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Organolanthanoids: XXII. [1] The synthesis and X-ray structure of dimeric $[YbCp_2F(THF)]_2$ (Cp = cyclopentadienyl; THF = tetrahydrofuran)

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Abstract

Reaction of $YbCp_2(DME)$ (Cp = cyclopentadienyl; DME = 1,2-dimethoxyethane) with perfluorodecalin or perfluoro(methylcyclohexane) in THF yields $[YbCp_2F(THF)]_2$. These are the first examples of C–F activation of saturated perfluorocarbons by a lanthanoid organometallic. The X-ray crystal structure of $[YbCp_2F(THF)]_2$ (monoclinic, $P2_1/c$, $a = 7.9901(12)$, $b = 20.411(4)$, $c = 8.5957(12)$ Å; $\beta = 104.70(2)°$, $Z = 2$, $R_1 = 0.0495$, for 1107 observed data) shows the complex to be dimeric with bridging fluorides and formal nine coordination for ytterbium. $YbCp_2F$ has also been obtained by oxidation of $YbCp_2(DME)$ with AgF or HgF_2. © 1998 Elsevier Science S.A.

Keywords: Ytterbium; Cyclopentadienyl; Oxidation; Fluoride; X-ray structure; C–F activation

1. Introduction

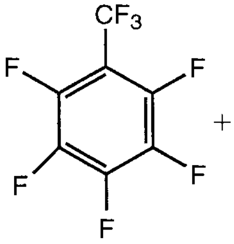
Cyclopentadienyl rare earth fluorides have proved elusive species. $(ScCp_2F)_3$ [2], $(Sm(Bu^tC_5H_4)_2F)_3$ [3], $Yb(C_5Me_5)_2F(L)$ (L = THF or Et_2O) [4], some $Yb_y(C_5Me_5)_xF_z$ [4–6] clusters, and the novel salt $[(Me_2N)_3SO]^+[Cp_3PrFPrCp_3]^-$ [7], represent the entire field of crystallographically characterised compounds. Since this paper was submitted, the complex $[Sm(C_5H_3(SiMe_3)_2\text{-}1,3)_2F]_2$ has also been reported [8]. In addition $Yb(MeC_5H_4)_2F(THF)$ was reported and was assumed to be monomeric by analogy with the C_5Me_5 compounds [4], and $Ln(C_5Me_5)_2F(OEt_2)$ (Ln = Sm, Eu) were also prepared [4]. There are no reported syntheses of unsubstituted $LnCp_2F$ complexes, and certainly none with products identified by X-ray crystallography [9,10]. We now report a facile new synthetic route to $YbCp_2F$ and the X-ray structure of $YbCp_2F(THF)$, which unexpectedly is a nine-coordinate, fluoride-bridged dimer.

2. Results and discussion

Oxidation of $YbCp_2(DME)$ with perfluorodecalin (Eq. (1)) or perfluoro(methylcyclohexane) (Eq. (2)) in THF, readily yields $YbCp_2F(THF)$ at room temperature.

$$\mathrm{YbCp_2(DME)} + \mathrm{C_{10}F_{18}} \xrightarrow[-\mathrm{DME}]{\mathrm{THF}} [\mathrm{YbCp_2F(THF)}]_2 + \text{unsaturated fluorocarbons} \tag{1}$$

$$\mathrm{YbCp_2(DME)} + \mathrm{C_6F_{11}CF_3} \xrightarrow[-\mathrm{DME}]{\mathrm{THF}} [\mathrm{YbCp_2F(THF)}]_2 \tag{2}$$

$+$  $+p$-, m- and o-H-$C_6F_4CF_3$

The genesis of this reaction lies in the successful oxidation of $YbCp_2$ with chloro-, bromo-, and iodo-ethanes

