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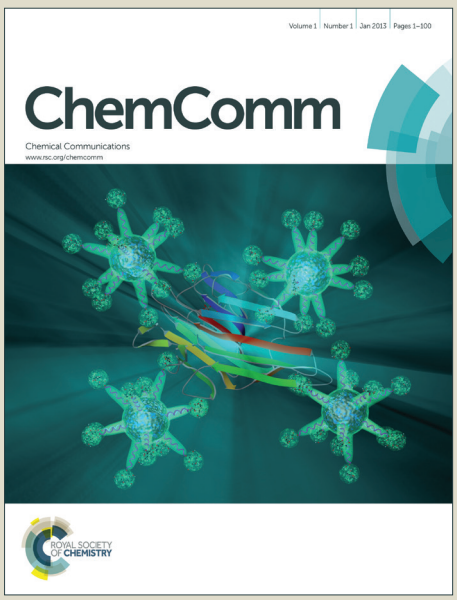

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A divalent heteroleptic lanthanoid fluoride complex stabilised by the tetraphenylcyclopentadienyl ligand, arising from C–F activation of pentafluorobenzene

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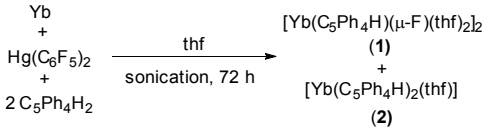
The divalent heteroleptic lanthanoid fluoride complex, $[Yb(C_5Ph_4H)(\mu\text{-}F)(thf)_2]_2$, as well as $[Yb(C_5Ph_4H)_2(thf)]$ and $[Yb(C_5Ph_4H)(C_6F_5)(thf)_2]$ were obtained from reactions of ytterbium metal with $Hg(C_6F_5)_2$ and tetraphenylcyclopentadiene under different conditions, and C–F activation of C_6F_5H by Yb metal was observed.

Establishing the divalent oxidation state for molecular compounds of the rare earth/lanthanoid elements not normally exhibiting this state has been the most dramatic recent development in divalent rare earth chemistry.[1-4] However, for elements normally exhibiting this state (Sm, Eu, Yb), significant synthetic challenges still exist. For example, divalent metal-organic lanthanoid hydrides are a comparatively recent development[5-7] and divalent organolanthanoid fluorides are unknown despite the considerable recent interest in heteroleptic lanthanoid(III) fluorides[8-12] and hydrogen for fluorine exchange reactions of heteroleptic cerium(III) hydrides.[12-14] The recent synthesis of a cerium(IV) terminal fluoride complex is also notable.[15] We now report the synthesis and spectroscopic and structural characterisation of the first divalent heteroleptic lanthanoid fluoride, $[Yb(C_5Ph_4H)(\mu\text{-}F)(thf)_2]_2$, together with syntheses of the octaphenylytterbocene, $[Yb(C_5Ph_4H)_2(thf)]$, and the half-sandwich complex $[Yb(C_5Ph_4H)(C_6F_5)(thf)_2]$, as well as the unexpected activation of pentafluorobenzene by ytterbium metal. Use of the tetraphenylcyclopentadienyl ligand provides bulk for stabilisation without the solubility problems associated with complexes of the bulkier pentaphenylcyclopentadienyl ligand, as exemplified by $[Yb(C_5Ph_5)_2]$.[16] Only one such lanthanoid complex has been reported viz. $[La(C_5Ph_4H)_2\{N(SiMe_3)_2\}]$.[17]

From the redox-transmetallation/protolysis (RTP) reaction between an excess of Yb metal, one equivalent of $Hg(C_6F_5)_2$ and two equivalents of $C_5Ph_4H_2$ in thf for 72 h, a small crop of orange single crystals of $[Yb(C_5Ph_4H)(\mu\text{-}F)(thf)_2]_2$ (**1**) (Scheme 1) was isolated after filtration and concentration of the thf solution. The expected product, $[Yb(C_5Ph_4H)_2(thf)]$ (**2**) also formed, as shown by ^{171}Yb NMR spectroscopy. An improved synthesis of **1** is outlined below.



