Journal of Alloys and Compounds 275–277 (1998) 891–893

Undercoordinated neodymium and samarium hydrides and alkyls: Their behaviour and stability in solution. Application in isoprene polymerization

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Abstract

The dimeric alkyl rare earth complexes $[Cp'_2SmMe]_2$ and $[Cp'_2NdMe]_2$ ($Cp'=C_5H_4tBu$) can be isolated in the solid state, whereas formation of the hydride $[Cp'_2NdH]_2$ does not occur and the hydride $[Cp'_2SmH]_2$ is only depicted in solution. Neodymium hydrides are characterized in solution as solvated (trisalkylboron) complexes of general formula $Cp'_2NdL_xHBEt_3$. By hydrogenolysis of a convenient alkyl derivative, a transient hydride Cp^Q_2NdH is formed ($Cp^Q=C_5H_4CH_2CH_2OCH_3$). This hydride is not stable and rapidly rearranges into the corresponding triscyclopentadienyl derivative Cp^Q_3Nd. It can be trapped by a hindered ketone such as pivalone, leading to the alkoxide $Cp^Q_2NdOCH(tBu)_2$. The complex $[Cp'_2NdMe]_2$ is not stable in THF and the analogous Cp^Q_2NdMe complex cannot be obtained from the corresponding chloride, using a solution of MeLi as alkylating reagent. Bimetallic Cp'_2NdMe_2Li is stable. Anionic allyl complexes of samarium and neodymium of general formula $(C_5H_4CMe_2)_2Ln(C_3H_5)_2Li(OR_2)_2$ were synthesized. These complexes are efficient catalysts for the *trans* 1–4 polymerization of isoprene. © 1998 Elsevier Science S.A.

Keywords: Alkyls; Hydrides; Isoprene polymerization; Neodymium; Rare earths; Samarium

1. Introduction

The well-known Cp^*_2LnH ($Cp^*=C_5Me_5$; Ln=Nd or Sm) hydrides [1] are highly reactive species which must be obtained by hydrogenolysis of convenient alkyl derivatives. They react with most common organic solvents and cannot be stored in solution. They polymerize ethylene but are inefficient towards α-olefins [2].

For the polymerization of α-olefins, we considered it was necessary to synthesize unsolvated hydrides of the early lanthanides, with less bulky ligands. This was undertaken from Cp'_2LnCl ($Cp'=C_5H_4tBu$) or Cp^Q_2LnCl ($Cp^Q=C_5H_4CH_2CH_2OCH_3$) as starting materials. Two methods were investigated, the hydridic route using $NaHBEt_3$ as reagent and the hydrogenolytic route via the intermediate formation of alkyl derivatives.

2. Experimental

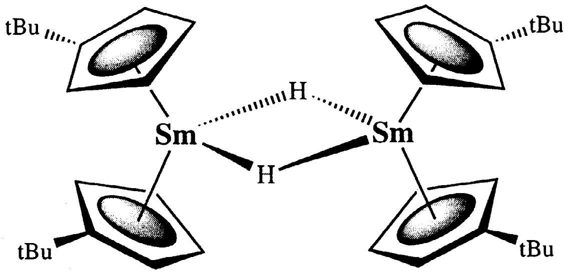
All experiments were performed under a dry nitrogen or argon atmosphere using standard glove box techniques. Starting materials were synthesized using described procedures [3].

Preliminary experiments were performed at the NMR scale and, for the stable species, syntheses were made in bulk. The new complexes were characterized by NMR, X-ray structural analysis or elemental analysis.

3. Results and discussion

3.1. Hydrides synthesis

From $(Cp'_2SmCl)_2$ (**1**) [4] and $NaHBEt_3$ in C_6D_6, the dimeric hydride $(Cp'_2SmH)_2$ (**2**) [5] was obtained (Scheme 1), whereas from $(Cp'_2NdCl)_2$ (**3**) [6] the sole triscyclopentadienyl derivative Cp'_3Nd was formed.



