Lanthanide Derivatives as Reagents or Catalysts for Organic Reactions*

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Abstract

A brief survey of use of lanthanide derivatives in organic chemistry is given in the introductory section. Organic chemistry mediated by $SmCp_2$ is then developed. Access to some organosamarium compounds using $SmCp_2$ is also mentioned. The second part of the paper is devoted to lanthanide catalysts. The selected examples involve catalysis by lanthanide alcoholates or various lanthanide salts.

Introduction

For a long time lanthanide derivatives were not considered by organic chemists to be a valuable help in synthesis (with the exception of ceric oxidations). In the last decade, however, there has been a progressive change in that attitude. Recent reviews [1—5] show the fast development of the use of lanthanide compounds as reagents and even as catalysts in organic transformations. Why has this evolution occurred? It comes from the availability of many lanthanides (as metals or salts) in conjunction with the needs of new methodologies in organic synthesis. Organic chemistry is of paramount importance for the preparation of fine chemicals or pharmaceuticals. New reactions giving milder experimental conditions, improved yields, higher chemoselectivity or stereoselectivity are always welcome. Transition metal complexes afforded in the past innovation in organic chemistry; it can be expected that the 4f-elements will make a contribution to the progresses of organic synthesis.

Some results involving low-valent lanthanide derivatives, mainly Sm(II) compounds, are presented. Catalytic reactions with lanthanide(III) alcoholates or lanthanide(III) salts are also discussed.

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Organic Chemistry Mediated by Sm(II) Compounds

Routes to Divalent Samarium Derivatives

Various ways to prepare divalent lanthanide derivatives have been reviewed [4]. A smooth preparation of samarium diiodide is now available [6, 7] (THF = tetrahydrofuran):
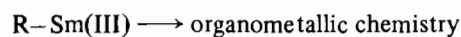
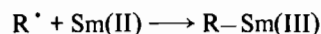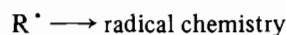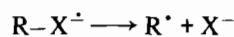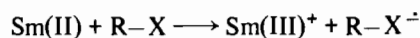$$Sm + ICH_2CH_2I \xrightarrow{THF} SmI_2 + CH_2{=}CH_2$$
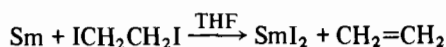
In turn, samarium diiodide is a good starting material to obtain other divalent samarium compounds through exchange reactions [7, 8]. By this method insoluble $SmCp_2$ can easily be obtained [7]:

$$SmI_2 + 2NaCp \xrightarrow{THF} SmCp_2 + 2NaI$$

(where Cp = cyclopentadienyl)
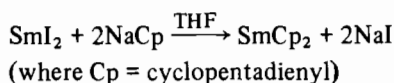
Reactions on Organic Substrates Expected with Sm(II)

Because of the strong reducing properties of Sm(II) salts, one can expect a set of electron-transfer reactions on an organic compound R—X where X is a leaving group:

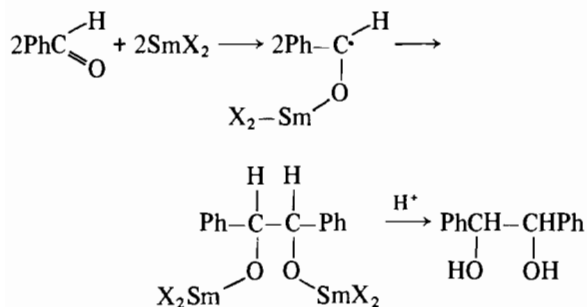$$Sm(II) + R{-}X \longrightarrow Sm(III)^+ + R{-}X^{\cdot -}$$

$$R{-}X^{\cdot -} \longrightarrow R^{\cdot} + X^-$$

$$R^{\cdot} \longrightarrow \text{radical chemistry}$$

$$R^{\cdot} + Sm(II) \longrightarrow R{-}Sm(III)$$

$$R{-}Sm(III) \longrightarrow \text{organometallic chemistry}$$

In the case of an organic compound with a $>C{=}O$ group one can also expect initial formation of $>C{=}O^{\cdot -}$.

