bu): X-ray crystallography has shown that the complexes $[Yb(OC_6H_2\text{-}2,6\text{-}t\mathrm{Bu}_2\text{-}4\text{-}X)_2F(THF)]_2$ (X = H or *t*Bu) are dimeric with bridging fluorides and five-coordinate ytterbium. In each case the fluoride bridging is somewhat unsymmetrical (0.04–0.07 Å), the differences being significant on consideration of the errors in bond lengths. Selected bond lengths and angles for the X = H complex and for the two crystallographically independent X = *t*Bu molecules are listed in Table 2, whilst the structure of $[Yb(OC_6H_3\text{-}2,6\text{-}t\mathrm{Bu}_2)_2F(THF)]_2$ is displayed in Figure 1, and that of molecule 1 of $[Yb(OC_6H_2\text{-}2,4,6\text{-}t\mathrm{Bu}_3)_2F(THF)]_2$ in Figure 2. The stereochemistry is very irregular, but can be regarded as distorted trigonal bipyramidal with an aryloxide oxygen and a fluorine apical (ArO–Yb–F 150–153°), and the other aryloxide oxygen, O(THF), and the other fluorine equatorial. A similar arrangement is observed in $[Yb(OC_6H_2\text{-}2,4,6\text{-}t\mathrm{Bu}_3)_2OH(THF)]_2$ [24] where the apical ArO–Yb–OH angle is somewhat larger [156.2(3)°] than the ArO–Yb–F angles (Table 2). A similar arrangement of Cp ring centres, THF oxygen, and bridging fluorides is observed in $[YbCp_2F(THF)]_2$,[21] $[Yb(MeCp)_2F(THF)]_2$, and $[YbCp_2F(OPPh_3)]_2$, (below), but the largest (transoid) angle, O(THF)–Yb–F, is only ca. 140°. Moreover, $[Yb(OAr)_2F(THF)]_2$ complexes have one of the bulky ligands in an apical position, whereas neither of the larger groups (Cp/MeCp) is apical in the cyclopentadienyl complexes. At first sight, the Yb–(μ-F) distances (Table 2) are surprisingly long for a five-coordinate complex, since they are comparable with those of the nine-coordinate dimers, $[YbCp_2F(THF)]_2$,[21] $[Yb(MeCp)_2F(THF)]_2$, and $[YbCp_2F(OPPh_3)]_2$ (see below), as well as those [2.206(5), 2.196(5) Å] of the two sets of Yb–(μ-F) bonds in eight-coordinate $[Yb_5(C_5Me_5)_6(\mu_4\text{-}F)(\mu_3\text{-}F)_2(\mu\text{-}F)_6]$.[3] On the basis of the data for the cyclopentadienyl compounds[3,21] and the variation of ionic radius with coordination number,[35] a Yb–(μ-F) distance of ca. 2.0 Å might be expected in $[Yb(OAr)_2F(THF)]_2$ complexes. This would be near terminal Yb–F distances [2.015(4), 2.026(2) Å] in monomeric eight-coordinate $[Yb(C_5Me_5)_2F(L)]$ (L = THF or Et_2O) complexes.[3] However there is actually quite wide variation in the limited range of bridging Yb–F distances reported[3,16,17,21]. Thus, Yb–(μ_3-F) distances for eight-coordinate Yb^{III} in $[Yb_5(C_5Me_5)_6(\mu_4\text{-}F)(\mu_3\text{-}F)_2(\mu\text{-}F)_6]$ are much longer [2.319(6)–2.468(6) Å] than Yb–(μ-F) above, and Yb–(μ_4-F) lenghts cover a narrower range (2.365–2.387 Å).[3] By contrast, Yb^{III}–(μ-F) distances for fluoride ions bridging Yb^{III} and Yb^{II} in seven-coordinate $[Yb_2(C_5Me_5)_4(\mu\text{-}F)]$[17] and eight-coordinate (for Yb^{III}) $[Yb_4(C_5Me_5)_6(\mu\text{-}F)_4]$[16] are very short at 2.084(2) and 2.129 ± 0.002 Å respectively. Even Sm–(μ-F) of eight-coordinate $[Sm(C_5H_4\text{-}t\mathrm{Bu})_2F]_3$ [20] and $[Sm\{C_5H_3\text{–}1,3\text{-}(SiMe_3)_2\}_2F]_2$ [19] differ by ca. 0.06 Å. In the present complexes, the relatively long (for coordination number 5) Yb–(μ-F) distances are attributed to steric crowding around ytterbium. The sum of the steric coordination numbers[36] of the ligands for the $[Yb(OAr)_2F(THF)]_2$ complexes is 8.0, whereas the values for the topologically related $[YbCp_2F(THF)]_2$ [21] and $[Yb(MeCp)_2F(THF)]_2$ are 7.3–7.5, indicative of less steric hindrance. Thus long Yb–(μ-F) bonds in the $[Yb(OAr)_2F(THF)]_2$ complexes are reasonable because of

Table 2. Selected bond lengths (Å) and angles (°) for $[Yb(OC_6H_3\text{-}2,6\text{-}tBu_2)_2F(THF)]_2$ and $[Yb(OC_6H_2\text{-}2,4,6\text{-}tBu_3)_2F(THF)]_2 \cdot 3$ THF

	$[Yb(OC_6H_3\text{-}2,6\text{-}tBu_2)_2F(THF)]_2$	$[Yb(OC_6H_2\text{–}2,4,6\text{-}tBu_3)_2F(THF)]_2 \cdot 3$ THF		
		molecule 1	molecule 2	
Yb(1)–F(1)	2.172(4)	2.170(4)	2.169(5)	Yb(2)–F(2)
Yb(1)–F(1a)	2.213(3)	2.239(4)	2.225(5)	Yb(2)–F(2a)
Yb(1)–O(1)	2.043(3)	2.061(6)	2.053(6)	Yb(2)–O(4)
Yb(1)–O(2)	2.062(4)	2.053(6)	2.073(5)	Yb(2)–O(5)
Yb(1)–O(3)	2.301(4)	2.315(6)	2.332(6)	Yb(2)–O(6)
Yb(1)–F(1)–Yb(1a)	111.3(1)	110.7(2)	111.1(2)	Yb(2)–F(2)–Yb(2a)
F(1)–Yb(1)–F(1a)	68.7(1)	69.3(2)	68.9(2)	F(2)–Yb(2)–F(2a)
O(1)–Yb(1)–F(1)	107.6(1)	102.8(2)	109.3(2)	O(4)–Yb(2)–F(2)
O(1)–Yb(1)–F(1a)	100.2(1)	152.7(2)	100.7(2)	O(4)–Yb(2)–F(2a)
O(1)–Yb(1)–O(2)	108.0(1)	109.1(2)	108.6(2)	O(4)–Yb(2)–O(5)
O(1)–Yb(1)–O(3)	112.9(1)	89.3(2)	113.7(2)	O(4)–Yb(2)–O(6)
O(2)–Yb(1)–F(1)	104.6(1)	109.7(2)	103.0(2)	O(5)–Yb(2)–F(2)
O(2)–Yb(1)–F(1a)	151.7(2)	98.1(2)	150.5(2)	O(5)–Yb(2)–F(2a)
O(2)–Yb(1)–O(3)	88.9(1)	113.1(2)	88.1(2)	O(5)–Yb(2)–O(6)
O(3)–Yb(1)–F(1)	130.6(2)	128.4(2)	129.1(2)	O(6)–Yb(2)–F(2)
O(3)–Yb(1)–F(1a)	77.3(1)	77.3(2)	77.4(2)	O(6)–Yb(2)–F(2a)

