



Full paper/Mémoire

Anionic and neutral bis(diimine)lanthanide complexes

Igor L. Fedushkin*, Olga V. Maslova, Anton N. Lukoyanov, Georgii K. Fukin

G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Tropinina 49, 603950 Nizhny Novgorod, Russia

ARTICLE INFO

Article history:

Received 28 December 2009

Accepted after revision 12 May 2010

Available online 29 June 2010

Keywords:

Diimines

Redox-active ligands

Lanthanides

ABSTRACT

Oxidation of ytterbium(II) complex $(\text{dpp-BIAN})\text{Yb}(\text{DME})_2$ (**1**) with dpp-BIAN affords an ionic compound $[(\text{dpp-BIAN})_2\text{Yb}]^- [(\text{dpp-BIAN})\text{Yb}(\text{DME})_2]^+$ (**2**) (dpp-BIAN = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene), in which the oxidation states of the metals in anionic and cationic counterparts are different. Structurally related lanthanum(III) complex $[(\text{dpp-BIAN})_2\text{La}]^- [(\text{dpp-BIAN})\text{La}(\text{DME})_2]^+$ (**3**) has been prepared reacting excess of metallic lanthanum with dpp-BIAN. Compound $[(\text{dpp-BIAN})_2\text{La}]^- [\text{K}(\text{Et}_2\text{O})_4]^+$ (**4**) has been isolated from the reaction of LaI_3 with three molar equivalents of potassium and one molar equivalent of dpp-BIAN in diethyl ether. The reaction of SmI_2 with dpp-BIAN and potassium affords complex $[(\text{dpp-BIAN})_2\text{Sm}]^- [\text{K}(\text{C}_6\text{H}_6)]^+$ (**5**). Treatment of compound **5** with 0.5 molar equivalent of iodine produces neutral complex $(\text{dpp-BIAN})_2\text{Sm}$ (**6**). Molecular structures of complexes **2–6** have been determined by X-ray crystallography.

© 2010 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

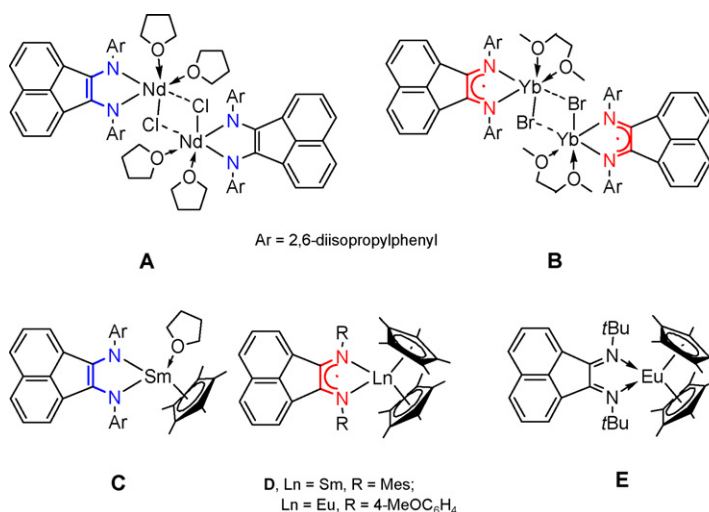
1. Introduction

Electronic and spatial features of 1,2-bis(arylimino)acenaphthenes (BIANs) provide for the formation of metal complexes that reveal remarkable molecular structures and reactivity. The most helpful ligand of the 1,2-bis(arylimino)acenaphthene family is 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN). The alkali metal reduction of dpp-BIAN results in the formation of its mono-, di-, tri-, and tetra-anions [1]. The redox-activity of dpp-BIAN has been further documented by the preparation of a series of group II [2] and XIII [3] metal complexes with the dpp-BIAN ligand in the radical-anionic and dianionic state. A shielding of the nitrogen lone pairs in dpp-BIAN by isopropyl groups of the phenyl substituents prevents the formation of dimeric structures with bridging dpp-BIAN ligands. This peculiarity of the dpp-BIAN ligand plays a crucial role in the formation of molecular species with direct metal-metal bonds, e.g. Zn–Zn [4], Ga–Ga [5], Zn–Ga [5], Li–Ga [6] and Na–Ga [6]. It is also suggested that the nitrogen lone pairs of the dpp-BIAN may contribute not

