ELSEVIER

Journal of Organometallic Chemistry 547 (1997) 157–165

Journal of Organometallic Chemistry

Unsolvated dimeric organometallic samarium hydride versus solvated trisalkylborane supported monomeric hydride

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Received 6 January 1997; received in revised form 13 March 1997

Abstract

The dimeric hydride $[Cp'_2SmH]_2$ and the monomeric trisalkylborohydride $Cp'_2SmHBEt_3(THF)_n$ ($Cp' = C_5H_4tBu$) are obtained from the starting dimeric chloride $[Cp'_2SmCl]_2$ by reaction with a hydridic reagent: $NaHBEt_3$. By hydrogenolysis of Cp'_2SmR ($R = CH_2SiMe_3$ or $CH(SiMe_3)_2$) in the presence of an ancillary ligand as PMe_3, a monomeric hydride: $Cp'_2SmH(PMe_3)_2$ is formed.

The trisalkylborohydride is fairly stable in solution when other new hydrides are only moderately stable: upon standing at room temperature, an irreversible transformation into Cp'_3Sm is observed. All hydrides react with propanone to give the corresponding alkoxide: $[Cp'_2SmOCHMe_2]_2$.

The new alkyl complex $[Cp'_2SmMe]_2$ is isolated and characterized by NMR and elemental analysis. After hydrogenolysis of this dimer or by reaction of one equivalent of $NaHBEt_3$ with the dimer $[Cp'_2SmCl]_2$, mixed bridged hydrides of the general formula $Cp'_2Sm(\mu\text{-}H)(\mu\text{-}X)SmCp'_2$ (X = Me or Cl) are formed. A mixed bridged chloroalkoxy complex $Cp'_2Sm(\mu\text{-}OCHR_2)(\mu\text{-}Cl)SmCp'_2$ is also obtained.

1. Introduction

Cyclopentadienyllanthanide hydrides and alkyls were first reported fifteen years ago [1], but interest in the chemistry of these extremely reactive species has recently intensified because of their activity as polymerisation catalysts for olefins, dienes or cyclic ethers [2].

Much of the investigation was performed in the bis(pentamethylcyclopentadienyl) series, and the hydrides Cp^*_2LnH ($Cp^* = C_5Me_5$) have been found very active for the polymerisation of ethylene [3]. Unfortunately, they did not polymerise α-olefins, but led to stable allyl complexes [4]. If this lack of reactivity can be ascribed to the steric hindrance due to the presence of two bulky Cp^* ligands, then to allow the polymerisation of α-olefins, it seemed necessary to use an early lanthanide, which offers the highest degree of coordination and possibly reactivity, associated with less bulky ligands.

In this way, recent significant results have been obtained with allyl complexes of lanthanum or neodymium [5]. Another way could be to use a mono-substituted cyclopentadienyl ligand leading — a priori — to less sensitive complexes toward oxygen and other poisons. It was reported that the shielding effect of the tertbutyl group is very efficient: crystals of $[C_5H_3tBu_2)_2LuH]_2$ are not destroyed by an exposure to air within a few minutes [6]. Because samarium is still a large lanthanide and the Cp' ring ($Cp' = C_5H_4tBu$) is much smaller than Cp^*, we proposed the synthesis of $Cp'_2Sm{-}H$ species. Moreover, samarium derivatives are very convenient for NMR studies in solution: these paramagnetic complexes do not exhibit large line broadening and well resolved NMR spectra can be obtained, even for complex mixtures. This paper reports the synthesis and reactivity of bis(terbutyl)cyclopentadienylsamarium hydrides.

2. Results

2.1. The hydridic route

2.1.1. In non coordinating solvents

When a stoichiometric amount of a toluene solution of $NaHBEt_3$ is added to a benzene solution of

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PII S0022-328X(97)00218-0

$[Cp'_2SmCl]_2$: **1** [7], a white precipitate of NaCl is immediately formed and the bright yellow solution becomes pale yellow. When the reaction is monitored by ^1H and ^{11}B NMR, a new set of signals is recorded which indicates the concomitant formation of BEt_3 ($\delta^{11}B = 86$ ppm) and $[Cp'_2SmH]_2$ **2** (Cp signals at $\delta = 18.5$ and 10.32 ppm, tBu at $\delta = -3.75$ ppm) and ca. 15% of Cp'_3Sm: **3** (Cp signals at $\delta = 21.46$ and 13.91 ppm, tBu at $\delta = -3.82$ ppm) [7].

$$\underset{\mathbf{1}}{[Cp'_2SmCl]_2}$$

$Cp' = C_5H_3tBu$

$$\xrightarrow{NaHBEt_3} \underset{\mathbf{2}}{[Cp'_2SmH]_2} + NaCl + BEt_3 + \underset{\mathbf{3}}{Cp'_3Sm}$$

The Sm–H signal of **2** is not found, but the hydridic nature of this complex is established by its chemical reactivity (see below). The dimeric structure of **2** is confirmed by comproportionation reactions with other dimeric complexes (see below). When the crude solution is distilled at room temperature under reduced pressure and the solvents trapped in a second NMR tube, BEt_3 can be identified. If the remaining part is now dissolved in benzene, the only complex present in the solution is Cp'_3Sm: **3**.

