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Short communication

Reactions of [(dpp-Bian)Ln(dme)$_2$] (Ln = Eu, Yb) with some oxidants

Svetlana V. Klementyeva [a,c,*], Alyona A. Starikova [b], Pavel A. Abramov [c]

[a] G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 603137 Tropinina str. 49, Nizhny Novgorod, Russian Federation
[b] Institute of Physical and Organic Chemistry, Southern Federal University, Stachka Ave. 194/2, 344090 Rostov-on-Don, Russian Federation
[c] Nikolaev Institute of Inorganic Chemistry, SB RAS, Prosp. Lavrentieva 3, 630090 Novosibirsk, Russian Federation

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ABSTRACT

Europium and ytterbium complexes [(dpp-Bian)Ln(dme)$_2$] (Ln = Eu (**1**), Yb(**2**), dme = 1,2-dimethoxyethane) with redox-active dianionic 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene ligand (dpp-Bian) have been tested in the reactions with nitrous oxide and sulfur. The reactions performed in 1:1 M ratio afford quantitatively neutral dpp-Bian, while the use of a half equivalent of oxidants leads to the europium complex with two radical-anionic dpp-Bian ligands [(dpp-Bian)$_2$Eu(dme)] (**3**) and the known ytterbium ionic compound [(dpp-Bian)$_2$Yb]$^-$[(dpp-Bian)Yb(dme)$_2$]$^+$ (**4**). The same products have been produced by the treatment of **1** and **2** with dpp-Bian. The oxidation of **1** and **2** with either sulfur dioxide or sulfur diimide ($(Me_3SiN{=})_2S$) proceeds with the total release of the neutral dpp-Bian. DFT calculations performed for **1** and **2** show pure ligand nature of the frontier molecular orbitals in both cases.

The 1,2-bis(arylimino)acenaphthenes (Bian) are considered to be very promising ligands for coordination compounds throughout the periodic table. The coordination chemistry of transition metals with redox-active Bian ligands has been developed since 1990s and a lot of complexes have been employed as homogeneous catalysts [1]. The application of *N*-aryl-substituted Bian and especially bulky 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-Bian) in coordination chemistry of non-transition metals have brought a number of interesting features caused by an amazing combination of redox-inactive main group metals and non-innocent dpp-Bian. Such a combination allows of extending reaction abilities of main group metal complexes over oxidative addition and reductive elimination [2]. In addition, some of them have been used as catalysts for hydroamination and hydroarylation of alkenes [3]. dpp-Bian serves as an “electron sponge” and can undergo from one to four electron reversible reduction steps, transforming into corresponding anion salts of alkali metals [4].

On the other hand, the f-block chemistry of Bian ligands is rather scanty. The reversible intramolecular electron-transfer in uranium complex with dpp-Bian ligand has been reported recently by Kiplinger et al. [5]. Only a few rare earth metal complexes based on Bian ligands are known to date [6–11]. Cowly et al. reported the treatment of lanthanocenes $(C_5Me_5)_2M\cdot(OEt_2)$ (M = Sm, Eu) with different Bian ligands for the first time and showed the influence of the choice of metal, ligand tuning, or ligand bulk on the zero, one, or two electron transfers from metals to Bian ligands [6]. The unique for rare earths chemistry phenomenon, namely temperature-induced redox isomerism, caused by metal-to-ligand electron transfer and Yb^{II}/Yb^{III} transformation, has been found out for some ytterbium complexes with redox-active dpp-Bian by Fedushkin et al. [7]. In addition, it was shown that the oxidation of divalent samarium derivative [(dpp-Bian)Sm(dme)$_2$] resulted invariably in the formation of novel complexes with trivalent samarium [8]. Continuing the search for new redox-isomeric systems based on europium complexes with dpp-Bian the oxidation of [(dpp-Bian)Eu(dme)$_2$] with different reagents have been recently reported by Fedushkin et al. [9] Noteworthy, in all cases the ligand-centered one-electron oxidation was observed and europium remained divalent. Noteworthy, a great contribution to the chemistry of ytterbium complexes with different redox-active ligands such as diazabutadienes [12], phenanthrolines [13] and bipyridines [14] has been made by Andersen et al. A comprehensive study on the reductive capacity of ytterbocenes with bulky diimines has been also reported by Trifonov et al. [15]

Herein, we report on the study of one- and two-electron oxidation of [(dpp-Bian)Ln(dme)$_2$] (Ln = Eu (**1**), Yb(**2**)) with nitrous oxide and sulfur as well as results of DFT calculations of initial lanthanide complexes **1** and **2**. In addition, preparation and characterization including single crystal X-ray diffraction of europium complex [(dpp-Bian)$_2$Eu(dme)] (**3**) with two radical-anionic dpp-Bian ligands will be discussed.

