



## Digest paper

## Recent progress in the chemistry of lanthanide–ligand multiple bonds

Qin Zhu<sup>b</sup>, Jun Zhu<sup>b,\*</sup>, Congqing Zhu<sup>a,\*</sup><sup>a</sup>State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China<sup>b</sup>State Key Laboratory of Physical Chemistry of Solid Surfaces, Fujian Provincial Key Laboratory of Theoretical Computational Chemistry and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

## ARTICLE INFO

## Article history:

Received 27 November 2017

Revised 27 December 2017

Accepted 29 December 2017

Available online 30 December 2017

## Keywords:

Lanthanide

Multiple bond

Metal-carbene

## ABSTRACT

Metal–ligand multiple bonds have received significant attention in the past few decades. A series of novel species with lanthanide–ligand multiple bonds have recently been isolated. This short review summarizes the synthesis and reactivity of these novel complexes.

© 2017 Elsevier Ltd. All rights reserved.

## Contents

Introduction	514
Lanthanide–carbon multiple bonds	515
Lanthanide–nitrogen multiple bonds	516
Lanthanide–oxygen multiple bonds	518
Conclusions and perspectives	520
Acknowledgements	520
References	520

## Introduction

Chemical bonding is the cornerstone of chemistry. In the past few decades, transition metal complexes containing metal–ligand multiple bonds have received increasing attention due to their extensive applications in synthetic chemistry and small-molecule activation.<sup>1–3</sup> Significant progress has been made in the chemistry of transition metal–ligand multiple bonds, especially for transition metal carbene complexes, which have revolutionized organic synthesis, culminating in the 2005 Nobel Prize in chemistry.<sup>4</sup>

In addition, a large number of metal–ligand multiple bonds involving the actinide elements,<sup>5</sup> as well as scandium and yttrium,<sup>6</sup> have been investigated. However, in comparison, examples of well-defined lanthanide–ligand multiple bonds lag far behind.

In principle, the 4f electrons in lanthanoid metals lie deep inside the electron shell, and as a result rarely participate in multiple bonding. Moreover, the bonding of lanthanides is principally ionic and highly polarized in nature. Therefore, the synthesis and stabilization of molecules containing lanthanide–ligand multiple bonds is a challenge.

In the past few years, organometallic chemists have made great developments in lanthanide chemistry,<sup>7</sup> especially in the chemistry of lanthanide–ligand multiple bonds. Some elegant examples of lanthanide–ligand multiple bonds in carbene (M=C), imido (M=N), and oxo (M=O) complexes have been reported. In this review, we will focus on the synthesis and reactivity of these novel complexes. However, NHC-type lanthanide carbene adducts are not included in this short review.<sup>8</sup>

\* Corresponding authors.

E-mail addresses: [jun.zhu@xmu.edu.cn](mailto:jun.zhu@xmu.edu.cn) (J. Zhu), [zcq@nju.edu.cn](mailto:zcq@nju.edu.cn) (C. Zhu).

## Lanthanide-carbon multiple bonds

Transition metal carbene complexes, which contain a metal-carbon double bond, are well-known as key intermediates in alkene metathesis. Back-donation from the metal to the carbon is important in the formation of metal-carbon double bonds. The back-donation effect is more common in the d-block transition metals compared with the f-block lanthanide metals. Therefore, metal-carbene complexes with d-block transition metals have been widely investigated. In contrast, for lanthanide metals, there are very limited examples of carbene complexes.

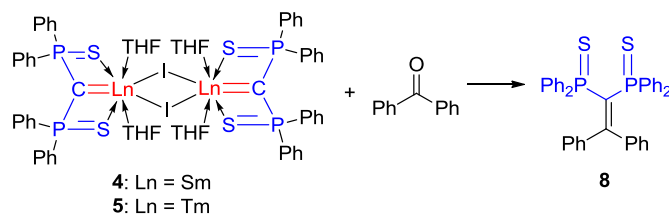
In 2000, Cavell and co-workers reported the synthesis of a samarium carbene complex by the double deprotonation of the bis(iminophosphorano)methane ligand.<sup>9</sup> As shown in Scheme 1, after treatment of the NCN-pincer type ligand **1** with samarium tris(dicyclohexylamide), the Sm-carbene complex **2** was isolated as a yellow solid. This was the first example of a lanthanide metal-carbon double bond with a dianionic carbene ligand. The bis(iminophosphorano)methane ligand is an useful precursor for the synthesis of lanthanide-carbene complexes, probably due to the bulky TMS group on the nitrogen atom and electron-rich nature of this ligand.

X-ray study showed that the Sm-carbon bond distance was shorter than the analogous distances in other neutral carbene ligand complexes of samarium. Based on this fact, as well as the P-N bond distances in the fused four-membered rings, the authors suggested that complex **2** has a delocalized structure.