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

Complex **1** (Fig. 1) crystallised in the monoclinic space group $P2_1/n$ as a symmetrical dimer. Each seven-coordinate ytterbium ion is coordinated by one C_5Ph_4H ring, two thf molecules and two bridging fluoride ions. The Yb–F bond lengths of **1** (Fig. 1) are longer than those of the trivalent complexes, $[Yb(Cp)_2F]_3$ (2.143(9)–2.18(1) Å)[18] and $[Yb(MeCp)_2F]_4$ (2.136(6)–2.173(6) Å),[18] mainly owing to the larger size of Yb^{2+} relative to Yb^{3+}.[19] The Yb–C(range) (2.773(3)–2.806(3) Å) of **1** is slightly longer than that of the divalent complex, $[Yb(C_5Ph_5)(CCPh)(thf)]_2$ (2.713(6)–2.740(6) Å),[20] which features two six-coordinate ytterbium ions.

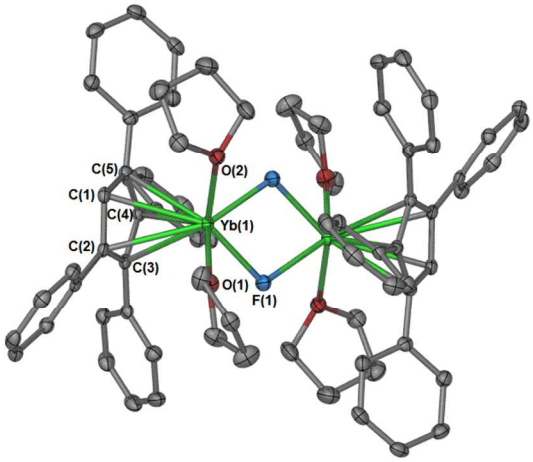


Fig. 1 Molecular structure of **1** shown with 50 % probability thermal ellipsoids. Selected bond lengths (Å): Yb(1)–C(range) = 2.773(3)–2.806(3), Yb(1)–centroid = 2.522, Yb(1)–F(1) = 2.2515(17), Yb(1)–F(1)$^{\#}$ = 2.2546(18), Yb(1)–O(1) = 2.458(2), Yb(1)–O(2) = 2.449(2). $^{\#}$ Generated by symmetry.

Retention of Yb–F binding in solution was established by multinuclear NMR spectroscopy (Fig. 2). In the $^{19}F\{^1H\}$ NMR spectrum, a signal corresponding to the fluoride ligands is observed at −81.82 ppm and it is flanked by ^{171}Yb satellites (abundance of ^{171}Yb ≈ 14.3 %)[21] ($^1J_{Yb,F}$ = 449 Hz). Coupling to two ^{171}Yb ions was not apparent in the $^{19}F\{^1H\}$ NMR spectrum due to the relatively low probability of having two such nuclei in the same molecule. In the ^{171}Yb NMR spectrum, a triplet with the same coupling constant is observed at 376 ppm (Fig. 2b), indicating that the complex remains dimeric in solution. In addition, a high resolution electrospray mass spectrum gave the isotopic cluster of the unsolvated dimer.

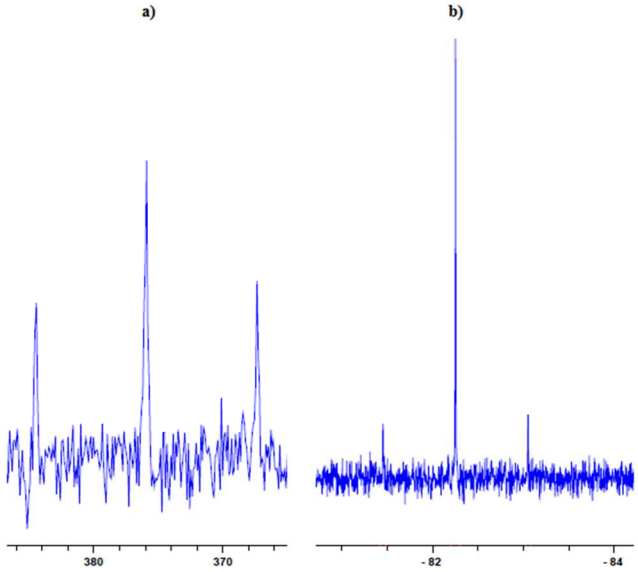
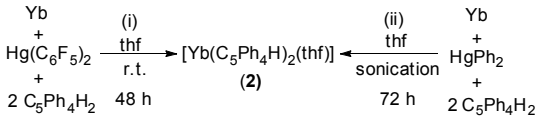


Fig. 2a) ^{171}Yb NMR, and **b)** $^{19}F\{^1H\}$, NMR spectra of **1** showing $^1J_{Yb,F}$ coupling ($^1J_{Yb,F}$ = 449 Hz).