When THF (about 2–10 eq) was added to the starting chloride **3**, before the hydridic reagent, the formation of

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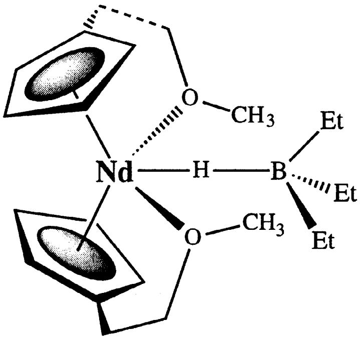
PII: S0925-8388(98)00478-2

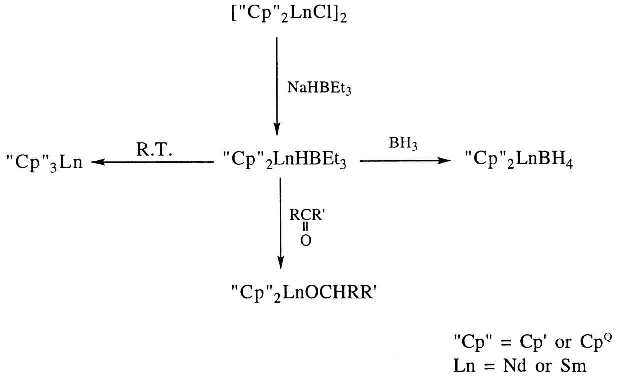
$Cp'_2Nd(THF)nHBEt_3$ was established by ^1H- and ^{11}B-NMR [7]. After removal of the solvent and dissolution of the crude solid in C_6D_6, the only product present in solution was Cp'_3Nd with unidentified insoluble species. When the oxygenated ligand was furnished with an intramolecular chelating ligand, $C_5H_4CH_2CH_2OCH_3$ (Cp^Q) [8], the more stable corresponding hydride $Cp^Q_2NdHBEt_3$ (**4**) was formed (Scheme 2). The solution containing **4** can be evaporated to dryness without complete redistribution, but all attempts to obtain crystals of **4** by storage of concentrated solutions for days only led to crystals of Cp^Q_3Nd.



All these moderately stable hydrides were characterized by NMR and by their chemical reactivity. They insert borane or ketones, affording the corresponding borohydrides or alkoxides (Scheme 3).

The Sm–H signal of **2** was not detected but it was established that this hydride did not exchange with deuterated benzene, because further reaction with a ketone led to the alkoxy derivative in which the Sm–O–C–H signal integration is correct [5].

The Nd–H–B signals were found at very low field in the range 150–200 ppm.



3.2. Alkyl synthesis and hydrogenolysis

Only the trisalkylborohydrides were obtained from the neodymium chlorides by the hydridic route. In order to obtain simple hydrides, it was planned to hydrogenolyse the alkyl derivatives in the presence of coordinating ligands to avoid disproportionation of the unstable "Cp_2"NdH moiety. Unfortunately, in the presence of oxygenated ligands such as THF, the known $(Cp'_2NdMe)_2$ was unstable and rearranged to give the triscyclopentadienyl derivative Cp'_3Nd. In contrast, the dimethyl anion Cp'_2NdMe_2Li (**5**) was obtained from **3** and two equivalents of 1 M methyllithium solution in diethylether. This anionic complex is stable.

The corresponding Cp^Q_2NdMe could not be obtained in an analogous way. Starting from Cp^Q_2NdCl, all attempts to replace the chloride ligand by MeLi led to complex mixtures of unidentified products. However, the expected alkyl derivative containing a bulky group, $Cp^Q_2NdCH(TMS)_2$ (**6**), could be isolated.