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to give $(LnCp_2X)_2$ (X = Cl, Br, I) [1], and in the use of perfluorodecalin as an oxidant in bis(cyclopentadienyl)Ti(Zr) systems [11,12]. This is the first oxidation of a Ln(II) complex with a saturated perfluorocarbon. Several $Ln(C_5Me_5)_2F(L)$ (Ln = Yb, Eu, Sm, L = Et_2O; Ln = Yb, L = THF) compounds and $Yb(MeC_5H_4)_2F(THF)$ have been prepared by oxidation of the appropriate substituted bis(cyclopentadienyl)lanthanoid(II) with perfluoroolefins including perfluoro-2,4-dimethyl-3-ethylpent-2-ene and perfluorocyclohexene and the reaction was often light induced [4]. Other reactions of $Yb(C_5Me_5)_2$ complexes with a suite of unsaturated fluorocarbons, gave polynuclear clusters [4] and mixed oxidation state ($Yb^{II,III}$) complexes [5,6]. The saturated fluorocarbons C_2F_6 and CF_3CH_3 were found to be unreactive [5,6]. Although the organic products were not investigated for Eq. (1), Eq. (2) with the simpler fluorocarbon reactant was shown to give perfluorotoluene and *p*-, *m*-, and *o*-$HC_6F_4CF_3$ in a ratio of 16:5:1:1. This indicates that defluorination of perfluoro(methylcyclohexane) is slower than defluorination of unsaturated intermediates, e.g., perfluoromethylcyclohexenes (see also Ref. [4]). Perfluorotoluene is an established product of other defluorination reactions of perfluoro(methylcyclohexane) [13], e.g., with sodium oxalate at 230°C [14], while defluorination of perfluorotoluene by Zn(Cu) occurs *para* to the CF_3 group probably via the radical anion [15]. In the present case, predominant formation of *p*-$HC_6F_4CF_3$ but with some of the other two isomers seems consistent with a radical anion intermediate, which would not be expected to defluorinate entirely regiospecifically. The relative reactivities in defluorination $C_{10}F_{18} > C_6F_{11}CF_3$, are consistent with reduction of these substrates by sodium benzophenone ketyl [16].

We have also prepared $YbCp_2F$ by oxidation of $YbCp_2(DME)$ with HgF_2 or AgF in THF (Eq. (3)) or DME (Eq. (4)).

$$2YbCp_2(DME) + HgF_2 \xrightarrow{THF} 2YbCp_2F + Hg\downarrow \qquad (3)$$

$$YbCp_2(DME) + AgF \xrightarrow[ii.\ THF]{i.\ DME} YbCp_2F + Ag\downarrow \qquad (4)$$

In these syntheses longer reaction times were required and the powdery products were recovered as nonsolvated complexes after drying. A disadvantage of this method is that even longer reaction times and excess metal oxidant are needed with aged samples of AgF or HgF_2. Recently Schumann reported the reaction of $Sm(Bu^tC_5H_4)_2$ with Me_3SnF in toluene to give $(Sm(Bu^tC_5H_4)_2F)_3$ and $Me_3SnSnMe_3$ [3]. Interestingly Roesky et al. used Me_3SnF to exchange fluoride for chloride in cyclopentadienyl (and substituted cyclopentadienyl) Group 4 systems [17]. $(ScCp_2F)_3$ [2] represented for several years the sole use of a metathesis reaction for the preparation of a bis(cyclopentadienyl) rare-earth fluoride, and it was prepared from reaction of ScF_3 with either $MgCp_2$ or NaCp. However very recently, Xie et al. [8] obtained $[Sm(C_5H_3(SiMe_3)_2\text{-}1,3)_2F]_2$ by accidental metathesis between the corresponding iodide and $AgSbF_6$, and then by the cleavage of $Sm(C_5H_3(SiMe_3)_2\text{-}1,3)_3$ with Me_3NHF.

