



ELSEVIER

Contents lists available at ScienceDirect

## Coordination Chemistry Reviews

journal homepage: [www.elsevier.com/locate/ccr](http://www.elsevier.com/locate/ccr)

## Review

## Lanthanides and actinides: Annual survey of their organometallic chemistry covering the year 2015



Frank T. Edelmann\*

Chemisches Institut der Otto-von-Guericke-Universität Magdeburg, D-39106 Magdeburg, Germany

## Contents

1. Introduction .....	30
2. Lanthanides .....	30
2.1. Lanthanide carbonyls and hydrocarbyls .....	30
2.1.1. Homoleptic compounds .....	30
2.1.2. Heteroleptic compounds .....	31
2.2. Lanthanide allyl and alkynyl complexes .....	49
2.3. Lanthanide cyclopentadienyl complexes .....	49
2.3.1. CpLnX, Cp <sub>2</sub> Ln and [Cp <sub>3</sub> Ln] <sup>-</sup> compounds .....	49
2.3.2. CpLnX <sub>2</sub> and Cp <sub>2</sub> LnX compounds .....	58
2.3.3. Cp <sub>3</sub> Ln and Cp <sub>3</sub> LnL compounds .....	62
2.3.4. Pentamethylcyclopentadienyl compounds .....	63
2.3.5. Pentalenyl, indenyl and fluorenyl compounds .....	70
2.4. Organolanthanide complexes with heteroatom five-membered ring ligands .....	71
2.5. Lanthanide arene complexes .....	75
2.6. Lanthanide cyclooctatetraenyl complexes .....	77
2.7. Lanthanide metallofullerenes .....	77
2.8. Heterobimetallic organolanthanide complexes .....	81
2.9. Organolanthanide catalysis .....	85
2.9.1. Organolanthanide-catalyzed polymerization reactions .....	85
2.9.2. Organolanthanide-catalyzed hydroamination and hydrophosphination reactions .....	99
2.9.3. Other organolanthanide-catalyzed reactions .....	100
2.10. Organolanthanides in organic synthesis .....	102
2.11. Organolanthanides in materials science .....	103
3. Actinides .....	104
3.1. Actinide hydrocarbyls .....	104
3.2. Actinide cyclopentadienyl compounds .....	109
3.2.1. Cp <sub>3</sub> An, CpAnX <sub>3</sub> , Cp <sub>2</sub> AnX <sub>2</sub> and Cp <sub>3</sub> AnX compounds .....	109
3.2.2. Pentamethylcyclopentadienyl compounds .....	111
3.3. Actinide arene complexes .....	117
3.4. Actinide cyclooctatetraenyl complexes .....	119
3.5. Organoactinides in catalysis .....	121
Acknowledgements .....	129
References .....	129

## ARTICLE INFO

## Article history:

Received 21 March 2016

Accepted 2 April 2016

Available online 3 May 2016

## ABSTRACT

This review summarizes the progress in organo-*f*-element chemistry during the year 2015. The year 2015 witnessed a slight increase of contributions in the fields of organolanthanide and organoactinide chemistry over 2014 (*ca.* 10% more). A continuing trend for many years which continued into 2015 was the investigation of highly reactive lanthanide alkyl complexes supported by non-cyclopentadienyl ligands

Dedicated to Professor Erwin Weiß, a pioneer of organometallic chemistry, on the occasion of his 90th birthday.

\* Tel.: +49 391 6758327; fax: +49 391 6712933.

E-mail address: [frank.edelmann@ovgu.de](mailto:frank.edelmann@ovgu.de)

<http://dx.doi.org/10.1016/j.ccr.2016.04.001>

0010-8545/© 2016 Elsevier B.V. All rights reserved.

## Keywords:

Lanthanides  
Actinides  
Cyclopentadienyl complexes  
Cyclooctatetraenyl complexes  
Organometallic chemistry

(e.g. amidinates,  $\beta$ -diketimines etc.). Many of these complexes found useful applications in homogeneous catalysis. Trinuclear rare-earth metal methylenide ( $\text{CH}_2^{2-}$ ) complexes are an emerging class of compounds that serve as methylenide transfer agents for the methylenation of carbonyl compounds. The range of rare-earth metal alkyl complexes bearing different types of carbene ligands have also been further expanded. Several new lanthanide phosphido and phosphinidene complexes have been stabilized by specially designed  $N,N'$ -chelating ligands. The range of fully characterized lanthanide(II) compounds of the type  $[\text{K}(2.2.2\text{-cryptand})][\text{Cp}'_3\text{Ln}]$  ( $\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$ ) has again been significantly expanded so that the +2 ions are now available for yttrium and all the lanthanides (except promethium, which was not studied due to its high radioactivity). The first well-defined lutetacyclopentadienes have been synthesized and their reactivity has been studied. The synthesis, structure, and reactivity of the extremely reactive yttrium metallocene ethyl complex  $\text{Cp}^*_2\text{Y}(\text{CH}_2\text{CH}_3)$ , including activation of methane, have been reported. Significant progress has also been made in the field of endohedral metallofullerenes. Notably, encapsulation of a large  $\text{La}_2\text{C}_2$  cluster inside  $\text{D}_5(450)\text{-C}_{100}$  induced a 5% axial compression of the cage, as compared with the structure of  $\text{La}_2@\text{D}_5(450)\text{-C}_{100}$ . The number of well-characterized heterometallic organolanthanide complexes has also witnessed a remarkable growth. An impressive number of interesting contributions have been published in the field of organolanthanide catalysis, with an emphasis on Ln-catalyzed olefin and diene polymerization. Approximately 20% of the papers published in 2015 were in the area of organoactinide chemistry. Notable results include the synthesis and characterization of homoleptic uranium(IV) tetrabenzyl complexes and a simple mono(imido) thorium complex and the first bis(imido) thorium complex,  $\text{K}[\text{Th}(=\text{NDipp})(\text{NR}_2)_3]$  and  $\text{K}_2[\text{Th}(=\text{NDipp})_2(\text{NR}_2)_2]$  ( $\text{Dipp} = 2,6\text{-diisopropylphenyl}$ ,  $\text{R} = \text{SiMe}_3$ ). The reactivity of the unusual base-free imido complex  $[\eta^5\text{-}1,2,4\text{-}(\text{Me}_3\text{C})_3\text{C}_5\text{H}_2]_2\text{Th}=\text{N}(\text{p-tolyl})$  has also been studied. A highly remarkable achievement in 2015 was the synthesis of crystalline molecular complexes of the  $[\{\text{C}_5\text{H}_3(\text{SiMe}_3)_2\}_3\text{Th}]^-$  anion containing thorium in the formal +2 oxidation state. Various unusual transformations have been achieved using the  $\text{Cp}^*_2\text{Th}$  platform. For example, a unique thorium phosphinidene complex obtained from the reaction of  $\text{Cp}^*_2\text{Th}(\text{CH}_3)_2$  with  $\text{H}_2\text{P}(2,4,6\text{-iPr}_3\text{C}_6\text{H}_2)$  has been prepared and structurally characterized. Other remarkable results include the preparation of novel actinide metallacyclocumulenes and metallacyclopentadienes. The synthesis of [3]thoro- and [3]uranocenophanes, the first structurally authenticated *ansa*-bridged actinocenes, has also been reported. Finally, significant progress has been made in the field of organoactinide catalysis.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