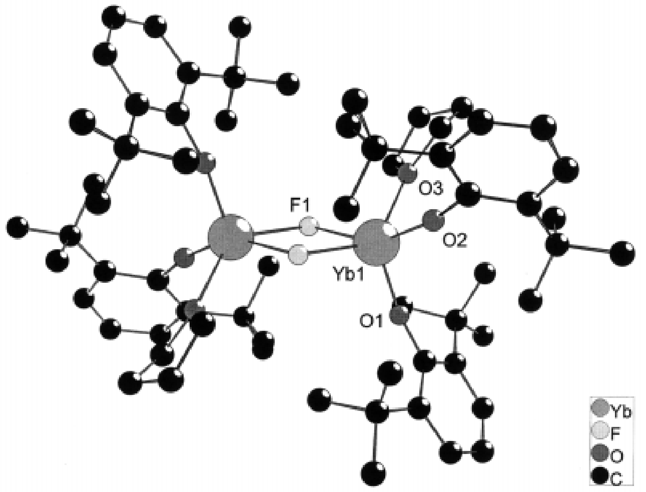

Figure 1. The molecular structure of $[Yb(OC_6H_3\text{-}2,6\text{-}tBu_2)_2F(THF)]_2$

crowding, and there are also relatively long Yb–O(THF) bonds (see below).

The average Yb–O(THF) distance (2.32 Å) is somewhat shorter than that [2.363(8) Å] of five-coordinate $[Yb(OC_6H_2\text{-}2,6\text{-}tBu)_2OH(THF)]_2$.[24] Subtraction of an extrapolated radius (from the data of Shannon[35]) for five-coordinate Yb^{3+} from Yb–O(THF) gives 1.51 Å, typical of values (1.48–1.59 Å) derived from Ln–O(THF) of low coordinate complexes with bulky aryloxides.[24,26,37] This is larger than subtraction values of 1.34 ± 0.05 Å derived from Ln–O(THF) of cyclopentadienyllanthanoid complexes[38] and specifically 1.37 Å from Yb–O(THF) of $[YbCp_2F(THF)]_2$ [21] and reflects bond lenghtening induced by steric crowding as noted for Yb–(μ-F) above. The Yb–OAr distances are comparable with those of both five-coordinate $[Yb(OC_6H_2\text{–}2,4,6\text{-}tBu_3)_2OH(THF)]_2$ [24] and $[Yb(OC_6H_3\text{-}2,6\text{-}Ph_2)_3(THF)_2]$,[37a] and subtraction of the 5-coordinate Yb^{3+} radius from <Yb–OAr> gives 1.25 Å, quite typical of values derived from data for low coordinate Yb^{II} and Yb^{III} aryloxides.[24,26,37]

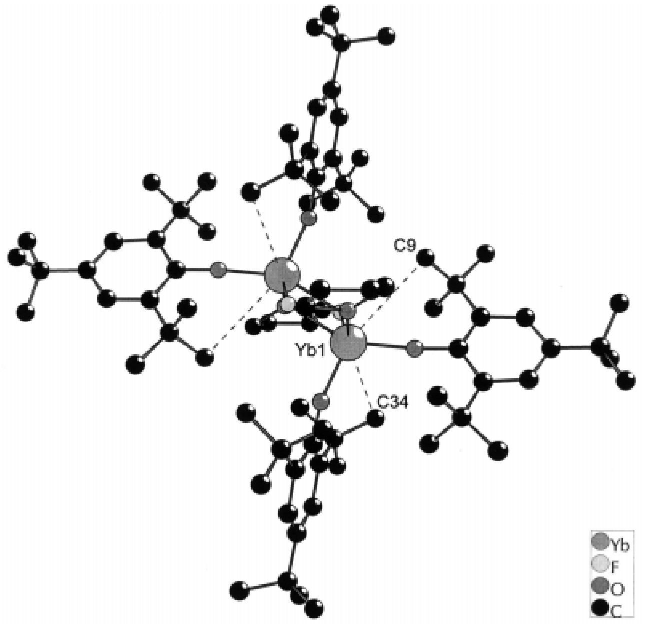

Figure 2. The molecular structure of molecule 1 of $[Yb(OC_6H_2\text{-}2,4,6\text{-}tBu_3)_2F(THF)]_2$ showing the close Yb···C(Me) contacts

Further evidence of considerable steric crowding in the $[Yb(OAr)_2F(THF)]_2$ complexes is provided by the existence of short Yb···C(Me) and C(Me)···C(Me) separations (Table 3) and the former are displayed for molecule 1 of $[Yb(OC_6H_2\text{-}2,4,6\text{-}tBu_3)_2F(THF)]_2$ in Figure 2. The listed Yb···C(Me) distances are less than the sum (3.94 Å) of the metallic radius of ytterbium[39] (which can be viewed as a pseudo van der Waals radius) and the van der Waals radius of a methyl group.[40] However these contacts are significantly longer than can be attributed to agostic Yb···C(alkyl) contacts (ca. 2.9–3.2 Å)[16,41] and are thus approaches induced by ligand congestion. The close C(Me)···C(Me) contacts that also reflect congestion are between methyls of *different tert*-butyl groups on the same or different Yb atoms. Their separations are less than two methyl van der Waals

Table 3. Non bonding close Yb···C and C(Me)···C(Me) contacts (Å) in $[Yb(OC_6H_2\text{-}2,6\text{-}t\mathrm{Bu}\text{-}4\text{-}X]_2$ complexes

Compound	X = H		X = *t*Bu molecule 1		X = *t*Bu molecule 2	
Yb···C(Me)	Yb(1)···C(28)	3.578(6)	Yb(1)···C(9)	3.65(4)	Yb(2)···C(67)	3.67(4)
	Yb(1)···C(8)	3.747(6)	Yb(1)···C(34)	3.65(2)	Yb(2)···C(48)	3.73(2)
C(Me)···C(Me)	C(14)···C(23)[a]	3.52(1)	C(17)···C(34)[a]	3.81(3)	C(57)···C(76)[a]	3.56(2)
	C(8)···C(22)[a]	3.77(1)	C(17)···C(27)[a]	3.86(3)	C(57)···C(75)[a]	3.96(3)
	C(9)···C(28)[b]	3.565(7)	C(8)···C(26)[b]	3.93(3)	C(48)···C(75)[a]	3.73(4)
	C(12)···C(27)[b]	3.790(9)	C(9)···C(35)[b]	3.81(3)	C(49)···C(67)[b]	3.65(3)
	C(12)···C(28)[b]	3.954(9)			C(66)···C(58)[b]	3.86(6)

[a] Both Me groups are on one Yb atom. – [b] Me groups on different Yb atoms.

radii. In addition to these contacts there are also a number just above the sum of the van der Waals radii.

