Tridentate CCC-Pincer Bis(carbene)-Ligated Rare-Earth Metal Dibromides. Synthesis and Characterization

Kui Lv[†,‡] and Dongmei Cui*[,†]

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China, and Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China

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*Summary: The first xylene-bridged bis(N-heterocyclic carbene) (bis(NHC))-ligated CCC-pincer rare-earth metal dibromides (PBNHC)LnBr$_2$(THF) (PBNHC = 2,6-(2,4,6-Me$_3$C$_6$H$_2$NCHCHNCCH$_2$)$_2$C$_6$H$_3$; **1**: Ln = Sc; **2**: Ln = Lu; **3**: Ln = Sm) were prepared by in situ treatment of a THF suspension of 2,6-bis(1-mesitylimidazolium methyl)-1-bromobenzene dibromides ((PBNHC-Br)·2HBr) and lanthanide trichlorides (LnCl$_3$) with dropwise addition of nBuLi at room temperature. The overall molecular structure of these complexes is an isostructrual monomer of a THF solvate. The monoanionic xylene-bridged bis(NHC)s bond to the central metal as a tridentate CCC-pincer moiety in a κC:κC:κC′ mode, which, in combination with the two trans-located bromo units, generates a twisted tetragonal-bipyramidal geometry.*

Introduction

Functionalized N-heterocyclic carbene (NHC) ligands, prepared via swiftly modifying the imidazolium salt with a pendant anionic group, have undergone an upsurge in research interest. These ligands are hemiliable and covalently bond to the metal centers, anticipated to tune the coordination sphere, rigidity, and chirality of the attached complexes, which has potential in the area of homogeneous catalysis.[1] The reported examples are transition metal complexes supported by hydroxy- (or phenoxy-) or amido group- modified NHCs[2−4] and Ni bromides stabilized by indenyl- or fluorenyl-NHCs.[5] Meanwhile, the "pincer" architecture, such as pincer phosphines and amines,[6−8] provides a preorganized backbone capable of blocking meridional or pseudo-meridional coordination sites of the metal center, leaving the remaining available for catalysis. Thus, pincer carbenes,[9−12] the combination of a pincer chelating effect with a strong electron-donating ylidene carbon, should provide functional complexes with enhanced stability, and the precise tailoring of the metal coordination sphere should enable the complexes to be used under harsher reaction conditions in most cases. To date CNC- and CPC-pincer-type bis(NHC)s attached transition metal complexes have been isolated and found to be active toward Suzuki coupling reaction,[7a,9−11,13−16] whereas only one CCC-pincer bis(NHC)-stabilized Pd complex was isolated,[13] and no lanthanide element-based counterparts have been reported, although those bearing amido-hydroxyl- and indenyl- or fluorenyl-modified NHC ligands have been obtained recently.[4a,17−19] Herein we report the preparation and characterization of the unprecedented xylene-bridged CCC-pincer bis(NHC)-ligated complexes based on various rare-earth metal centers.

Results and Discussion

Treatment of 2,6-bis(bromomethyl)-1-bromobenzene with 1-mesitylimidazole in 1,4-dioxane under reflux for 24 h afforded the xylene-bridged bis(imidazolium) salt (2,6-(2,4,6-Me$_3$C$_6$H$_2$-NCHCHNCCH$_2$)$_2$-1-Br-C$_6$H$_3$)·2HBr ((PBNHC-Br)·2HBr) in high yield (>90%) (Scheme 1). The ^{1}H NMR spectrum of

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* Corresponding author: Fax: +86-431-85262773. E-mail: dmcui@ciac.jl.cn.

[†] Changchun Institute of Applied Chemistry.

[‡] Graduate School of the Chinese Academy of Sciences.

