



## Review

## Lanthanides and actinides: Annual survey of their organometallic chemistry covering the year 2017



Frank T. Edelmann

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

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## ABSTRACT

This review summarizes the progress in organo-*f*-element chemistry during the year 2017. This year witnessed a significant increase of publications in the fields of organolanthanide and -actinide chemistry over 2016 (195 vs. 155 publications). The journal *Organometallics* dedicated a special issue to the topic “Organometallic Actinide and Lanthanide Chemistry”.

Notable among homoleptic lanthanide alkyl species are the unsolvated homoleptic tris(alkyl)lanthanide compounds  $\text{Ln}[\text{C}(\text{SiHMe}_2)_2\text{Ph}]_3$  ( $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$ ) and  $\text{Ce}[\text{C}(\text{SiHMe}_2)_3]_3$ . A continuing trend for many years which continued into 2017 was the study of reactive lanthanide mono- and bis(alkyl) complexes supported by a variety of non-cyclopentadienyl ligands such as monoanionic NPN ligands, amidinates,  $\beta$ -diketiminates, chelating carbene ligands (methanediides), amino-bis(phenolates) etc. Also notable is a series of heteroleptic lanthanide complexes containing direct Ln-Si bonds like e.g.  $[(\text{Me}_3\text{Si})_2\text{Si}(\text{OMe})_2\text{Yb}(\text{THF})]$ . Reactions of yttrium and lutetium metallocyclopentadienes with  $\text{P}_4$  afforded the first lanthanide *cyclo*- $\text{P}_3$  complexes. The bulky scorpionate ligand  $\text{Tp}^{\text{Me}_2}$  (= tris(3,5-dimethylpyrazolyl)borate) played an important role in the synthesis of novel lanthanide polysulfide complexes such as  $(\text{Tp}^{\text{Me}_2})\text{Y}(\kappa_4\text{-S}_5)(\text{THF})$ . In the area of Ln cyclopentadienyl complexes, unusual  $\text{Ln}^{2+}$ -in-*crypt* complexes of the type  $[\text{Ln}(\text{crypt})(\text{THF})][\text{Cp}'_3\text{Ln}]_2$  ( $\text{Ln} = \text{Sm}, \text{Eu}$ ; *crypt* = 2.2.2-cryptand;  $\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$ ) have been reported. The carbonate-bridged samarium(III) dimers  $(\mu\text{-CO}_3)[\text{Cp}_2^{\text{Sm}}]_2$  and  $(\mu\text{-CO}_3)[\text{Cp}_2^{\text{Sm}}]_2$  have been prepared from reactions of reaction of  $\text{CO}_2$  with the base-free divalent samarium complexes  $\text{Cp}_2^{\text{Sm}}$  ( $\text{Cp}^{\text{tt}} = 1,3\text{-}^i\text{Bu}_2\text{C}_5\text{H}_3$ ) and  $\text{Cp}_2^{\text{Sm}}$  ( $\text{Cp}^{\text{tt}} = 1,2,4\text{-}^i\text{Bu}_3\text{C}_5\text{H}_2$ ). A particularly remarkable achievement in 2017 was the successful synthesis of a dysprosium metallocene single-molecule magnet,  $[(\text{Cp}^{\text{tt}})_2\text{Dy}][\text{B}(\text{C}_6\text{F}_5)_4]$ , with a record anisotropy barrier and a record magnetic blocking temperature of 60 K. The accessibility of well-defined organocerium(IV) compounds has been significantly broadened by the isolation of a series of heteroleptic tris(cyclopentadienyl) Ce(IV) complexes such as  $\text{Cp}'_3\text{Ce}(\mu\text{-OC}_6\text{H}_4\text{O})\text{CeCp}'_3$  or  $\text{Cp}'_3\text{CeCl}$ . Two novel cationic dysprosium ammonia metallocene complexes have been prepared by treatment of the tetraphenylborate precursor  $[\text{Cp}_2^{\text{Dy}}][(\mu\text{-Ph})_2\text{BPh}_2]$  with  $\text{NH}_3$ . The complexes  $\text{Cp}_2^{\text{Ln}}[(\text{Me}_3\text{SiN}=\text{S})_2\text{S}]$  ( $\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$ ) were the first Ln complexes with a redox-active sulfur diimide ligand. The dinuclear ytterbium metallocenes  $(\mu\text{-Me})[\text{Cp}_2^{\text{Yb}}]_2$  and  $(\mu\text{-Me})[\text{Cp}_2^{\text{Yb}}]_2(\text{Me})$  have been prepared from  $\text{Cp}_2^{\text{Yb}}$  using MeCu as methyl transfer reagent. Moreover, the synthesis and structural characterization of novel indigo-bridged dilanthanide complexes,  $[(\mu\text{-ind})\{\text{Cp}_2^{\text{Ln}}\}_2]^{n-}$  ( $\text{Ln} = \text{Gd}, \text{Dy}$ ;  $n = 0, 1, 2$ ) have been described. For the first time, solvent-free mechanochemistry was utilized to synthesize lanthanide tris(pentamethylcyclopentadienyl) complexes,  $\text{Cp}_3^{\text{Ln}}$  ( $\text{Cp}^* = \text{pentamethylcyclopentadienyl}$ ), by ball-milling  $\text{Cp}_2^{\text{Ln}}(\mu\text{-Ph})_2\text{BPh}_2$  and  $\text{KCp}^*$  as solids. Another highlight in the field of organolanthanide chemistry was the successful isolation of the unusual quadruple-decker cerium(II) sandwich complex  $[\text{K}(2.2.2\text{-crypt})_2][\{\{\text{KL}_3\text{Ce}(\mu\text{-}\eta^6\text{-C}_7\text{H}_8)\}_2\text{Ce}\}][\text{L} = \text{OSi}(\text{O}^i\text{Bu})_3]$ . Also along this line, the new lanthanide inverse sandwich complexes  $\text{KLn}_2(\text{C}_7\text{H}_7)[\text{N}(\text{SiMe}_3)_2]_4$  ( $\text{Ln} = \text{Gd}, \text{Dy}, \text{Er}$ ) and  $\text{K}(\text{THF})_2\text{Er}_2(\text{C}_7\text{H}_7)[\text{N}(\text{SiMe}_3)_2]_4$  with bridging cycloheptatrienyl ligands were synthesized. An oxidation reaction of  $\text{Li}[\text{Sc}(\text{COT}')_2]$  with  $\text{CoCl}_2$  afforded a mixture of the expected triple-decker complex  $\text{Sc}_2(\text{COT}')_3$  and the novel complex  $\text{Sc}_2\{\mu\text{-BTHP}\}(\text{COT}')_2$  ( $\text{BTHP}^{2-} = \text{bis}(3,5\text{-bis}(\text{trimethylsilyl})\text{-1,3a,6,6a-tetrahydropentalene-1-yl})\text{diide}$ ). Another remarkable achievement in this field was the synthesis of the first bis( $\eta^9$ -cyclononatetraenyl) complex of an *f*-element, namely the europium(II) sandwich complex  $\text{Eu}(\text{Cnt})_2$  ( $\text{Cnt} = \text{cyclononatetraenyl monoanion}$ ). Significant progress has also been made in the field of endohedral metallofullerenes, including the first examples of *N*-heterocyclic carbene adducts of metal carbide cluster fullerenes, the successful isolation and structural characterization of a series of giant carbide cluster metallofullerenes, and the synthesis, isolation, and trifluoromethylation of two isomers of