2.1.2. In the presence of coordinating ligands

If the above experiments are reproduced, without the crude solution being distilled, but 0.1 ml of THF being added instead, the signals of **2** and BEt_3 disappear and the new spectra are interpreted in the terms of the formation of $Cp'_2SmHBEt_3(THF)_2$: **4**. A ^{11}B signal is now recorded at 45.6 ppm and the Sm–**H**–B signal is found at $\delta = -23$ ppm whereas the ^1H Cp signals are at 12.2 and 10.8 ppm and the tBu signal at 0.98 ppm.

When THF (4 eq.) is added before the hydridic reagent, the same spectra are recorded, but the concurrent formation of **3** is significantly reduced (to ca. 5% instead of 15 or 20%). After 24 h at ambient temperature the spectrum remains unchanged. The solvents are then evaporated, the residue dissolved in deuteriated benzene: the signals of **4** are still present, THF signals integrate for 8H, the percentage of **3** remains low, near 15%. After 10 min at 50°C this percentage increases to 30%. When solutions containing **4** are kept at room temperature, the proportion of **3** increases slowly: 40% of **3** is present after three days.

$$\underset{\mathbf{2}}{[Cp'_2SmH]_2} \xrightarrow[BEt_3]{THF} \underset{\mathbf{4}}{Cp'_2SmHBEt_3(THF)_2}$$

When PMe_3 (1 or 2 eq.) is added before $NaHBEt_3$, the same types of spectra are obtained, with new Cp signals at 13.7 and 11.07 ppm. These results are in good agreement with the formation of the hydride $Cp'_2SmHBEt_3(PMe_3)_2$ **4'**; **3** is also present (10%).

$$\underset{\mathbf{1}}{[Cp'_2SmCl]_2} \xrightarrow{PMe_3} Cp'_2SmCl(PMe_3)_n$$

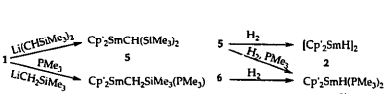
$$\xrightarrow{NaHBEt_3} \underset{\mathbf{4'}}{Cp'_2SmHBEt_3(PMe_3)_2}$$

Complex **4'** is not as stable as **4**: after 5 h at room temperature, the spectra show significant modifications, the signals became larger, the amount of **3** increases and some new signals appear. After three days, only **3** is present in the solution, and an unidentified brown precipitate deposits.

It is noteworthy that, when triisopropylphosphine is added instead of trimethylphosphine before $NaHBEt_3$, the dimeric hydride **2** is obtained (Cp signals at 18.4 and 10.33 ppm). It seems that the basic, but much more bulky trisisopropylphosphine is sterically unable to coordinate the chloride **1** and, therefore, does not take part in the reaction with $NaHBEt_3$.

2.2. Hydrogenolysis experiments

The alkyl derivatives $Cp'_2SmCH(SiMe_3)_2$ **5** and $Cp'_2SmCH_2SiMe_3(PMe_3)$ **6** are synthesized in NMR tubes by mixing a stoichiometric amount of **1** with the convenient LiR reagent in deuteriated benzene. To get **6** it is necessary to coordinate the phosphine before the addition of RLi to avoid the redistribution leading to **3**. These complexes are characterized by ^1H NMR and used without further purification.



After degassing, the tubes are pressurized with H_2 (1 atm). The hydrogenolysis of **5** is slow at room temperature: after 6 h, ca. 30% of the hydride **2** and 20% of the triscyclopentadienyl **3** are formed and about 40% of **5** is still present. When the hydrogenolysis is performed in the presence of PMe_3, the monomeric hydride **2'** (Cp signals at 11.8 and 11.1, tBu at -0.97 ppm) is obtained. The latter is also obtained by hydrogenolysis of **6**.

2.3. Mixed bridged hydrides

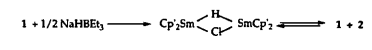
2.3.1. Hydridic route

When the progressive addition of $NaHBEt_3$ to dimeric **1** is monitored by NMR, the signals of **1** decrease and

the signals of the hydride **2** increase. After addition of one equivalent of $NaHBEt_3$ for two Sm–Cl units, ca. 30% of **1** is still present, **2** is formed in ca. 30% yield and a new set of signals: four Cp and one tBu is recorded (Cp: $\delta = 18.95$, 17.35 and 10.58, 10.33 ppm; tBu: $\delta = -2.29$ ppm). The amount of this new product is about 40% (estimated by integration of the Cp signals at 50°C).

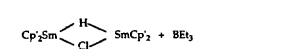
When equal amounts of **1** and **2** in benzene solution are mixed, the same set of signals is also recorded, near the signals of **1** and **2**.

These facts can be interpreted by the formation of a dinuclear mixed bridged chlorohydride $Cp'_2Sm(\mu\text{-}H)(\mu\text{-}Cl)SmCp'_2$ **7**. This dinuclear form is in equilibrium with both the dimeric chloride **1** and hydride **2**.



This equilibrium is temperature dependent: the proportion of **7** increases upon raising the temperature. However, heating of the mixture led to the formation of a considerable amount of **3**.