$[YbCp_2F(THF)]_2$ crystallised as yellow blocks during Eq. (1) as the characteristic purple colour of $YbCp_2(THF)_2$ was discharged. The product had the empirical composition $YbCp_2F(THF)$ and showed appropriate absorptions for cyclopentadienyl (1011 and 774 cm^{-1}) and coordinated THF ligands (1066 and 873 cm^{-1}) in the infrared spectrum. The far infrared spectrum has an absorption band at 298 cm^{-1} which is assigned to ν(Yb–F) and is appropriately placed from reduced mass calculations based on ν(Yb–Cl) [1] of dimeric $YbCp_2Cl$ [18,19], assuming that the change in coordination number from eight to nine has little effect on the Yb–halogen bond strength. Additionally it is near to the terminal ν(Ln–F) absorptions reported for monomeric eight coordinate $Ln(C_5Me_5)_2F(Et_2O)$ (Ln = Yb, 303; Eu, 311; Sm, 304 cm^{-1}) [4], and somewhat lower than for the assumed monomeric $Yb(MeC_5H_4)_2F(THF)$ (326 cm^{-1}) [4]. The mass spectrum of the complex showed the presence of THF in the early scans and above 300°C unsolvated ions with a maximum m/z of 901 ($Yb_3Cp_5F_3^+$), along with a series of fragments with one, two or three ytterbium atoms. The detection of trinuclear ions in the mass spectrum of the solvated dimer upon heating, suggests the formation of $(YbCp_2F)_3$, analogous to $(ScCp_2F)_3$ [2] and $(Sm(Bu^tC_5H_4)_2F)_3$ [3]. The highest mass feature $Yb_3Cp_5F_3^+$ is comparable with those observed for the unsolvated trimers $(ScCp_2F)_3$ [2] and $(Sm(Bu^tC_5H_4)_2F)_3$ [3] and a similar fragmentation pattern is obtained.

Fig. 1 displays the molecular structure of $[YbCp_2F(THF)]_2$, while atomic coordinates and selected bond distances and angles are given in Tables 1 and 2 respectively. The compound is a dimer situated on a crystallographic inversion centre, with asymmetrically bridging fluorides and formal nine coordination about ytterbium. The structure is similar to those of $[LnCp_2Cl(THF)]_2$ (Ln = Nd [20], Er [21]), $[Sm(MeC_5H_4)_2Cl(THF)]_2$ [22] and the bis(cyclopentadienyl)hydridolanthanoid complexes $[LuCp_2H(THF)]_2$ [23], $[Ln(MeC_5H_4)_2H(THF)]_2$ (Ln = Y, Er) [24], and $[Y(1,3\text{-}Me_2C_5H_3)_2H(THF)]_2$ [25]. (Other hydrido complexes with these stoichiometries are also likely to be dimeric [24–27]). The structural similarity between hydrido and fluoro complexes, reflects the similarity in size between hydrogen and fluorine (van der Waals radii 1.20 and 1.35 Å) [28]. With $LnCp_2Cl(THF)$, the dimeric structure observed for Ln = Nd or Er is evidently too crowded for the smaller Ln = Lu, and a less hindered monomeric eight coordinate structure is

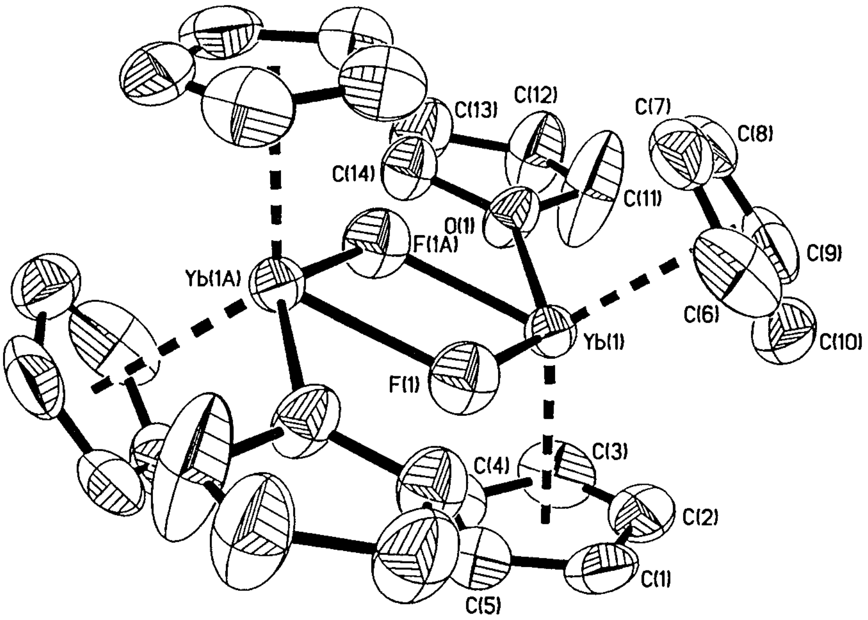

Fig. 1. The molecular structure of[YbCp$_2$F(THF)]$_2$.

adopted [29]. Conversely, the reduction in ligand size from C$_5$Me$_5$ to Cp leads to a change from monomeric Yb(C$_5$Me$_5$)$_2$F(THF) [4] to dimeric nine coordinate [YbCp$_2$F(THF)]$_2$ (Fig. 1) to achieve steric saturation. The sum of the steric coordination numbers of the ligands [30] is approximately the same for the two structures.