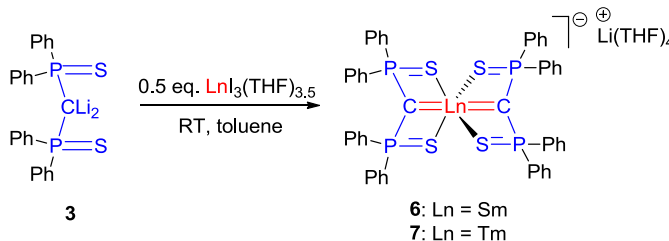
Floch, Nief, Mézailles, and co-workers used the SCS-pincer type dianionic ligand **3** to synthesize samarium and thulium carbene complexes.<sup>10</sup> By the reaction of  $\text{SmI}_3(\text{THF})_{3.5}$  or  $\text{TmI}_3(\text{THF})_{3.5}$  with one equivalent of dianionic ligand **3**, the lanthanide-carbene complexes **4** and **5** were generated, respectively (Scheme 2). Complex **5** represents the first late-lanthanide alkylidene complex.

The Ln=C double bond in these species showed nucleophilic character similar to the Schrock-type transition metal carbene complexes. After treatment of complex **4** or **5** with benzophenone, the Wittig-like reaction product **8** was formed (Scheme 3). This result shows that the electronic characters of early- and late-lanthanide carbenes are similar.

Interestingly, treatment of  $\text{SmI}_3(\text{THF})_{3.5}$  or  $\text{TmI}_3(\text{THF})_{3.5}$  with two equivalents of dianionic ligand **3** led to the formation of the first homoleptic samarium and thulium carbene complexes **6** and **7**, which contain two Ln=C bonds (Scheme 4).



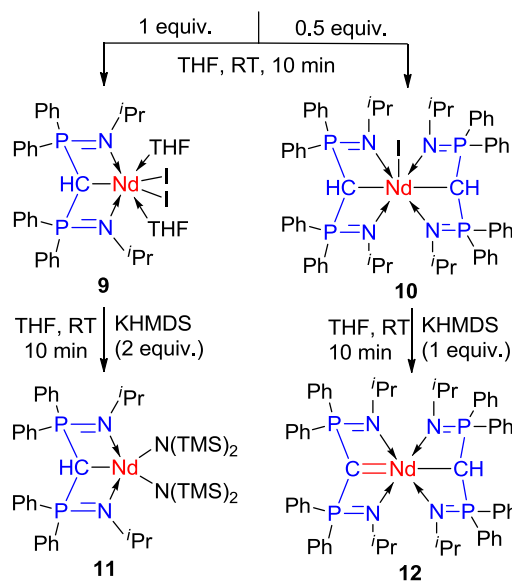
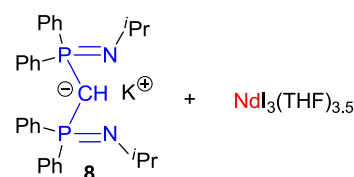
Scheme 3.



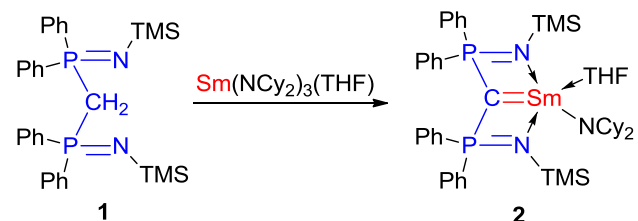
Scheme 4.

Therefore, the use of different ratios of the ligand and the metal will lead to the formation of different products. Floch and co-workers found that treatment of monoanionic ligand **8** with  $[\text{NdI}_3(\text{THF})_{3.5}]$  in a 1:1 ratio enabled the synthesis of the neodymium iodide complex **9** (Scheme 5), whereas a 2:1 ligand: metal ratio yielded bisalkyl neodymium complex **10**.<sup>11</sup> The first lanthanide alkyl-carbene mixed complex **12** was formed by treating one equivalent of KHMDS with **10** in THF, whereas the reaction of two equivalents of KHMDS with complex **9** afforded the new alkyl neodymium complex **11**.

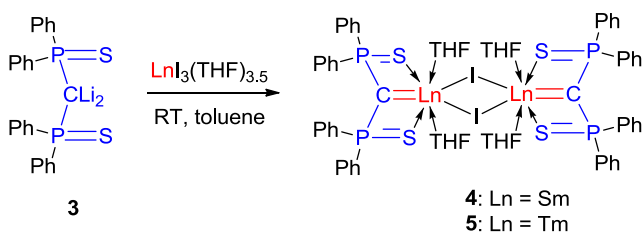
The monoanionic NCN-type pincer ligand **13** was also found to react with  $\text{LaI}_3(\text{THF})_4$  to yield the alkyl lanthanum complex **14**



Scheme 5.



Scheme 1.



Scheme 2.

Download English Version:

<https://daneshyari.com/en/article/7830663>

Download Persian Version:

<https://daneshyari.com/article/7830663>

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