This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
The divalent heteroleptic lanthanoid fluoride complex, \([\text{Yb(C}_5\text{Ph}_5\text{H})(\mu-F)(\text{thf})_2]_2\), as well as \([\text{Yb(C}_5\text{Ph}_5\text{H})(\text{thf})_2]_2\) and \([\text{Yb(C}_5\text{Ph}_5\text{H})(\text{C}_5\text{F}_5)(\text{thf})_2]_2\) were obtained from reactions of ytterbium metal with \(\text{Hg(C}_5\text{F}_5)_2\) and tetraphenylcyclopentadienyl ligand under different conditions, and C–F activation of \(\text{C}_5\text{F}_5\text{H}\) 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, \([\text{Yb(C}_5\text{Ph}_5\text{H})(\mu-F)(\text{thf})_2]_2\), together with syntheses of the octaphenyl ytterbocene, \([\text{Yb(C}_5\text{Ph}_5\text{H})(\text{thf})_2]_2\), and the half-sandwich complex \([\text{Yb(C}_5\text{Ph}_5\text{H})(\text{C}_5\text{F}_5)(\text{thf})_2]_2\), 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 \([\text{Yb(C}_5\text{Ph}_5\text{H})]_2\).\(^ {16}\) Only one such lanthanoid complex has been reported viz. \([\text{La(C}_5\text{Ph}_5\text{H})(\text{N(SiMe}_3)_2])_2\].\(^ {17}\)

From the redox-transmetallation/protolysis (RTP) reaction between an excess of Yb metal, one equivalent of \(\text{Hg(C}_5\text{F}_5)_2\) and two equivalents of \(\text{C}_5\text{Ph}_5\text{H}_2\) in thf for 72 h, a small crop of orange single crystals of \([\text{Yb(C}_5\text{Ph}_5\text{H})(\mu-F)(\text{thf})_2]_2\) (1) (Scheme 1) was isolated after filtration and concentration of the thf solution. The expected product, \([\text{Yb(C}_5\text{Ph}_5\text{H}_2](\text{thf})_2\] (2) also formed, as shown by \(^ {17}\)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 \(P2_1/\alpha\) as a symmetrical dimer. Each seven-coordinate ytterbium ion is coordinated by one \(\text{C}_5\text{Ph}_5\text{H}\) 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, \([\text{Yb(Cp)}_3\text{F}]_2\) (2.143(9)–2.18(1) Å)\(^ {18}\) and \([\text{Yb(MeCp)}_2\text{F}]_2\) (2.136(6)–2.173(6) Å)\(^ {18}\) mainly owing to the larger size of \(\text{Yb}^{2+}\) relative to \(\text{Yb}^{3+}\). The Yb–(C-range) (2.773(3)–2.806(3) Å) of 1 is slightly longer than that of the divalent complex, \([\text{Yb(C}_5\text{Ph}_5\text{H})(\text{C}_5\text{F}_5)(\text{thf})_2]_2\) (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 \(^{171}Yb = 14.3 \%\)) \(^{21}J\{^1H,F\} = 449 \) 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 \(-81.82 \) ppm and it is flanked by \(^{171}Yb \) satellites (abundance of \(^{171}Yb ≈ 14.3 \%\)).

In the \(^{1}H \) NMR, and \(^{19}F\{^1H\} \) NMR spectra of 1 showing \(^1J\{Yb,F\} \) coupling (\( \Delta \{Yb,F\} = 449 \) 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 HgPh\(_3\) and sonating the reaction mixture for 72 h. Dark orange single crystals of 2 were obtained by crystallisation from toluene. In contrast to \([Yb(C_5Ph_5H)_2(thf)]\), \(^{22}\) 2 has good thermal stability.

\[
\begin{align*}
\text{Yb}^+ & + \text{Hg}(C_5F_5)_{12}^{+} \overset{\text{r.t.}}{\underset{\text{thf}}{\rightarrow}} [\text{Yb}(C_5Ph_5H)_2(\text{thf})]^+ \overset{\text{sonication}}{\rightarrow} \text{HgPh}_2^+ \\
2 \text{C}_5\text{Ph}_5\text{H}_2 & \overset{48 \text{ h}}{\rightarrow} 2 \text{C}_5\text{Ph}_5\text{H}_2
\end{align*}
\]

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\(_5\)Ph\(_5\)H ligands and one thf molecule. The Yb–C\(_{range}\) (2.627(5)–2.806(6) \(\text{Å}\)) is much wider than observed for 1 or \([Yb(C_5Ph_5)_2] \) (2.652(2)–2.680(2) \(\text{Å}\)). \(^{26}\) In 2, there is evidence of C–H···C(\(\pi\)) interactions (see CIF). Similar to what has been observed in \([\text{M}C_5\text{Ar}_5\text{H}]\) \((\text{M} = \text{Yb, Ba, Ar = Ph; M = Sm, Yb, Eu, Ca, Sr, Ba, Ar = C}_3\text{C}_6H_{18}\text{Bu}_3\text{p})\) complexes, \(^{16, 23-25}\) although the number of such interactions in 2 is lower than in \([\text{M}C_5\text{Ar}_5\text{H}]\) complexes.