When THF is added to the mixture, the signals of **2** and **7** disappear and only **1** and the monomeric solvated hydride **4** are present. In the same manner, when THF is added before addition of $NaHBEt_3$, only **4** is formed.



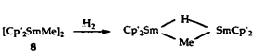
2.3.2. Hydrogenolysis

The new methyl complex $[Cp'_2SmCH_3]_2$ **8** was synthesized from **1** and a diethylether solution of methyllithium. After usual workup, the unsolvated dimeric **8** was isolated as yellow microcrystals and identified by NMR and elemental analysis. No crystal suitable for X-ray analysis could be obtained.

$$[Cp'_2SmCl]_2 \xrightarrow{MeLi} [Cp'_2SmMe]_2$$

1 **8**

The hydrogenolysis experiments are monitored by NMR. Hydrogenolysis (1 atm H_2) is found to be slow: after 2 days, ca. 60% of **8** is consumed and the complete consumption requires one week. The NMR spectra show the formation of only small amounts of the unsolvated dimeric hydride **2**, the major component exhibits four Cp signal ($\delta = 12.13$, 16.7,11.25 and 11.12 ppm), one tBu signal at -2.21 ppm and one methyl signal at -20 ppm. This set of signals is in good agreement with the formation of the bridged complex $Cp'_2Sm(\mu\text{-}H)(\mu\text{-}Me)SmCp'_2$ **9**. Hydrido-alkyl bridged lanthanoid complexes were recently described [8]. The formation of **9** is not observed in the presence of coordinating solvents.



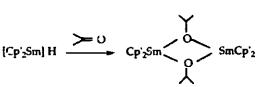
2.4. Reactivity of $[Cp'_2SmH]_2$ 2 and other hydrides

BH_3 in toluene solution reacts immediately with **2** to give the known borohydride $[Cp'_2SmBH_4]_2$ [9]. The same complex has been obtained by a comproportionation reaction between **3** and $Sm(BH_4)_3(THF)_3$, followed by the removal of the solvents.

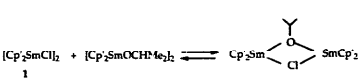
$$[Cp'_2SmH]_2 + 2BH_3 \rightarrow [Cp'_2SmBH_4]_2$$

2

Propanone reacts with **2**, **2'**, **4** or **4'** to give the alkoxide **10**. This new complex is identified by comparison with a sample obtained by alcoholysis of the methyl derivative **8**.



Addition of one equivalent of propanone to the crude mixture containing **1**, **2** and **7** led to the formation of the new chloroalkoxy bridged complex $Cp'_2Sm[\mu\text{-}OCH(CH_3)_2](\mu\text{-}Cl)SmCp'_2$ **11** identified by comparison with an authentic sample obtained by mixing stoichiometric amounts of **1** and **10** in toluene or in C_6D_6.



3. Discussion

3.1. Unsolvated complexes

Polymeric forms are not common for unsolvated derivatives $(C_5H_4R)_2LnX$ of the early lanthanides [10]. Trimetallic units (cristallised with solvated alkali metal ions) were often reported, but only for late lanthanide (Er, Lu, Y) complexes, containing non substituted Cp

Table 1
^{1}H NMR data of dimeric complexes

	Cp	tBu	Other
$[Cp'_2SmCl]_2$ **1**	17.5 12.3	−1.92	
$[Cp'_2SmH]_2$ **2**	18.5 10.32	−3.75	H not found
$[Cp'_2SmMe]_2$ **8**	14.6 11.93	−0.94	−26.1 (Me)
$[Cp'_2SmOCH(CH_3)_2]_2$ **10**	14.95 13.98	0.34	−8.2(CH_3) −39.4 (CH)

rings [11]. Most of the complexes of the early lanthanides are dimeric, except for those containing very bulky X ligands (X = $CHSi(CH_3)_2$ for example). The starting chloride $[Cp'_2SmCl]_2$ is known to be dimeric [7] and preliminary X-ray analysis of $[Cp'_2SmOiPr]$ also reveals a dimeric structure [12]. Though the structure of other complexes $[Cp'_2SmX]_2$ (X = Me, H) has not been established by X-ray analysis or otherwise, one can consider these complexes as dimers, on the basis of the known structure of other analogous complexes: $[Cp'_2NdMe]_2$ [13] and $[Cp''_2SmH)_2]$ ($Cp'' = C_5H_3tBu_2$) [9].

When two dimers of general formula $[Cp'_2SmX]_2$ and $[Cp'_2SmY]_2$ are mixed together in a non coordinating solvent, new complexes $[Cp'_2Sm\mu X\text{-}\mu YCp'_2]$ are obtained (**7** and **11**). The comproportionation is not complete and the three partners can be observed in solution. Exchange is slow at ambient temperature and could not be detected by spin saturation transfer. NMR data of these new complexes are reported in Tables 1 and 2. The presence of an unsymmetrical bridge allows the observation of four Cp signals. Neutral complexes with unsymmetrical bridges are not so numerous as the dimers but some have been described: a μ-H, μ-Cl bridged complex, $[Me_2Si(C_5H_3tBu_3)_2Yb]_2(\mu H\text{-}\mu Cl)$ [14] and a μ-H, μ-alkyl complex [15]. The formation of the hydrido/methyl dinuclear complex **9** during hydrogenolysis of the methyl bridged dimer **8** is postulated in view of the NMR data, because four Cp signals are also found. This complex is more resistant towards hydrogenolysis than **8**: After one week, **8** is almost entirely consumed and only traces of **2** are found. A similar stability towards hydrogenolysis has been reported for the previously described μ-H, μ-alkyl complex [15].