Primarily, these inorganic oxidants were chosen as convenient reagents for preparation of lanthanide oxide and sulfide complexes alike to the known lanthanocene species $(\eta^5\text{-}C_5Me_5)_2Ln$ [16]. Unfortunately, the interaction of **1** and **2** with N_2O or $1/8S_8$ in molar ratio of 1:1

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* Corresponding author at: G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 603137 Tropinina str. 49, Nizhny Novgorod, Russian Federation.

E-mail address: sklementyeva_2010@mail.ru. (S.V. Klementyeva).

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afforded neutral dpp-Bian in quantitative yield [17], thus indicating two-electron oxidation of dianionic dpp-Bian ligand in the lanthanide complexes.

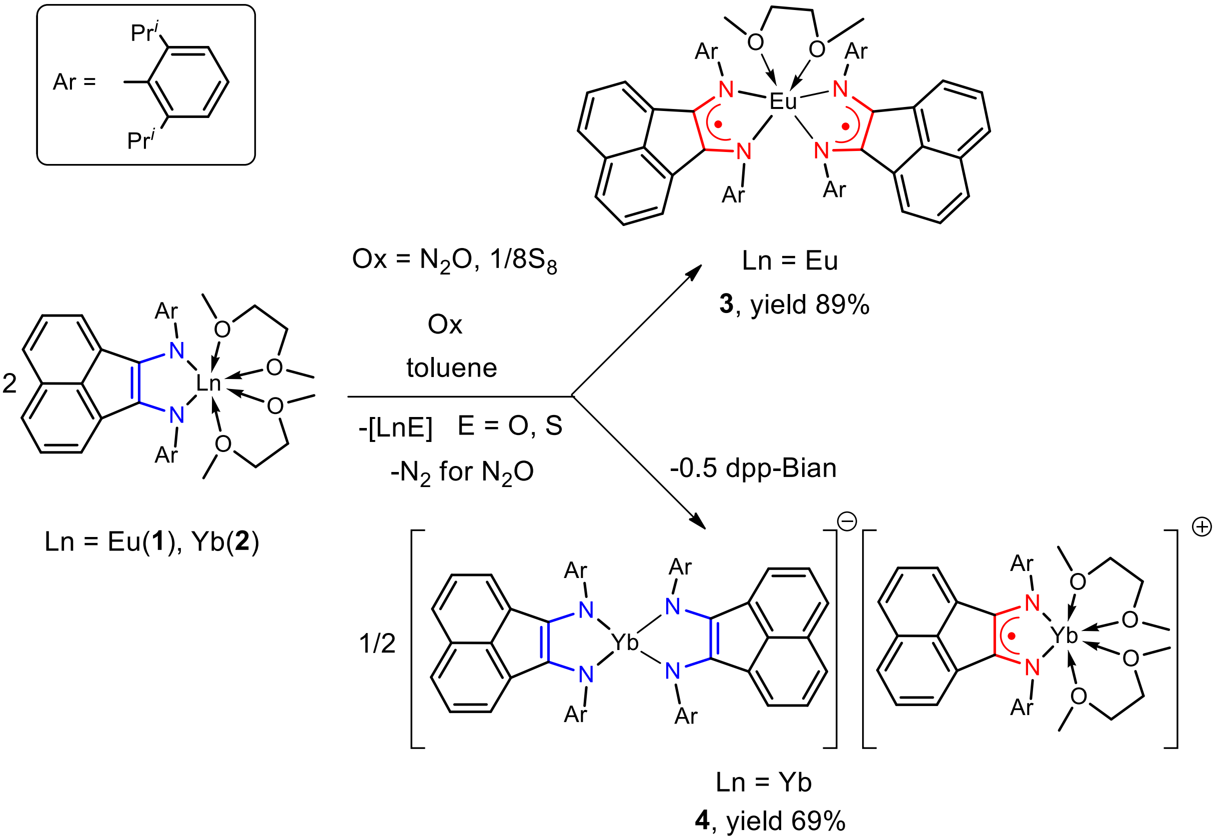
The use of a half equivalent of oxidants led to the europium complex with two radical-anionic dpp-Bian ligands [(dpp-Bian)$_2$Eu(dme)] (**3**) and the known ytterbium ionic compound [(dpp-Bian)$_2$Yb]$^-$[(dpp-Bian)Yb(dme)$_2$]$^+$ (**4**) (Scheme 1) [18,19]. Noteworthy, complex **4** is a mixed valence Yb^{III}/Yb^{II} compound in contrast to compound **3**, which is obviously a complex of divalent europium. In other words, the complex **4** contains Yb^{III} ion, whereas no europium equivalent is observed, because ytterbium is more easily oxidized from the Yb^{II} to the Yb^{III} state than europium according to their redox behavior both in aqueous and non-aqueous solutions [20].

