# Synthesis and First Structural Characterization of Lanthanide(II) Aryls: Observation of a Schlenk Equilibrium in Europium(II) and Ytterbium(II) Chemistry

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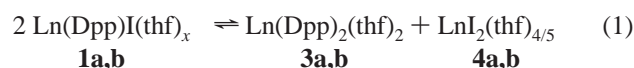
The use of lanthanoid(II) reagents in organic synthesis has developed considerably over the last two decades.[1,2] Most of the attention has been given to the unique reducing agent samarium-(II) iodide and to other mainly π-bonded samarium species. However, there is a growing interest in synthetic applications of divalent σ-bonded organolanthanoid complexes of the composition RLnX (Ln = Sm, Eu, Yb; X = Br, I). The first compounds of this type were obtained almost thirty years ago by Evans and co-workers from organic iodides and lanthanoid metals in THF.[3] It was found later that these reagents show some unique reactivity toward various electrophiles[4−7] Unfortunately, little characterization of such intermediates has been performed. As a consequence, only limited information[8,9] is available on the structure of these molecules or the exact nature of the reactive species (type **1**−**5** see below) which may be present in solution.
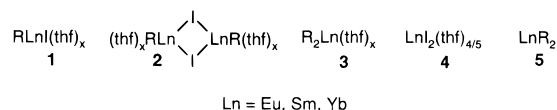
By using very bulky silylated alkyl groups as ligands, dimeric complexes [Yb{C(SiMe$_3$)$_2$(SiMe$_2$R′)}I(OEt$_2$)]$_2$ (R′ = Me, CH= CH$_2$, OMe) of type **2** were synthesized and structurally characterized only recently by Smith and co-workers.[10,11] They also reported the crystal structures of two donor-free lanthanide alkyls Ln{C(SiMe$_3$)$_3$}$_2$ (Ln = Eu, Yb)[11] which are bent in the solid state.[10] Very recently the structural characterization of a solvated samarium(II) alkyl[12] was published. In addition, several solvated ytterbium(II) dialkyls have been characterized by NMR spectroscopy.[13,14] Much less structural information is available for lanthanide(II) aryls.[15] The synthesis of perfluorated ytterbium(II) diaryls, in particular Yb(C$_6$F$_5$)$_2$(thf)$_4$ was pioneered by Deacon et al.[16] Although the reactivity of these compounds was studied

in depth, structural data is not available yet. The simplest ytterbium diaryl YbPh$_2$ is accessible by transmetalation from HgPh$_2$ and activated Yb metal in THF.[17] However, this compound was characterized only very poorly, and its true composition, presumably YbPh$_2$(thf)$_4$, is not known.

In this paper the synthesis and characterization of the *m*-terphenyl derivatives Yb(Dpp)I(thf)$_3$ (**1b**) and Eu(Dpp)$_2$(thf)$_2$ (**3a**) (Dpp = 2,6-Ph$_2$C$_6$H$_3$) are described. In addition to the solid-state structures of **1b** and **3a**, which appear to be the first structurally authenticated lanthanoid(II) aryls, the crystal structure of EuI$_2$-(thf)$_5$ (**4a**) is reported. Compounds **1b** and **3a** were obtained from reactions of DppI with lanthanoid metals in THF.[18] In the case of the ytterbium derivative the expected monosubstituted ytterbium aryl **1b** is isolated in good yield. Going to europium surprisingly affords the disubstituted lanthanoid aryl **3a** and europium diiodide as main products. Apparently the different solubility of the species present in solution is responsible for the different shift of the Schlenk-like equilibrium. This is consistent with the isolation of the ytterbium diaryl **3b** by changing the solvent from THF to toluene.[18]

$$2\ \underset{\textbf{1a,b}}{Ln(Dpp)I(thf)_x} \ \rightleftharpoons\ \underset{\textbf{3a,b}}{Ln(Dpp)_2(thf)_2} + \underset{\textbf{4a,b}}{LnI_2(thf)_{4/5}} \qquad (1)$$
Ln = Eu (a), Yb (b)

In the case of the ytterbium compound it is possible for the first time to detect all three species which are present in THF solution, using ^{171}Yb and ^{13}C NMR spectroscopy as a probe. Therefore, the ^{171}Yb NMR spectrum[20] of **1b** in THF-d_8 solution shows a main signal at 677 ppm. Smaller resonances of equal height at 927 and 457 ppm are assigned to the diaryl species Yb-(Dpp)$_2$(thf)$_2$ **3b** and solvated ytterbium(II) iodide YbI$_2$(thf)$_4$ **4b**,[21]