This review summarizes the progress in organo-*f*-element chemistry during the year 2015. The year 2015 witnessed an increase of ca. 10% more contributions in this field over 2014. In this review mainly regular scientific papers are covered, while patents and conference abstracts *etc.* have mostly been excluded.

## 2. Lanthanides

### 2.1. Lanthanide carbonyls and hydrocarbyls

#### 2.1.1. Homoleptic compounds

The vibrational frequencies for a selected set of transition metal carbonyl complexes have been computed using various forms of density functional theory (B3LYP, BP86, M06, and M06-L), employing several different basis sets. The computed frequencies for the carbonyl stretches were compared to the experimental values obtained from gas phase infrared spectra of isolated neutrals and ions. Included in this study was the cationic yttrium carbonyl species  $\text{Y}(\text{CO})_8^+$  [1]. Design criteria for two-coordinate dysprosium complexes with favorable SMM (single molecule magnet) properties have been theoretically examined with *ab initio* calculations, with the result that the task for synthetic chemists pursuing lanthanide-

based SMMs is clear: Any  $\text{Dy}^{\text{III}}$  complex with only two anionic donor atoms is desirable, where the presence of weak agostic-type interactions should have negligible effects. However, the coordination of solvent molecules such as THF has catastrophic consequences on the  $U_{\text{eff}}$  (energy barrier to magnetic relaxation) values. If such *pseudo*-two-coordinate  $\text{Dy}^{\text{III}}$  complexes such as  $[\text{Dy}\{\text{C}(\text{SiR}_3)_3\}_2]^+$  or  $[\text{Dy}\{\text{N}(\text{SiR}_3)_2\}_2]^+$  can be isolated, they should be accompanied by a phenomenal increase to the current record magnetic relaxation barrier, which should result in much higher blocking temperatures, leading the way to technologically relevant high-temperature lanthanide SMMs [2]. Two isomers of  $\text{La}(\text{C}_3\text{H}_2)$ , namely  $\eta^2$ -propadienylidene-lanthanum,  $\text{La}(\eta^2\text{-CCCH}_2)$ , and deprotilanthanacyclobutadiene,  $\text{La}(\text{HCCCH})$ , have been identified from the reaction mixture of neutral La atom activation of propyne in the gas phase (*cf.* Fig. 1). The two isomers were characterized with mass-analyzed threshold ionization spectroscopy combined with electronic structure calculations and spectral simulations.  $\text{La}(\eta^2\text{-CCCH}_2)$  and  $\text{La}(\text{HCCCH})$  were formed by concerted 1,3- and 3,3-dehydrogenation, respectively. Both isomers prefer a doublet ground state with a La 6s-based unpaired electron, and  $\text{La}(\eta^2\text{-CCCH}_2)$  is slightly more stable than  $\text{La}(\text{HCCCH})$ . Ionization of the neutral doublet state of either isomer produces a singlet ion state by removing the La-based electron. The geometry change upon ionization results in the excitation of a symmetric metal–hydrocarbon

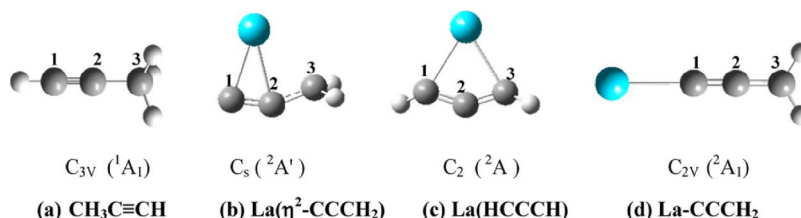


Fig. 1. Structures of  $\text{CH}_3\text{C}\equiv\text{CH}$  (a),  $\text{La}(\eta^2\text{-CCCH}_2)$  (b),  $\text{La}(\text{HCCCH})$  (c), and  $\text{La-CCCH}_2$  (d). Reprinted with permission from Ref. 3. Copyright 2015 American Chemical Society.

Download English Version:

<https://daneshyari.com/en/article/1299035>

Download Persian Version:

<https://daneshyari.com/article/1299035>

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