Abstract: Reaction of [Yb(Cp)(dme)] (Cp = cyclopentadienyl, dme = 1,2 dimethoxyethane) with bis(diphenylphosphano)methane dioxide (H2dppmO2) leads to deprotonation of the ligand H2dppmO2 and oxidation of ytterbium, forming an extremely air-sensitive product, [YbIII(HdppmO2)3] (1), a six-coordinate complex with three chelating (OPCHPO) HdppmO2 ligands. Complex 1 was also obtained by a redox transmetallation/protolysis synthesis from metallic ytterbium, Hg(C6F5)2, and H2dppmO2. In a further preparation, the reaction of [Yb(C6F5)2] with H2dppmO2, not only yielded compound 1, but also gave a remarkable tetranuclear cage, [Yb4(µ-HdppmO2)6(µ-F)6] (2) containing two [Yb(µ-F)2] rhombic units linked by two fluoride ligands and the tetranuclear unit is encapsulated by six bridging HdppmO2 donors. The fluoride ligands of the cage result from C-F activation of pentafluorobenzene and concomitant formation of p-H2C6F4 and m-H2C6F4, the last being an unexpected product.

Keywords: ytterbium; phosphine oxide; methanide; C-F activation; fluoride cage

1. Introduction

Phosphane oxide ligands, and especially triphenylphosphane oxide, are popular ligands for rare earth metals [1–4]. Complexation is aided by the oxophilic nature of lanthanoid ions and is enhanced by the polarity of the P+-O- bonds. The spear-like donor functionality limits steric repulsion close to the metal but provides steric protection further away. Some use has been made of these ligands in solvent extraction/separation of lanthanoids [5]. They have also been used in the stabilisation and crystallization of highly reactive organolanthanoids, aryloxides and organoamides, including pyrazolates [6–13]. Interestingly, [YbCp2(dme)] (Cp = cyclopentadienyl, dme = 1,2 dimethoxyethane) undergoes complexation with Ph3PO without the occurrence of a redox reaction to give [YbCp2(OPPh3)2] [6,8]. More recently attention has turned to chelating phosphane oxides with bis(diphenylphosphano)methane dioxide attracting particular attention [14–20]. Still more recently, reactions of yttrium and lanthanum tris(bis(trimethylsilyl)amide) complexes with bis(diphenylphosphano)- and bis(dimethylphosphano)-methane dioxide led to the deprotonation and formation of homoleptic rare earth complexes of bis(phosphane-oxide)methane species (Scheme 1, previous work, reaction 1a) [14]. We now report that the reaction of dicyclopentadienylytterbium(II) with bis(diphenylphosphano)methane dioxide (H2dppmO2) does not lead to a simple complexation giving [YbCp2(H2dppmO2)], as with Ph3PO [6], but rather both deprotonation and oxidation occur, to give the tris(bis(diphenylphosphane oxide)methanido)ytterbium(III) complex, [Yb(HdppmO2)3] (1) (Scheme 1, present work, reaction 1b). The compound 1 was also prepared by a redox transmetallation (RTP) reaction between Yb metal, Hg(C6F5)2, and bis(diphenylphosphano) methane dioxide (Scheme 1, present work, reaction 1b). However, the reaction of bis(pentafluorophenyl)ytterbium and bis(phosphano)methane dioxide not only yields
1, but also forms a (hexafluorido)tetraytterbium(III) cage \([\text{Yb}_4(\mu-\text{HdppmO}_2)_6(\mu-\text{F})_6] (2)\) by C-F activation of pentafuoroobenzene (Scheme 1, present work, reaction 1c). The paper provides new synthetic paths to bis(phosphine oxide)methanide complexes and a remarkable fluoride-bridged cage.

**Scheme 1.** Previous studies (reaction 1a [14]) and our current work (1b and 1c) on rare earth complexes from reactions of \(\text{H}_2\text{dppmO}_2\).