The cen–Yb–cen (cen = centroid of the Cp rings) angle (Table 2) is as expected for nine coordinate lanthanoid cyclopentadienyls (113–129°) [20–25,31–37] and below the range for eight coordinate analogues (127–140°) [9,10,18,19,38–41]. The Yb–F–Yb and F–Yb–F angles (Table 2) are very similar to those in representative bis(cyclopentadienyl)hydrido(tetrahydrofuran)lanthanoid dimers (Table 3), confirming the fluoride/hydride analogy. Increased steric repulsion associated with the larger chloride ligands of [LnCp$_2$Cl(THF)]$_2$ leads to opening of the angle at the metal and to a smaller angle at the bridging atom (Table 3). In the bis(cyclopentadienyl)fluorolanthanoid trimers, the X–M–X angles are ≥ 15° higher than in nine coordinate [YbCp$_2$F(THF)]$_2$. They are more typical of eight coordinate (MCp$_2$(μ-X))$_2$ (X = halogen) environments

Table 1
Atomic coordinates and equivalent isotropic displacement coefficients for [YbCp$_2$F(THF)]$_2$

	x	y	z	U_{eq} (Å^2)^a
Yb	0.0277(1)	0.0838(1)	0.4364(1)	0.058(1)
F(1)	0.1324(12)	0.0030(4)	0.6053(1)	0.093(2)
O(1)	− 0.2190(15)	0.1078(5)	0.2166(16)	0.079(4)
C(1)	0.3516(27)	0.0989(14)	0.4170(39)	0.117(9)
C(2)	0.2581(34)	0.1461(11)	0.3144(39)	0.097(7)
C(3)	0.1538(39)	0.1191(13)	0.1926(37)	0.109(8)
C(4)	0.1777(33)	0.0486(12)	0.2098(29)	0.100(7)
C(5)	0.2974(25)	0.0389(9)	0.3477(23)	0.076(5)
C(6)	0.0765(43)	0.1397(15)	0.7240(26)	0.118(10)
C(7)	− 0.1059(40)	0.1283(10)	0.6702(36)	0.105(8)
C(8)	− 0.1637(32)	0.1688(11)	0.5475(33)	0.098(7)
C(9)	− 0.0249(43)	0.2035(9)	0.5282(34)	0.110(8)
C(10)	0.1280(34)	0.1817(11)	0.6320(34)	0.095(6)
C(11)	− 0.2767(46)	0.1722(11)	0.1510(42)	0.186(20)
C(12)	− 0.3985(38)	0.1661(11)	0.0045(38)	0.137(11)
C(13)	− 0.4530(30)	0.0959(11)	− 0.0120(37)	0.119(9)
C(14)	− 0.3408(26)	0.0628(8)	0.1288(26)	0.086(5)

[a] Equivalent isotropic U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2
Selected bond distances and angles for [YbCp$_2$F(THF)]$_2$