Table 2
^{1}H NMR data of unsymmetrical dinuclear complexes

	Cp	tBu	Other
$Cp'_2Sm(\mu\text{-}H)(\mu\text{-}Cl)SmCp'_2$ **7**	17.35 10.30 18.95 10.58	−2.39	H not found
$Cp'_2Sm(\mu\text{-}H)(\mu\text{-}Me)SmCp'_2$ **9**	17.13 11.24 16.7 11.12	−2.21	−22 (Me)
$Cp'_2Sm[\mu\text{-}OCH(CH_3)_2]$-$(\mu\text{-}Cl)SmCp'_2$ **11**	17.54 12.96 15.75 12.49	−0.73	−6.58 (CH_3) −30 (H)
$Cp'_2Sm(\mu\text{-}Me)(\mu\text{-}Cl)$-$SmCp'_2$ **12**	16.53 12.02 15.72 11.83	−1.39	−24.5 (CH_3)

Table 3
^{1}H NMR data of $[Cp'_2SmCl]_2$ in the presence of coordinating ligands

Ligand	Cp	tBu	Ligand
None	17.5 12.3	−1.92	
$PiPr_3$ 2 eq	17.5 12.31	−1.92	
PMe_3 1 eq	17.18 12.19	−1.75	0.40
PMe_3 1.5 eq	16.50 11.98	−1.47	0.47
PMe_3 2 eq	16.50 11.96	−1.35	0.51
THF 2 eq	17.41 12.27	−1.83	3.42 1.34
THF 20 eq	11 broad	−1.14	id
THF d_8	10.49 10.39	0.45	id

The NMR spectra of these unsolvated complexes generally exhibit well separated Cp signals; the largest difference in the chemical shift ($\Delta\delta$ = ca. 8 ppm) is recorded for the hydride **2**. For mixed dinuclear complexes, the chemical shifts of the Cp signals are very close to those of the parent compounds.

3.2. Opening of the bridged dimers by ancillary ligands

In the Tables 3 and 4, and Table 5 are reported the NMR data of the solvated species $[Cp'_2SmX, L]$ (X = Cl, H, Me; L = THF or PMe_3) in the presence of a stoichiometric quantity (or an excess) of an ancillary ligand.

The chemical shift of the H atoms of $[Cp'_2SmCl]_2$ is not strongly affected by the addition of 1 or 2 equivalents of PMe_3: $\Delta\delta = 1$ and 0.3 ppm (Cp) and 0.5 ppm (tBu) or by addition of 4 equivalents of THF: $\Delta\delta = 0.1$ and 0.05 ppm (Cp), 0.1 ppm (tBu). The coordination of these ligands is reversible, and the dimeric starting materials were recovered after distillation of the solvents and pumping off the solids. Therefore, it seems reasonable to believe that only one molecule of Lewis base is weakly coordinated to each metal atom of the dimer, without opening of the bridge, leading to complexes analogous to the known $[(C_5H_4Me)_2Sm(THF)\mu\text{-}Cl]_2$ which is dimeric in the solid state as established by X-ray structural analysis [16].

More than 10 equivalents of THF are necessary to bring about any great modification of the NMR spectrum of $[Cp'_2SmCl]_2$: when 20 eq. of THF are added to

Table 4
^{1}H NMR data of $[Cp'_2SmH]_2$ in the presence of THF or (PMe_3) and BEt_3

Ligand	Cp	tBu	THF(PMe_3)	BEt_3
None	18.5 10.32	−3.75		
2 PMe_3	13.7 11.07	−1.79	0.24	1.14 −4.9
2 THF	12.11 11.26	−0.05	2.10 0.55	1.10 −5.14
3 THF	12.16 11.07	0.08	2.80 1.95	1.22 5.26
4 THF	12.17 11.02	0.09	0.07 1.09	0.94 −5.28
10 THF	12.17 11.95	0.12	3.37 1.31	id.
50 THF	12.15 10.81	0.13	3.51 1.43	id
100 THF	12.15 10.02	0.13	3.51 1.43	id

Table 5
^{1}H NMR data of $[Cp'_2SmMe]_2$ in the presence of oxygenated ligands

	Cp	tBu	Me
None	14.6 11.93	−0.94	−26.1
Diethylether 10 eq	14.6 11.93	−0.94	−26.1
THF 10 eq	14.6 11.93	−0.94	−26.1
THF 100 eq	13.7 11.5	0.01	−25
THF d_8	7.84 7.63	0.62	6.43

a benzene solution, a new large unresolved Cp signal is observed at 11 ppm and the tBu signal is shifted of 0.8 ppm. The monomeric adduct obtained by dissolving the dimer in deuteriated THF exhibits two neighbour Cp signals at $\delta = 10.5$ and 10.4 ppm. Quite similar values ($\delta = 10.1$ and 9.5 ppm) were observed for the above mentioned $[(C_5H_4Me)_2Sm(THF)\mu\text{-Cl}]$, when dissolved (probably with bridges opening) in deuteriated THF.