**2. Results and Discussion**

**2.1. Synthesis and Characterisation of \([\text{Yb}(\text{HdppmO}_2)_3]\) 1**

Initially, an attempt was made to prepare \([\text{YbCp}_2(\text{H}_2\text{dppmO}_2)]\) by reaction of \([\text{YbCp}_2(\text{dme})]\) (dme = 1,2-dimethoxyethane) with an equimolar amount of bis(diphenylphosphane)methane dioxide (\(\text{H}_2\text{dppmO}_2\)) (Scheme 2, Route 1), analogous to the reaction conditions used in the preparation of \([\text{YbCp}_2(\text{OPPh}_3)_2]\) [6]; instead, an oxidation reaction occurred and the tris[bis(diphenylphosphate oxide)methanido]ytterbium(III) complex, \([\text{Yb}(\text{HdppmO}_2)_3]\) 1 was isolated, together with CpH and unreacted \([\text{YbCp}_2(\text{dme})]\). The \(^{31}\text{P}(^{1}\text{H})\) NMR spectrum revealed a considerably deshielded \(^{31}\text{P}(^{1}\text{H})\) signal at 39.1 ppm (c.f \(\text{H}_2\text{dppmO}_2\) 24.5 ppm) (See Figure S1a,c) and the \(^1\text{H}\) NMR spectrum showed the formation of CpH indicative of deprotonation of \(\text{H}_2\text{dppmO}_2\). In addition, the presence of unreacted \([\text{Yb Cp}_2(\text{dme})]\) was also detected in the reaction mixture. (See Supplementary Materials, Figure S1b, Table S1).

**Scheme 2.** Rational synthesis of \([\text{Yb}(\text{HdppmO}_2)_3]\) 1.
To facilitate a rational synthesis and effective utilization of \([\text{YbCp}_2(\text{dme})]\), the reaction stoichiometry was increased to a 3:1 ratio of \(\text{H}_2\text{dppmO}_2\): \([\text{YbCp}_2(\text{dme})]\), resulting in the isolation of crystalline \(1\) in 65% yield. NMR spectroscopy of the reaction mixture shows complete consumption of the \([\text{YbCp}_2(\text{dme})]\) (See Supplementary Materials, Figure S1f). Thus, both protolysis and redox processes are observed in the reaction of \([\text{YbCp}_2(\text{dme})]\) with \(\text{H}_2\text{dppmO}_2\) (Scheme 2, route 2). With the same mole ratio the reaction was carried out in an NMR tube in \(d_8\)-toluene, revealing a resonance at 4.79 ppm attributable to \(\text{H}_2\) gas formation [21–23] (See Figure S2c). The composition of \(1\) was established by microanalysis and high-resolution mass spectrometry which revealed the \([\text{M}+\text{H}]^+\) ion (see Experimental Section 3.4).

The infrared spectrum of the extremely air- and moisture-sensitive \(1\) shows very strong \(\nu(\text{P}=\text{O}, \text{cm}^{-1})\) absorptions at 1154, 1120, 1081 and 1061 (Figure 1, top), which are very different from those of free ligand (1212, 1197 and 1176 \text{cm}^{-1}) (Figure 1, bottom). A strong band of the ligand at 1111 \text{cm}^{-1} can be assigned to the X-sensitive mode \(q\), involving P-C stretching [24,25]. This is not unduly shifted or enhanced in intensity on coordination as indicated by the spectra of \(\text{Ph}_3\text{P}=\text{O}\) complexes [24] and presumably contributes to the intensity of the 1120 \text{cm}^{-1} band of the complex. Weaker C-H in-plane deformation modes of the ligand at 1083 and 1027 \text{cm}^{-1} are unlikely to be affected by coordination. The shifts of \(\nu(\text{P}=\text{O})\) are reminiscent of the shift of \(\nu(\text{C}=\text{O})\) of the diketo form of beta-diketones to \(\nu_{as}(\text{C}=\text{O})\) of \(\beta\)-diketone complexes [26]. The absorption bands of \(1\) (see Experimental Section 3.4) are somewhat similar to those listed for \([\text{M}(\text{dppmO}_2)_3]\) [14] (\(\text{M} = \text{Y}, \text{La}\)), where absorptions at 1148 (\(\text{M} = \text{Y}\)) and 1076, 1050 \text{cm}^{-1} (\(\text{M} = \text{La}\)) are assigned to \(\nu(\text{P}=\text{O})\). On the other hand, in the complex \([\text{Ln}(\text{H}_2\text{dppmO}_2)_4]\beta^3\), containing neutral \(\text{H}_2\text{dppmO}_2\), the absorptions at 1197 and 1098 \text{cm}^{-1} are assigned to \(\nu(\text{P}=\text{O})\) [15], though the latter may be a slightly shifted \(q\) vibration, thereby indicating that the absorptions are little affected when the ligand is neutral. Similarly, \([\text{Ga}(\text{Bu})_3(\text{H}_2\text{dppmO}_2)]\) has strong bands at 1210, 1187, 1170 (\(\nu\text{ P}=\text{O}\)) and 1110 (\(q\)), and medium C-H deformation bands at 1075 and 1028 \text{cm}^{-1}, all near free ligand values, but the complex of the deprotonated ligand \([\text{Ga}(\text{Bu})_3(\text{H}_2\text{dppmO}_2)]\) has strong bands at 1195, 1165, 1110, 1076, 1060 \text{cm}^{-1} [27], which are similar to those of \(1\), apart from the first value.