Bond	Distance (Å)	Bond	Distance (Å)
Yb(1)–F(1)	2.215(9)	Yb(1)–O(1)	2.410(11)
Yb(1)–F(1a)	2.161(9)	Yb(1)... Yb(1a)	3.6507(13)
Yb(1)–C(1)	2.65(2)	Yb(1)–C(6)	2.66(2)
Yb(1)–C(2)	2.66(2)	Yb(1)–C(7)	2.66(2)
Yb(1)–C(3)	2.65(3)	Yb(1)–C(8)	2.65(2)
Yb(1)–C(4)	2.63(2)	Yb(1)–C(9)	2.63(2)
Yb(1)–C(5)	2.63(2)	Yb(1)–C(10)	2.60(2)
Yb(1)–cen(1)^a	2.374	Yb(1)–cen(2)^b	2.374
Angle	Degrees	Angle	Degrees
O(1)–Yb(1)–F(1)	139.8(3)	F(1)–Yb–F(1a)	66.9(4)
O(1)–Yb(1)–F(1a)	72.9(3)	F(1)–Yb(1)–cen(1)^a	99.7
O(1)–Yb(1)–cen(1)^a	98.9	F(1)–Yb(1)–cen(2)^b	100.1
O(1)–Yb(1)–cen(2)^b	98.5	cen(1)^a–Yb(1)–cen(2)^b	123.9
F(1a)–Yb(1)–cen(1)^a	116.4	F(1a)–Yb(1)–cen(2)^b	119.6
Yb(1)–F(1)–Yb(1a)	113.1(4)		

[a] Cen(1) is the centroid of the Cp ring C(1)–C(5).
[b] Cen(2) is the centroid of the Cp ring C(6)–C(10).

Table 3
Selected angles involving Ln and bridging atoms (X) for $LnCp_2X$ complexes

Complex	X–M–X	M–X–M	Reference
$[Y(MeC_5H_4)_2H(THF)]_2$	66(3)	114(3)	[24]
$[LuCp_2H(THF)]_2$	62(2)	118(3)	[23]
$[NdCp_2Cl(THF)]_2$	73.7(1)	106.3[a]	[20]
$[Sm(Bu^tC_5H_4)_2F]_3$	82.8(3)	157.2(3)	[3]
	84.9(3)	152.7(5)	
$(ScCp_2F)_3$	86.6(3)	153.5(4)	[2]
	86.2(3)	153.9(5)	
	86.7(3)	152.9(4)	

[a] Angle calculated from reported data.

[18,19,39–41], and appear to be part of a mechanism to reduce steric repulsion between $LnCp_2$ units, especially with small bridging groups such as fluoride [2,3] and hydride [25]. It is noteworthy that in $Sm(C_5Me_5)_2Cl$ the large C_5Me_5 groups give rise to a trimer [42]. In the present structure the least squares plane formed by one ytterbium, the associated oxygen donor atom and the two bridging fluorides almost bisects the corresponding cen(1)–Yb–cen(2) wedge, and this appears to be a general feature of dimeric nine-coordinate bis(cyclopentadienyl)lanthanoid complexes [23–25,31–37].

The Yb–F distances, 2.161, 2.215 Å, are quite short for bridging interactions and correspond to Yb–F bond lengths found in $Yb_5(C_5Me_5)_6(\mu_4\text{-F})(\mu_3\text{-F})_2(\mu\text{-F})_6$ (av. 2.201 Å) [3], in which ytterbium is eight coordinate. This shortness is emphasized by the fact that ⟨Yb–F⟩ is 0.11 Å shorter than ⟨Sm–F⟩ of the recently reported $[Sm(C_5H_3(SiMe_3)_2\text{-}1,3)_2F]_2$ [8], although only a 0.04 Å difference is expected from the appropriate ionic radii [43]. The Yb–F distances are more comparable with Ln–F distances in eight coordinate $(Sm(Bu^tC_5H_4)_2F)_3$ (av. 2.262 Å) [3] when the difference in ionic radii is considered. However as expected, they are longer than terminal Ln–F distances in $Yb(C_5Me_5)_2F(THF)$ (2.026) [4] and $Yb(C_5Me_5)_2F(Et_2O)$ (2.015 Å) [4]. Subtraction of the ionic radius for nine coordinate Yb^{3+} [43] from the Yb–F distances gives 1.12 and 1.17 Å for $[YbCp_2F(THF)]_2$. These are at the lower end of values similarly derived for $Yb_5(C_5Me_5)_6(\mu_4\text{-F})(\mu_3\text{-F})_2(\mu\text{-F})_6$ (av. 1.22) [4], $(ScCp_2F)_3$ (av. 1.18) [2], $(Sm(Bu^tC_5H_4)_2F)_3$ (av. 1.18 Å) [3] or $[Sm(C_5H_3(SiMe_3)_2\text{-}1,3)_2F]_2$ (av. 1.22) [8]. A similar treatment of the mixed valence complexes $Yb_2(C_5Me_5)_4(\mu\text{-F})$ [5] and $Yb_4(C_5Me_5)_6(\mu\text{-F})_4$ [6] is inappropriate given the difficulties in assigning integral oxidation states. As a comparison, values derived from terminal Yb–F distances in the monomeric complexes $Yb(C_5Me_5)_2F(THF)$ and $Yb(C_5Me_5)_2F(Et_2O)$ are 1.04 and 1.03 Å, respectively [4].

