



Review

Lanthanides and actinides: Annual survey of their organometallic chemistry covering the year 2013



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ABSTRACT

This review summarizes the progress in organo-*f*-element chemistry during the year 2013. The year 2013 witnessed a significant increase of contributions in the fields of organolanthanide and organoactinide chemistry over 2012 (*ca.* 16% more). An unbroken trend for many years which continued into 2013 was the investigation of highly reactive lanthanide alkyl complexes supported by non-cyclopentadienyl

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ligands (e.g., amidinates, aminopyridinates, β -diketimines, etc.). Many of these complexes found useful applications in homogeneous catalysis. Three classes of compounds stand out for having become increasingly important in 2013: carbene complexes of lanthanides and uranium, organolanthanide hydrido clusters, and heterometallic organolanthanide compounds. Notable among the 2013 highlights in the field of organolanthanide chemistry is the successful synthesis of the first carbene complex of tetravalent cerium, $\text{Ce}(\text{BIPM}^{\text{TMS}})(\text{ODipp})_2$ ($\text{BIPM}^{\text{TMS}} = [\text{C}(\text{PPh}_2\text{NSiMe}_3)_2]^{2-}$, $\text{Dipp} = 2,6$ -diisopropylphenyl). Two new scandium terminal imido complexes have also been reported. Without doubt a major highlight was the isolation of first examples of crystallographically characterizable complexes of Tb^{2+} , Pr^{2+} , Gd^{2+} , and Lu^{2+} . This finding demonstrates that Ln^{2+} ions are now accessible in soluble molecules for all of the lanthanides except radioactive promethium. Also quite remarkable is the europium(II) metallocene $\text{Eu}(\text{Cp}^{\text{BIG}})_2$ ($\text{Cp}^{\text{BIG}} = (4\text{-}^n\text{BuC}_6\text{H}_4)_5\text{-cyclopentadienyl}$) which exhibits bright orange photoluminescence at room temperature. The class of lanthanide hydride clusters has been largely expanded in 2013, including a series of heterometallic species such as the first heterotrimetallic (Lu/Re/W) and several hexanuclear heterobimetallic Y_4/M_2 - and Y_5/M -polyhydride ($\text{M} = \text{Mo}, \text{W}$) cluster complexes. The same is true for various heterometallic organolanthanide compounds, including, e.g., the unusual new $3d/4f$ polyphosphide complexes $(\text{Cp}^+ \text{Fe})_2 \text{P}_{10}[\text{Sm}(\eta^5\text{-C}_5\text{Me}_4\text{R})_2]_2$ ($\text{R} = \text{Me}, ^n\text{Pr}$) and several novel complexes comprising direct bond between lanthanides and main group elements and transition metals. The chemistry of endohedral lanthanide fullerenes continued to attract significant interest in 2013. For example, it was discovered that the Lewis acid CuCl_2 is a suitable reagent for the isolation of a broad array of endohedral fullerenes containing metal, metal carbide, metal nitride, and metal oxide clusters, as well as for the separation of their structural isomers. $\text{YCN}@\text{C}_{82}$ was shown to be the first endohedral metallofullerenes entrapping a metal cyanide. Several new catalytic applications of organolanthanide compounds have also been uncovered, such as the Ln-catalyzed carbostannylation of olefins and terminal alkynes. Ca. 20% of all publications covered in this review were in the area of organoactinide chemistry. Significant progress has been made in the synthesis and characterization of actinide alkyl complexes, e.g., the preparation of first genuine uranyl(VI) alkyl complex, $[\text{Li}(\text{DME})_{1.5}]_2[\text{UO}_2(\text{CH}_2\text{SiMe}_3)_4]$. A rich chemistry has been developed around new uranium carbene complexes containing, e.g., the $\text{BIPM}^{\text{Dipp}}$ ligand ($\text{BIPM}^{\text{Dipp}} = [\text{C}(\text{PPh}_2\text{NDipp})_2]^{2-}$; $\text{Dipp} = \text{C}_6\text{H}_3\text{Pr}_2\text{-}2,6$). Truly remarkable was the identification of the +2 oxidation state for uranium in a crystalline molecular complex, $[\text{K}(2.2.2\text{-cryptand})][(\text{C}_5\text{H}_4\text{SiMe}_3)_3\text{U}]$, which was made by flash reduction of $\text{Cp}'_3\text{U}$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$) in a column of potassium graphite in the presence of 2.2.2-cryptand. A reinvestigation of the chemistry of $(\text{COT})_2\text{Th}$ with neutral Lewis bases provided access to novel bent sandwich complexes $(\text{COT})_2\text{Th}(\text{L})$.