![Figure 1](image-url) Figure 1. The infrared spectrum of complex \([\text{Yb}(\text{HdppmO}_2)_3]\) \(1\) (top) and free ligand \(\text{H}_2\text{dppmO}_2\) (below) in Nujol mull.

2.2. Solid State Structure of \([\text{Yb}(\text{HdppmO}_2)_3]\) \(1\)

Slow evaporation of a solution of \(1\) in acetonitrile yielded polychromatic blocks of compound \(1\)-MeCN which crystallised in the triclinic space-group (P \(\overline{1}\)) with a molecule of lattice acetonitrile in the asymmetric unit. A single-crystal X-ray structure determination of \(1\) shows a six-coordinate complex, having a slightly distorted octahedral stereochemistry (Figure 2) for ytterbium with cis and trans O–Yb–O angles in the ranges...
of 85.01(6)–93.23(6)° and 174.1(6)–176.86(6)°, respectively (See Table S4). Although the structure is similar to those of [M(HdppmO)] (M = La or Y) [14], the structures are not isomorphous, possibly owing to the presence of lattice solvent in 1-MeCN. The Yb-O bond lengths (2.1953(16)–2.2263(14) Å) are in the range of comparable reported amide complexes, namely, (a) [Yb[PO(C6H5)2]3] [28]; (2.199(6)–2.219(6) Å) and (b) [Yb[PO(C6H5)2]2] [29]; (2.18(2)–2.28(2) Å). The Yb-O bond lengths of 1 are shorter than those in [Yb(H2dppmO2)2Cl]+ where the ytterbium atom is bound to neutral H2dppmO2 (Yb-O 2.250(3)–2.338(3) Å) [16]. The P-O and P-C bond lengths in 1 range between 1.5152(16)–1.5317(16) Å and 1.706(2)–1.714(2) Å, respectively, which are different from those of the free ligand H2dppmO2 [30] (P-O: 1.486(2) Å and P-C:1.815(2) Å) indicating partial double bond character for P-O and P-C bonds in the chelate ring as reported in the case of the La and Y analogues [(M(HdppmO)2)] [14]. However, the P-O double bond character is reduced on coordination, whilst the double bond character of the P-C bond is considerably increased, owing to charge delocalization on deprotonation.

![Figure 2](image-url)

Figure 2. The molecular structure of [Yb(HdppmO2)3] 1. All hydrogen atoms are omitted for clarity except backbone methanide protons. Lattice acetonitrile is omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and bond angles (°) can be found in Table S4.

2.3. Properties of [Yb(HdppmO2)3] 1 in Solution

The 1H NMR spectrum of compound 1 in CD2Cl2 (see Supplementary Materials) is broad owing to the paramagnetic nature of the complex. The two broad singlets observed at ~3.26 and 7.45 ppm are assigned to methanide and aromatic protons, respectively. The methanide CH− proton is upfield shifted by ~6 ppm relative to the CH2 resonance of the free ligand (3.56 ppm) [31] indicating it is highly shielded in comparison to other [M(HdppmO2)3] complexes (M = Y (δH = 2.26 ppm), M = La (δH = 2.28 ppm)) [14] presumably owing to YbIII paramagnetism. This pronounced shielding of the methanide proton was supported by Natural Bond Orbital (NBO) analysis on complex 1 (see Supplementary Materials).
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Materials for full details). It was observed that Natural Population Analysis (NPA) revealed substantial negative natural charge of $-1.43$ at the methanide carbon (see Table S2), where $q_C$ of CH$^-$ was significantly more negative than the aromatic carbon atoms attached to the phosphorus atom ($-0.395$ to $-0.425$) in 1, implying high shielding of the CH$^-$ proton in the $^1$H NMR spectrum, as observed experimentally (See Table S2). The positive natural charge for Yb(III) was calculated to be $1.84$ which is in the range as mentioned in the literature [32].