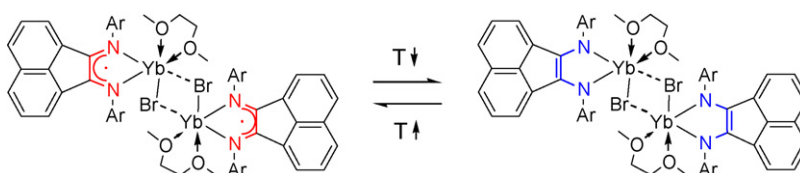
only in the metal-nitrogen bonding (π -component), but also in the metal-metal bonding. A review concerning development of the coordination chemistry of BIAN ligands with s- and p-block elements has been published recently [7]. By comparison, lanthanide complexes with BIAN ligands have been studied much less and are limited by 13 compounds. Some of them are presented in Scheme 1 showing the structures **A** [8], **B** [9], and **C–E** [10]. Within the lanthanide series, the ytterbium derivative $[(\text{dpp-BIAN})\text{Yb}(\mu\text{-Br})(\text{DME})_2]$ (**B**) is a sole example that exhibits a thermally induced reversible metal-to-ligand electron transfer in solution – redox isomerism phenomenon (Scheme 2) [9]. This phenomenon is characterized by existence of two electronic isomers with different charge distribution. The low temperature isomer is always represented by species with a more oxidized metal ion M^{n+1} and the high temperature isomer consists of the reduced metal ion M^n . Originally, such electron transfer was observed in the bis(*o*-benzosemiquinone)cobalt complex [11]. In order to get more insight in the redox-isomeric transformation involving the rare earth element, we started preparation of the ytterbium complex with two dpp-BIAN ligands. Although we have not succeed the preparation of desired neutral ytterbium complex $(\text{dpp-BIAN})_2\text{Yb}$, a series of anionic bis(dpp-BIAN)lanthanide

* Corresponding author.

E-mail address: igorfed@iomc.ras.ru (I.L. Fedushkin).



Scheme 1.



Scheme 2.

complexes have been synthesized and characterized by single crystal X-ray analysis. Indeed, the neutral samarium derivative (dpp-BIAN)₂Sm has been isolated and studied by X-ray crystallography.

2. Results and discussion

2.1. Syntheses and characterization of the newly prepared compounds

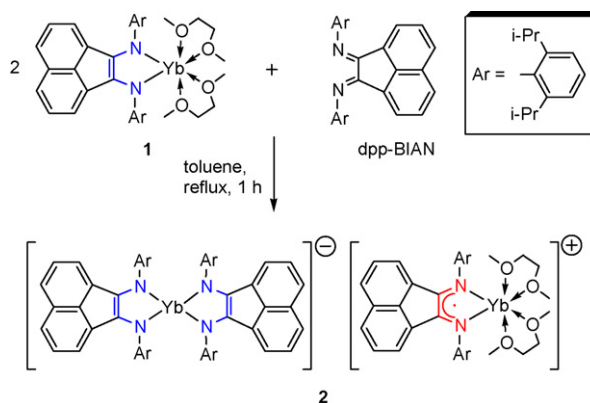
The reaction of (dpp-BIAN)Yb(DME)₂ (**1**) [9] with dpp-BIAN in DME proceeds slowly at reflux and is accompanied by a color change from red-brown to blue-green. When equimolar amounts of the reagents were used even after attainment of the final blue-green color, a remarkable amount of free dpp-BIAN is still present in the reaction mixture. In toluene, the reaction of **1** with 0.5 molar equivalent of dpp-BIAN completes within 1 h at reflux and affords complex [(dpp-BIAN)₂Yb][(dpp-BIAN)Yb(DME)₂] (**2**) as deep blue crystals (Scheme 3).

Since in the course of the synthesis of compound **1** from ytterbium metal and dpp-BIAN in DME at reflux the reaction mixture turned first blue-green and then red-brown, we suggest that reduction of dpp-BIAN with ytterbium proceeds via intermediate formation of complex **2**, which with an excess of the metal gives compound **1**.

In order to obtain the analogous complex with lanthanum, for which, in contrast to ytterbium, the oxidation state +3 is common, dpp-BIAN was reacted with an excess of lanthanum metal in diethyl ether.

At ambient temperature, the reaction proceeds slowly and affords blue microcrystalline powder after stirring the reaction mixture for 7 days. Extraction of the product with DME and crystallization from toluene affords complex [(dpp-BIAN)₂La][(dpp-BIAN)La(DME)₂] (**3**) as deep green crystals (Scheme 4).

The presence of the paramagnetic dpp-BIAN radical-anion in complex **2** prevents its characterization by NMR spectroscopy and, on the other hand, the ESR spectroscopy is useless for characterization of complex **2** due to the presence of trivalent ytterbium. Unexpectedly, the ¹H NMR spectrum of diamagnetic compound **3** in THF-d₈ is also less informative: a broadening of all of the signals may be indicative for dynamic processes in metal coordination



Scheme 3.

Download English Version:

<https://daneshyari.com/en/article/171171>

Download Persian Version:

<https://daneshyari.com/article/171171>

[Daneshyari.com](https://daneshyari.com)