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Communication

The first lanthanide (II) diorganophosphide complex with planar coordination at phosphorus: synthesis, crystal and molecular structure of $[(\text{mesityl})_2\text{P}]_2\text{Yb}(\text{THF})_4$

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Summary – The title compound **2** was prepared by oxidative addition of ytterbium metal to the P–P bonds of 1-dimesitylphosphido-2,3,4,5-tetramethylphosphole or tetramesitylbiphosphine, or by reaction of Mes_2PK with ytterbium diiodide in THF. Although the P–Yb bond is a single bond in the structure of **2**, the tricoordinated P atom is planar.

Ytterbium / complex / phosphole / phosphide

Although the molecular chemistry of lanthanide compounds in the + II oxidation state is currently restricted to the elements samarium, europium and ytterbium, it has nevertheless stirred considerable interest recently, because of the unique combination of their strong reducing properties, especially for samarium(II), and strong Lewis acidity [1]. The most widely studied compounds include SmI_2 in THF solution [2], which is now a commercially available reagent, and organometallic complexes of Yb(II) and Sm(II) with the pentamethylcyclopentadienyl (Cp*) ligand [1,3]. Inorganic compounds of these metals with hard amido ligands are also well known [4]. However, quite recently, studies have appeared in which Ln(II) cations are coordinated to the softer organosulfide, selenide or telluride ligands [5-7]. We have previously shown that the dibenzophospholide ligand, an unusual diorganophosphide, was η^1-coordinated through the soft P atom to Sm(II) [8]. This compound was prepared by insertion of Sm into the P–P bond of a bis(dibenzophospholyl). Since insertion of Yb metal into a P–S bond of a 1-phenylthiophosphole was also successful, yielding a π-phospholylytterbium(II) thiolate dimer [9], we reasoned that insertion of Yb metal into the P–P bond of a 1-dimesitylphosphidophosphole (mesityl = 2,4,6-trimethylphenyl) would give a π-phospholylytterbium(II) dimesitylphosphide compound. We hoped that the bulky mesityl groups on phosphorus would give a monomeric structure for this compound. A transition from dimeric to monomeric Yb(II) thiolate complexes is observed with increasing bulk on the thiolate organic substituent [6, 7].

1-Dimesitylphosphido-2,3,4,5-tetramethylphosphole [10] **1**, could be prepared by reaction of potassium 2,3,4,5-tetramethylphospholide [11] with dimesitylbromophosphine. Thereafter, we tried the insertion reaction of Yb metal in slight excess (activated with *ca* 2-5% (m/m) HgCl_2) into the P–P bond of **1** in tetrahydrofuran (THF). Within 48 h, the reaction mixture turned dark red and a yellow precipitate **2** formed and was isolated. Investigation of this material by NMR showed a broad singlet at −39.7 ppm in the ^{31}P spectrum and only resonances due to the mesityl group in the ^1H and ^{13}C spectra. These results suggested that the product was not the expected π-phospholylytterbium dimesitylphosphide compound, but an ytterbium(II) bis(dimesitylphosphide). This material was recrystallized in warm THF and an X-ray crystal study confirmed that the structure of **2** was that of $\text{Yb}(\text{PMes}_2)_2(\text{THF})_4$ [12] (Mes = mesityl). Ytterbium does indeed insert into the P–P bond of **1**, but disproportionation occurs because of the lower solubility of **2**. Since the synthesis of **2** is not efficient (the phospholyl moiety is lost in the process), two other methods were tried, and were successful. In the first, **2** was obtained by direct insertion of Yb metal into the P–P bond of $\text{Mes}_2\text{P–PMes}_2$ [13] whereas in the second, **2** could be obtained by an anionic route, *ie* by reaction of Mes_2PK with $\text{YbI}_2(\text{THF})_2$ (fig 1).

A PLATON plot of **2** is presented in figure 2; **2** crystallized in the tetragonal space group $I4_1/a$ (No 88) [14], with the Yb at the origin of the lattice, which means that the molecule must have S_4 symmetry. This in turn implies three things : a) that the Yb atom lies

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* Correspondence and reprints