Table 4. Selected bond lengths and angles for $[YbCp_2F]_3$ and $[Yb(MeCp)_2F]_4$

Distance (Å)		Angle (°)	
$[YbCp_2F]_3$			
Yb(1)–F(1)	2.147(9)	Yb(1)–F(1)–Yb(2)	154.1(4)
Yb(1)–F(3)	2.16(1)	Yb(1)–F(3)–Yb(3)	148.9(4)
Yb(2)–F(1)	2.146(9)	Yb(2)–F(2)–Yb(3)	154.6(4)
Yb(2)–F(2)	2.157(9)	F(1)–Yb(2)–F(2)	85.5(3)
Yb(3)–F(2)	2.143(9)	F(1)–Yb(1)–F(3)	88.7(3)
Yb(3)–F(3)	2.18(1)	F(2)–Yb(3)–F(3)	88.1(3)
<Yb–C>	2.59	Cen(1)–Yb(1)–F(1)	106.4
Yb(1)–Cen(1)	2.33	Cen(1)–Yb(1)–F(3)	107.2
Yb(1)–Cen(2)	2.33	Cen(2)–Yb(1)–F(1)	107.7
Yb(2)–Cen(3)	2.31	Cen(2)–Yb(1)–F(3)	109.7
Yb(2)–Cen(4)	2.31	Cen(1)–Yb(1)–Cen(2)	129.5
Yb(3)–Cen(5)	2.32	Cen(3)–Yb(2)–F(1)	107.6
Yb(3)–Cen(6)	2.32	Cen(3)–Yb(2)–F(2)	107.9
		Cen(4)–Yb(2)–F(1)	108.8
		Cen(4)–Yb(2)–F(2)	108.9
		Cen(3)–Yb(2)–Cen(4)	129.4
		Cen(5)–Yb(3)–F(2)	106.8
		Cen(5)–Yb(3)–F(3)	107.9
		Cen(6)–Yb(3)–F(2)	109.4
		Cen(6)–Yb(3)–F(3)	107.4
		Cen(5)–Yb(3)–Cen(6)	129.4
$[Yb(MeCp)_2F]_4$			
Yb(1)–F(1)	2.163(6)	F(1)–Yb(1)–F(2)	91.4(3)
Yb(1)–F(2)	2.173(6)	Yb(2)–F(1)–Yb(1)	178.9(4)
Yb(2)–F(1)	2.136(6)	F(1)–Yb(2)–F(2)	92.2(3)
Yb(2)–F(2)	2.145(6)	Yb(2)–F(2)–Yb(1)	168.4(3)
<Yb–C>	2.59	Cen(1)–Yb(1)–F(1)	107.6
Yb(1)–Cen(1)	2.31	Cen(1)–Yb(1)–F(2)	110.4
Yb(1)–Cen(2)	2.29	Cen(2)–Yb(1)–F(1)	107.1
Yb(2)–Cen(3)	2.31	Cen(2)–Yb(1)–F(2)	107.1
Yb(2)–Cen(4)	2.31	Cen(1)–Yb(1)–Cen(2)	127.2
		Cen(3)–Yb(2)–F(1)	106.5
		Cen(3)–Yb(2)–F(2)	108.0
		Cen(4)–Yb(2)–F(1)	107.9
		Cen(4)–Yb(2)–F(2)	108.0
		Cen(3)–Yb(2)–Cen(4)	128.2

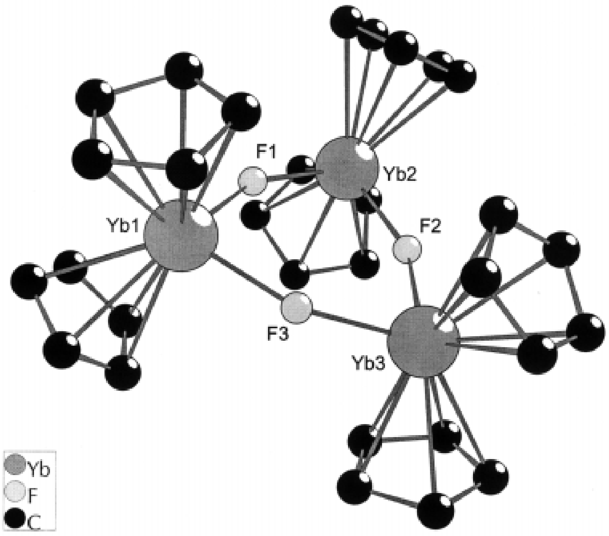

Figure 3. The molecular structure of $[YbCp_2F]_3$

2. $[YbCp_2F]_3$: Unsolvated bis(cyclopentadienyl)fluoroytterbium(III) crystallizes as a trimer with eight-coordinate ytterbium ions, and is the first *unsolvated unsubstituted* cyclopentadienyllanthanoid fluoride to be structurally characterized, though similar trimers have been observed for $[ScCp_2F]_3$,[15] $[Sm(C_5H_4\text{-}t\mathrm{Bu})_2F]_3$,[20] and $[Sm(C_5Me_5)_2Cl]_3$.[42] Selected bond lengths and angles are given in Table 4 and the structure is shown in Figure 3. The structure features a planar Yb_3F_3 ring with near equal Yb–F bond lengths, but with one Yb–F–Yb and one F–Yb–F angle slightly different from the other two. However, these slight variations are of little consequence and the structure is sufficiently symmetrical for ν(Yb–F) to be infrared inactive and observed only in the Raman spectrum (Table 1). There is little variation in <Ln–C> bond lengths between $[YbCp_2F]_3$ (Figure 3) and $[ScCp_2F]_3$,[15] $[Sm(C_5H_4\text{-}t\mathrm{Bu})_2F]_3$ [20] and $[Sm(C_5Me_5)Cl]_3$ [42] and in <Ln–F> between the three fluorides, when allowance is made for variation in Ln^{3+} radii. Thus subtraction of the ionic radius for eight-coordinate Ln^{3+} from <Ln–C> gives 1.61, 1.60, 1.63, and 1.65 Å for the respective compounds. These values are in the normal range[43] and compare with 1.60 Å similarly derived from <Yb–C> of $[YbCp_2F(THF)]_2$.[21] A similar subtraction from <Ln–F> of the first three compounds gives 1.17, 1.18, and 1.17 Å, respectively. Values from <Ln–F> of $[YbCp_2F(THF)]_2$ [21] (1.15 Å) and $[Sm\{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}_2F]_2$ [19] (1.22 Å) lie either side of the values for the trimers, and all are well below similarly derived values (1.36 and 1.41 Å) for the two different Yb–F bonds of the bulky $[Yb(OAr)_2F(THF)]_2$ complexes (above). Of the four trimeric bis(cyclopentadienyl)lanthanoid(III) halide structures (Figure 3 and refs.[15,20,42]), the present complex has the largest X–Ln–X (X = Cl or F) angle and the smallest Ln–X–Ln angle, a result that is unexpected since the group contains the complex of the much smaller Sc^{3+}. Although the cen–Yb–cen (cen = centroid of a Cp ring) angle is in the range (127–140°) for 8-coordinate complexes, it is close to the overlap with the range (113–129°) for 9-coordinate complexes (see literature cited in ref.[21]). The sum of the steric coordination numbers of the ligands[36] is quite low at 6.1, especially compared with 7.3 for $[YbCp_2F(THF)]_2$, and highlights the surprising failure to obtain a solvate from DME. A dimer with chelating DME and 10-coordinate ytterbium would have a sum of steric coordination numbers of 7.9. Whilst comparable with the value 8.0 for $[Yb(OAr)_2F(THF)]_2$ complexes, it may be too large when other alternatives are available. A monomer with chelating DME would have a reasonable value of 6.85, but the molecule would have only one stable Yb–F bond per Yb compared with two in dimers and trimers. However, a dimer with unidentate DME (known refs.[28,44] in lanthanoid chemistry) would allow two Yb–F bonds/Yb and a reasonable steric coordination number sum of 7.0. Despite this, the sterically unsaturated $[YbCp_2F]_3$ is preferred. With this structure, the non bonding Yb(n)···Yb(m) separations [(1)/(2) 4.186; (1)/(3) 4.185; (2)/(3) 4.196 Å] and F(n)···F(m) separations [(1)/(2) 2.885; (1)/(3) 2.975; (2)/(3) 2.981 Å] exceed those for the solvated dimer $[Yb(MeCp)_2F(THF)]_2$ (Yb···Yb 3.666 Å; F···F 2.465 Å). From the structural data for $[Sm(C_5H_3\text{-}1,3\text{-}(SiMe_3)_2)_2F]_2$,[19] a Yb···Yb separation of ca. 3.60 Å in the unsolvated dimer "$[YbCp_2F]_2$" can be estimated. This reinforces the lack of crowding revealed by steric coordination numbers.

