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Review

Lanthanides and actinides: Annual survey of their organometallic chemistry covering the year 2005

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Abstract

This article give a comprehensive overview of the chemistry of organolanthanide and organoactinide complexes published in the year 2005. Besides synthetic and structural aspects of all new compounds, the review also covers applications of organolanthanide and -actinide complexes in homogeneous catalysis, organic synthesis, and materials science.

Keywords: Lanthanides; Actinides; Cyclopentadienyl complexes; Cyclooctatetraenyl complexes; Organometallic chemistry

1. Introduction

This review summarizes the progress in organo-*f*-element chemistry during the year 2005. The year 2005 has witnessed a remarkable increase in research activities in this area.

2. Lanthanides

2.1. Lanthanide carbonyls

The electronic and geometric structure of scandium monocarbonyl ScCO has been investigated through coupled cluster (CC) and multireference variational methods (MRCI) combined with large basis sets. The bonding in this simple molecule is rather complicated and could be attributed mainly to π-conjugation effects between the Sc and CO π-electrons, along with weak σ-charge transfer from CO to the Sc atom [1]. Matrix-isolated $Sc_2[\eta^2(\mu_2\text{-CO})]$ molecules have been produced by co-deposition of laser-ablated Sc atoms with CO in excess argon at 7 K and investigated using FT-IR spectroscopy. It was shown that $Sc_2[\eta^2(\mu_2\text{-CO})]$ is an unprecedented homoleptic dinuclear metal carbonyl with an asymmetrically bridging and *side-on*-bonded CO. There is evidence that it is an intermediate to CO dissociation [2].

2.2. Lanthanide hydrocarbyls

2.2.1. Neutral homoleptic compounds

Ab initio and DFT calculations have been performed on a series of simple organometallic compounds of the formula MCH_n with $n = 1$–3. The main electronic characteristics of methylidynes, methylidenes, and methyl-metals have been described for first-row early transition metals, including the scandium species ScCH, $ScCH_2$, and $ScCH_3$. $ScCH_2$ exhibits a bent structure and therefore constitutes a candidate to present α-agostic bonds [3]. A major achievement in organolanthanide chemistry reported in 2005 was the synthesis of the elusive homoleptic alkyls trimethylyttrium and trimethyllutetium. The synthetic strategy employed involves donor-induced cleavage of the corresponding homoleptic lanthanide tetramethylaluminates as illustrated in Scheme 1. The elimination of trimethylaluminum could be achieved with the Lewis base donors THF or diethyl ether. Polymeric $[YMe_3]_n$ and $[LuMe_3]_n$ were isolated as white powders which are insoluble in aliphatic and aromatic solvents. The lutetium derivative detonates spontaneously when exposed to air. Preliminary investigations into the reaction behavior of $[LnMe_3]_n$ were performed using the yttrium derivative and are summarized in Scheme 1 [4].

Reaction of $o\text{-}Me_2NC_6H_4CH_2K$ with YCl_3 in THF yielded $(o\text{-}Me_2NC_6H_4CH_2)_3Y$ in the form of light yellow crystalline plates in 59% yield (Scheme 2, Ln = Y). The crystal structure shows three bidentate benzyl ligands bound to Y, which has a prismatic coordination sphere. The La analogue was prepared similarly (41% yield, Scheme 2, Ln = La) and is isostructural to the yttrium derivative, but shows more extensive multihapto bonding of the benzyl ligands to the larger metal atom (short aryl–La interactions) [5].

2.2.2. Heteroleptic compounds

Cationic yttrium methyl complexes have been prepared by protonation of formally trianionic precursors as illustrated in Scheme 3. The crystal structure of $[YMe_2(THF)_5][BPh_4]$ has been determined by X-ray diffraction. Fig. 1 shows the pentagonal-bipyramidally coordinated yttrium center with the methyl groups in the *trans*-positions [6].

A family of scandium and yttrium tris[(trimethylsilyl)methyl] complexes with neutral N_3 donor ligands has been reported. The synthetic routes are summarized in Scheme 4. Representatives of all three types of trialkyls have been structurally characterized by X-ray diffraction. As an example, the molecular structure of $[HC(Me_2pz)_3]Sc(CH_2SiMe_3)_3$ is shown in Fig. 2 [7].

X-ray crystallography and variable-temperature (VT) NMR spectroscopy revealed a structural diversity within the known series of neutral 12-crown-4 supported tris(trimethylsilylmethyl) complexes $(12\text{-crown-}4)Ln(CH_2SiMe_3)_3$ (Ln = Sc, Y, Sm, Gd–Lu) in the solid-state as well as in solution. VT NMR spectroscopy indicates fluxional 12-crown-4 coordination on the NMR time scale. The X-ray crystal structure determination of $(12\text{-crown-}4)Sc(CH_2SiMe_3)_3$ revealed incomplete 12-crown-4 coordination (Fig. 3). The molecule adopts a three-legged "piano-stool" geometry with the 12-crown-4 ligand bonded facially through only three oxygen atoms. Thus the coordination geometry around Sc is best described as distorted octahedral [8].

The neutral precursors of the type $(12\text{-crown-}4)Ln(CH_2SiMe_3)_3$ and $Ln(CH_2SiMe_3)_3(THF)_n$ ($n = 2,3$; Ln = Sc, Y, Lu) have been utilized in the preparation of a series of mono- and di-cationic trimethylsilylmethyl lanthanide complexes sup-