Comparison between Chemistry Induced by SmI_2 and $SmCp_2$

Organic chemistry induced by SmI_2 began to be extensively investigated in the period 1977—1980 [9] and is presently in fast development (for references to recent publications see ref. 1). It is therefore very attractive to try to compare the behaviour of SmI_2 and $SmCp_2$ in some reactions, with the hope of

finding selectivities associated with one or the other compound. Some information has begun to evolve [10] and will be presented here.
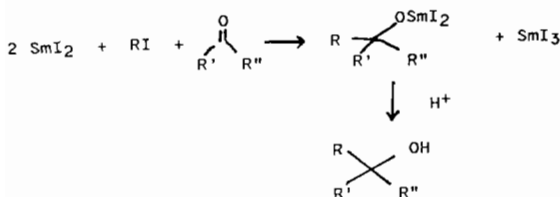
Pinacol formation from aromatic aldehydes such as benzaldehyde is very fast in the presence of SmI_2 [11]. The same reaction was observed with $SmCp_2$ [10]:

$$2PhC\overset{H}{\underset{O}{\diagdown}} + 2SmX_2 \longrightarrow 2Ph-\overset{H}{\underset{\underset{Sm-X_2}{O}}{C}} \longrightarrow$$

$$\underset{\underset{X_2Sm}{\overset{O}{|}} \underset{SmX_2}{\overset{O}{|}}}{Ph-\overset{H}{\underset{|}{C}}-\overset{H}{\underset{|}{C}}-Ph} \xrightarrow{H^+} \underset{HO \quad OH}{PhCH-CHPh}$$

(X = I or Cp)

This reaction occurs in a few minutes in THF at room temperature and is typical of an electron transfer.

Another analogy between SmI_2 and $SmCp_2$ is their ability to reduce organic iodides (RI) into alkanes (RH) by heating in THF. Interestingly, there is no need to hydrolyse the reaction mixture; THF is the hydrogen source (presumably through H abstraction from $R\cdot$ or by proton abstraction by an RSm(III) species). The Barbier reaction (one-pot reaction) between a ketone and an organic iodide was found especially easy by using SmI_2 [9]:

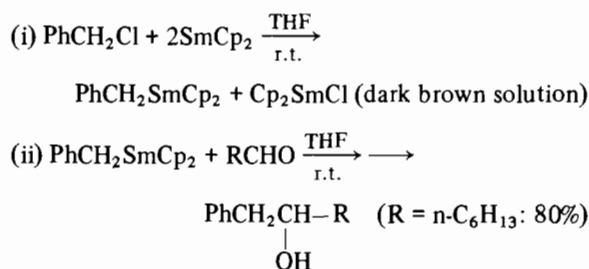$$2\ SmI_2 + RI + \underset{R' \quad R''}{\overset{O}{\overset{||}{C}}} \longrightarrow \underset{R' \quad R''}{R\diagdown\diagup OSmI_2} + SmI_3$$

$$\downarrow H^+$$

$$\underset{R' \quad R''}{R\diagdown\diagup OH}$$

The reaction was not clean with aldehydes (R' = H) because of by-products coming from a subsequent Oppenauer oxidation. By using $SmCp_2$ instead of SmI_2 it was discovered [10] that the Barbier reaction on aldehydes gives reasonable yields of the expected secondary alcohol, for example:

$$CH_3(CH_2)_5CHO + I(CH_2)_3CH_3 + 2SmCp_2 \longrightarrow \xrightarrow{H^+}$$

$$\underset{OH}{CH_3(CH_2)_5-CH-(CH_2)_3CH_3}$$
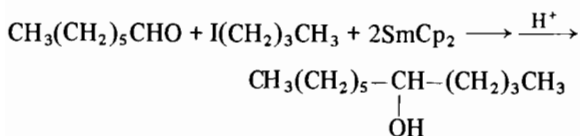
In this case the reaction was performed for 1 h at room temperature and gave after the usual workup 59% of the product.