3. $[Yb(MeCp)_2F]_4$: Crystallization of this heteroleptic fluoride from DME as a tetramer with eight-coordinate Yb^{III} is particularly surprising. Not only is the complex not solvated, but it is the first tetrameric bis(cyclopentadienyl)lanthanoid(III) fluoride. Previously only an unsolvated dimer,[19] trimers,[15,20] and a solvated dimer[21] have been isolated. The nearest similar structure is the mixed oxidation state ($Yb^{II,III}$) $[Yb_4(C_5Me_5)_6(\mu\text{-}F)_4]$,[16] which has eight-coordinate Yb^{III} and five-coordinate Yb^{II}. Selected bond lengths and angles for $[Yb(MeCp)_2F]_4$ are given in Table 4.

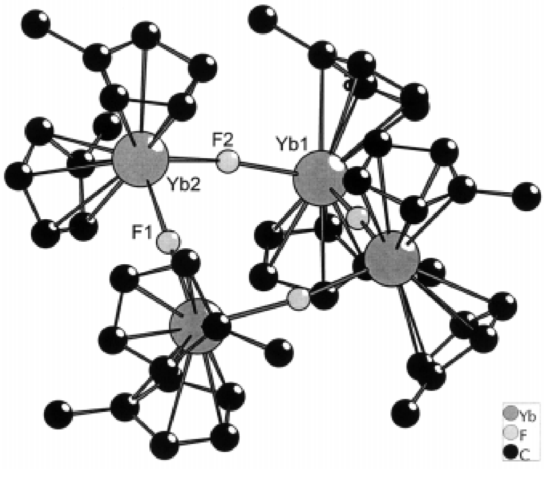

Figure 4. The molecular structure of $[Yb(MeCp)_2F]_4$

The structure is displayed in Figure 4. The eight-membered Yb_4F_4 ring is puckered with Yb–F–Yb angles near linear and F–Yb–F angles near 90° (Table 4). Similar F–Yb–F angles are observed in $[Yb_4(C_5Me_5)_6(\mu\text{-}F)_4]$,[16] but the Yb–F–Yb angles [160.0(2), 157.3(2)°] show much greater deviation from linearity than in $[Yb(MeCp)_2F]_4$. The four fluorine atoms are near coplanar (max. deviation 0.007 Å) with the plane parallel to the [101] plane, but the two different ytterbium atoms are very substantially displaced [Yb(1) +0.605 Å; Yb(2) −0.575 Å] from the F_4 plane. In $[Yb_4(C_5Me_5)_6(\mu\text{-}F)_4]$ the Yb^{III} atoms are similarly displaced from the F_4 plane, but the Yb^{II} atoms are only slightly displaced.[16] The average Yb–C and Yb–F distances are virtually identical with those of $[YbCp_2F]_3$, and subtraction of the ionic radius[35] for eight-coordinate Yb^{3+} gives 1.60 and 1.17 Å respectively. Although the methylcyclopentadienyl ligand is somewhat bulkier than Cp, the cen–Yb–cen angles are marginally smaller for the MeCp complex and are approaching the limit for eight-coordinate complexes (see literature cited in ref.[21]). As with $[YbCp_2F]_3$, the sum of the steric coordination numbers for the ligands[36] is small at 6.3, and contrasts 7.5 for the solvated dimer $[Yb(MeCp)_2F(THF)]_2$ (below). Again, a solvated monomer "$[Yb(MeCp)_2F(DME)]$" with chelating DME or a dimer solvated with unidentate DME are sterically viable. Formation of a tetramer leads to even longer Yb···Yb and F···F separations (4.296/4.299 and 3.088/3.106 Å, respectively) than in the trimer with the *less bulky* ligand. Whilst this should minimise non-bonding interactions, several molecules with closer Ln···Ln and F···F separations are isolable. In particular, the highly crowded $[Yb(OAr)_2F(THF)]_2$ dimers have average Yb···Yb separations of 3.635 Å and average F···F separations of 2.49 Å.

4. $[YbCp_2F(OPPh_3)]_2$ and $[Yb(MeCp)_2F(THF)]_2$: Both complexes were established as fluoride-bridged dimers with nine-coordinate ytterbium. The structures are displayed in Figure 5 and Figure 6, and bond length and angle data are compared with those of $[YbCp_2F(THF)]_2$ in Table 5. Two independent molecules are observed for the phosphane oxide complex, but data are listed for only one owing to the low precision of the determination. A structure was needed for the previously reported[3] $[Yb(MeCp)_2F(THF)]$, since both monomeric $[Yb(C_5Me_5)_2F(THF)]$[3] and dimeric $[YbCp_2F(THF)]_2$[21] structural analogues exist.

The arrangement of centroids of the cyclopentadienyl rings, the fluorines, and the oxygen donor atom can be viewed as distorted trigonal bipyramidal with oxygen and one bridging fluoride in the apical positions. For the phosphane oxide complex, within the error limits, the Yb–C, Yb–F, and Yb–O distances show no unexpected features. The bond lengths of $[Yb(MeCp)_2F(THF)]_2$ show interesting trends, when compared with those of $[YbCp_2F(THF)]_2$.[21] From <Yb–C> and <Yb–F> values, there is a hint of bond lengthening in the methylcyclopentadienyl compound, but the size of the estimated standard deviations in the earlier determination[21] makes the comparison uncertain. However Yb–O(THF) is clearly larger for $[Yb(MeCp)_2F(THF)]_2$. Subtraction of the ionic radius for nine-coordinate Yb^{3+} gives 1.45 Å, which is higher than usual (1.34 ± 0.05 Å)[38] for THF complexes of

Table 5. Selected bond lengths and angles of [Yb(MeCp)$_2$F(THF)]$_2$, [YbCp$_2$F(THF)]$_2$,[21] and [YbCp$_2$F(OPPh$_3$)]$_2$