In the series (Ln(HdppmO$_2$)$_3$) Ln = La, Y [14], Yb (this work) the calculated charge decreases 2.30, 2.00, 1.84, respectively, as the size of the ion decreases, reflecting increased ligand to metal charge transfer in the same sequence. The $^{31}$P{$^1$H} NMR spectrum of complex 1 shows a singlet at 39.1 ppm with a coordination shift of 14.2 ppm (H$_2$dpmpO$_2$; 24.9 ppm), and is similar to the reported [M(HdppmO)$_3$] (M = Y (37.8 ppm), La (35.4 ppm)) [14], hence the effect of deprotonation outweighs paramagnetic effects in $^{31}$P{$^1$H} NMR spectroscopy (see Figure S5b).

To examine the solution behavior further, $^1$H NMR spectra were recorded for complex 1 in CD$_2$Cl$_2$ from 25 °C to −75 °C (Figure 3). On lowering the temperature from 25 °C to 5 °C, coalescence was observed until −15 °C when the peaks were resolved (Figure 3). At −55 °C, sharp peaks are seen with no further changes below. This phenomenon can be rationalised by a conformational equilibrium [33] in 1. At 25 °C the conformers are found to be highly fluxional, while at −55 °C the dynamic equilibrium between the conformers ceases, whereas in case of the reported [M(HdppmO)$_3$] (M = Y, La) complexes, they are found to be fluxional even at −80 °C [14].

![Figure 3](image)

**Figure 3.** Variable temperature (VT) $^1$H NMR spectrum of complex 1 showing aromatic region only, at 25, −15 and −55 °C in CD$_2$Cl$_2$. Full $^1$H NMR spectra can be found in Figure S7a.

The presence of conformers is further supported by close analysis of the solid-state structure. Three six-membered YbO$_2$P$_2$C metallacycles, present in 1, exhibit a combination of boat and twist-boat conformers within the solid-state (Figures 4 and 5). The torsion angles of the O-P-O atoms in the metallacycle are all significantly different for all the three metallacycle rings in both the boat and twist-boat conformations (Table 1).
This indicates that at 25 °C there is a rapid intramolecular dynamic process within complex 1. As the temperature reaches −15 °C, the spectrum indicates the interconversion process slowing down between the possible conformers. At −55 °C the intramolecular dynamic process ceases as resolved peaks are distinctly observed. This indicates the possibility of phenyl groups frozen in the axial and equatorial positions at −55 °C, where there are mirror image peaks (See Figure S7b). Thereby, we can conclude that at 25 °C, complex 1 is highly fluxional, but at −55 °C the fluxionality is lost. Variable temperature $^{31}$P/$^1$H NMR spectroscopy did not show much variation within the temperature range of 25 °C to −75 °C other than a slight shift to a higher frequency (See Figure S7c).

![Figure 4](image-url1)

Figure 4. Arrangement of phenyl groups on P atoms within the metallacycle of complex.

![Figure 5](image-url2)

Figure 5. Boat and twist-boat conformers of the metallacycles in complex 1.

| O-P-P-O Mean Plane   | Torsion Angle (°) | Conformer     |
|----------------------|-------------------|---------------|
| O1-P1-P2-O2          | 8.03 (11)         | boat form     |
| O3-P3-P4-O4          | 30.05 (8)         | twist-boat    |
| O5-P5-P6-O6          | 4.18 (11)         | boat form     |
2.4. Synthesis of 1 by the RTP Method