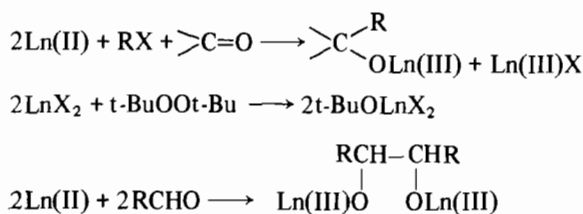All attempts to modify the Barbier reaction with SmI_2 in order to get first an organosamarium species

failed. It was not possible to obtain these compounds in a first step, by reaction between SmI_2 and organic halides [12]. It was therefore an exciting finding [13] that $SmCp_2$ and some organic halides such as $PhCH_2Cl$ are able to give a Barbier reaction on a ketone (one-pot reaction) as well as a Grignard-like reaction. In this case $SmCp_2$ first reacts with $PhCH_2Cl$ to lead to a THF-soluble organosamarium species (stable at room temperature) which is able to further react with ketones or various electrophiles (including D_2O). For example:

(i) $PhCH_2Cl + 2SmCp_2 \xrightarrow[r.t.]{THF}$

$\quad PhCH_2SmCp_2 + Cp_2SmCl$ (dark brown solution)

(ii) $PhCH_2SmCp_2 + RCHO \xrightarrow[r.t.]{THF} \longrightarrow$

$$\underset{OH}{PhCH_2CH-R} \quad (R = n\text{-}C_6H_{13}: 80\%)$$

A route is then opened to new organosamarium compounds [13]. It is interesting to point out that $(C_5Me_5)_2Yb$ and $PhCH_2Cl$ do not give stable organometallic species [14].

Reaction Catalyzed by Lanthanides

Catalyzed reactions are the most appreciated in organic synthesis since they minimize the amount of auxiliary materials. Several classes of lanthanide derivatives are able to induce catalytic reactions, namely $(Cp'_2LnH)_2$, LnX_3, $Ln(OR)_{3-m}X_m$, Ln-(β-diketonate)$_3$ (where Cp' stands for C_5Me_5 and X stands for a halide, carboxylate or cyclopentadienyl group). Very high catalytic activities were found for some hydrido-complexes in hydrogenation or polymerization of some olefins [15–18]. Lanthanide alcoholates give rise to some useful catalysts; we shall summarize some of the results that we obtained. Chemistry starting from divalent lanthanides gives several routes to trivalent lanthanide alcoholates [19]:

$$2Ln(II) + RX + {\diagup}{\diagdown}C{=}O \longrightarrow {\diagup}{\diagdown}C\overset{R}{\underset{OLn(III)}{\diagdown}} + Ln(III)X$$

$$2LnX_2 + t\text{-}BuOOt\text{-}Bu \longrightarrow 2t\text{-}BuOLnX_2$$

$$2Ln(II) + 2RCHO \longrightarrow \underset{Ln(III)O \quad OLn(III)}{\overset{RCH-CHR}{}}$$

In addition to the classical preparation of $Ln(OR)_3$ from metal and ROH, it is also able to perform the reaction in the presence of a stoichiometric amount of iodine, leading to iodoalcoholates (19):