	[Yb(MeCp)$_2$F(THF)]$_2$	[YbCp$_2$F(THF)]$_2$ [a]	[YbCp$_2$F(OPPh$_3$)]$_2$ molecule 2
Distance (Å)			
Yb(1)–F(1)	2.186(3)	2.161(9)	2.18(2)
Yb(1)–F(1a)	2.231(3)	2.215(9)	2.20(2)
Yb(1)–O(1)	2.490(4)	2.41(1)	2.19(2)
<Yb–C>	2.67	2.64	2.65
<Yb–Cen>	2.39	2.37	2.37
Yb···Yb	3.666	3.651	3.686
Angle (°)			
F(1)–Yb(1)–F(1a)	67.8(1)	66.9(4)	65.1(9)
Yb(1)–F(1)–Yb(1a)	112.2(1)	113.1(4)	114.9(9)
O(1)–Yb(1)–F(1)	73.5(1)	72.9(3)	76.2(8)
O(1)–Yb(1)–F(1a)	141.2	139.8(3)	141.3(8)
O(1)–Yb(1)–Cen(1)	97.0	98.9	100
O(1)–Yb(1)–Cen(2)	98.5	98.5	97
Cen(1)–Yb(1)–Cen(2)	125.2	123.9	124
Cen(1)–Yb(1)–F(1)	114.0	116.4	120
Cen(1)–Yb(1)–F(1a)	100.9	99.7	98
Cen(2)–Yb(1)–F(1)	120.8	119.6	116
Cen(2)–Yb(1)–F(1a)	98.7	100.1	100

[a] Numbering of F(1) and F(1a) inverted from that reported (ref.[21]) to correspond to that used [Yb(1)–F(1) shortest] in the present molecules.

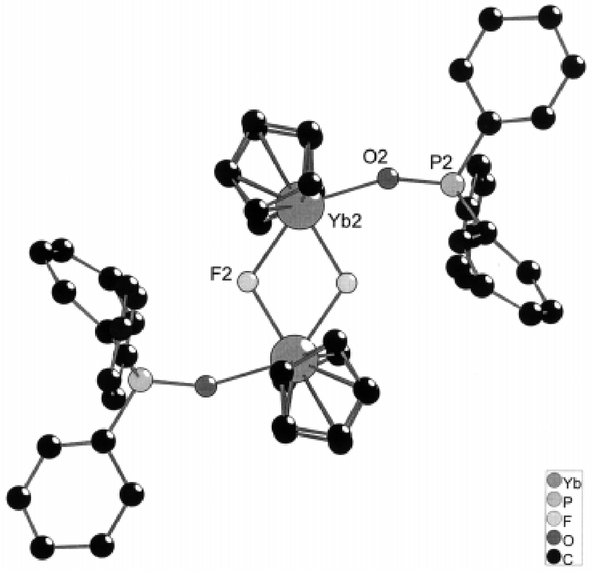

Figure 5. The molecular structure of molecule 2 of [YbCp$_2$F(OPPh$_3$)]$_2$

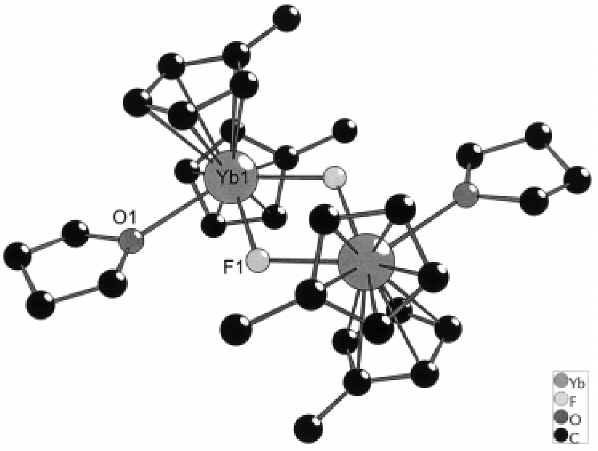

Figure 6. The molecular structure of [Yb(MeCp)$_2$F(THF)]$_2$

cyclopentadienyllanthanoids, e.g. 1.37 Å for [YbCp$_2$F(THF)]$_2$ [21] and 1.34 Å for monomeric [Yb(C$_5$Me$_5$)$_2$F(THF)], and approaching values (1.49–1.59 Å)[24,26,37] derived from Yb-O(THF) of THF complexes of bulky lanthanoid aryloxides (see e.g. [Yb(OAr)$_2$F(THF)]$_2$ above). Thus the small increase in cyclopentadienyl ligand bulkiness from [YbCp$_2$F(THF)]$_2$ to [Yb(MeCp)$_2$F(THF)]$_2$ (sum of ligand steric coordination numbers 7.3 and 7.5 respectively) is sufficient to weaken the Yb–O bond significantly. It also becomes apparent why [Yb(C$_5$Me$_5$)$_2$F(THF)][3] is monomeric, not dimeric. The dimer would have a ligand steric coordination number sum of 8.2, higher even than for [Yb(OAr)$_2$F(THF)]$_2$ (8.0), and THF would plausibily be dissociated, whereas the steric coordination number sum for the monomer is 7.2, comparable with [YbCp$_2$F(THF)]$_2$, permitting an uncrowded Yb–O bond.

From the packing diagrams, it is evident that the molecules of the above dimers, trimer, and tetramer are well separated and non interacting. In [YbCp$_2$F]$_3$, the trimeric molecules are parallel to one another in alternating layers, whilst in [Yb(MeCp)$_2$F]$_4$ the planes of the four fluorines of the tetramers align parallel to the [101] plane. The two independent molecules of [Yb(OC$_6$H$_2$-2,4,6-tBu$_3$)$_2$-F(THF)]$_2$ are perpendicular to each other.

Conclusions

The present study establishes that a range of heteroleptic lanthanoid fluorides can be prepared, including aryloxides, and that considerable structural variety is exhibited. A heteroleptic aryloxide chloride analogous to the

$[Yb(OAr)_2F(THF)]_2$ complexes is known, viz. $[Sm(OC_6H_2\text{-}2,6\text{-}t\mathrm{Bu}_2\text{-}4\text{-}Me)_2Cl(THF)]_2$,[45] but the larger iodide gives a slightly more crowded monomer $[Ln(OAr)_2I(THF)_2]$ (Ln = Sm[45] or Yb[46]). There are both chloride and hydride analogues of $[Ln(Cp\ \text{or}\ MeCp)_2FL]_2$ where L = THF (see ref.[21] and literature cited therein), but not for L = Ph_3PO, and $[Sm(C_5Me_5)_2Cl]_3$ [42] is related to $[YbCp_2F]_3$. However there is no homocyclic chloride tetramer structurally similar to $[Yb(MeCp)_2F]_4$.[12–14] Although the tetramer $[GdCp_2Cl]_4$ is known, the structure is a dimer of dimers with a ladder arrangement[13]. Isolation of $[YbCp_2F]_3$ and $[Yb(MeCp)_2F]_4$ unsolvated from DME is striking, and contrasts the formation of $[Yb(Cp\ \text{or}\ MeCp)_2F(THF)]_2$. The corresponding DME complexes would have the more unusual[28,44] unidentate DME and appear unable to compete with the very uncrowded unsolvated trimer and tetramer.