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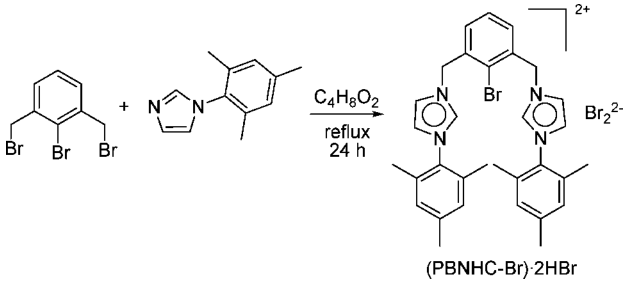
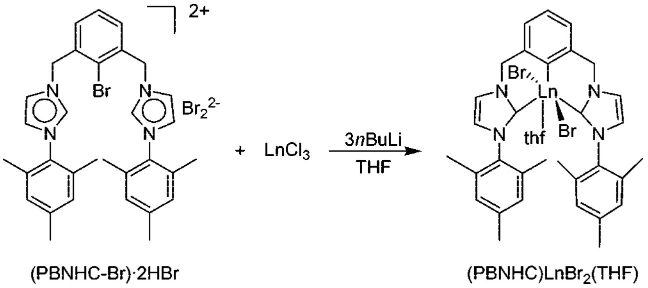
Scheme 1. Synthesis of CCC-Pincer-Type Bis(NHC) Ligand



Scheme 2. Synthesis of Complexes 1 (Ln = Sc), 2 (Ln = Lu), and 3 (Ln = Sm)



(PBNHC-Br)·2HBr exhibited a singlet at 10.4 ppm, typical for the ylidene proton NHC-*H*,[18,19] while the methylene protons gave a singlet at 6.1 ppm, consistent with the symmetric pincer geometry of the molecule. To a THF suspension of (PBNHC-Br)·2HBr and LnCl$_3$, 3.0 equiv of *n*BuLi in hexane was added dropwise *in situ* at room temperature under vigorous stirring, which gradually generated a clear yellow solution. Evaporation of the THF solvent left residues, which were extracted with toluene. Filtration and removal of toluene gave solids, which were dissolved by THF. The resultant solution was cooled to −30 °C to afford yellow crystals of (PBNHC)LnBr$_2$(THF) (Ln = Sc (**1**); Lu (**2**); Sm (**3**)) in moderate yields within 24 h (Scheme 2). ^{1}H NMR spectrum analysis of **1** and **2** (**3** is paramagnetic) revealed the absence of the ylidene proton, indicative of the completeness of the reaction. Meanwhile the formation of M−σ-C bonding between metal ions and the ylidene carbons was confirmed by ^{13}C NMR spectra, which displayed the typical resonances around δ 190.04−197.43 ppm,[18] downfield shifted as compared with 126.19 ppm in the ligand precursor.

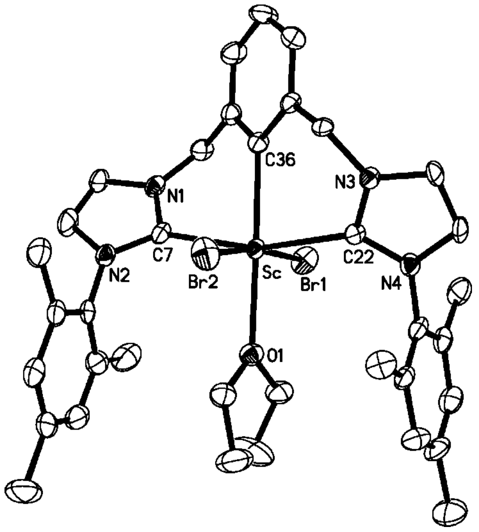


Figure 1. ORTEP drawing of the molecular structure of **1** with 40% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes 1−3

	Ln = Sc	Ln = Lu	Ln = Sm
Ln−C(7)	2.397(8)	2.486(7)	2.584(7)
Ln−C(22)	2.383(8)	2.482(7)	2.587(7)
Ln−C(36)	2.341(8)	2.443(8)	2.575(8)
Ln−O(1)	2.317(6)	2.415(5)	2.533(6)
Ln−−Br(1)	2.586(2)	2.687(1)	2.789(1)
Ln−Br (2)	2.590(2)	2.675(1)	2.772(1)
C(7)−Ln (1)−C(22)	163.9(3)	158.9(3)	152.4(2)
Br(1)−Ln(1)−Br(2)	171.17(7)	168.48(4)	166.05(4)