Hydrogenolysis of **6** did not afford the corresponding hydride derivative, only Cp^Q_3Nd is formed. Nevertheless, the transient hydride could be trapped: when hydrogenolysis was performed in the presence of a hindered ketone such as pivalone, which does not insert in the Nd–C bond of **6**, the corresponding alkoxide **7** was obtained in high yield

$$\underset{\mathbf{6}}{Cp^Q_2NdCH(TMS)_2} \xrightarrow[tBu_2CO]{H_2} [Cp^Q_2NdH + tBu_2CO] \rightarrow \underset{\mathbf{7}}{Cp^Q_2NdOCHtBu_2}$$

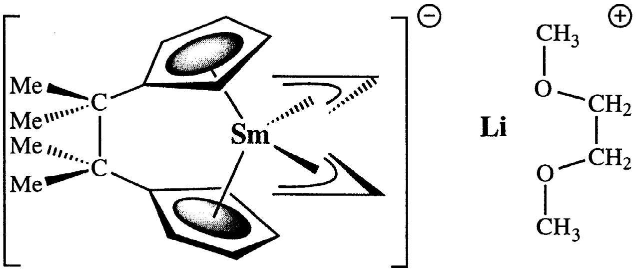
It then appears that monomeric Cp^QNdH and Cp^QNdMe are only transient species, unable to be stabilised by dimerization, whereas the corresponding chloride is easily isolated. This chloride was found to be monomeric by X-ray crystal structure analysis (only the lanthanum derivative is dimeric) [9].

3.3. Precursors for diene polymerization

The above hydrides and alkyls were of poor stability. To avoid disproportionation into triscyclopentadienyl derivatives, it was necessary to use ansa cyclopentadienyl ligands. For this purpose, the bridged Grignard reagent $(C_5H_4CMe_2CMe_2C_5H_4)(MgCl)_2$ was a convenient precursor [10]. The formation of the samarium derivative $(C_5H_4CMe_2CMe_2C_5H_4)SmCl(THF)_2$ has been reported [11] and the X-ray crystal structure has been described [12], but it has been impossible to reproduce this synthesis in bulk; after workup, the NMR spectra of the crude powder did not show the formation of a definite material. In fact, it has been established by NMR that a mixture of $SmCl_3(THF)_3$ and of a stoichiometric amount of $(C_5H_4CMe_2CMe_2C_5H_4)(MgCl)_2$ in benzene or toluene led to a solution of $(C_5H_4CMe_2CMe_2C_5H_4)SmCl,MgCl_2(THF)_n$, one equivalent of $MgCl_2$ being eliminated by filtration. Treatment of this solution to eliminate the coordinated magnesium salt was unsuccessful and led to considerable decomposition. The X-ray crystal structure of this material has been described [13]. Crude solutions of this bimetallic were used for further syntheses.

Neutral alkyl complexes could not be obtained when a stoichiometric amount of RLi was used (obviously for steric reasons: the cone angle of the ansa Cp ligand is much smaller than that of two tBuCp rings) whereas, from two equivalents of RLi ($R = CH_2SiMe_3$, $CH(SiMe_3)_2$, C_3H_5), the corresponding dialkyl anions were obtained (ca. 60% yield). It is noteworthy that the dimethyl anion Cp'_2NdMe_2Li (**5**) is fairly stable towards the disproportion reaction leading to Cp'_3Nd.

The samarium bisallyl anionic complex **8** (Scheme 4) has been obtained analytically pure. The analogous neodymium bisallyl was also formed, but it was isolated mixed with salts and some organometallic impurities



Both complexes were tested as catalysts for the polymerization of isoprene (50°C, atm. pressure, cat/substrate 5×10^{-4}). After 5 h stirring, using the samarium derivative as catalyst, quite pure (>96%) *trans*polyisoprene was isolated in 75–90% yield. The neodymium complex exhibited similar, but slightly slower, activity.

Under the same conditions, the dioxane adduct of allyllithium was found to have very low catalytic activity. It was assumed that the catalytic performances of the lanthanide complexes should be related to the easy dissociation of one allylic ligand allowing diene coordination. This is in good accordance with Schumann and Taube [14,15], who reported that the same stereocontrol was obtained for neutral and anionic rare earth complexes.

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