The composition of **3** was determined by elemental analysis. The strong absorption at 1514 cm^{-1} in the IR spectrum of **3** indicates the sesquialteral character of C—N bonds of radical-anionic dpp-Bian ligands [18]. The complex **3** is soluble in common organic solvents such as aromatic hydrocarbons, ethers, *etc.* The broad absorption band with maximum at 513 nm [18] in the electronic absorption spectrum of **3** (Fig. S7) confirms the presence of radical anions of dpp-Bian [4b].

The molecular structure of the complex **3** was determined by single-crystal X-ray diffraction. The complex **3** crystallizes in the triclinic space group *P*-1 with two formula units and four toluene molecules per unit cell. The asymmetric unit contains the full molecule, as depicted in Fig. 1 with the selected bond lengths and angles. The coordination sphere of europium atom consists of coordinated 1,2-dimethoxyethane molecule and two bidentate chelating ligands – radical-anionic dpp-Bian, providing a coordination number of six. Coordination environment around the metal center may be described as the distorted trigonal prism. The bases of prism are formed by the nitrogen atoms N1, N3 and oxygen atom O1 and by the nitrogen atoms N2, N4 and oxygen atom O2, respectively. The corresponding geometrical parameters of both dpp-Bian moieties in **3** are very close to each other and evidently point out their radical-anionic state. The all four N—C bonds (av. 1.331 Å) and the both central C—C bonds (av. 1.456 Å) in dpp-Bian ligands in **3** are well comparable with those bonds found in other lanthanide complexes with dpp-Bian radical-anion [7–10]. The mentioned nitrogen carbon bond lengths are substantially shorter, while the central carbon carbon bond lengths are longer than those in lanthanide complexes of dpp-Bian dianion, for example, starting compounds **1** (av. 1.387 Å and 1.404 Å, respectively) [9a] and **2** (av. 1.386 Å and 1.409 Å, respectively) [7a]. The Eu–N distances are close to each other (av. 2.635 Å) and elongated than those distances in **1** (av. 2.460 Å) [9a] indicating a weaker interaction of europium(II) cation with dpp-Bian radical-anion in comparison with the metal-ligand interaction in the complex **1** with dianionic dpp-Bian. The Eu–O distances (av. 2.604 Å) with coordinated dme molecule are almost coincident with those distances in the complex **1** (av. 2.601 Å) [9a].

Noteworthy, the same compound **4** was isolated heretofore by the oxidation of **2** with dpp-Bian [10]. Taking into account this fact we attempted to oxidize europium complex **1** with equimolar amount of dpp-Bian. As a result we succeeded in the preparation of the target compound **3** under the same conditions (Scheme 2) [21]. In fact, the europium complex with two dpp-Bian radical-anionic species was prepared for the first time by the oxidation of **1** with dpp-Bian in dme and isolated as solvate with partial content of Et$_2$O and dme as coordinated solvents [22].

This fact allowed us to suggest that when a 2:1 complex/oxidant ratio is employed, the oxidant oxidizes a half of the initial complexes **1** or **2** to give LnE (Ln = Eu, Yb, E = O, S) (Scheme 1). An equivalent of the formally dianionic (dpp-Bian)$^{2-}$ is oxidized by two electrons in the process and the liberated neutral dpp-Bian immediately reacts with the remaining reactants to give the observed products **3** or **4**, respectively (Scheme 2).



Scheme 1. Reactions of **1** and **2** with oxidants.

