Hydride derivatives of Group 4 metals
with the ansa-(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$ ligand

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Abstract

The dinuclear hydrides [M(CpSi$_2$Cp)H(μ-H)]$_2$ [M = Zr (1), Hf (2); (CpSi$_2$Cp) = [(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$]] have been synthesized by reaction of the corresponding dichloro compounds M(CpSi$_2$Cp)Cl$_2$ [M = Zr, Hf] with LiBHEt$_3$ in a molar ratio of 1 : 2. Related deutero derivatives [M(CpSi$_2$Cp)D(μ-D)]$_2$ [M = Zr (3), Hf (4)] were obtained by using LiBDEt$_3$. When the same reaction was carried out with Ti(CpSi$_2$Cp)Cl$_2$, the formation of unidentified titanium(III) species was observed. These compounds have been characterized by the usual analytical and spectroscopic methods. The ^{1}H NMR study of the reaction of complex 1 with traces of water in deuterated tetrahydrofuran shows that the terminal hydrides are more reactive than the bridging hydrides, and only one of the terminal hydrides reacts selectively. Complex 1 shows a rigid behaviour in the NMR time scale between −80°C (500 MHz) and +80°C (300 MHz).

Keywords: Zr; Hf; Si; *Ansa*-cyclopentadienyl complexes; Silylcyclopentadienyls; Hydrides
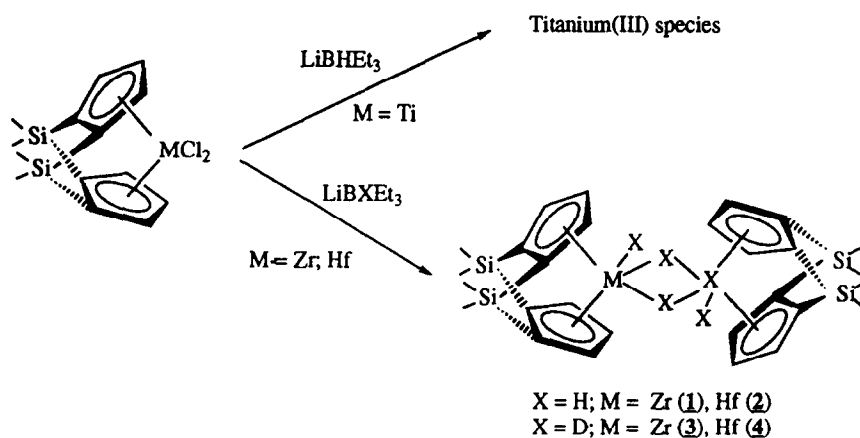
1. Introduction

New cyclopentadienyl hydrides of the early transition metals have been reported since the first compound of this type, ZrCp$_2$HCl, was synthesized [1]. The replacement of the cyclopentadienyl ligand C$_5$H$_5$ by substituted rings provides access to hydride complexes with new properties.

The study of the reactivity of the early transition metal hydrides has shown that they are potentially valuable reagents for several organometallic reactions. The reactivity of zirconocene hydrides with olefins and acetylenes has been investigated [2]. [Zr(η^5-C$_5$H$_5$)$_2$H$_2$]$_x$ and related zirconocene hydrides have been found to be active as catalysts for olefins and acetylene hydrogenation [3]. The unusual chemical reactivity of zirconocene hydrides towards CO has also been studied [4]. Recently, new reactions with the participation of Group 4 metal hydrides have been proposed. The NMR study permits the conclusion that zirconocene(IV) hydride bridged dimers, with "cation-like" silylium ligands, are the active species in a catalytic dehydrocoupling of

phenylsilane [5]. Cationic d^0 hydrides [Zr(η^5-C$_5$H$_5$)$_2$H]$^+$ and [Zr(η^5-C$_5$H$_5$)$_2$H(L)]$^+$ are of interest in relation to their activity in Ziegler–Natta olefin polymerization catalysis [6]. These cationic hydride species are the expected products of β-H elimination or hydrogenolysis reactions of the chain-transfer step in ZrCp$_2$X$_2$-based catalysts [7]. Some zirconium cationic derivatives in which the ion pair contains carborane anions linked to zirconium by a β-H–Zr bridge have also been described [8].