Experimental Section

General: The lanthanoid(II) reactants and lanthanoid(III) products are extremely air- and moisture-sensitive, hence all operations were carried out under purified Ar or N_2. Unless indicated otherwise, handling methods and solvent purification were as described previously.[47] – Infrared spectra (4000–600 cm^{-1}) were obtained for Nujol mulls between NaCl plates with a Nicolet 5PC-FTIR-spectrometer or as KBr disks with a Bruker 66V/S instrument. Far infrared spectra (600–50 cm^{-1}) were recorded for polyethylene disks with a Bruker IFS 66V/S spectrometer. – The Raman spectrum was obtained for a solid sample in a sealed capillary with a Bruker FRA 106/S instrument. – Mass spectra were recorded with a Varian MAT CH5-DF mass spectrometer. The aryloxofluoroytterbium(III) complexes showed only ligand ions and the data are not listed. For the cyclopentadienylfluoroytterbium(III) compounds, clusters with the correct isotope pattern for the assignments given were observed. – The Energy Dispersive Analysis through X-ray (EDAX) measurement was carried out with an ECON IV PV 9900–26 instrument, II. Physikalische Institut, Universität zu Köln. – Metal analysis were effected as described previously.[47] Fluorine analyses for samples sealed under Ar in gelatin capsules were carried out by the method of Campbell.[48] Perfluorodecalin and perfluoro(methylcyclohexane), from Avocado Chemicals, were dried over molecular sieves (4 Å), degassed, and vacuum transferred to storage vessels. Ytterbium(II) aryloxides were prepared as described previously[26] and had IR spectra in agreement with those reported. Far IR spectra – for comparison with trivalent complexes (below): $[Yb(OC_6H_3\text{-}2,6\text{-}t\mathrm{Bu}_2)_2(THF)_3]$: ṽ = 590 w cm^{-1}, 534 m (br), 490 w, 459 w, 441 m, 383 w, 333 s, 309 m, 270 w, 184 w, 143 w (br). $[Yb(OC_6H_2\text{-}2,6\text{-}t\mathrm{Bu}_2\text{-}4\text{-}Me)_2(THF)_3]$: ṽ = 577 m cm^{-1}, 564 w, 527 s (br), 501 s, 353 s, 302 s, 223 w, 180 w, 149 w, 116 w. $[Yb(OC_6H_2\text{-}2,4,6\text{-}t\mathrm{Bu}_3)_2(THF)_3]$: ṽ = 578 vw cm^{-1}, 537 m, 519 s, 491 vw, 447 m, 358 s (br), 263 w (br), 170 w, 144 m, 87 w. The divalent ytterbocenes $[YbCp_2(DME)]$ and $[Yb(MeCp)_2(THF)]$ were also prepared by reported methods.[49]

Bis(aryloxo)fluorolanthanoid(III) Complexes $[Yb(OAr)_2F(THF)]_2$: The appropriate $[Yb(OC_6H_2\text{-}2,6\text{-}t\mathrm{Bu}_2\text{-}4\text{-}R)_2(THF)_3]$ (R = H, Me, *t*Bu) complex (ca. 0.30–0.40 mmol) and perfluorodecalin (mol ratio 4:1) were stirred in THF (2.5 mL) at room temperature for 48 h. The resulting suspension was heated to 50 °C and then cooled to room temperature, when the deposited solid was filtered off and washed twice with THF (0.5 mL) and dried for at least 3 h under vacuum. The products were obtained as bright orange microcrystalline powders in 25–30% yield.

Di{bis(2,6-di-*tert*-butylphenolato)(μ-fluoro)(tetrahydrofuran)ytterbium(III)}: IR (Nujol): ṽ = 3077 w cm^{-1}, 3063 w, 1584 w, 1410 s, 1358 m, 1316 w, 1260 s, 1246 s, 1200 m, 1130 w, 1105 m, 1036 w, 1003 m, 953 w, 924 w, 914 w, 870 s, 821 w, 750 s, 662 m. – Far-IR: ṽ = 589 w cm^{-1}, 573 w, 562 w, 547 s, 526 w, 494 m, 451 m, 387 s (br), 338 vs, 304 m, 279 m, 207 s, 140 w, 125 w. – $C_{64}H_{100}F_2O_6Yb_2$ (1349.52): calcd. F 2.82, Yb 25.64; found F 2.59, Yb 25.41. Single crystals were obtained by storage of a THF solution in a dry box for 4 weeks.

Di{bis(2,6-di-*tert*-butyl-4-methylphenolato)(μ-fluoro)(tetrahydrofuran)ytterbium(III)}: IR (KBr disk): ṽ = 3059 w cm^{-1}, 2955 s, 2913 s, 2869 m, 1459 m, 1419 s, 1386 m, 1356 w, 1260 s (br), 1219 m, 1202 w, 1149 w, 1122 w, 1067 w, 1020 m, 915 w, 887 w, 861 m, 830 m, 807 w, 780 w. – Far-IR: ṽ = 577 w cm^{-1}, 563 w, 537 vs, 401 w (sh), 381 s (br), 356 m, 325 w (sh), 314 m, 302 m, 219 w, 190w. – $C_{68}H_{108}F_2O_6Yb_2$ (1408.70): calcd. F 2.70, Yb 24.62; found F 2.50, Yb 24.53.

Di{(μ-fluoro)(tetrahydrofuran)bis(2,4,6-tri-*tert*-butylphenolato)ytterbium(III)}: IR (Nujol): ṽ = 3067 w cm^{-1}, 1584 w, 1408 s, 1360 m (sh), 1260 s, 1246 s, 1200 w, 1130 w, 1105 w, 1036 w, 1003 w, 953 w, 914 w, 870 m, 822 w, 797 w, 750 s, 662 w. – Far-IR: ṽ = 539 s cm^{-1}, 475 w (sh), 461 m, 375 s (br), 359 s (sh), 304 m, 273 w, 206 m, 183 w. – $C_{80}H_{132}F_2O_6Yb_2$ (1574.00): calcd. F 2.41, Yb 21.99; found F 2.42, Yb 22.18. Single crystals of the complex as a tris(tetrahydrofuran) solvate were obtained by storage of a saturated THF solution at –20 °C for 2 d, and were shown to contain fluorine by EDAX measurements.

Bis(cyclopentadienyl)fluoroytterbium(III) Complexes. – Tri{bis(cyclopentadienyl)(μ-fluoro)ytterbium(III)}: To a solution of $[YbCp_2(DME)]$ (1.0 g, 2.5 mmol) in DME (10 mL), perfluoro(methylcyclohexane) (0.23 g, 0.51 mmol) was added. The biphasic system was stirred for 48 h at room temperature. The resulting yellow precipitate was filtered off and washed twice with DME (3 mL). The product was dried for 3 h under vacuum (yield 45%). – IR (Nujol): ṽ = 3077 w cm^{-1}, 2708 w, 1653 w, 1576 w, 1152 w, 1067 w, 1011 s, 774 vs, 667 w, 621 w. – Far IR: ṽ = 480 s (br) cm^{-1}, 265 m, 230 w, 194 m, 114 w. – Raman Spectrum: ṽ = 938 w cm^{-1}, 629 s, 336 m, 119 m. – MS (20 eV, 260 °C), *m*/*z* (%): 901 (100) $[Yb_3Cp_5F_3]^+$, 836 (2.5) $[Yb_3Cp_4F_3]^+$, 644 (10) $[Yb_2Cp_4F_3]^+$, 625 (5.4) $[Yb_2Cp_4F_2]^+$, 579 (38) $[Yb_2Cp_3F_2]^+$, 533 (2.6) $[Yb_2Cp_2F_2]^+$, 369 (18) $[YbCp_3]^+$, 304 (76) $[YbCp_2]^+$, 239 (31) $[YbCp]^+$, 173 (1.6) $[Yb]^+$, 66 (41) $[CpH]^+$, 65 (27) $[Cp]^+$, 39 (24) $[HF_2]^+$, 19 (57) $[F]^+$. – $C_{30}H_{30}F_3Yb_3$ (966.69): calcd. F 5.90, Yb 53.70; found F 5.66 Yb 53.36. – A saturated DME solution was stored for 3 weeks at –20 °C giving yellow crystals of the title compound suitable for X-ray crystallography. An analogous preparation using perfluorodecalin gave the compound in 49% yield.