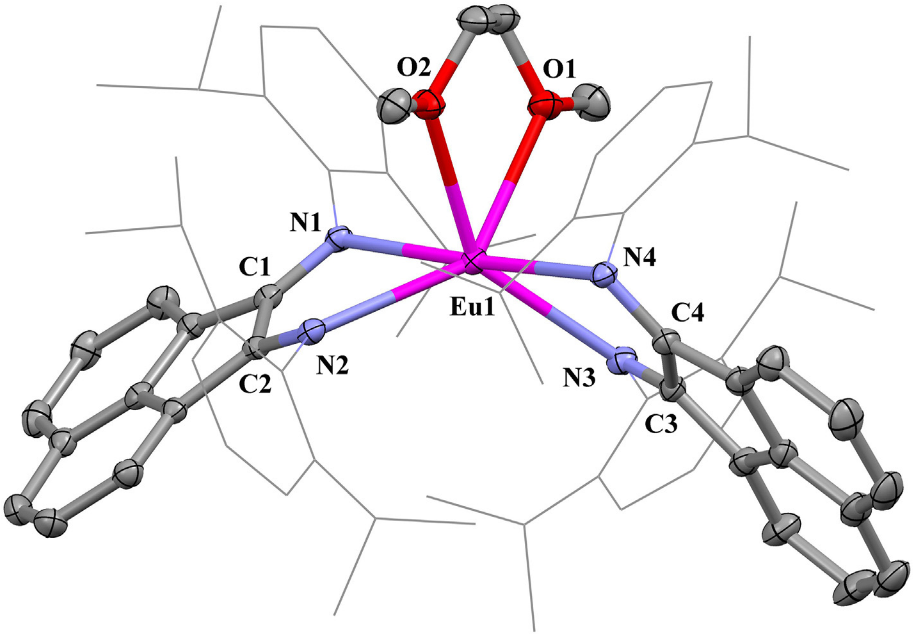
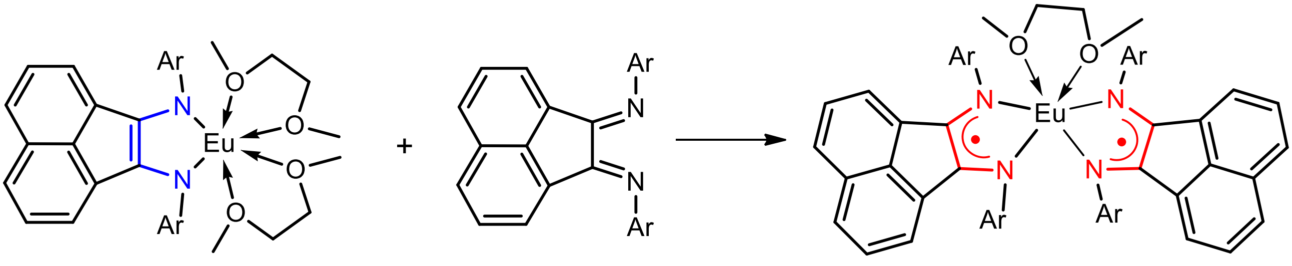


Fig. 1. Molecular structure of **3**, omitting hydrogen atoms. The thermal ellipsoids are drawn at the 50% probability. The selected bond lengths (Å) and angles (°): Eu1–O1 2.6071 (17), Eu1–O2 2.6003 (17), Eu1–N1 2.6325 (19), Eu1–N2 2.6412 (19), Eu1–N3 2.6588 (19), Eu1–N4 2.6067 (19), N1–C1 1.326(3), N2–C2 1.331(3), C1–C2 1.460 (3), N3–C3 1.334(3), N4–C4 1.331(3), C3–C4 1.453 (3), O1–Eu1–O2 61.14 (6), N1–Eu1–N2 65.61 (6), N3–Eu1–N4 65.90 (6).

On the other hand, one-electron oxidation of a number of ytterbium and europium complexes containing along with dpp-Bian other non-innocent ligands have been recently reported [7–10]. For example, ancillary ligands such as 2,2′-bipyridine, sterically hindered 1,4-diazabutadiene-1,2 or 2-ethoxy-3,6-di-tert-butylphenolate are coordinated as bidentate ligands in chelating mode [9c], thus stabilizing dpp-Bian in any reducing state to be coordinated to the lanthanides. In addition, the final charge distribution in the prepared compounds depends undoubtedly on the redox-properties of all the components, namely lanthanide ion and combination of redox-active ligands, in each case. Thus, when chelating ligands are absent in the reaction mixture, the liberation of neutral dpp-Bian becomes quite probable.