The Yb–O distance (Table 2) lies between Y–O (2.46(1) Å) of nine coordinate $[Y(MeC_5H_4)_2H(THF)]_2$ [24] and Lu–O (2.387(5)Å) of nine coordinate $[LuCp_2H(THF)]_2$ [23], as is appropriate for the ionic sizes [43]. It is significantly shorter than Er–O (2.490(6) Å) of $[ErCp_2Cl(THF)]_2$, well beyond what is expected from the difference in Ln^{3+} radii [43], and may reflect the higher electronegativity of fluorine than chlorine. Subtraction of the ionic radius for nine coordinate Yb^{3+} from Yb–O gives 1.37 Å, which corresponds closely to the value (1.34 ± 0.05 Å) for a range of relatively uncrowded Ln–O(THF) bonds in cyclopentadienyllanthanoid ether complexes [44]. The ⟨Yb–C⟩ distance (2.64 Å) is unexceptional. The Yb···Yb separation (Table 2) is analogous to those of nine coordinate hydride bridged complexes (3.52–3.68 Å) [23–25], and much smaller than that for $[ErCp_2Cl(THF)]_2$ (4.42 Å) [21], where the increased size of the bridging atom has a major effect.

3. Experimental

3.1. General remarks

All the ytterbium complexes are extremely air- and moisture-sensitive. Thus, all reactions and manipulations of these compounds were carried out under purified nitrogen or argon, using Schlenk-, vacuum line- and dry box-techniques. Analytical and spectroscopic methods and instrumentation were generally as described previously [45]. IR spectra (4000–650 cm^{-1}) were obtained for compounds in dry Nujol. Far infrared spectra (650–100 cm^{-1}) of complexes were obtained as vaseline mulls between polyethylene plates with a Bruker IFS 120 HR or Perkin 180 spectrometer. In listed mass spectra, each m/z value corresponds to the main peak of a cluster with the appropriate isotope pattern. Solvent, nitrogen, and argon purification has been given previously [45]. Ytterbium powder was from Rhone-Poulenc, Phoenix, Arizona. Silver(I) fluoride (Fluka) and mercury(II) fluoride (Harshaw Chemical, Ohio, USA) were standard commercial anhydrous samples and were used without purification. Perfluorodecalin and perfluoro(methylcyclohexane) were from Aldrich, and were degassed by alternating freeze/thaw cycles and then vacuum transferred before use. Bis(cyclopentadienyl)(1,2-dimethoxyethane)ytterbium(II) was prepared by the reported method [46].