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

C<sub>84</sub>-based monometallic cyanide clusterfullerenes (CYCFs). In the field of heterometallic organolanthanide complexes, several unique lanthanide ferrocenophane complex such as [Li(THF)<sub>4</sub>][DyFc<sub>3</sub>(THF)<sub>2</sub>Li<sub>2</sub>] and [Li<sub>2</sub>X(THF)<sub>6</sub>][Dy<sub>3</sub>Fc<sub>6</sub>Li<sub>2</sub>(THF)<sub>2</sub>] (X = I, Cl; Fc = ferrocene dianion) have been reported. The trapping of a rare [W<sub>2</sub>(CO)<sub>10</sub>]<sup>2-</sup> anion with an unsupported W–W bond has been achieved in the mixed-valent samarium (II/III)/tungsten complex [(μ-OC)<sub>2</sub>W<sub>2</sub>(CO)<sub>8</sub>][(THF)<sub>2</sub>Sm<sup>II</sup>(N<sub>4</sub>Et<sub>8</sub>)Sm<sup>III</sup>(THF)<sub>2</sub>] ((N<sub>4</sub>Et<sub>8</sub>)<sup>4-</sup> = *meso*-octaethylcalix [4] pyrrolide). Once again, an impressive number of interesting contributions have been published in 2017 in the field of organolanthanide catalysis, with an emphasis on Ln-catalyzed olefin and diene polymerization reactions. Notable results among polymerization reactions include, among many others, the organoscandium-catalyzed copolymerization of ethylene with aminoalkenes, the highly syndiospecific styrene-ethylene copolymerization catalyzed by allyl *ansa*-lanthanidocene catalysts, the highly efficient syndiospecific chain-transfer polymerization of styrene using anisoles as chain-transfer agents (CTAs), and the *cis*-1,4-selective copolymerization of ethylene and butadiene catalyzed by thiophene-fused cyclopentadienyl-ligated scandium pre-catalysts. An efficient organoyttrium-catalyzed method to produce unusual polymer brushes with bottle brush architecture has also been developed. Other interesting findings in the field of organolanthanide catalysis include e.g. the first diastereodivergent enantioselective synthesis of bicyclic aminocyclopropanes by asymmetric carboamination/annulation of cyclopropenes with aminoalkenes, and the enantioselective yttrium-catalyzed C(sp<sup>3</sup>)–H bond addition of 2-methyl azarenes to substituted cyclopropenes. The use of organolanthanide complexes in organic synthesis and as precursors in materials science has decreased significantly in 2017 as compared to 2016.