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(18) All manipulations were carried out under strictly anaerobic and anhydrous conditions using argon as inert atmosphere. (a) **1b**·(thf)$_{0.5}$: Yb chips (0.93 g, 5.37 mmol) were added at ambient temperature to a stirred solution of DppI[19] (1.42 g, 4.0 mmol) in THF (60 mL). After an induction period of several minutes a color change to orange was observed. Stirring was continued for 1 h, whereupon the resulting red-brown solution was carefully decanted from the excess of Yb metal. The volume of the solution was reduced to incipient crystallization under reduced pressure. Storage in a −30 °C freezer overnight afforded **1b**·(thf)$_{0.5}$ as thin orangered needles. yield 2.28 g (2.92 mmol, 73%); mp 110−125 °C (dec, crystals gradually turn black); NMR data in THF-d_8: values for **3b** are given in brackets ^{1}H NMR δ 1.77 (m, OCH$_2$C*H*$_2$, 14H), 3.63 (m, OC*H*$_2$CH$_2$, 14H), 6.97−7.78 (m, aryl-*H*, 13H); ^{13}C NMR δ 26.4 (OCH$_2$*C*H$_2$), 68.2 (O*C*H$_2$CH$_2$), 124.4 [124.2] (*m*-C$_6$H$_3$), 125.0 [125.2] (*p*-C$_6$H$_3$), 126.0 [126.1] (*p*-Ph), 128.2 [128.1] (*o*-Ph), 130.4 [129.9] (*m*-Ph), 151.5 [150.7] (*i*-Ph), 152.1 [151.5] (*o*-C$_6$H$_3$), 199.4 [201.4] (*i*-C$_6$H$_3$). The assignment is based on ^{13}C DEPT experiments and comparison to coupled ^{13}C spectra of DppH and DppI. ^{171}Yb NMR δ 677 [927] ($w_{1/2}$ = 8 Hz [12 Hz]). (b) Isolation of **3b**: **1b** was treated with a 20:1 mixture of toluene and THF. Storage of the filtered solution in a −60 °C freezer gave tiny red rhombi of **3b** in ∼10% yield. According to a preliminary X-ray structural study **3b** is essentially isostructural to **3a**. (c) **3a**·(thf): The synthesis was accomplished in a manner similar to that of the preparation of **1b** with use of an Eu ingot (4.8 g, 31.6 mmol) and DppI (1.07 g, 3.0 mmol). Crystallization from THF yielded a mixture of orange (**3a**) and yellow (**4a**) crystals, which proved difficult to separate. Further experimental details and additional spectroscopic data will be reported in the full paper. Owing to the lability of the coordinated and cocrystallized THF ligands satisfactory elemental analytical data for **1b**, **3a**, **3b**, and **4a** could not be obtained.

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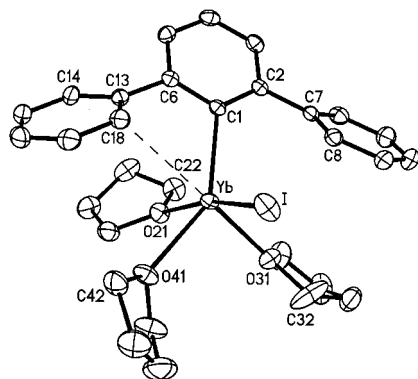
Figure 1. Molecular structure of **1b**, showing the numbering scheme. Hydrogen atoms and the cocrystallized THF molecule have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Yb−C(1) 2.529-(4), Yb···C(18) 3.104(5), Yb−I 3.1148(5), Yb−O(21) 2.424(3), Yb−O(31) 2.377(4), Yb−O(41) 2.463(4), C(1)−Yb−I 106.7(1), Yb−C(1)−C(2) 126.5(3), Yb−C(1)−C(6) 116.5(3).
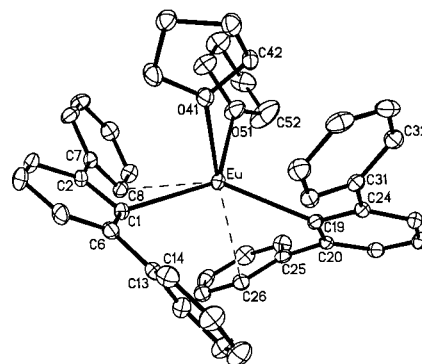

Figure 2. Molecular structure of **3a**, showing the numbering scheme. Hydrogen atoms and the cocrystallized THF molecule have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Eu−C(1) 2.606-(4), Eu−C(19) 2.623(4), Eu···C(8) 3.218(4), Eu···C(26) 3.153(4), Eu−O(41) 2.501(3), Eu−O(51) 2.494(4), C(1)−Eu−C(19) 135.3(1), O(41)−Eu−O(51) 77.8(1), Eu−C(1)−C(2) 112.2(3), Eu−C(1)−C(6) 120.6(3), Eu−C(19)−C(20) 111.9(3), Eu−C(19)−C(24) 129.5(3).