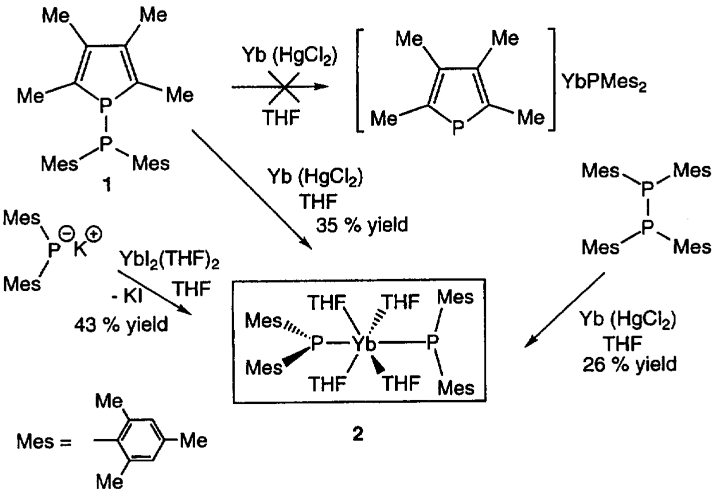

Fig 1

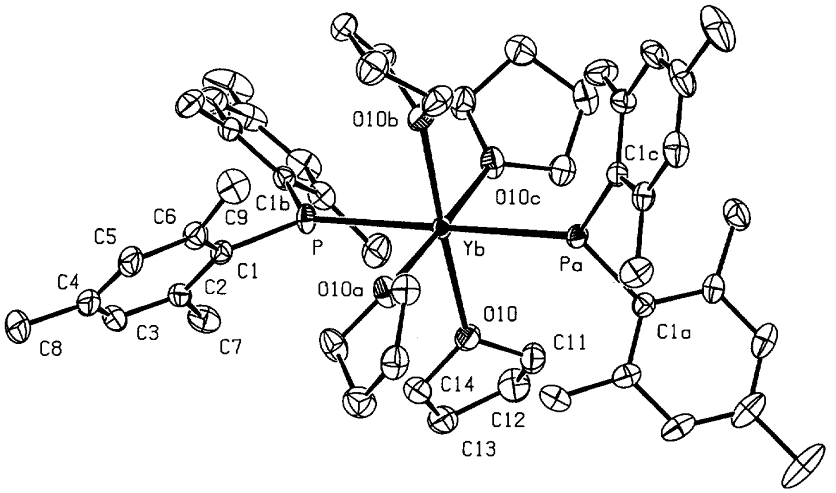

Fig 2. A PLATON plot of one molecule of **2** with ellipsoids scaled at 50% probability level. Selected bond lengths (Å) and angles (degrees) : Yb-P 2.925(2), Yb-O 2.439(4), P-C 1.837(5), C-P-C 102.5(3), C-P-Yb 128.8(2), P-Yb-O(10) 91.30(8), P-Yb-O(10b) 88.70(8), O(10)-Yb-O(10b) 90.0(4), O(10)-Yb-O(10a) 177.4(2).

in the middle of the P to Pa distance; b) that the coordination around phosphorus is *rigorously planar*; and c) that the C-P-P′-C′ dihedral angles are exact multiples of 90°. These results can be compared with an interesting work by G Rabe [15] that we recently became aware of. In his study, Rabe was able to prepare the less bulky Yb(PPh$_2$)$_2$(THF)$_4$, closely related to **2**, by reaction of YbI$_2$ or YbI$_3$ with Ph$_2$PK, or Yb[N(SiMe$_3$)$_2$]$_2$ with Ph$_2$PH. However in contrast to our case, no reaction occurred from the interaction of Ph$_2$P–PPh$_2$ with Yb metal. The crystal structure of Yb(PPh$_2$)$_2$(THF)$_4$, which also displays a linear P–Yb–P bonding pattern, is different from that of **2** because the coordination around phosphorus is now *pyramidal* (sum of angles = 332.7°); the P–Yb bond lengths are similar in both cases. Interestingly, a crystallographically imposed planarity of phosphorus has also been found by Aspinall [16] and coworkers in a bulky La(III)–PPh$_2$ complex; this planarity was attributed to steric crowding. The comparison of the structures of **2** and Yb(PPh$_2$)$_2$(THF)$_4$ supports this hypothesis in view of the mostly steric difference between phenyl and mesityl. Of course, planar coordination at phosphorus is known in the case of transition metal compounds in which there are phosphorus-metal double bonds [17]. Further chemical studies of **2** are in progress.

References and notes

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14 X-ray structure of **2** ($C_{52}H_{76}O_4P_2Yb$) : data collected at −150°C on an Enraf-Nonius CAD4 Diffractometer using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71037$ Å), tetragonal space group $I4_1/a$ (no 88), $a = 16.823(2)$ Å, $c = 18.371(2)$ Å, $V = 5\,199.4$ (1.8) Å^3, $Z = 4$, ρ_{calc} 1.278 g/cm^3, $\mu = 18.9$ cm^{-1}, $F(000) = 2\,080$, 2θ max = 60°, No of measured reflexions : 3 466 unique, 2 540 with $F^2 > 3\sigma(F^2)$, solution by direct methods, anisotropic refinement for all non-hydrogen atoms, hydrogens included as fixed contributions in the final least-squares refinements, final agreement factors : $R = 0.042$, $R_w = 0.067$, GOF = 1.41

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