For the hydride **2**, obtained by the hydride route, drastic changes in the spectra are recorded after addition of one eq. of THF per samarium moiety: the two well separated Cp signals ($\delta = 18.5$ and 10.3 ppm) of the starting material now appear very close at 12.1 and 11.2 ppm. These chemical shifts are only slightly modified by the subsequent addition of 2 to 100 eq. of THF. The coordination of BEt_3, as shown by the ^{11}B NMR spectra unambiguously establish the monomeric nature of the complex in the presence of THF (similar coordination of BEt_3 was also observed for neodymium hydrides [17]). The assistance of BEt_3 as Lewis acid is not necessary to open the bridge. The same chemical shifts changes were observed for **2**, obtained by hydrogenolysis of **5** the addition of PMe_3 afforded a new hydridic species with two Cp signals at 11.8 and 11.1 ppm. Subsequent addition of PMe_3 or THF did not lead to significant change of these signals.

It appears from Tables 1–4 that a large difference between the Cp signals is generally observed for the unsolvated bridged structures, whereas in monomeric solvated species this difference becomes very small: $\Delta\delta = 0.2$ ppm for $Cp'_2SmCl(THF)_n$ and 0.1 ppm for $Cp'_2SmMe(THF)_n$, and $\Delta\delta = 0.7$ ppm for $Cp'_2SmH(THF)_2$, **2'**. We propose that this is related to the electron deficiency of the metal in the unsolvated dimers which would induce electron density transfer from the ligand to the metal allowing the signals to be shifted.

This fact, which seems to be general for this type of complexes of samarium, is of importance: a correlation might be possible between the NMR data and the structure of the complexes in solution.

Concerning the alcoxyde $[Cp'_2SmOiPr]_2$, **10**, which is a dimer in the solid state, it is noteworthy that the addition of THF (10 to 100 eq.) does not imply modifications of the ^{1}H NMR spectrum. Thus, THF seems to be not strong enough to open the Sm–O–Sm bridges, and this complex remains dimeric in solution.

3.3. Stability of the alkyls derivatives

Complexes **5** and **8** are stable in solution whereas **6** is only observable in the presence of PMe_3. All attempts to obtain **6** free from ancillary ligand have failed, only the tris derivative Cp_3Sm **3** was formed. Generally the form in which a Cp_2LnX unit is formed, i.e., an electron deficient dimer or a monomeric solvate $Cp_2LnX(solvent)$, depends on whether the solvent (or an ancillary ligand) will strongly coordinate to the metal and whether the X group is a good bridging ligand. It seems that the CH_2SiMe_3 ligand does not allow the dimerisation (which is easy for the methyl derivative) and is too small to prevent the disproportionation with formation of **3**. The very bulky $CH(SiMe_3)_2$ ligand is known to allow the formation of stable alkyls [9] and **5** is probably monomeric.

3.4. Nature of $[Cp'_2SmH]_2$ 2 and hydrides 2', 4, 4', 7 and 9

The hydridic nature of **2** was established unambiguously by its chemical reactivity:

— BH_3 in toluene solution reacted immediately with **2** to give the known borohydride $[Cp'_2SmBH_4)]_2$. The obtention of a tetraborohydride or a dihydrodialkylborate by BH_3 or BHR_2 insertion in an organometallic (f element) M–H bond was previously described [18].

— The reaction with propanone afforded the alkoxide **10** identified by comparison with an authentic sample obtained by alcoholysis of the methyl derivative **8**. The alkoxide **10** was also obtained from the other hydridic species **2'**, **4** and **4'**. The same alkoxyde **10** was also prepared by alcoholysis of **3**.

— The structure of **2'** was first established by chemical correlation: it was formed by hydrogenolysis of the alkyl complexes **6** and **5** (after addition of PMe_3 in this latter case). It was also formed by addition of PMe_3 on the dimer **2**.

— The hydrido-chloro bridged complex **7** (always obtained mixed with **2** and unreacted **1**) treated by the stoichiometric amount of propanone afforded the chloroalkoxyde **11** (mixed with ca. 20% of **1** and **10**). It is noteworthy that the comproportionation reaction between pure **1** and **10** leads to 80% of **11**; the same experiments conducted from **1** and **2** lead only to ca. 50% of **7**.

— Treatment of the hydrido-methyl complex **9** with propanone afforded a new alkoxo-compound; its NMR spectrum showed one isopropyl group per two $(tBuCp)_2Sm$ unit.

3.5. Stability of the hydrides

Solutions containing **2'** cannot be concentrated and evaporated to dryness nor stored at ambient temperature

even for a few hours without noticeable or complete decomposition to give **3**.