In order to obtain information on the formation of 1, we investigated the synthesis of a possible intermediate, \([\text{Yb}(C_5\text{Ph}_5\text{H})(C_6\text{F}_5)(\text{thf})]\) (3). Stirring an excess of Yb metal, one equivalent of Hg(C\(_5\)F\(_5\)) 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 \(^{1}H \) NMR spectroscopy after protolysis of a sample suspended in CD\(_2\)CN. Variable temperature \(^{19}F\{^1H\} \) and \(^{171}Yb \) NMR studies did not show any Yb–F coupling, nor did the related complex, \([\text{Yb}(C_5\text{Me}_5)(C_6\text{F}_5)(\text{thf})]_2\). \(^{26}\) 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 \(^{1}H \) 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 \([\text{Yb}(C_5\text{Ph}_5\text{H})(C_6\text{F}_5)(\text{thf})]_2\) (3) does not seem to be the precursor of 1 (Scheme 4), even though trivalent \([\text{LnL}_3(C_6\text{F}_5)]\) complexes have been shown to form the corresponding \([\text{LnL}_2\text{F}]\) complexes. \(^{8-10, 12}\)

Given that the only other source of fluorine is the C\(_5\)F\(_5\)H 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\(_5\)F\(_5\)H 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$_6$F$_5$H$_2$, which was also detected by GC/MS studies of a hydrolysed reaction mixture.

$$\text{Yb} + 2\text{C}_6\text{F}_5\text{H}_2 \rightarrow \text{[Yb(C}_6\text{F}_5\text{H}_2\text{H}(\text{thf})]} \rightarrow \text{[Yb(C}_6\text{F}_5\text{H}_2\text{H}+\text{F}(\text{thf})]}_2$$

$$2\text{C}_6\text{F}_5\text{H}_2 \rightarrow \text{2C}_6\text{F}_5\text{H}_2$$

Scheme 4. Proposed formation of 1.

Its formation could result from the reduction of C$_6$F$_5$H to form a C$_6$F$_5$H radical followed by hydrogen abstraction from the solvent (Scheme 4); (b) monitoring the RPT reaction by $^{19}$F/$^1$H NMR spectroscopy showed a decrease in the amount of C$_6$F$_5$H over time after prolonged stirring of the reaction mixture at room temperature with a concomitant increase in the amount of I and C$_6$F$_5$H$_2$; (c) addition of C$_6$F$_5$H to the Yb/H$_2$P/C$_6$F$_5$H$_2$ 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 RPT 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$_6$F$_5$H resulted in the formation of C$_6$F$_5$H$_2$, some [Yb(C$_6$F$_5$)$_2$], and insoluble [YbF$_6$(thf)$_2$]. After removal of soluble products, the removal of [YbF$_6$(thf)$_2$] was demonstrated by reaction of the insoluble residue with 2 to give the fluoride 1 (see a related reaction of YbCl$_2$), confirming the steps of Scheme 4.

$$\text{Yb} + 2\text{C}_6\text{F}_5\text{H}_2 \rightarrow \text{[Yb(C}_6\text{F}_5\text{H}_2\text{H}(\text{thf})]} + \text{2Yb}$$

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, the reduction of a fluorocarbon by an elemental lanthanoid to yield an insoluble 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 RPT reactions with the bulky C$_6$F$_5$H$_2$ ligand. The steric bulk of this ligand made the isolation of the first divalent heteroleptic ytterbium fluoride complex possible.

We thank the Australian Research Council (ARC Discovery: DP 130100152), the Faculty of Science (Monash University) for a Dean's Scholarship to RPK, the CNRS and the Université de Reims for support. We would also like to thank Dr Jun Wang for assistance with X-ray crystallography. Part of this research was undertaken on the MXI beamline at the Australian Synchrotron, Victoria, Australia.

Notes and references

*Email: glen.deacon@monash.edu, florian.jaroschik@univ-reims.fr, peter.junk@jcu.edu.au

1. J. Name, 2012, 00, 1-3 | 3

ChemComm Accepted Manuscript

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