Recently, two types of compounds, namely sulfur diimide and sulfur dioxide, have been successfully involved in coordination chemistry of lanthanide. These substances may serve as one-electron oxidants and may be coordinated to the metal in chelating mode being in reduced state. It has been shown that lanthanocenes $(\eta^5\text{-}C_5Me_5)_2Ln(THF)_2$ (Ln = Eu, Yb, Sm) quantitatively reduce sulfur diimide $(Me_3SiN{=})_2S$ giving lanthanide complexes $[LLn(\eta^5\text{-}C_5Me_5)_2]$ with radical anion ligand $L = [(Me_3SiN{=})_2S]^-$ [23]. In addition, the activation of sulfur dioxide with lanthanocenes resulting in the formation of a number of sulfinate lanthanide complexes and dithionite derivatives as minor products in the case of ytterbium and samarium has been reported [24]. In contrast, reactions of complexes **1** and **2** containing dianionic dpp-Bian ligand with either $(Me_3SiN{=})_2S$ or SO_2, which were proceeded under the same conditions [17] lead to the quantitative elimination of neutral dpp-Bian. Thus, the oxidation of [(dpp-Bian)Ln(dme)$_2$] with such stronger oxidants occur as two-electron process in spite of their chelating abilities.

In order to realize the reaction ability of divalent lanthanide complexes with dianionic dpp-Bian ligand with respect to oxidants, the DFT calculations for **1** and **2** were performed (for more details see ESI). The optimized geometries of the complex **1** and **2** (Figs. S2 and S5) are in a good accordance with the X-ray analysis data of these compounds [7a,9a]. It was shown that the frontier molecular orbitals of both lanthanide complexes are localized on the redox-active dpp-Bian ligand and neither europium nor ytterbium participates in the formation of them (Figs. 2, S3, S4, S6). Moreover, the shapes of the frontier MOs for **1** and **2** are nearly identical, thus only the HOMO of complex **2** is shown in Fig. 2. Noteworthy, the HOMO is substantially localized on the diamide N-C-C-N system of dianionic dpp-Bian ligand indicating the possibility of electron withdrawing from the ligand first, but not from the metal. It may be considered as an indirect evidence for oxidation of dianionic dpp-Bian species rather than oxidation of divalent Eu^{II} or Yb^{II} in the complexes **1** and **2**, respectively, upon the influence of oxidants.



1

3, yield 92%

Scheme 2. Synthesis of complex **3**.

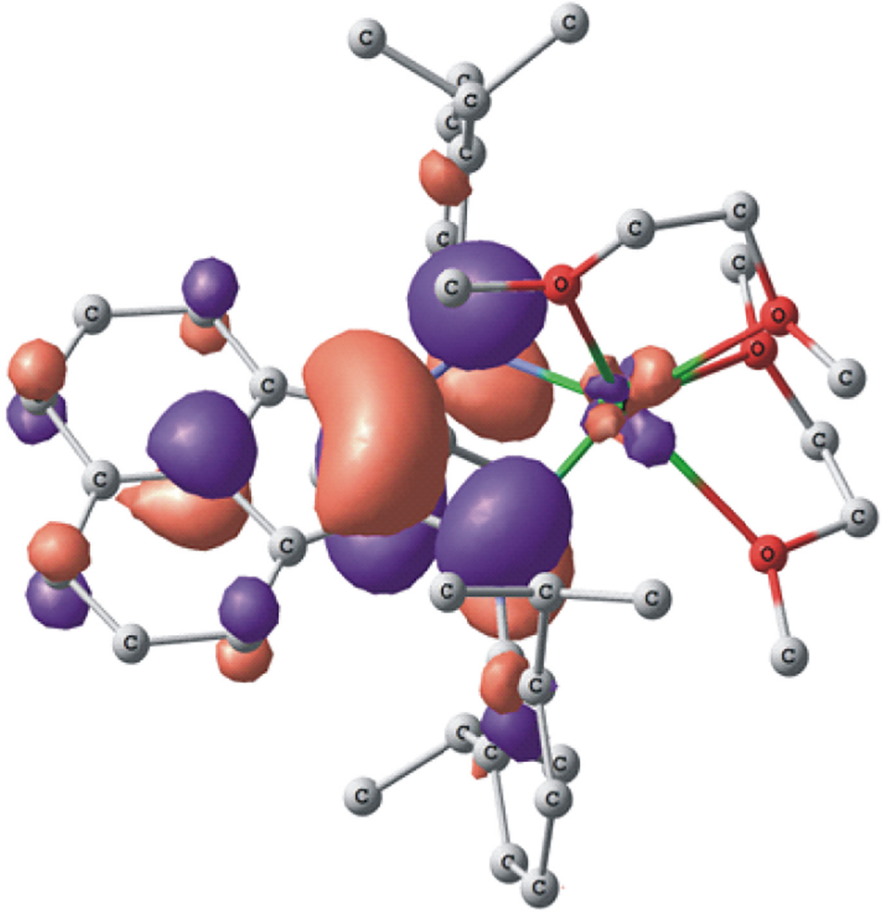


Fig. 2. HOMO of **2** calculated by DFT B3LYP/6-31G(d,p)/SDD method.