In organoactinide chemistry, a rare homoleptic uranium(III) tris(aryl) complex, (Terph)<sub>3</sub>U (Terph = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>4</sub>-4-<sup>t</sup>Bu)<sub>2</sub>), has been reported, and the synthesis and reactivity of homoleptic uranium (IV) tetrabenzyl complexes have been studied. Also notable among non-cyclopentadienyl actinide complexes is the phosphorano-stabilized Th(IV) carbene complex Th(CHPhPh<sub>3</sub>)[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>. Moreover, the synthesis, characterization, and reactivity of new heteroleptic Th and U complexes supported by the macrocyclic TMTAA ligand (TMTAA = tetramethyl-tetraazaannulene) have been reported. Interesting derivative chemistry has been developed around the bis(NHC)borate-supported thorium bis(phosphido) complex Th(Bc<sup>Mes</sup>)<sub>2</sub>[HP(Mes)]<sub>2</sub> (Bc<sup>Mes</sup> = [H<sub>2</sub>B(C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>Mes)<sub>2</sub>]<sup>-</sup>, Mes = 2,4,6-trimethylphenyl). A novel uranium μ-phosphido complex have also been prepared and structurally characterized, and the formation of a uranium-coordinated η<sup>1</sup> cyaphide (CP<sup>-</sup>) ligand *via* activation and C–O bond cleavage of the phosphoethynolate (OCP<sup>-</sup>) anion has been reported. Thorough reactivity studies have been carried out for actinide metallocene complexes such as ThCp<sup>''</sup><sub>3</sub> (Cp<sup>''</sup> = [C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>-1,3], [η<sup>5</sup>-1,3-(Me<sub>3</sub>C)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>]<sub>2</sub>U(η<sup>4</sup>-C<sub>4</sub>Ph<sub>2</sub>), Cp<sup>''</sup><sub>4</sub>U (Cp<sup>''</sup> = C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>), Cp<sup>''</sup><sub>2</sub>U[η<sup>4</sup>-C<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub>], Cp<sup>''</sup><sub>2</sub>U(bipy), Cp<sup>''</sup><sub>2</sub>Th=N(mesityl)(DMAP) (DMAP = 4-dimethylaminopyridine) and Cp<sup>''</sup><sub>2</sub>Th[CHPhPh<sub>3</sub>]X (X = Br, I). The complexes Cp<sup>''</sup><sub>2</sub>Th(EHTipp)<sub>2</sub> (E = P, As; Tipp = 2,4,6-triisopropylphenyl) have been used to access Th–E multiple bonds as in the terminal phosphinidene complex [K(2,2,2-cryptand)][Cp<sup>''</sup><sub>2</sub>Th = PTipp(PHTipp)]. The synthesis, structure, and reactivity of the sterically crowded Th<sup>3+</sup> complex Cp<sup>''</sup><sub>3</sub>Th have also been investigated in detail. Remarkable achievements have been made in 2017 in the organometallic chemistry of neptunium and plutonium. Structurally characterized compounds included e.g. Cp<sub>3</sub>Np, Cp<sub>3</sub>Np(NCMe)<sub>2</sub>, K[NpCp<sub>4</sub>], and Cp<sub>3</sub>Np. Yet another highlight in this field was the first identification of the formal +2 oxidation state of plutonium in the organometallic complex [K(2,2,2-cryptand)][Pu<sup>II</sup>Cp<sup>''</sup><sub>3</sub>]. This complex was prepared by reduction of Cp<sup>''</sup><sub>3</sub>Pu with KC<sub>8</sub> in the presence of 2,2,2-crypt and structurally characterized by X-ray diffraction. In a second contribution, the first X-ray crystal structure determination of an organometallic plutonium(IV) complex, the tetrasubstituted plutonocene complex Pu(1,3-COT<sup>''</sup>)(1,4-COT<sup>''</sup>) [COT<sup>''</sup> = η<sup>8</sup>-bis(trimethylsilyl)cyclooctatetraenyl], has been reported. Interesting studies involving organoactinides complexes in homogeneous catalysis have addressed e.g. the dimerization of aldehydes.

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## Contents

1. Introduction	131
2. Lanthanides	132
2.1. Lanthanide carbonyls and hydrocarbyls	132
2.1.1. Homoleptic compounds	132
2.1.2. Heteroleptic compounds	133
2.1.3. Silyl-based compounds	143
2.2. Lanthanide allyl and alkynyl complexes	145
2.3. Lanthanide cyclopentadienyl complexes	145
2.3.1. CpLnX, Cp <sub>2</sub> Ln and [Cp <sub>3</sub> Ln] <sup>-</sup> compounds	145
2.3.2. CpLnX <sub>2</sub> and Cp <sub>2</sub> LnX compounds	146
2.3.3. Cp <sub>3</sub> Ln and Cp <sub>3</sub> LnL compounds	149
2.3.4. Pentamethylcyclopentadienyl compounds	151
2.3.5. Pentalenyl, indenyl and fluorenyl compounds	155
2.4. Organolanthanide complexes with heteroatom five-membered ring ligands	156
2.5. Lanthanide arene complexes	158
2.6. Lanthanide cycloheptatrienyl and cyclooctatetraenyl complexes	162
2.7. Lanthanide metallofullerenes	167
2.8. Heterobimetallic organolanthanide complexes	170

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