Tetra{(μ-fluoro)bis(methylcyclopentadienyl)ytterbium(III)}: To $[Yb(MeCp)_2(THF)]$ (1.06 g, 2.6 mmol) and perfluorodecalin (0.30 g, 0.66 mmol), DME (2.5 mL) was added. The solution became emerald green and the biphasic system was stirred for 24 h at room temperature. An orange solid was precipitated after 2 h. This was filtered off and washed twice with DME (0.5 mL) and dried for 3 h under vacuum (yield 25%). – IR (KBr): ṽ = 3083 w cm^{-1}, 2927 m, 2864 m, 1703 w, 1634 w, 1534 w, 1486 w, 1454 m, 1381 w, 1350 w, 1237 w, 1038 s, 933 m, 830 s, 768 vs, 623 w. – Far IR: ṽ = 470 vs (br) cm^{-1}, 328 s, 260 s, 230 m, 197 m, 164 w, 144 w. – MS (20 eV, 205 °C), *m*/*z* (%): 971 (44) $[Yb_3(MeCp)_5F_3]^+$, 957 (29)

Table 6. Crystallographic data for $[Yb(OC_6H_3\text{-}2,6\text{-}tBu_2)_2F(THF)]_2$ and $[Yb(OC_6H_2\text{-}2,4,6\text{-}tBu_3)_2F(THF)]_2 \cdot 3$ THF

	$[Yb(OC_6H_3\text{-}2,6\text{-}tBu_2)_2F(THF)]_2$	$[Yb(OC_6H_2\text{-}2,4,6\text{-}tBu_3)_2F(THF)]_2 \cdot 3$ THF
Empirical formula	$C_{64}H_{100}F_2O_6Yb_2$	$C_{92}H_{156}F_2O_9Yb_2$
Formula weight [g/mol]	1349.52	1790.25
Temperature [K]	293(2)	123(2)
Radiation Mo-K_α [pm]	71.073	71.073
Crystal system	orthorhombic	triclinic
Space group	*Pbca* (Nr. 61)	$P\bar{1}$ (No. 2)
Cell dimensions [Å, °]	$a = 19.628(2)$ $b = 15.567(2)$ $c = 20.728(2)$	$a = 15.871(3)$ $b = 16.098(3)$ $c = 19.346(3)$ $\alpha = 92.96(2)$ $\beta = 106.24(2)$ $\gamma = 101.41(2)$
Volume/10^6 [pm^3]	6333(1)	4622(1)
Z	4	2
Density [g/cm^3] calcd.	1.415	1.286
Absorption coefficient [mm^{-1}]	2.844	1.961
$F(000)$	2759	1876
2θ range	$3.88° < 2\theta < 45°$	$4.0° < 2\theta < 42°$
Diffractometer	STOE-IPDS	STOE-IPDS
Number of reflections collected	40376	25790
Data/restraints/parameters	4138/0/334	9493/0/901
Goodness of Fit	0.905	1.000
R indices [$I > 2\sigma(I)$]	$R1 = 0.0291$, $wR2 = 0.0364$	$R1 = 0.0504$, $wR2 = 0.1257$
R indices (all data)	$R1 = 0.0613$, $wR2 = 0.0388$	$R1 = 0.0636$, $wR2 = 0.1365$

Table 7. Crystallographic data for $[YbCp_2F]_3$, $[Yb(MeCp)_2F]_4$, $[Yb(MeCp)_2F(THF)]_2$, and $[YbCp_2F(OPPh_3)]_2$

	$[YbCp_2F]_3$	$[Yb(MeCp)_2F]_4$	$[Yb(MeCp)_2F(THF)]_2$	$[YbCp_2F(OPPh_3)]_2$
Empirical formula	$C_{30}H_{30}F_3Yb_3$	$C_{48}H_{56}F_4Yb_4$	$C_{32}H_{44}F_2O_2Yb_2$	$C_{56}H_{50}F_2O_2P_2Yb_2$
Formula weight [g/mol]	966.69	1401.09	844.75	1200.98
Temperature [K]	293(2)	293(2)	293(2)	293(2)
Radiation Mo-K_α [pm]	71.073	71.073	71.073	71.073
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	*Cc* (Nr. 9)	*Ia* (Nr. 9)	$P2_1/c$ (Nr. 14)	$P\bar{1}$(No. 2)
Cell dimensions [Å, °]	$a = 17.331(3)$ $b = 15.544(2)$ $c = 10.691(2)$ $\beta = 91.59(2)$	$a = 11.820(2)$ $b = 8.5812(9)$ $c = 22.470(4)$ $\beta = 92.98(4)$	$a = 8.575(1)$ $b = 19.444(2)$ $c = 9.313(1)$ $\beta = 98.05(2)$	$a = 10.525(5)$ $b = 12.481(7)$ $c = 22.35(2)$ $\alpha = 97.2(1)$ $\beta = 92.63(1)$ $\gamma = 106.0(6)$
Volume/10^6 [pm^3]	2878.9(7)	2276.1(6)	1537.4(3)	2789(4)
Z	4	2	2	2
Density [g/cm^3] calcd.	2.230	2.044	1.825	1.430
Absorption coefficient [mm^{-1}]	9.290	7.839	5.817	3.432
F(000)	1787	1320	820	1180
2θ range	$5.14° < 2\theta < 50.50°$	$5.86° < 2\theta < 50.00°$	$4.88° < 2\theta < 56.20°$	$4.92° < 2\theta < 37.50°$
Diffractometer	STOE-IPDS	STOE-IPDS	STOE-IPDS	STOE-IPDS
Number of reflections collected	10357	7833	14262	10478
Data/restraints/parameters	4994/2/277	3648/1/262	3454/0/172	4163/9/297
Goodness of Fit	1.000	0.985	0.941	0.703
R-indices [$I > 2\sigma(I)$]	$R1 = 0.0420$, $wR2 = 0.0737$	$R1 = 0.0282$, $wR2 = 0.0604$	$R1 = 0.0315$, $wR2 = 0.0575$	$R1 = 0.0719$, $wR2 = 0.1566$
R-indices (all data)	$R1 = 0.0639$, $wR2 = 0.0769$	$R1 = 0.0344$, $wR2 = 0.0622$	$R1 = 0.0615$, $wR2 = 0.0637$	$R1 = 0.1701$, $wR2 = 0.1876$