In order to examine the redox transmetallation protolysis (RTP) protocol [34] an excess of metallic Yb was treated with Hg(C₆F₅)₂ and H₂dppmO₂, in THF at room temperature for 15 min (Scheme 3). Analysis of the reaction mixture by $^{19}$F[¹H] NMR spectroscopy revealed peaks at −139.8, −155.5 and −163.4 ppm corresponding to the formation of C₆F₅H [35] and a small peak at −140.2 ppm, assigned to $p$-H₂C₆F₄ [35] (See Figure S8). The $^{31}$P[¹H] NMR spectrum showed a sharp resonance at 39.8 ppm indicative of complex 1. Recrystallisation of this extremely air- and moisture sensitive compound from dry acetonitrile gave polychromatic blocks of complex 1 in a 71% yield. This simple one-pot procedure should be applicable to all rare earth elements, and does not require a prior synthesis of metal precursors, e.g., of tris[bis(trimethylsilyl)amido]-lanthanoid(III) complexes [14]. This is the first synthesis of a methanido-lanthanoid complex by this method, but should be widely applicable, for example to $\beta$-diketonates.

Scheme 3. One pot RTP synthesis of complex 1.

2.5. Synthesis of [Yb₄(µ-HdppmO₂)$_6$(µ-F)$_6$] 2

RTP reactions between Yb metal, Hg(C₆F₅)₂, and a protic reagent LH (LH = a weak protic acid e.g., phenols, amines, CpH, pyrazoles, amidines etc.) proceed through a [Yb(C₆F₅)$_2$] intermediate, which is protolysed to give pentafluorobenzene and Yb[II]L$_2$, but when Yb[III]L$_3$ is the final product, YbL$_2$ is further oxidised by Hg(C₆F₅)$_2$ to give YbL$_2$(C₆F₅), which is protolysed to give YbL$_3$ [34]. Since [Yb(C₆F₅)$_2$] is a key intermediate in RTP syntheses, we examined the reaction of independently prepared [Yb(C₆F₅)$_2$] [36,37] with H₂dppmO₂. It also provides a comparison with the reactions of [YbCP$_2$(dme)] (as discussed in Section 2.1).

[Yb(C₆F₅)$_2$] was prepared by reacting an excess of Yb with Hg(C₆F₅)$_2$ (Scheme 4). Addition of the filtered [Yb(C₆F₅)$_2$] solution to H₂dppmO₂ in THF in a 1:3 ratio afforded a solution colour change from red/orange to colorless over 20 min. The $^{19}$F[¹H] NMR spectrum of an aliquot of the reaction mixture revealed seven peaks, identified as corresponding to the major products; pentafluorobenzene (−139.6, −155.59 and −163.5 ppm) [35] and 1,2,4,5-tetrafluorobenzene (−140.7 ppm) [35] and minor product, 1,2,3,5-tetrafluorobenzene (−114.2, −133.1 and −167.5 ppm) [38] (See Figure S9a). The corresponding $^{31}$P[¹H] NMR spectrum of the reaction mixture shows a sharp peak at 39.1 ppm corresponding to compound 1. (see Figure S9b).

A small amount of colourless blocks was deposited from a concentrated reaction mixture aliquot added to $d_6$-benzene. The crystals were subjected to X-ray single crystal structure determination which revealed the presence of the C-F activation product [Yb$_4$(µ-HdppmO$_2$)$_6$(µ-F)$_6$]-6THF-3C$_6$D$_6$ 2 (Figure 5). Compound 2 is obtained in low yield and is insoluble in most deuterated organic solvents ($d_6$-benzene, $d_6$-thf, CD$_3$CN, CD$_2$Cl$_2$ and $d_5$-toluene) inhibiting analysis in the solution state.
work, 1,2,3,4-tetrafluorobenzene formation has been observed in C-F activation reactions with 1,2,4,5-tetrafluorobenzene. Ytterbium (and Eu) can activate C$_2$(L = ytterbium atoms. Six bridging (O,O’) HdppmO ate [Yb(HdppmO)$\cdot$6THF $\cdot$3C$_6$D$_6$$_2$ (Figure 5). Compound 2 is obtained in low yield and is unselectively with the m$_F$ atoms of C$_6$F$_5$H by single electron transfer to generate [Yb(HdppmO)$_2$F] and isomeric m- and p-C$_6$H$_4$F$_4$ radicals which capture hydrogen radicals from the solvent to give m- and p-C$_6$H$_4$F$_4$. Complex 2 is then formed by the rearrangement of the [Yb(HdppmO)$_2$F] (Scheme 5).