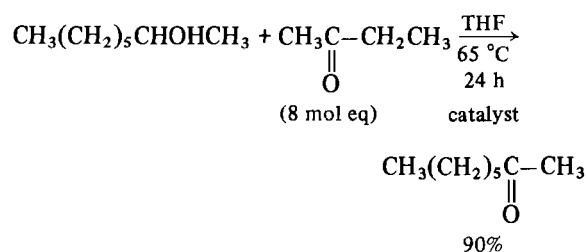$$Ce + ROH + I_2 \longrightarrow Ce(OR)I_2$$
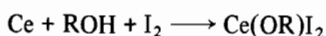
Complex t-BuOSmI$_2$, cleanly obtained from SmI$_2$ and t-BuOOt-Bu, was extensively studied for its catalytic properties. It is a catalyst for the selective isomerization in good yields of terminal epoxides into methylketones [20]:

$$R-CH\overset{O}{\overbrace{\qquad}}CH_2 + 0.1 \text{ eq t-BuOSmI}_2 \xrightarrow[60\,°C]{THF} R-\overset{O}{\overset{\parallel}{C}}-CH_3$$
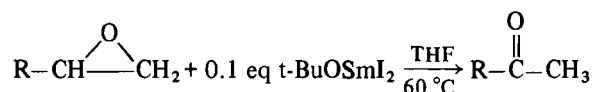
The alternate isomerization into the aldehyde RCH$_2$-CHO does not occur, even in a trace amount. The mechanism of this unusual transformation was discussed; a selective ring opening was proposed through mild activation by coordination of oxygen to samarium, followed by nucleophilic attack of iodide ion to the less-hindered side.
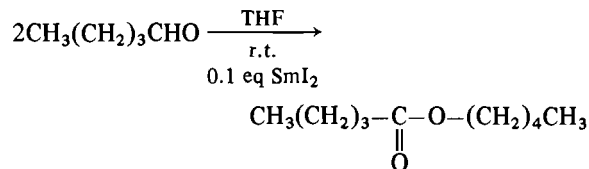
Another useful application of t-BuOSmI$_2$ is as catalyst in oxido—reduction reactions of Meerwein—Ponndorf—Verley—Oppenauer type (MPV/O reactions). These reactions involve reduction of a ketone by an alcohol (or *vice-versa*) through hydride transfers and are usually mediated by aluminium alcoholates in stoichiometric amounts. We found that 0.1 mol eq of t-BuOSmI$_2$ was enough to catalyse the MPV/O reactions by heating in THF [19]. For example, butanone is a good oxidant for many secondary alcohols, a typical case is below:

$$CH_3(CH_2)_5CHOHCH_3 + CH_3\overset{\parallel}{\underset{O}{C}}-CH_2CH_3 \xrightarrow[65\,°C]{THF}$$

(8 mol eq)   24 h
                    catalyst

$$CH_3(CH_2)_5\overset{\parallel}{\underset{O}{C}}-CH_3$$

90%

It is interesting to point out that SmI$_2$ itself in place of t-BuOSmI$_2$ efficiently catalyzes the same reaction; 90% yield was obtained under the same conditions with 0.1 mol eq SmI$_2$ at 25 °C for 24 h [21]. The actual catalyst is not SmI$_2$, which rapidly disappears in the presence of the excess of butanone. It has been established that the catalytic activity is related to the formation of a samarium β-ketoalcoholate arising from aldolisation of butanone. A tentative structure has been assigned to this complex:
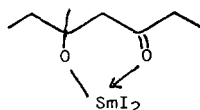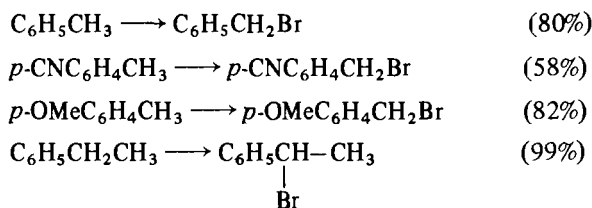

Diiodosamarium was also found to be a superior catalyst for the Tischenko reaction, which allows the transformation of an aldehyde into an ester. The reaction is carried out at room temperature in a few hours [21]:

$$2CH_3(CH_2)_3CHO \xrightarrow[\substack{r.t.\\0.1\text{ eq SmI}_2}]{THF}$$

$$CH_3(CH_2)_3-\overset{\parallel}{\underset{O}{C}}-O-(CH_2)_4CH_3$$

It is not SmI$_2$ which is the actual catalyst of this reaction; presumably CH$_3$(CH$_2$)$_3$CH$_2$OSmI$_2$ is formed. A catalytic cycle can easily arise starting from this samarium alcoholate.