respectively. All three signals are relatively sharp with line widths <15 Hz, there is no evidence for an additional monomer dimer equilibrium. The presence of a genuine reversible equilibrium (eq 1) which is accessible from both sides is demonstrated by further NMR experiments. Therefore, adding YbI_2 to a solution of **3b** in THF generates **1b** again. Moreover, addition of an excess of YbI_2 to either **1b** or **3b** shifts the equilibrium to the left and suppresses the formation of **3b** (see Supporting Information). The ^{13}C NMR of **1b** at ambient temperature shows the presence of **1b** and **3b** in a proportion of 67 and 33%, respectively. Due to its limited solubility the quota of **1b** decreases to 40% at 263 K and 30% at 233 K. This is in accordance with the isolation of pure **1b** by crystallization at low temperatures. If the isolated mother liquor, which is enriched in **3b**, is rewarmed to ambient temperature, the original **1b**/**3b** ratio is observed again. It should be noted that **1b** is thermally labile in THF solution and slowly decomposes with a half-time of ~1 d at 293 K.

In the solid state[22] **1b** consists of well-separated monomeric units as shown in Figure 1. The ytterbium atom is bound to the *ipso*-carbon atom of the terphenyl group, to the terminal iodo substituent, and to three THF molecules. The Yb−C(1) distance of 2.529(4) Å is the first experimentally determined value for a Yb(II)−C(sp^2) σ-bond. As expected for the different oxidation state, this distance is ~0.12 Å longer than the corresponding bond length in Yb(III)−C(aryl) compounds.[23−25] Similar distances are found in Yb(II) alkyls, which cover a range of 2.47 to 2.58 Å.[9] The Yb−I distance of 3.1148(5) Å may be compared with the Yb−I bond length in hexa-coordinate $YbI_2(thf)_4$ **4b** which was determined to be 3.103(1) Å.[21] The average Yb−O(thf) bond length in **1b** (2.421 Å) is slightly longer than the distance (av. 2.386 Å) found in **4b**. The distorted tetragonal pyramidal coordination in **1b** leaves room for an additional weak $\eta^1-\pi$-arene interaction[26,27] (Yb···C(18) 3.104(5) Å) to one *o*′-phenyl carbon atom of the terphenyl ligand. As a consequence quite

different Yb−C(1)−C(2) and Yb−C(1)−C(6) angles of 126.5-(3)° and 116.5(3)° are observed.

The molecular structure of Eu(Dpp)$_2$(thf)$_2$ **3a** is depicted in Figure 2. The Eu center shows a distorted tetrahedral coordination by two aryl ligands and two THF molecules. The different size of the ligands is clearly reflected by the rather distinct C(1)−Eu−C(19) and O(41)−Eu−O(51) angles of 135.3(1)° and 77.8-(1)°. With a value of 2.615 Å the average Eu−C distance is close to the average bond length in two-coordinate Eu{C(SiMe$_3$)$_3$}$_2$ (2.609 Å).[11] Apparently a possible shortening in **3a** caused by a different hybridization of the σ-bonded carbon atom is compensated by the lower coordination number in the dialkyl. The average Eu−O(thf) distance of 2.498 Å is in the expected range. A notable feature is the considerable displacement of the Eu atom from the C(1)−C(6) and C(19)−C(24) aromatic planes by 1.503 and 0.790 Å. This can be interpreted in terms of the high ionic character of the metal−carbon bonds and steric crowding in the molecule. As in the case of **1b** additional metal-$\eta^1-\pi$-arene interactions (Eu···C(8) 3.218(4) Å, Eu···C(26) 3.153(4) Å) are observed, which are accompanied by different Eu−C(*ipso*)−C(*ortho*) angles.

The second product of the reaction of DppI and Eu metal was identified by X-ray structural analysis as $EuI_2(thf)_5$ (**4a**). Thermally labile crystals of **4a**, which rapidly decompose above ~0 °C, are isomorphous to the Sm derivative $SmI_2(thf)_5$. The structure of the latter compound was established some years ago,[28] although the refinement converged at the high conventional R value of 15%. However, in the case of **4a** it was possible to obtain reasonably accurate bond parameters[29] for the pentagonal−bipyramidal-coordinated Eu atom. Reactivity studies of **1b**, **3a**, and **3b** are in hand.

Supporting Information Available: ^{171}Yb NMR spectra of **1b** and **3b**, and X-ray structural information on **1b**, **3a**, and **4a** (PDF). X-ray crystallographic files (CIF) for **1b**, **3a**, and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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