The hydride **2** is more stable and solutions can be stored for a few days; the disappearance of the hydride is complete within ten days. When freshly prepared solution of **2** are evaporated the percentage of **3** increases from 15 to 30%. To successfully obtain the electron deficient dimer **2** it seems necessary to start from a dinuclear structure, which is retained during the synthesis:

— By the hydridic route, one can assume that when the $HBEt_3$ anion reacts with the dimeric chloride **2**, only one Sm–Cl–Sm bridge is opened and the elimination of BEt_3 and NaCl occurs with the concomitant formation of a new Sm–H–Sm bridge, to form the (doubly bridged) hydrido-chloro complex **7**. This complex is in equilibrium with the dimers **1** and **2**, and during the ligand exchanges variable quantity of Cp'_3Sm, **3** are also formed. The addition of the second eq. of hydridic reagent allows, by the same way, the formation of the dimer **2**.

— Hydrogenolysis of lanthanide alkyls has been known for years [1,10] to form the corresponding hydrides. The transient formation of the monomeric Cp'_2SmH likely occurs when $Cp'_2SmCH(SiCH_3)_2$, **5** is left under hydrogen; but in concurrence with the dimerisation which leads to **2**, the disproportionation of the unstable hydride moiety is observed, leading to a high percentage (nearly 60%) of **3**. In contrast, hydrogenolysis of the dimer **8**, performed in a non coordinating solvent, does not lead to large amount of **3** but first to a new dinuclear hydrido-alkyl derivative.

Non surprisingly the tris(alkylborane) supported hydride **4** is the most stable the decomposition into **3** is slow and solutions can be stored during days, but crystals could not be obtained, even by treatment of concentrated solutions with pentane.

The different hydrides: dimeric or tris alkylborane supported, do not react with the toluene, as does Cp'_2SmH [19]. During the storage of hydride solutions in the presence of toluene, the formation of **3** occurs but no new paramagnetic signals consistent with the formation of a benzyl derivative were observed. This is not surprising: It is known [20] that the reactivity of the monoalkyl substituted or unsubstituted Cp complexes is very similar (except that the former which exhibit a better solubility) and the Cp_2LnH hydrides [21] are synthesized in the presence of toluene and do not react with it.

Syntheses of related complexes containing a (alane supported) Cp'_2SmH moiety were reported: $[(Cp'_2Sm\mu_3\text{-}H)(\mu_2\text{-}H_2AlH)(THF)]_2$ [22] and $[(Cp'_2Sm_2(\mu_2\text{-}H)(\mu_3\text{-}H)_2Al(\mu_2\text{-}H)_2(TMEDA)]_2$ [23]. These complexes were characterized in the solid state by the X-ray crystal structure determination. Nothing was mentioned about their structure in solution and no NMR data are available, nevertheless, one could assume that the aluminohydride bridging moiety remains coordinated when the compounds are dissolved in a convenient solvent.

3.6. Formation of Cp'_3Sm 3

The formation of **3** is observed when hydrides or alkyls are synthesized or during the attempts to get crystals, when solution are stored for days. The mechanism of these reactions was not really investigated, several factors may be involved. The rearrangement is favoured by the concentration of crude solution, by raising of the temperature and likely by the presence of salts in THF solution: in the synthesis of **1** in THF the formation of **3** (5 to 15%) is observed. After removal of the salts from the crude product and after removal of **3** by cold pentane, no further formation of **3** is observed in non polar solvents.

In a polar medium, one can postulate that the liberation of a Cp′ ligand occurs after the coordination to the metal of the starting material of solvent molecules or chloride ions; this allows the rapid reaction of the Cp anion on a Cp'_2SmH moiety leading to **3**.

In non polar solvents, the ligand exchanges generally occur by concerted bimolecular reactions, favoured by the concentration. The disproportionation of a Cp'_2SmH unit could lead to a mixture containing **3** and a dihydride species:

$$2(Cp'_2SmH)_2 \rightarrow 2Cp'_3Sm + (Cp'SmH_2)_2$$

No signals corresponding to the dihydride could be depicted in crude mixtures; however such a complex could be insoluble in benzene or toluene. In an other set of experiment from neodymium hydrides, a set of signals consistent with the formation of such monocyclopentadienyl-dihydride species was observed.

4. Conclusion

Samarium hydrides were characterized in solution. The dimeric unsolvated hydride **2** is moderately stable. It was not possible to increase significantly its stability by coordinating phosphine or THF ligands. This led to monomeric solvated forms which invariably rearrange and lead to the known Cp'_3Sm. In contrast the monomeric hydride **4** which is coordinated to a trisalkylborane molecule is fairly stable.

5. Experimental

5.1. General procedures

All experiments were performed under a dry nitrogen or argon atmosphere using standard Schlenk or glove

box (JACOMEX) techniques. Solvents were stored under argon on sodium-benzophenone and distilled immediately before use. The compounds Cp'_3Sm [7], $Li(CHTMS)_2$ [24] and $LiCH_2TMS$ [25] were synthesized following published methods. KCp′ was made by action of KH over Cp′H [26] For the synthesis of $Sm(BH_4)_3(THF)_3$ the procedure was slightly modified ($TlBH_4$ was used instead of $NaBH_4$) [27].

The ^1H NMR spectra were collected on a Bruker AC-200 spectrometer. The ^{11}B NMR spectra were recorded on a Bruker DRX-500 spectrometer at 160 MHz and the chemical shifts were measured versus BF_3, Et_2O in $CDCl_3$ as an external reference. The elemental analyses have been performed on a Fisons EA 1108 apparatus or at the Service Central d'Analyse du CNRS.

