



## Review

## Lanthanides and actinides: Annual survey of their organometallic chemistry covering the year 2012



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## ABSTRACT

This review summarizes the progress in organo-*f*-element chemistry during the year 2012. A continuing trend in organolanthanide research is a strong emphasis on applications of organolanthanide complexes in homogeneous catalysis and materials science. Reactive lanthanide alkyl complexes supported by ligands other than cyclopentadienyl rings also continue to attract continuing interest. Currently, the study of organo-rare-earth-based SMMs is another exciting topic in organolanthanide chemistry.

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Notable among the highlights in organolanthanide chemistry is the synthesis of the first molecular complexes of holmium and erbium in the +2 oxidation state which have been generated by reducing Cp<sub>3</sub>Ln (Cp' = C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>; Ln = Ho, Er) with KC<sub>8</sub> in the presence of 18-crown-6 in Et<sub>2</sub>O at –35 °C. The direct P<sub>4</sub> activation using scandium and yttrium complexes has been achieved for the first time under mild conditions. Two novel P<sub>n</sub>-containing products, [(NN<sup>fc</sup>)Sc]<sub>4</sub>P<sub>8</sub> and [(NN<sup>fc</sup>)Sc]<sub>3</sub>P<sub>7</sub>, were isolated from reactions of P<sub>4</sub> with the scandium arene complexes (μ-naphthalene)[(NN<sup>fc</sup>)Sc]<sub>2</sub> and (μ-anthracene)[(NN<sup>fc</sup>)Sc]<sub>2</sub> (NN<sup>fc</sup> = 1,10'-fc(NSi<sup>t</sup>BuMe<sub>2</sub>)<sub>2</sub>, fc = ferrocenylene). A steady increase in research activities focussed on endohedral lanthanide metallofullerenes has been observed in 2012. Highly remarkable in this field was the discovery that complexation of endohedral metallofullerenes with TiCl<sub>4</sub> can provide an efficient route for separation and purification of lanthanide metallofullerenes from empty fullerenes in large scale. Ca. 24% of all relevant papers published in 2012 were in the area of organoactinide chemistry, which continues to produce exciting results. A major achievement in organoactinide chemistry was the finding that (C<sub>5</sub>Me<sub>4</sub>H)<sub>3</sub>U reacts with 1 equiv. of NO to form the first *f*-element nitrosyl complex, (C<sub>5</sub>Me<sub>4</sub>H)<sub>3</sub>UNO, as a dark brown solid.

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## 1. Introduction

This review summarizes the progress in organo-*f*-element chemistry during the year 2012. 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 papers published in 2012 were in the area of organoactinide chemistry, although the latter continues to produce exciting results. Patents have been included as long as they were clearly related to the use of organo-*f*-element complexes.

## 2. Lanthanides

### 2.1. Lanthanide hydrocarbyls

#### 2.1.1. Homoleptic compounds

Reactions of Group 3 metal atoms with carbon monoxide in solid argon have been studied using matrix isolation infrared absorption spectroscopy. Lanthanide monocarbonyls LnCO were produced spontaneously on annealing. The observations on LnCO (Ln = Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er) were new. The structure, bonding, and C–O stretch infrared frequencies have been investigated theoretically. It was found that the covalent M–C bonding contains both M ← C σ donation from the carbon lone pair, and M 5*d* → CO 2π\* back donation contributions. In addition to the open 4*f*<sup>*n*</sup> shells, the total spin, as found earlier, may have contributions from an M “σ doughnut” and the M–C π-bond, in a σ1π1, σ1π2 high-spin, or σ2π1 low-spin configuration. They form at least a single-bond, and those with the σ1π2 configuration approach a double bond in length. The weakening of the C–O bonding was shown to be related to the back donation to the antibonding C–O 2π\* orbital [1].

#### 2.1.2. Heteroleptic compounds

The optical spectra of the mono-THF, mono-triphenylphosphin oxide and bis-cyclohexylisocyanide adducts of the tris[bis(trimethylsilyl)amido]samarium(III) moiety, Sm[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, as well as those of the bis-THF adduct and the bis-triphenylphosphin oxide adduct of the tris[bis(dimethylsilyl)amido]samarium(III) moiety have been recorded at room temperature and low temperatures. From the spectra obtained, the underlying crystal field splitting patterns could be derived and simulated by fitting the free parameters of a phenomenological Hamiltonian [2]. The gas phase reaction of La<sup>+</sup> cations with acetone has been investigated using density functional theory (=DFT). Both ground and excited state potential energy surfaces have been investigated in detail. The results showed that the reaction starts with the formation of an O-attached complex. All