Complex **2** could be obtained as the sole isolable ytterbium-containing product under two different reaction conditions (Scheme 2): (i) a mixture with a stoichiometric amount of Yb was stirred at room temperature for 48 h instead of sonication; or (ii) using $HgPh_2$ instead of $Hg(C_6F_5)_2$ and sonicating the reaction mixture for 72 h. Dark orange single crystals of **2** were obtained by crystallisation from toluene. In contrast to $[Yb(C_5Ph_5)_2]$,[16] **2** has good solubility in toluene. Furthermore, unlike $[Ba(C_5Ph_4H)_2\{thf\})]$,[22] **2** has good thermal stability.



Scheme 2. Synthesis of **2**.

The sandwich complex **2** (Fig. 3) crystallised in the monoclinic space group $P2_1/n$. The seven-coordinate ytterbium ion of the open sandwich complex is bound by two C_5Ph_4H ligands and one thf molecule. The Yb–C(range) (2.627(5)–2.806(6) Å) is much wider than observed for **1** or $[Yb(C_5Ph_5)_2]$ (2.652(2)–2.680(2) Å).[16] In **2**, there is evidence of C–H···C(π) interactions (see CIF) similar to what has been observed in $[M(C_5Ar_5)_2]$ (M = Yb, Ba, Ar = Ph; M = Sm, Yb, Eu, Ca, Sr, Ba, Ar = $C_5(C_6H_4nBu\text{-}p)_5$) complexes,[16, 23-25] although the number of such interactions in **2** is lower than in $[M(C_5Ar_5)_2]$ complexes.

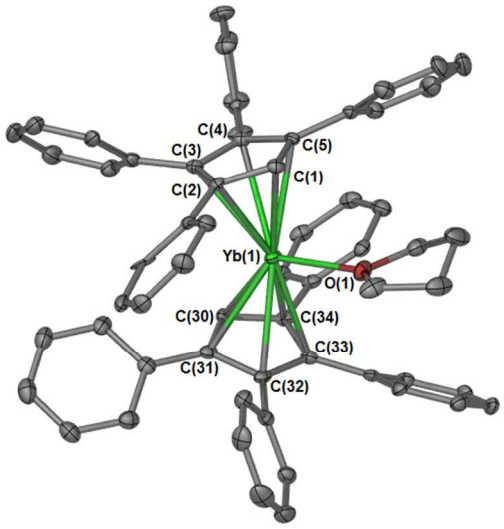
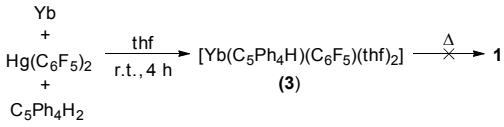


Fig. 3 Molecular structure of **2** shown with 50 % probability thermal ellipsoids. Selected bond lengths (Å): Yb–C(range) = 2.627(5)–2.806(6), Yb(1)–centroid(1) = 2.440, Yb(1)–centroid(2) = 2.448, Yb(1)–O(1) = 2.369(4).

In order to obtain information on the formation of **1**, we investigated the synthesis of a possible intermediate, $[Yb(C_5Ph_4H)(C_6F_5)(thf)_2]$ (**3**). Stirring an excess of Yb metal, one equivalent of $Hg(C_6F_5)_2$ and only one equivalent of ligand in thf at room temperature for 4 h gave a high yield of **3** (Scheme 3).

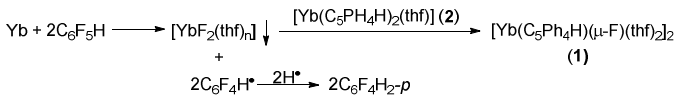


Scheme 3. Synthesis of **3**.