All the syntheses from 10 mg of **1** were performed in NMR tubes after dissolution in 0.4 ml of C_6D_6 and monitored by ^1H NMR. Yields were generally estimated by integration of the cyclopentadienyl signals or sometimes by integration of the tBu signals.

6. $(Cp'_2SmCl)_2$, 1

It was synthesized according to Wayda's method [7] but using KCp′ in toluene instead of LiCp′ in THF. Anal. Found: C, 50.04; H, 6.00. $C_{36}H_{52}Sm_2Cl_2$. Calc.: C, 50.49; H, 6.12.

6.1. Hydrides

6.1.1. Hydride $[Cp'_2SmH]_2$, 2

(a) 10 mg of **1** were dissolved in C_6D_6 and 23.7 μl of a 1 M toluenic solution of $NaHBEt_3$ were added by a syringe. After 30 min at room temperature, the consumption of the starting materials was complete and ca. 85% of **2** and ca. 15% of **3** were formed. After 5 days, the solution contained 50% of **2** and 50% of **3**.

(b) To a solution of the hydride **2** (containing 15% of **3**) obtained from 8 mg of **1** and 19.7 μl of $NaHBet_3$ as described above, 9 μl of a toluenic solution of BH_3, SMe_2 (2M) were added. The solution contained the borohydride $[Cp'_2Sm\text{-}BH_4]_2$ as the major product.

6.1.2. Hydride $Cp'_2SmHBEt_3(THF)_2$, 4

In a similar experiment, THF (2 eq./Sm) was added to **1**. After addition of 0.5 eq. of $NaHBEt_3$ (11.7 μl), the solution contained unreacted solvated **1** (ca. 50%), hydride **4** (ca. 50%) and a small amount (ca. 3%) of **3**. After complete addition of $NaHBEt_3$ (23.4 μl), only **4** and 5% of **3** were present. No significant change occurred after 24 h at room temperature. After removal of the solvents and redissolution in C_6D_6, the solution contained 10% of **3**. The same sample was heated 15 min at 50°C, the amount of **3** raised up to 30%.

6.1.3. Hydride $Cp'_2SmHBEt_3(PMe_3)_2$, 4′

The same experiment was performed with addition of PMe_3 (5 μl, 2 eq/Sm) instead of THF. The solution contained **4′** (65%), **3** (20%) and 15% of unidentified products. After 10 min at 50°C, the amount of **3** was 50%.

6.2. Hydrogenolysis experiments

6.2.1. From $Cp'_2SmCH(SiMe_3)_2$, 5

(a) 10 mg of **1** and 4 mg of $LiCH(SiMe_3)_2$ were dissolved in C_6D_6. The orange solution containing **5** [δ C_6D_6 = 18.55 (CH), 15.70 and 10.06 (Cp), −1.58 (broad, $SiMe_3$), −3.75 (tBu)] and a small amount of **3** (5%) was frozen, degassed and pressurised with H_2 (1 atm). A slow reaction occurred; after 6 h, the yellow solution contained 50% of unreacted **5** and equivalent amounts of **2** and **3** were formed. After 2 days, only **3** was present with traces of **5** and **2**.

(b) To a solution of **5** obtained in the same way, 2.3 μl of PMe_3 were added. After 6 h under hydrogen pressure (1 atm), 98% of the starting material was consumed; the solution contained **2′** [δ C_6D_6 = 11.80 and 11.07 (Cp), 0.30 (PMe_3), −1.00 (tBu)] (75%) and **3** (25%).

6.2.2. From $Cp'_2SmCH_2SiMe_3(PMe_3)$, 6

To 10 mg of **1** dissolved in C_6D_6, were added first 2.3 μl of PMe_3, then 2.1 mg of $LiCH_2SiMe_3$. After stirring by ultra-sounds the solution contained **6** [δ C_6D_6 = 11.75 and 10.39 (Cp), 10.4 (broad, CH_2), 1.16 (PMe_3), −0.49 (tBu)] and a very small amount of **3** (2%). After 4.5 h under hydrogen (1 atm), the hydrogenolysis was nearly complete; **2′** (85%), **3** (8%), **6** (2%) and some impurities were present.

6.2.3. Mixed bridged hydride $Cp'_2Sm(\mu\text{-}H)(\mu\text{-}Cl)SmCp'_2$, 7

(a) 10 mg of **1** were dissolved in 0.4 ml of C_6D_6 and 11.7 μl of a 1 M solution of $NaHBEt_3$ was added by a syringe. After 15 min, the solution contained less than 5% of **3** and a mixture of **1**, **2** and **7** in the rate 1/1/3. The amount of **3** increased slowly (10% after 4 h at room temperature).

In the same tube, 11.7 μl of the solution of $NaHBEt_3$ was added. The yellow–orange solution contained only the dihydride **2** and ca. 15% of **3**. After 24 h, the amounts of **2** and **3** were 60% and 40%, respectively.

(b) To a solution of **2** prepared from 10 mg of **1** and 23.4 μl of $NaHBEt_3$, 8 mg of **1** were added. After stirring, the NMR spectrum of the solution was the same as above described.