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1. Introduction

This review summarizes the progress in organo-*f*-element chemistry during the year 2013. The year 2013 witnessed an increase of ca. 16% more contributions in this field over 2012. In this review mainly regular scientific papers are covered, while patents, conference abstracts, etc. have mostly been excluded.

2. Lanthanides

2.1. Lanthanide hydrocarbyls

2.1.1. Homoleptic compounds

The topology of the electron density of d^0 lanthanide compounds at subatomic resolution has been studied. In this contribution it was pointed out that accurate X-ray diffraction experiments allow for a reconstruction of the electron density distribution of solids and molecules in a crystal and that the basis for the reconstruction of the electron density is in many cases a multipolar expansion of the X-ray scattering factors in terms of spherical harmonics, a so-called multipolar model. This commonly used ansatz splits the total electron density of each pseudoatom in the crystal into (i) a spherical core, (ii) a spherical valence, and (iii) a nonspherical valence contribution. Previous studies, for example, on diamond and α -silicon had already shown that this approximation is no longer valid when ultrahigh-resolution diffraction data are taken into account. In this study the results of an analysis of the calculated electron density distribution in the d^0 transition metal compounds $[\text{LnCH}_3]^{2+}$ ($\text{Ln} = \text{Sc}, \text{Y}, \text{and La}$) at subatomic resolution have been reported. By a detailed molecular orbital analysis, it was demonstrated that due to the radial nodal structure of the $3d$, $4d$, and $5d$ orbitals involved in the Ln–C bond formation a

significant polarization of the electron density in the inner electronic shells of the Ln atoms is observed. It was further shown that these polarizations have to be taken into account by an extended multipolar model in order to recover accurate electron density distributions from high-resolution structure factors calculated for $[\text{LnCH}_3]^{2+}$ compounds [1]. The gas-phase reactivity of methyl fluoride with selected first-row transition metal monocations (Sc^+ , Ti^+ , V^+ , and Zn^+) has been theoretically investigated. The thermochemical and kinetics study showed that early transition-metal cations exhibit a much more active chemistry than the latest transition metal monocation Zn^+ . It was shown that the strong C–F bond in methyl fluoride can be activated by scandium, titanium, and vanadium monocations yielding the metal fluoride cation, MF^+ . However, the rate efficiencies vary dramatically along the period 0.73 (Sc), 0.91 (Ti), and 0.028 (V) in agreement with the experimental observation [2]. A detailed computational study on the equilibrium geometries, stability and vibrational frequencies of a series of $\text{Sc}(\text{CO})_n$ ($n = 1\text{--}7$), $\text{Sc}(\text{CO})_7^-$ and $\text{Sc}(\text{CO})_6^{3-}$ has been reported using density functional theory functionals and the coupled cluster (single-point) method with 6-311+G(3df) basis set. It was shown that the obtained sequential and average CO binding energies of $\text{Sc}(\text{CO})_n$ ($n = 4\text{--}7$), $\text{Sc}(\text{CO})_7^-$ and $\text{Sc}(\text{CO})_6^{3-}$ are comparable to those of experimentally known species, i.e., smaller scandium carbonyls ($n < 3$) and the analog $\text{Ti}(\text{CO})_7^+$. In addition, the studied $\text{Sc}(\text{CO})_n$ complexes generally favor the low-spin ground state (doublet) structures except ScCO and $\text{Sc}(\text{CO})_3$ that are in the quartet states. The previously uncertain spectrum bands were assigned to $\text{Sc}(\text{CO})_4$ and $\text{Sc}(\text{CO})_5$ in this work. In all, the appreciable stability suggested that the 18-electron first-row transition metal carbonyls, i.e., $\text{Sc}(\text{CO})_7^-$ and $\text{Sc}(\text{CO})_6^{3-}$ could be accessible experimentally [3]. In a closely related study, theoretical calculations and experimental observations on octacoordinate metal carbonyls of scandium and

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