Scheme 4. Protolysis reaction for the formation of 1 and [Yb$_4$(µ—HdppmO)$_6$(µ—F)$_6$] 2.

2.6. Solid State Structure of [Yb$_4$(µ-HdppmO)$_6$(µ-F)$_6$] 2

The X-ray structure of 2 (Figure 6) shows four ytterbium centres bridged by six HdppmO$_2$ and six fluoride ions with each metal centre adopting slightly distorted octahedral geometry. The tetra-nuclear structure of 2 can be regarded as a dimer of dimers. It is based on a Yb$_2$F$_6$ cage with alternating single and double bridges between adjacent ytterbium atoms. Six bridging (O,O’) HdppmO$_2$ ligands form the periphery of the cage and also alternate between double and single ligand bridges with the pairs corresponding to single fluoride bridges and vice versa. Two [Yb(µ-F)$_2$] rhombic units are linked by two fluoride ligands. By contrast, the iso-stoichiometric cages reported earlier, [Yb$_4$F$_6$L$_6$] (L = p-HC$_6$F$_4$N(CH$_2$)$_2$NR$_2$; R = Me or Et), consist of one rhombic [Yb(µ-F)$_2$] unit linked on both sides by two metal centres via four M—F—M units, and the amide ligands are chelating not bridging [39]. In the case of 2, the Yb-O bond lengths (2.162(2)—2.189(2) Å) are slightly shorter than those of compound 1 (2.1953(16)—2.2263(15) Å), probably due to the electronegative fluoride co-ligands. The P-O bond lengths (1.515(2)—1.524(2) Å) are relatively longer and P-C$_H$ lengths (1.695(4)—1.712(4) Å) are relatively shorter than those in the free ligand H$_2$dpmpz$_2$ (P-O 1.486(2) Å and P-C$_H$ 1.812(2) Å) [30] indicating partial double bond character of P-O and P-C bonds. The P-O and P-C bond lengths are very close to those of 1. The Yb-F bond lengths in [Yb(µ-F)$_2$] are slightly shorter than those which link two rhombic units (Figure 5). Overall, the Yb-F bond lengths in compound 2 are in the range of previously reported complexes (c.f. [Yb$_4$ (p-HC$_6$F$_4$N(CH$_2$)$_2$NMe$_2$)$_6$F$_6$], 2.150(2)—2.190(2) Å) [39].

Inhibited by low solubility, was also characterized by elemental analysis (see Experimental Section 3.4). The formation of 2 by C-F activation, utilising an organolanthanoid, is very rare in being accompanied by the formation of 1,2,3,4-tetrafluorobenzene along with 1,2,4,5-tetrafluorobenzene. Ytterbium (and Eu) can activate C$_6$F$_5$H with the formation of the observed p-C$_6$F$_4$H$_2$, though the reaction is slow [40,41]. However, in the present reaction, the Yb metal is separated before C$_6$F$_5$H is generated by protolysis. In previous work, 1,2,3,4-tetrafluorobenzene formation has been observed in C-F activation reactions that accompany the redox transmetallation between Sm metal and Hg(C$_6$F$_5$)$_2$ [42], but there was no report of the formation of m-C$_6$F$_4$H$_2$. A possibility source of two tetrafluorobenzenes is that [Yb(HdppmO)$_2$], the initial product of protolysis of [Yb(C$_6$F$_5$)$_2$], reacts unselectively with the m-F and p-F atoms of C$_6$F$_5$H by single electron transfer to generate [Yb(HdppmO)$_2$F] and isomeric m- and p-C$_6$H$_4$F$_4$ radicals which capture hydrogen radicals from the solvent to give m- and p-C$_6$H$_4$F$_4$. Complex 2 is then formed by the rearrangement of the [Yb(HdppmO)$_2$F] (Scheme 5)
Figure 6. The molecular structure of \([\text{Yb}_4(\mu-\text{HdppmO}_2)_{6}(\mu-\text{F})_6]\). All hydrogen atoms are omitted for clarity except backbone methanide protons. Displacement ellipsoids are drawn at the 30% probability level. The lattice solvents THF and C\textsubscript{6}D\textsubscript{6} have been omitted and phenyl groups drawn in wire frame for better clarity. Symmetry operator = 1 − x, +y, 1/2 − z. Selected bond lengths (Å) and bond angles (°) can be found in Table S4.