The molecular structures of complexes **1**−**3** were determined by X-ray diffraction analysis as, surprisingly, THF-solvated monomeric rare-earth metal dibromides, not the designated dichlorides (Figure 1, complex **1**). The monoanionic CCC-pincer bis(NHC) ligand coordinates to the central metal ion in a κC:κC:κC′ tridentate mode, adopting a pseudo-meridional conformation. The two NHC moieties are *anti*-arranged, and the two N-aryl rings are almost parallel to each other and to the coordinating THF ring. The two bromo groups are disposed in *trans*-positions with large angles varying from 166.05(4)° to 171.17(7)° (Table 1). These ligands generate square-bipyramidal geometry around the metal center. The average Ln−C$_{\mathrm{carbene}}$ bond lengths, 2.390(8) Å in **1**, 2.484(7) Å in **2**, and 2.585(7) Å in **3**, fall in the reasonable range for the linkage of a lanthanide metal ion and an ylidene carbon.[18] The Ln−C$_{\mathrm{phenyl}}$ bond length of 2.341(8) Å in **1**, 2.443(8) Å in **2**, and 2.575(8) Å in **3** is comparable to those reported in the literature.[20] The average Sc−Br bond length of 2.5879(18) Å in **1** is shorter than 2.6812(10) Å of Lu−Br in **2** and much shorter than 2.7804(10) Å of Sm−Br in **3**, well consistent with the trend of ionic radii of the corresponding lanthanide elements. In contrast, the C$_{\mathrm{carbene}}$−Sc−C$_{\mathrm{carbene}}$ bond angle of 163.9(3)° in **1** is larger than 158.9(3)° of C$_{\mathrm{carbene}}$−Lu−C$_{\mathrm{carbene}}$ in **2** and 152.4(2)° of C$_{\mathrm{carbene}}$−Sm−C$_{\mathrm{carbene}}$ in **3**, the inverse of the previously mentioned trend. This is due to the more distorted structure of the Sc-centered complex. Because the smaller the ionic radius is, the bulkier the environment of the metal center, the much distorted structure is obtained, leading to a larger bite angle. Similarly, the Br−Sc−Br bond angle of 171.17(7)° in **1** is larger than Br−Lu−Br of 168.48(4)° in **2** and Br−Sm−Br of 166.05(4)° in **3**.

As the NMR monitoring technique could not provide information about this, the mechanism for the generation of these bromo complexes is still ambiguous. It should be noted that the stepwise addition of the three kinds of reagents instead of the above-mentioned *in situ* method, for instance, treatment of (PBNHC-Br)·2HBr (or LnCl$_3$) with *n*BuLi for 0.5 h followed by adding LnCl$_3$ (or (PBNHC-Br)·2HBr), was unsuccessful and yielded unknown products. This result indicated that the intermediates were unstable, and the presence of the third reagent to ensure the immediate transformation to the eventual target complexes was necessary.

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Conclusion

We have demonstrated that CCC-tridentate pincer bis(NHC)-ligated rare-earth metal dibromides could be prepared by *in situ* treatment of a mixture of the corresponding imidazolium salts and $LnCl_3$ and *n*BuLi. The resultant complexes represent the first example of a xylenyl-functionalized CCC-pincer bis(NHC)-stabilized rare-earth metal complex. Significantly, X-ray diffraction analysis revealed that the complexes were monomeric dibromides, which are convenient precursors of alkyl, amido counterparts or important homogeneous catalysts.

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Supporting Information Available: Experimental details and CIF files for complexes **1**, **2**, and **3** and ORTEP drawings for complexes **2** and **3** are available free of charge via the Internet at http://pubs.acs.org.

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