$[Yb_3(MeCp)_4(Cp)F_3]^+$, 942 (7.2) $[Yb_3(MeCp)_3(Cp)(C_5H_4)F_3]^+$, 700 (18) $[Yb_2(MeCp)_4F_2]^+$, 686 (5.4) $[Yb_2(MeCp)_3(Cp)F_2]^+$, 621 (82) $[Yb_2(MeCp)_3F_2]^+$, 607 (21) $[Yb_2(MeCp)_2(Cp)F_2]^+$, 594 (1.1) $[Yb_2(MeCp)(Cp)(C_5H_6)F_2]^+$, 542 (10) $[Yb_2(MeCp)_2F_2]^+$, 528 (1.4) $[Yb_2(MeCp)_2(Cp)F_2]^+$, 463 (3.3) $[Yb_2(MeCp)F_2]^+$, 411 (16) $[Yb_3(MeCp)_3]^+$, 397 (4.1) $[Yb(MeCp)_2(Cp)]^+$, 332 (100) $[Yb(MeCp)_2]^+$, 318 (14) $[Yb(MeCp)(Cp)]^+$, 253 (39) $[Yb(MeCp)]^+$, 239 (3.6) $[Yb(Cp)]^+$, 174 (2.2) $[Yb]^+$, 79 (57) $[MeCp]^+$, 67 (10.3) $[CpH]^+$. – $C_{48}H_{56}F_4Yb_4$ (1401.09): calcd. F 5.42, Yb 49.40; found F 5.27, Yb 49.61. Single crystals for X-ray analysis were obtained by isothermal evaporation of DME in a U-tube, with the solution in one arm at room temperature, and the other arm cooled in liquid nitrogen.

Di{bis(cyclopentadienyl)(μ-fluoro)(triphenylphosphane oxide)-ytterbium(III)}: $[YbCp_2(DME)]$ (0.59 g, 1.5 mmol) and perfluorodecalin (0.17 g, 3.8 mmol) were stirred in THF (4 mL) at room temperature for 24 h. The colour of the solution changed to dark brown and a yellow solid precipitated. To this mixture, THF (4 mL) and $OPPh_3$ (0.42 g, 1.5 mmol) were added. After stirring for 24 h at room temperature and 3 d at 50 °C, the resulting yellow precipitate was filtered off. The pale yellow solid was washed twice with

THF (2 mL) and dried for 3 h under vacuum (yield 34%). – IR (KBr): $\tilde{\nu}$ = 3084 m cm^{-1}, 3059 m, 1650 w, 1591 w, 1486 w, 1438 s, 1179 s (br), 1124 s, 1098 m, 1071 w, 1012 s, 926 w, 873 w, 846 w, 779 s (br), 747 s, 726 s, 692 s. – Far IR: $\tilde{\nu}$ = 540 s cm^{-1}, 514 w, 476 s, 458 s (br), 421 w, 389 w, 306 m, 292 m, 254 m, 225 w, 203 m (sh), 195 s, 141 w, 117 w. – MS (20 eV, 280 °C), *m*/*z* (%): 902 (1.7) $[Yb_3Cp_5F_3H]^+$, 643 (0.7) $[Yb_2Cp_3F_2(C_5H_4)]^+$, 578 (1.4) $[Yb_2Cp_2F_2(C_5H_4)]^+$, 513 (0.3) $[Yb_2CpF_2(C_5H_4)]^+$, 369 (8.8) $[YbCp_3]^+$, 304 (18) $[YbCp_2]^+$, 278 (57) $[OPPh_3]^+$, 277 (100) $[OPPh_2(C_6H_4)]^+$, 239 (15) $[CpYb]^+$, 201 (17) $[OPPh_2]^+$, 185 (8.6) $[PPh_2]^+$, 154 (3.6) $[Ph_2]^+$, 77 (4.3) $[Ph]^+$, 65 (2.9) $[Cp]^+$, 39 (3.5) $[HF_2]^+$. – $C_{56}H_{50}F_2O_2P_2Yb_2$ (1200.98): calcd. F 3.16; found F 3.22. Slow evaporation of the THF filtrate in a U-tube yielded yellow needles of $[YbCp_2F(OPPh_3)]_2$ suitable for X-ray crystallography.

Di{(μ-fluoro)bis(methylcyclopentadienyl)(tetrahydrofuran)ytterbium(III)}: $[Yb(MeCp)_2(THF)]$ (0.76 g, 1.8 mmol) and perfluorodecalin (0.21 g, 4.5 mmol) were stirred for 48 h in THF (2.5 mL) at room temperature. The mixture was warmed up to 50 °C for 2 h and then slowly cooled. The microcrystalline precipitate was filtered off and washed twice with 0.5 mL of THF (yield 24%). – IR (Nujol): $\tilde{\nu}$ = 3079 w cm^{-1}, 1239 w, 1067 w, 1049 m, 1034 m, 932 m, 835 s, 766 vs, 616 w. – Far IR: $\tilde{\nu}$ = 468 vs (br) cm^{-1}, 331 s, 268 s, 229 m, 197 m, 116 w. – MS (20 eV, 215 °C), *m*/*z* (%): 970 (47) $[Yb_3(MeCp)_4(CpCH_2)F_3]^+$, 956 (29) $[Yb_3(MeCp)_4(C_5H_4)F_3]^+$, 943 (7.7) $[Yb_3(MeCp)_3(Cp)_2F_3]^+$, 700 (12) $[Yb_2(MeCp)_4F_2]^+$, 684 (3.4) $[Yb_2(MeCp)_3(Cp)F_2]^+$, 621 (38) $[Yb_2(MeCp)_3F_2]^+$, 609 (8.6) $[Yb_2(MeCp)_2(C_5H_7)F_2]^+$, 542 (4.9) $[Yb_2(MeCp)_2F_2]^+$, 528 (1.1) $[Yb_2(MeCp)(Cp)F_2]^+$, 411 (29) $[Yb(MeCp)_3]^+$, 397 (7.3) $[Yb(MeCp)_2(Cp)]^+$, 332 (100) $[Yb(MeCp)_2]^+$, 318 (17) $[Yb(MeCp)(Cp)]^+$, 253 (51) $[Yb(MeCp)]^+$, 239 (6.6) $[Yb(Cp)]^+$, 174 (2.2) $[Yb]^+$, 79 (66) $[MeCp]^+$, 39 (12) $[HF_2]^+$. – $C_{32}H_{44}F_2O_2Yb_2$ (844.75): calcd. F 4.50, Yb 41.00; found F 4.29, Yb 41.38. – Single crystals were obtained by isothermal evaporation of the filtrate in a U-tube. An attempt to effect a similar synthesis with perfluoro(methylcyclohexane) at room temperature for 7 d showed the reaction to be very slow.

X-ray Structure Determination: Crystals were mounted in 0.2/0.3 mm diameter glass capillaries under dry argon in a glove box. Data sets were measured with an IPDS diffractometer (imaging plate system STOE) using Mo-K_α radiation and a graphite monochromator (Table 6 and Table 7). Structure determinations were carried out with the programs SHELX-96 and SHELX-97.[50] Numerical absorption corrections for $[YbCp_2F]_3$, $[Yb(MeCp)_2F]_4$, $[Yb(MeCp)_2F(THF)]_2$, and $[Yb(OC_6H_2\text{-}2,6\text{-}t\mathrm{Bu}_2\text{-}4\text{-}X)_2F(THF)]_2$ were run after crystal face optimisation (X-Shape[51] and X-RED[52]). Neutral atom scattering factors were from International Tables, vol. C.[53] Complete lists of atomic coordinates, bond lengths and angles, thermal parameters, and hydrogen atom coordinates are available from the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-136401–136406. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB121EZ (UK) [Fax: (int. code) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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