Lewis acidity of many lanthanide derivatives is useful for the catalysis of various chemical transformations, such as acetal formation or Diels-Alder reaction [23]. This explains in part a reaction that we extensively investigated [24], the use of molecular bromine for benzylic bromination of many alkylbenzenes (for a preliminary note see ref. 25). A catalytic amount of La(OAc)$_3$ is an excellent catalyst for this reaction (which is usually performed with the much more expensive *N*-bromosuccinimide). The compound is dissolved in CCl$_4$ to which is added 0.1 mol eq of La(OAc)$_3$. A solution of bromine in CCl$_4$ is added dropwise to the heated solution (reflux) of the aromatic compound, the reaction is over after a few hours. Yields are quite good with this procedure; the product is obtained without nuclear bromination:

C$_6$H$_5$CH$_3$ ⟶ C$_6$H$_5$CH$_2$Br   (80%)

p-CNC$_6$H$_4$CH$_3$ ⟶ *p*-CNC$_6$H$_4$CH$_2$Br   (58%)

p-OMeC$_6$H$_4$CH$_3$ ⟶ *p*-OMeC$_6$H$_4$CH$_2$Br   (82%)

$$C_6H_5CH_2CH_3 \longrightarrow C_6H_5\overset{\displaystyle}{\underset{Br}{C}H}-CH_3 \quad (99\%)$$

Nuclear bromination competes with benzylic substitution when the aromatic ring is too electron-rich (*p*-cresol, methylnaphthalene, etc.). The mechanism of the reaction was investigated; it was shown that La(OAc)$_3$ is completely insoluble in CCl$_4$ and rapidly fixed the dropwise-added bromine. This fixation is very likely complexation of bromine by the lanthanide centre acting as a Lewis acid. This complex is easily photolyzed by ambient light to give radicals Br$^•$ which act in the usual way to lead to radical substitution in the benzylic position of the alkyl benzenes which are close to the catalyst. This picture has been supported by a set of experiments [24].

Lanthanide trichlorides are quite strong Lewis acids and are useful catalysts in some reactions. Thus Friedel—Crafts reactions were recently reinvestigated by replacing AlCl$_3$ by lanthanide trichlorides [26]. We found [27] that SmCl$_3$ (0.1 mol eq) is a very suitable catalyst for the formation of an ether from an allylic alcohol. The procedure is simple since it involves only reflux in ClCH$_2$CH$_2$Cl as solvent. For example:
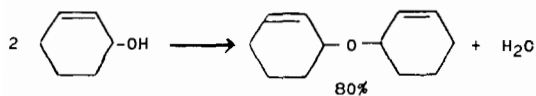
Another application of catalysis by $LaCl_3$ acting as a Lewis acid is the clean condensation of some silicon reagents on benzaldehyde with C–C bond formation [28]:
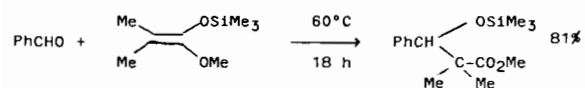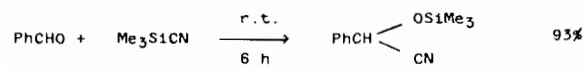
Conclusions

Lanthanide derivatives have to be seriously considered by organic chemists as useful aids in devising reactions. This was illustrated by some of our recent results in the field of divalent and trivalent lanthanides. One can expect that new reagents with specific properties will be developed by the suitable change of ligands around the metal centre. Catalysis is also a promising field; progress can be expected by tuning the Lewis acidity of the complex thanks to new ligands and to the proper choice of the lanthanide.

Acknowledgements

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