6.2.4. Synthesis of $[Cp'_2SmMe]_2$, 8

(a) In a NMR tube, 10 mg of **1** (0.024 mmol) were dissolved in C_6D_6 and 15 μl of MeLi (1.6 M in

diethylether) were added and the solution immediately analyzed. The consumption of **1** was complete and the formation of **8** was nearly quantitative. with traces (less than 2%) of **3**.

(b) A solution of 457 mg (1.07 mmol) of **1** in 20 ml of toluene was added slowly at room temperature to a stirred solution of MeLi (0.73 ml of 1.6 M solution in diethylether) in 15 ml of toluene. 15 min after the end of the addition, the pale yellow solution was filtered and toluene was removed under reduced pressure at room temperature. To eliminate **3**, the yellow–orange powder was cooled with liquid nitrogen, 1 ml of pentane was condensed and immediately separated after liquefaction. The crude yellow powder (347 mg, yield 80%) still contained ca. 5% of **3** (by NMR). To obtain an analytically pure sample (free of **3** and of LiCl) as a microcrystalline yellow powder, five cycles of extraction with 5 ml of pentane at room temperature were necessary. Each extraction was followed — after evaporation of the solvent — by washing with 0.5 ml of cold pentane, as described above, to eliminate last traces of **3**. Anal. Found: C, 56.56; H, 7.14. $C_{38}H_{58}Sm_2$. Calc.: C, 55.96; H, 7.17.

6.2.5. *Mixed bridged hydride* $Cp'_2Sm(\mu\text{-}H)(\mu\text{-}Me)SmCp'_2$, **9**

10 mg of **8** were dissolved in C_6D_6, the solution was frozen, degassed and pressurized with H_2. A slow reaction occurred, after 2 days the solution contained 60% of unchanged **8**, a very small amount of **3**, traces of the dihydride **2** and ca. 40% of the mixed hydride **9**. During the reaction the percentage of **3** increased: after 7 days, the reaction was complete, **3** (30%), **9** (25%) and **2** (25%) were present in the solution with non identified components.

6.2.6. *Alkoxide* $[Cp'_2Sm\text{-}OCH(CH_3)_2]_2$, **10**

(a) To a solution of 200 mg (0.47 mmol) of **1** in toluene (30 ml), were added 0.33 ml of an etheral solution (1.6 M) of MeLi (0.52 mmol). The solution turned pale yellow while LiCl deposited. After 20 min, a solution of isopropanol (40 μl; 0,52 mmol) in toluene (10 ml) was added. The mixture turned deep yellow immediately and was allowed to stand at room temperature for 2 h. The solvents were evaporated off and pentane (40 ml) was added. After filtration, concentration to ca. 15 ml, and standing 24 h at room temperature, large yellow crystals were obtained. Concentration of the mother liquor (ca. 5 ml) gave a second crop of crystals (total yield: 96 mg; 45,3%). Anal. Found: C, 54.73; H, 7.25. $C_{42}H_{66}Sm_2O_2$. Calc.: C, 55.85; H, 7.31.

(b) 383 mg (0.75 mmol) of **3** were dissolved in pentane and 57.4 μl (0,75 mmol) of isopropanol were added slowly by a syringe. The yellow–brown solution was stirred 12 h, filtered and the solvent was removed. After addition of 4 ml of pentane (at 0°C) the solution was filtered; after concentration, 85 mg of yellow–brown crystals were obtained (yield 25%). The sample was contaminated by ca. 5% of **3**.

(c) To a solution of the hydride **2** (containing 15% of **3**) obtained from 10 mg of **1** and $NaHBEt_3$ as described above, 1.3 μl of propanone were added. The red orange solution contained **10** and unchanged **3**.

The same experiment performed from the hydrides **2'**, **4** and **4'** afforded also **10**.

In the presence of a large excess (10 to 100 eq.) of THF the NMR spectrum of **10** is not altered.

6.2.7. *Mixed chloroalkoxide* $Cp'_2Sm(\mu\text{-}OCH(CH_3)_2)(\mu\text{-}Cl)SmCp'_2$, **11**

(a) 9.8 mg of **1** and 10.1 mg of **10** were dissolved in C_6D_6 and stored 48 h at room temperature. The solution contained ca. 40% of **11** and 30% each of **1** and **10**. After heating 4 h at 65°C the rates were 70%, 15%, 15% respectively, they became unchanged after 16 h at 65°C.

(b) To a solution obtained as above from 4 mg of **1** and 4.7 μl of $NaHBEt_3$ and containing the hydrochloride **7** (mixed with **1** and **2**, 25% each and **3**, 5%), 0.4 μl of propanone were added. After 1 h, the solution contained ca. 65% of **11**, 20% of **10** and 10% of **3**.

6.2.8. *Mixed chloroalkoxide* $Cp'_2Sm(\mu\text{-}CH_3)(\mu\text{-}Cl)SmCp'_2$, **12**

A solution of **8** is prepared from 10 mg of **1** and MeLi (ether solution, 14 μl); the solvents are evaporated, 0.4 ml of C_6D_6 and 9 mg of **1** are added. With the signals of **1** and **8**, a set of new signals is observed and tentatively attributed to **12**.

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