Complex **3** was characterised by multinuclear NMR spectroscopy and the number of thf molecules was determined by ^1H NMR spectroscopy after protolysis of a sample suspended in CD_3CN. Variable temperature $^{19}F\{^1H\}$ and ^{171}Yb NMR studies did not show any Yb–F coupling, nor did the related complex, $[Yb(C_5Me_5)(C_6F_5)(thf)_3]$.[26] Complex **3** is moderately stable in thf but it decomposes gradually in aromatic solvents with the formation of unidentified fluoroarenes, as indicated by both the ^1H and $^{19}F\{^1H\}$ NMR spectra. No formation of **1** was observed during the decomposition process. Acceptable microanalysis results for **3** could not be obtained due to poor stability in the solid state. Heating a thf solution of **3** did not afford **1**. Thus, the divalent complex $[Yb(C_5Ph_4H)(C_6F_5)(thf)_2]$ (**3**) does not seem to be the precursor of **1** (Scheme 4), even though trivalent $[LnL_2(C_6F_5)]$ complexes have been shown to form the corresponding $[LnL_2F]$ complexes,[8-10, 12]

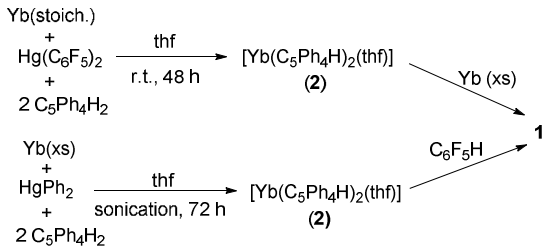
Given that the only other source of fluorine is the C_6F_5H formed in the redox-transmetallation/protolysis (RTP) reaction (Scheme 1), we consider that the excess Yb metal (activated by amalgamation with Hg) reacts with C_6F_5H to form $YbF_2(thf)_n$, which then undergoes ligand redistribution with one equivalent of **2** to form **1** (Scheme 4). This hypothesis is substantiated by the following observations: (a) the $^{19}F\{^1H\}$ NMR spectrum of a reaction mixture

showed the presence of $C_6F_4H_2$-*p*, which was also detected by GC/MS studies of a hydrolysed reaction mixture.



Scheme 4. Proposed formation of **1**.

Its formation could result from the reduction of C_6F_5H to form a $C_6F_4H^{\cdot}$ radical followed by hydrogen abstraction from the solvent (Scheme 4); (b) monitoring the RTP reaction by $^{19}F\{^1H\}$ NMR spectroscopy showed a decrease in the amount of C_6F_5H over time after prolonged stirring of the reaction mixture at room temperature with a concomitant increase in the amount of **1** and $C_6F_4H_2$-*p*; (c) addition of C_6F_5H to the Yb/$HgPh_2$/$C_5Ph_4H_2$ reaction mixture after 72 h of sonication led to the formation of some **1** (Scheme 5); (d) addition of excess Yb metal to the stoichiometric RTP reaction after 48 h led to the formation of **1** in 44 % isolated yield (Scheme 5); and (e) compellingly, direct reaction of I_2-activated Yb metal with C_6F_5H resulted in the formation of $C_6F_4H_2$-*p*, some $[Yb(C_6F_5)_2]$, and insoluble $[YbF_2(thf)_n]$. After removal of soluble products, the presence of $[YbF_2(thf)_n]$ was demonstrated by reaction of the insoluble residue with **2** to give the fluoride **1** (see a related reaction of $YbCl_2$),[27] confirming the steps of Scheme 4.



Scheme 5. Additional experiments for the formation of **1**.

Although divalent lanthanoid complexes have been known to reduce fluorocarbons to yield trivalent heteroleptic fluoride complexes,[28-31] the reduction of a fluorocarbon by an elemental lanthanoid to yield an isolable divalent heteroleptic fluoride complex is unprecedented and we are attempting to see whether or not this approach can be extended to other systems.

In conclusion, three new divalent ytterbium complexes have been prepared by RTP reactions with the bulky C_5Ph_4H ligand. The steric bulk of this ligand made the isolation of the first divalent heteroleptic ytterbium fluoride complex possible.

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Notes and references

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Electronic Supplementary Information (ESI) available: [synthetic details and crystallographic information]. See DOI: 10.1039/c000000x/

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