3.2. Syntheses

3.2.1. Di[bis(cyclopentadienyl)-μ-fluoro(tetrahydrofuran)ytterbium(III)]

3.2.1.1. From perfluorodecalin. $YbCp_2(DME)$ (0.79 g, 2.0 mmol) was dissolved in THF (8 ml) and perfluorodecalin (0.46 g, 1.0 mmol) added by syringe. The resulting biphasic mixture, was stirred for 8 h to give a yellow precipitate and a yellow brown solution. The precipitate was dissolved by heating the mixture to boiling and upon slow cooling to room temperature, golden yellow blocks were observed. They were filtered off and washed with 5 ml THF (three times) and dried at 10^{-3} mm Hg for 5 h. Yield 0.42 g (53%). Anal. Found: Yb, 43.6. $C_{28}H_{36}O_2F_2Yb_2$ Calc.: Yb, 43.9%. IR: ν 3088w, 2710w, 1653w, 1346w(sh), 1252w, 1174w, 1066m, 1011s, 922w, 873m, 774vs, 670w, 622w, 552w, 480s, 406m, 298m, 264m, 196m cm^{-1}. MS: m/z 901 [5, $Yb_3Cp_5F_3^+$]; 836 [0.4, $Yb_3Cp_4F_3^+$]; 776 and 771 overlapping [0.3, $Yb_3Cp_3F_3^+$ and $Yb_3Cp(C_5H_4)_3^+$]; 705 [0.5, $Yb_3Cp(C_5H_4)F_3^+$]; 644 [5, $Yb_2Cp_4F_2^+$]; 625 [1, $Yb_2Cp_4F^+$]; 579 [21, $Yb_2Cp_3F_2^+$]; 558 [0.8, $Yb_2Cp(C_5H_4)_2F^+$]; 533 [2, $Yb_2Cp_2F_3^+$]; 514 [5, $Yb_2Cp_2F_2^+$]; 495 [2, $Yb_2Cp_2F^+$]; 468 [5, $Yb_2CpF_3^+$]; 449 [6, $Yb_2CpF_2^+$]; 428 [0.8, Yb_2CpF^+]; 403 [13, $Yb_2F_3^+$]; 384 [6, $Yb_2F_2^+$]; 369 [19, $YbCp_3^+$]; 304 [44, $YbCp_2^+$]; 239 [65, $YbCp^+$]; 193 [13, YbF^+]; 174 [19, Yb^+]; 129 [10, $CpC_5H_4^+$]; 65 [100, Cp^+]. Minor features due to incorporation of Cl ions from the mass spectrometer source were observed at 597 [$Yb_2Cp_3FCl^+$] and 662 [$Yb_2Cp_4FCl^+$] similar to previous reports [1]. Vis–near IR [λ_{max} (e)] (THF): 337(56), 941(2), 976(3) nm (dm^3 mol^{-1} cm^{-1}).

3.2.1.2. From perfluoro(methylcyclohexane). $YbCp_2$(DME) (0.79 g, 2.0 mmol) was dissolved in THF (6 ml) and perfluoro(methylcyclohexane) (0.35 g, 1.0 mmol) added by syringe. The reaction mixture was stirred for 72 h to give a yellow precipitate and a yellow brown solution. The volatiles were removed in vacuo and collected in a liquid N_2 cooled trap. The yellow brown residues were dissolved in boiling THF (5 ml) and upon slow cooling the crystalline yellow title compound was obtained and isolated as above. Yield 0.41 g (52%). Anal. Found: Yb, 43.6. $C_{28}H_{36}O_2F_2Yb_2$ Calc.: Yb, 43.9%. IR and MS were identical with those given above. The ^{19}F NMR spectrum of the volatiles collected revealed the following fluorocarbons: C_7F_{14} (perfluoro(methylcyclohexane)), C_7F_8 (octafluorotoluene), p-$HC_6F_4CF_3$ (4-H-heptafluorotoluene), m-$HC_6F_4CF_3$ (3-H-heptafluorotoluene), and o-$HC_6F_4CF_3$ (2-H-heptafluorotoluene) in a ratio of 60:16:5:1:1 respectively.

3.2.2. Bis(cyclopentadienyl)fluoroytterbium(III)

3.2.2.1. From HgF_2. To a mixture of $YbCp_2$(DME) (0.78 g, 2.0 mmol) and HgF_2 (0.24 g, 1.0 mmol) was added THF (20 ml) and the reaction mixture was stirred for a period of 72 h with periodic warming, after which time it was yellow brown and contained precipitated mercury. The solution was filtered and then taken to dryness yielding a yellow powder which was dried at 10^{-3} mm Hg for 3 h with periodic warming. Yield 0.45 g (70%). Anal. Found: C, 37.0, 36.3; H, 4.2, 3.9; Yb, 53.2. $C_{10}H_{10}FYb$ Calc.: C, 37.3, H, 3.1; Yb, 53.7%. IR: ν 3090w, 2800w, 2710w, 1440w, 1010s, 790sh, 780s, 725m, 664m, 466m, 300w, 250s cm^{-1}. MS: m/z (no metal containing peaks) 66 [100, CpH^+]; 65 [55, Cp^+]. Vis–near IR [λ_{max} (e)] (THF): 362sh(204), 916(4), 945(5), 979sh(7), 984(16), 1031(3) nm (dm^3 mol^{-1} cm^{-1}).