Scheme 5. Proposed mechanism for C-F activation and formation of complex 2.

3. Materials and Methods
3.1. General Procedures

All the lanthanoid metals and lanthanoid(II) and (III) products are highly air- and moisture-sensitive, hence operations were carried out under nitrogen using standard Schlenk-line and glovebox techniques. Ytterbium metal was purchased as metal in-
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gots from Santoku or Eutectix. [YbCp₂(dme)] [43], H₂dppmO₂ [44], Hg(C₆F₅)₂ [45] and [Yb(C₆F₅)₂] [36,37] were synthesised by literature procedures. THF was dried and deoxygenated by refluxing over Na metal and distillation from calcium hydride, whereas MeCN was dried and deoxygenated by refluxing over and distillation from calcium hydride. The dried solvents were stored over 4 Å molecular sieves. Infrared spectra (4000–650 cm⁻¹) were obtained with Nujol mulls between NaCl plates with a Perkin-Elmer 1600 FT-IR spectrometer. Room temperature (25 °C) ¹H and ³¹P{¹H} NMR spectra were recorded with a Bruker DPX 300 instrument using d₈-toluene, C₆D₆ or CD₂Cl₂. The solvents were dried over 4 Å molecular sieves for 48 h, and resonances were referenced to residual hydrogen-atom resonances of the deuterated solvent.

3.2. Single Crystal X-ray Structure Determination

Crystals for X-ray structure analysis were grown using saturated solutions in acetonitrile (1), or THF-C₆D₆ (2). Crystals 1 and 2 were immersed in paratone, and were measured on a Rigaku SynergyS diffractometer. The SynergyS operated using microsource Cu-Kα radiation (λ = 1.54184 Å) at 123 K. Data processing was conducted using the CrysAlisPro software suite [46]. Structural solutions were obtained by ShelXT [47] and refined using full-matrix least-squares methods against F² using SHELXL [48], in conjunction with Olex2 [49] graphical user interface. All hydrogen atoms were placed in calculated positions using the riding model.

3.3. Computational Studies

All calculations reported were performed using the Gaussian 09 suite of programs. The coordinates for the calculations were directly taken from X-ray structure of compound 1. The calculations were performed on complex 1 using the basis set def2-TZVP [50–54]/6-31G (d, p) [50–52,55,56] for carrying out natural bond analysis and MO6L was chosen as functional for our study. def2-TZVP is a basis set used for Yb metal [57] and the 6-31G (d, p) basis set is used for C, H, O and P. Full details are in the Supplementary Materials.

3.4. Experimental Section

3.4.1. Preparation of [Yb{(Ph₂PO)₂CH}]₃ (1)

Method 1: [YbCp₂(dme)] (30 mg, 0.076 mmol) and H₂dppmO₂ (95.2 mg, 0.228 mmol) in dry THF (5 mL) at room temperature, were stirred for 30 min. The solution was evaporated and 10 mL of dry MeCN were added. The volume of the solution was concentrated by half to obtain extremely air- and moisture-sensitive polychromatic crystals of 1, 70 mg, 65% yield. M.P decomp. temp at 380 °C. ¹H NMR (at 25 °C 400 MHz, CD₂Cl₂) δ 7.22 (s, 60H), −3.14 (s, 3H). ¹H NMR (at −75 °C 400 MHz, CD₂Cl₂) δ 13.71–12.68 (m, 11H), 8.75 (s, 13H), 8.18 (s, 6H), 5.91 (s, 13H), 5.28 (s, 11H), −3.98 (s, 3H). ³¹P{¹H} NMR (at 25 °C, 162 MHz, CD₂Cl₂) δ 39.20. HRMS(m/z) calcld. for C₇₅H₆₃O₆P₆Yb 1420.2526 (M+1); found 1420.2518 (M+1, 0.08%). IR spectrum (1700–650) cm⁻¹ /Nujol 1676(w), 1590(w), 1573(w), 1438(s), 1308(m), 1262(s), 1120(vs), 1081 and 1062(vs), 1026(s), 999(w), 947 and 932(vs), 812(s), 745(s), 722(s), 692(s). Elemental analysis calcld (%) for C₇₅H₆₃O₆P₆Yb (loss of MeCN lattice solvent): C 63.47, H 4.47; found C 63.50, H 4.65.