possible pathways starting with C–O, C–H, and C–C activation have been searched. It was shown that these reactions can lead to four different products, (<sup>1</sup>LaO<sup>+</sup> + C<sub>3</sub>H<sub>6</sub>, <sup>2</sup>LaCH<sub>2</sub>COCH<sub>3</sub><sup>+</sup> + H, <sup>1</sup>LaCOCH<sub>2</sub><sup>+</sup> + CH<sub>4</sub> and <sup>1</sup>LaCH<sub>2</sub><sup>+</sup> + CH<sub>3</sub>CHO) [3]. It has been reported that deep-blue solutions of Y<sup>2+</sup> formed from Y(NR<sub>2</sub>)<sub>3</sub> (R = SiMe<sub>3</sub>) and excess potassium in the presence of 18-crown-6 at –45 °C under vacuum in diethyl ether react with CO at –78 °C to form colorless crystals of the (CO)<sup>–</sup> radical complex, {[ (R<sub>2</sub>N)<sub>3</sub>Y(μ-CO)<sub>2</sub> ] [K<sub>2</sub>(18-crown-6)<sub>2</sub> ] }<sub>*n*</sub>. It was shown that the polymeric structure contains trigonal bipyramidal [(R<sub>2</sub>N)<sub>3</sub>Y(μ-CO)<sub>2</sub>]<sup>2–</sup> units with axial (CO)<sup>–</sup> ligands linked by [K<sub>2</sub>(18-crown-6)<sub>2</sub>]<sup>2+</sup> dications. By-products such as the ynediolate, [(R<sub>2</sub>N)<sub>3</sub>Y]<sub>2</sub>(μ-OC≡CO){[K(18-crown-6)]<sub>2</sub>(18-crown-6)}, in which two (CO)<sup>–</sup> anions are coupled to form (OC≡CO)<sup>2–</sup>, and the insertion/rearrangement product, {(R<sub>2</sub>N)<sub>2</sub>Y[OC(=CH<sub>2</sub>)Si(Me<sub>2</sub>)NSiMe<sub>3</sub>]}[K(18-crown-6)], were common in these reactions that give variable results depending on the specific reaction conditions. The CO reduction in the presence of THF forms a solvated variant of [(R<sub>2</sub>N)<sub>3</sub>Y]<sub>2</sub>(μ-OC≡CO){[K(18-crown-6)]<sub>2</sub>(18-crown-6)}, the ynediolate [(R<sub>2</sub>N)<sub>3</sub>Y]<sub>2</sub>(μ-OC≡CO)[K(18-crown-6)(THF)<sub>2</sub>]<sub>2</sub>. CO<sub>2</sub> reacted analogously with Y<sup>2+</sup> to form the (CO<sub>2</sub>)<sup>–</sup> radical complex, {[ (R<sub>2</sub>N)<sub>3</sub>Y(μ-CO<sub>2</sub>)<sub>2</sub> ] [K<sub>2</sub>(18-crown-6)<sub>2</sub> ] }<sub>*n*</sub>, that has a structure similar to that of {[ (R<sub>2</sub>N)<sub>3</sub>Y(μ-CO)<sub>2</sub> ] [K<sub>2</sub>(18-crown-6)<sub>2</sub> ] }<sub>*n*</sub>. Analogous (CO)<sup>–</sup> and (OC≡CO)<sup>2–</sup> complexes of lutetium were isolated using Lu(NR<sub>2</sub>)<sub>3</sub>/K/18-crown-6, namely {[ (R<sub>2</sub>N)<sub>3</sub>Lu(μ-CO)<sub>2</sub> ] [K<sub>2</sub>(18-crown-6)<sub>2</sub> ] }<sub>*n*</sub>, [(R<sub>2</sub>N)<sub>3</sub>Lu]<sub>2</sub>(μ-OC≡CO){[K(18-crown-6)]<sub>2</sub>(18-crown-6)}, and [(R<sub>2</sub>N)<sub>3</sub>Lu]<sub>2</sub>(μ-OC≡CO)[K(18-crown-6)(Et<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> [4].

A nucleophilic carbene complex of scandium has been successfully employed as stoichiometric carbene transfer agent in a transmetalation process. All reactions depicted in Scheme 1 proceeded very smoothly, being complete within 15 min at room temperature. It was pointed out that this novel transformation does allow circumventing redox competitive processes. As such it opens the way for the synthesis of “SCS” carbene complexes of oxidized and oxidizing metal centers [5].

It has been reported that reactions of LnCl<sub>3</sub> (Ln = Y, Nd, Sm, Yb) with the enol-functionalized imidazolium salt H<sub>2</sub>LBr (L = 4-OMe-C<sub>6</sub>H<sub>4</sub>COCH{C(NCHCHN<sup>i</sup>Pr)}) and NaN(SiMe<sub>3</sub>)<sub>2</sub> in a molar ratio of 1:4:1 in THF at room temperature afforded the corresponding novel enol-functionalized *N*-heterocyclic carbene (NHC) lanthanide amides L<sub>2</sub>LnN(SiMe<sub>3</sub>)<sub>2</sub> (Ln = Y, Nd, Sm, Yb) in moderate yields (37–40%) as outlined in Scheme 2. Their molecular structures of have been determined by X-ray structure analyses. All complexes adopt monomeric structures in which each five-coordinated metal is coordinated by two NHC ligands and one amido group in a distorted trigonal bipyramid geometry [6].

The synthesis of an yttrium phosphonium methylide complex and its reaction with benzophenone according to Scheme 3 has

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