In conclusion, it was shown that reactions of [(dpp-Bian)Ln(dme)$_2$] (Ln = Eu (**1**), Yb(**2**)) with oxidants may occur with partial and full (two-electron) oxidation of dianionic dpp-Bian ligands depending on the molar ratio of reagents. The two-electron oxidation of **1** and **2** results in the liberation of the neutral dpp-Bian from lanthanides, while the deficiency of oxidants leads to the formation of the europium complex with two radical-anionic dpp-Bian ligands [(dpp-Bian)$_2$Eu(dme)] (**3**) and the known ytterbium ionic compound [(dpp-Bian)$_2$Yb]$^-$[(dpp-Bian)Yb(dme)$_2$]$^+$ (**4**), indicating the different behavior of **1** and **2**. DFT calculations performed for complexes **1** and **2** point the localization of the HOMO on the diamide N-C-C-N system of dianionic dpp-Bian ligand, thus confirming the primary oxidation of dpp-Bian.

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Appendix A. Supplementary data

Supplementary data associated with this article including materials and methods, spectroscopic and crystallographic data with selected refinement details for **3** as well as computational details for **1** and **2** can be found as electronic supplementary information in the online version at https://doi.org/10.1016/j.inoche.2018.04.004.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre under the reference number CCDC 1812314 for **3** and may be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

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[18] The reactions of **1** and **2** with nitrous oxide in molar ratio of 2:1. N_2O (0.25 mmol) was condensed onto a solution of $[(\text{dpp-Bian})Ln(dme)_2]$ (Ln = Eu, 416 mg; Yb, 426 mg; 0.5 mmol) in 30 ml of toluene at −90 °C. The resulting mixture was stirred for 1 h while slowly warming up to room temperature and turning colour of the mixture. The reaction mixture turned cherry-red in the case of europium. Then it was stored overnight without stirring. The solvent was removed by slow evaporation leaving dark red crystals of **3** · $2C_7H_8$ (314 mg, yield 89%) suitable for single crystal X-ray diffraction analysis. Anal. calcd (%) for $C_{83}H_{98}N_4O_2Eu$ (1319.66): C 75.54, H 7.86, N 4.24; found C 75.22, H 7.73, N 4.31%. IR (Nujol) ν, cm^{-1}: 1603 (w), 1582(w), 1514(s), 1495(m), 147(s), 1409(s), 1352(m), 1336(m), 1312(s), 1279(w), 1252(m), 1238(m), 1212(m), 1182(s), 1121(m), 1109(m), 1080(s), 1056(m), 1040(m), 1011(w), 961(w), 937(m), 873(m), 839(m), 817(m), 796(m), 787(w), 770(s), 761(s), 732(s), 695(m), 668(w), 631(w), 612(w), 598(m), 536 (w), 510(w), 480(w), 464(w). UV/vis (298 K, dme): λ 513 nm. In the case of ytterbium the reaction mixture turned blue-green and deep-blue fine crystals of **4** precipitated, which were collected by filtration (175 mg, yield 69%). IR spectrum of **4** matches with the literature [10]. The toluene was removed by slow evaporation from blue-green solution leaving a mixture of yellow-orange dpp-Bian and another crop of deep-blue crystals of **4**.

[19] The reactions of **1** and **2** with sulfur in molar ratio of 2:1. At ambient temperature $[(\text{dpp-Bian})Ln(dme)_2]$ (Ln = Eu, 416 mg; Yb, 426 mg; 0.5 mmol) and S_8 (8 mg, 0.25 mmol) were dissolved in 30 ml of toluene and the resulting mixture was stirred for 5 h while the colour of the mixture turned, then stirred for 24 h. The further work-up as described above for nitrous oxide gave crystals of **3** · $2C_7H_8$ (289 mg, yield 82%) and **4** (158 mg, yield 62%), respectively.

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