Method 2: Yb metal (166.2 mg, 0.960 mmol), Hg(C₆F₅)₂ (128.3 mg, 0.239 mmol) and H₂dppmO₂ (200 mg, 0.480 mmol), stirred for 15 h at room temperature in dry THF. The reaction mixture was filtered and dried under vacuum. Anhydrous MeCN was added to the crude product followed by concentration of the solution to yield extremely air- and moisture-sensitive polychromatic blocks of compound 1. The unit cell values of the crystals (by SCXRD studies) matched that of compound 1 (Yield = 241 mg, 71%).

Full crystal and refinement data for complexes 1 and 2 can be found in the Supplementary Materials.
3.4.2. Preparation of [Yb₄{(Ph₂PO)₂CH}₆F₆] (2)

Yb metal (166.2 mg, 0.960 mmol) and Hg(C₆F₅)₂ (128.3 mg, 0.239 mmol) in dry THF were stirred for 2 h at room temperature and the reaction mixture was filtered into a THF solution of H₂dppmO₂ (300 mg, 0.717 mmol) and stirred for 20 min at room temperature. The reaction mixture was filtered, and an aliquot of the solution in C₆D₆ was subjected to NMR analysis in a Young’s NMR tube. The NMR solution yielded extremely air- and moisture-sensitive colourless block crystals identified as compound 2. Yield of 2 (17 mg, 2.2%). An attempt was made to obtain the infrared spectrum of 2 but it had limited stability in Nujol and turns black gradually. Gradual decomposition is also apparent in the X-ray oil. ¹⁹F[¹[H] NMR of the reaction mixture (376 MHz, C₆D₆) δ = −139.6, −155.59 and −163.5 (C₆F₅H), −140.7 (1,2,4,5-C₆F₄H), and −114.2, −133.1 and −167.5 (1,2,3,5-C₆F₄H). Elemental analysis calculated (%) for C₁₅₀H₁₂₀O₁₂P₁₂Yb₁F₁₆ (loss of lattice solvent 3 × C₆D₆ + 6 × thf) C 54.62, H 3.85 found C 54.59 H 3.89. HRMS (m/z) calculated for Yb(HdppmO₂)₃ + Ph₂P(O)OH + H: 1638.3031 found 1638.3168. The rest of the reaction solution was evaporated to dryness and anhydrous MeCN was added to the crude product followed by concentration of the solution to yield extremely air- and moisture-sensitive colourless block crystals of compound 1 (Yield = 230 mg, 68%).

4. Conclusions

The complex, [Yb(HdppmO₂)₃] 1, with a chelating O,O’-donor set of bis(diphenylphosphane oxide)methanide ligands, has been obtained by oxidative protolysis of [YbC₆P₂(dme)] with H₂dppmO₂, by a redox transmetallation/protolysis reaction between Yb metal, Hg(C₆F₅)₂ and H₂dppmO₂, and by oxidative protolysis of [Yb(C₆F₅)₂] with H₂dppmO₂. The latter reaction also yielded a novel fluoride-bridged cage, [Yb₄(µ-HdppmO₂)₆(µ-F)₆] 2, with a core of Yb atoms alternately singly and doubly bridged by fluoride, YbFYbF₂YbFYbF₂. The fluoride ligands are derived from C-F activation of pentafluorobenzene giving p-H₂C₆F₄ and, unexpectedly, m-H₂C₆F₄. The RTP synthesis provides a simple one pot route for all rare earth tris{bis(diphenylphosphane oxide)methanides}, and also for other analogous phosphine oxide-derived species and potentially methanidolanthanoid species in general.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27227704/s1, including NMR spectra, additional experimental, X-ray and refinement data, bond lengths and angle data and DFT calculations.

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