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Review

Lanthanides and actinides: Annual survey of their organometallic chemistry covering the year 2011

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Contents

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ABSTRACT

This review summarizes the progress in organo-*f*-element chemistry during the year 2011. A continuing trend in organolanthanide research is a strong emphasis on applications of organolanthanide complexes in homogeneous catalysis and, to a lesser extent, materials science. Roughly 24% of all relevant

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papers published in 2011 were in the area of organoactinide chemistry, which continues to produce exciting results. Quite remarkable is a steady increase in research activities focussed on lanthanide and actinide carbene complexes.

1. Introduction

This review summarizes the progress in organo-*f*-element chemistry during the year 2011. A continuing trend in organolanthanide research is a strong emphasis on applications of organolanthanide complexes in homogeneous catalysis and, to a lesser extend, materials science. Roughly 24% of all relevant papers published in 2011 were in the area of organoactinide chemistry, although the latter continues to produce exciting results.

2. Lanthanides

2.1. Lanthanide hydrocarbyls

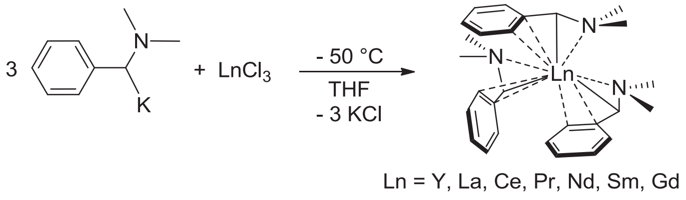
2.1.1. Homoleptic compounds

The synthesis and reactivity of a series of homoleptic α-metalated N,N-dimethylbenzylamine rare-earth metal complexes have been described. The compounds were synthesized using salt metathesis reactions between $LnCl_3$ and α-K(DMBA) (Scheme 1; Ln = Y, La, Ce, Pr, Nd, Sm, Gd; DMBA = *N*,*N*-dimethylbenzylamide). All seven complexes were found to be free of coordinating solvent, and no formation of any anionic “ate” species was observed. The ligands in these complexes displayed η^4-coordination to the metal center [1].

Subsequently, the reactivity of the Y and La derivatives was investigated *via* various protonolysis reactions using silylamines, anilines, and phenols to generate a diverse array of other homoleptic lanthanide complexes as illustrated in Scheme 2 [1].

2.1.2. Heteroleptic compounds

A matrix infrared spectroscopic and computational investigation of the lanthanide–methylene complexes CH_2LnF_2 with single Ln—C bonds has been published in 2011. Laser-ablated lanthanide metal atoms were condensed with CH_2F_2 in excess argon at 6 K or neon at 4 K. New infrared absorption bands were assigned to the oxidative addition product methylene lanthanide difluorides on the basis of deuterium substitution and vibrational frequency calculations with density functional theory (DFT). Two dominant absorptions in the 500 cm^{-1} region were identified as lanthanide–fluoride stretching modes for this very strong infrared absorption. The predominantly lanthanide–carbon stretching modes were found to follow a similar trend of increasing with metal size and have characteristic 30 cm^{-1} deuterium and 14 cm^{-1} ^{13}C isotopic shifts. The electronic structure calculations showed that these CH_2LnF_2 complexes are not analogous to the simple transition and actinide metal methylidenes with metal–carbon double bonds that have been investigated previously, because the lanthanide metals (in the +2 or +3 oxidation state) do not appear to form a π-type bond with the CH_2 group. The DFT and *ab initio* correlated molecular orbital theory calculations predicted that these complexes exist as multiradicals, with a Ln—C σ bond and a single electron on C-2p weakly coupled with f_x (x = 1 (Ce), 2 (Pr), 3 (Nd), *etc.*) electrons in the adjacent Ln-4*f* orbitals. The Ln—C σ bond is composed of about 15% Ln-5*d*,6*s* and 85% C-sp^2 hybrid orbital. The Ln orbital has predominantly 6*s* and 5*d* character with more *d*-character for early lanthanides and increasing amounts of *s*-character across the row. The Ln—F bonds are almost purely ionic. Accordingly, the argon–neon matrix shifts were large (13–16 cm^{-1}) for the ionic Ln—F bond stretching modes and small (~1 cm^{-1}) for the more covalent Ln—C bond stretching modes [2]. Reactions of laser-ablated scandium, yttrium, lanthanum, and several lanthanide metal atoms with dimethyl ether have been studied using matrix isolation infrared spectroscopy. Identifications of the major products, $Ln(CH_3OCH_3)$ and CH_3OLnCH_3 (Ln = Sc, Y, La, Ce, Gd, Tb, Yb, Lu), were supported by experiments with deuterium substitution as well as theoretical calculations. It was found that most ground-state metal atoms react with dimethyl ether to give the $Ln(CH_3OCH_3)$ complexes spontaneously on annealing, which isomerize to the CH_3OLnCH_3 insertion products with visible irradiation (Fig. 1). Density functional calculations revealed that the $Ln(CH_3OCH_3)$ complexes possess C_{2v} symmetry with metal atoms bound to the oxygen side of dimethyl ether, and bent geometries were found for the inserted CH_3OLnCH_3 molecules with direct Ln—O and C—O bonds. All of these products were found to have the same ground states as their corresponding metal atoms except for Tb. Although the $Lu(CH_3OCH_3)$ complex has been predicted to be a stable molecule, it was not observed in the experiment owing to the low energy barrier for the subsequent C—O bond insertion reaction [3].



Scheme 1. Synthesis of α-Ln(DMBA)$_3$.

In a similar manner, lanthanide metal atoms, produced by laser ablation, have been condensed with CH_3F in excess Ar at

$$\alpha\text{–La(DMBA)}_3 + 2\ \text{HOAr} \xrightarrow[\text{THF}]{} \text{La(DMBA)(OAr)}_2\text{(THF)} + 2\ \text{HDMBA}$$

$$\alpha\text{–Ln(DMBA)}_3 + 3\ \text{HOAr} \xrightarrow[\text{THF}]{} \text{Ln(OAr)}_3 + 3\ \text{HDMBA}$$

$$\alpha\text{–Ln(DMBA)}_3 + 3\ \text{H}_2\text{NAr}' \xrightarrow[\text{THF}]{} \text{Ln(NHAr}')_3 + 3\ \text{HDMBA}$$

$$\alpha\text{–Ln(DMBA)}_3 + 3\ \text{HN(SiMe}_3)_2 \xrightarrow[\text{THF}]{} \text{Ln[N(SiMe}_3)_2]_3 + 3\ \text{HDMBA}$$

Ln = Y, La

Scheme 2. Protonolysis reactions of α-Ln(DMBA)$_3$ (Ar = 2,6-di-*tert*-butylphenyl, 4-*tert*-butylphenyl; Ar′ = 2,6-diisopropylphenyl, 4-*tert*-butylphenyl).