3.2.2.2. From AgF. To a mixture of $YbCp_2$(DME) (0.76 g, 1.9 mmol) and AgF (0.23 g, 1.8 mmol) was added DME (40 ml) and the reaction mixture stirred for a period of 7 days with periodic warming, after which time it was yellow brown and contained precipitated silver. The solution was filtered and the solvent removed in vacuo yielding a yellow powder. THF (20 ml) was added and the solution was stirred for 30 days, giving some yellow crystals. These were separated from the mother liquor which was evaporated and the resulting yellow powder dried at 10^{-3} mm Hg for 3 h with periodic warming. Yield 0.33 g (56%). The yellow powder was identified spectroscopically as $YbCp_2F$, by IR and Vis–near IR spectra, which corresponded to those of the previous product. MS (yellow crystals): m/z 644 [1, $Yb_2Cp_4F_2^+$]; 579 [2.5, $Yb_2Cp_3F_2^+$]; 514 [0.5, $Yb_2Cp_2F_2^+$]; 449 [0.5, $Yb_2CpF_2^+$]; 369 [1, $YbCp_3^+$]; 304 [4, $YbCp_2^+$]; 258 [0.3, $YbCpF^+$]; 239 [45, $YbCp^+$]; 193 [5, YbF^+]; 174 [15, Yb^+]; 66 [100, CpH^+]; 65 [60, Cp^+].When aged metal fluorides were used an excess of these reagents and longer reaction times were required.

3.3. X-ray structure determination

3.3.1. Crystal-refinement data

$C_{28}H_{36}O_2F_2Yb_2$; $M = 788.67$; monoclinic; space group, $P2_1/c$ (C_{2h}^5; No. 14); $a = 7.9901(12)$, $b = 20.411(4)$ and $c = 8.5957(12)$ Å; $\beta = 104.70(2)°$; $U = 1355.9(4)$ Å^3; $D_c = 1.932$ g cm^{-3}; $Z = 2$; $F(000) = 756$; $\mu_{Mo} = 7.577$ mm^{-1}; the crystal was mounted in a 0.4 mm diameter glass capillary under a dry argon atmosphere in the dry box; colour: yellow; $N = 1588$; $N_o = 1107$; $R_{1_{(obs.)}} = 0.0495$, $\omega R_{2_{(obs.)}} = 0.1068$, $R_{1_{(all)}} = 0.0734$, $\omega R_{2_{(all)}} = 0.1140$; $n_v = 155$; $T = 293(2)$ K. Other specific procedural details: reflection weights, $w = [\sigma^2(F_o)^2 + (0.0615P)^2]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$; measured on a Stoe Imaging Plate Diffraction System; software: SHELXS-86 and SHELXL-93.

3.3.2. Structure determination

A unique data set was measured within the limit $5.6 \leq 2\theta \leq 44°$; monochromatic Mo K$\alpha$ ($\lambda = 0.71073$ Å) was employed. N independent reflections were obtained (see Section 3.3.1), N_o with $I > 2\sigma$ being considered 'observed' and were used for the calculation of R factors$_{(obs.)}$, but are irrelevant to the choice of reflections used in the refinement. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{\mathrm{iso}})_{\mathrm{H}}$ were constrained at appropriate values. Residuals R_1 $(R_1 = \Sigma||F_{\mathrm{o}}| - |F_{\mathrm{c}}||/\Sigma|F_{\mathrm{o}}|)$ and ωR_2 $(\omega R_2 = \{\Sigma[w(F_{\mathrm{o}}^2 - F_{\mathrm{c}}^2)^2]/\Sigma[w(F_{\mathrm{o}}^2)^2]\}^{1/2})$, are quoted at convergence. Neutral atom complex scattering factors were employed [47]. The structure is displayed in Fig. 1, and selected bond distances and angles are given in Table 2. Complete lists of atomic coordinates, bond distances and angles, thermal parameters and hydrogen atom coordinates are available from the Cambridge Crystallographic Data Centre.

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