Ansa-metallocene complexes of the early transition metals have received considerable attention in recent years [9]. The presence of two cyclopentadienyl rings bridged by a single SiMe$_2$ group restricts the mobility of the cyclopentadienyl ligand, providing a more rigid system that renders the activation of their C–H bonds more difficult. We are interested in isolating and studying the reactivity of cyclopentadienyl Group 4 metal complexes by using the doubly bridged bis(dimethylsilanodiyl)dicyclopentadienyl dianion [(SiMe$_2$)$_2$(η^5-C$_5$H$_3$)$_2$]$^{2-}$ as a ligand that increases the stereorigidity of the complex. Different mono- and oligo-nuclear transition metal derivatives containing this type of ligand have been reported [10], but few Group 4 metal complexes are known [11].

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Scheme 1.

Here, we report the synthesis and characterization of new dinuclear zirconium and hafnium hydrides with the double dimethylsilanodiyl bridged dicyclopentadienyl ligand $\{M[(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]H(\mu\text{-}H)\}_2$ [M = Zr (1), Hf (2)] and the related deutero derivatives $\{M[(SiMe_2)_2\text{-}(\eta^5\text{-}C_5H_3)_2]D(\mu\text{-}D)\}_2$ [M = Zr (3), Hf (4)]. A detailed NMR study of compound 1 shows a rigid behaviour in the NMR time scale between -80 and $+80°C$ and allows observation of the spectral features of the different cyclopentadienyl protons and hydride sustituents.

2. Discussion of synthetic and spectroscopic results

The dichloro compounds $M(CpSi_2Cp)Cl_2$ [M = Zr, Hf; $(CpSi_2Cp) = [(SiMe_2)_2(\eta^5\text{-}C_5H_3)_2]]$ react when stirred with 2 equivalents of $LiBHEt_3$ in toluene at room temperature to give the dinuclear hydrides $[M(CpSi_2Cp)H(\mu\text{-}H)]_2$ [M = Zr (1), Hf (2)] as shown in Scheme 1. Related deutero derivatives $[M(CpSi_2Cp)\text{-}$ $D(\mu\text{-}D)]_2$ [M = Zr (3), Hf (4)] are obtained by using $LiBDEt_3$. When the same reaction is carried out with $Ti(CpSi_2Cp)Cl_2$ the formation of unidentified titanium(III) species is observed.

In common with the known Group 4 hydrides, 1–4 are very air and moisture sensitive, making characterization by elemental analysis difficult. The ^1H NMR spectrum of compound 1 at room temperature in benzene-d_6 shows: two triplets at δ -3.21 and δ 3.45, characteristic of bridged and terminal Zr–H protons respectively; four singlets for the methyl protons of the $SiMe_2$ bridges; three signals assignable to cyclopentadienyl ring protons (Table 1, Fig. 1). Similar features are observed for compound 2 (δ 0.65, bridging Hf–H and δ 8.67, terminal Hf–H). These spectra are consistent with the dinuclear structure proposed for related Group 4 metal compounds [3c,12].

The spin-lattice relaxation times for protons in compound 1 were measured at 193 K. H_b and H_t show characteristic T_1 values of classical hydrides [13]. The

Table 1
^1H NMR data for complexes 1 and 2 in C_6D_6 at 298 K (chemical shifts [ppm], spin-lattice relaxation times $\{T_1\}$ [a] [seg] and spin–spin coupling constants [Hz])

Complex	H_1	H_2	H_3	H_b	H_t	Me_{endo}		Me_{exo}	
1	7.32	6.04	6.82	-3.21	3.45	0.365	0.507	0.526	0.540
(Zr)	{1.15}	{0.81}	{0.93}	{0.44}	{0.635}	{0.64}	{0.59}	{0.97}	{1.03}
	$^3J_{H_1\text{-}H_2} = 2.75$, $^4J_{H_1\text{-}H_3} = 1.5$, $^3J_{H_2\text{-}H_3} = 2.75$, $^2J_{H_1\text{-}H_t} = 0.5$, $^2J_{H_2\text{-}H_b} = 0.2$, $^2J_{H_t\text{-}H_b} = 7.0$									
2	7.19	5.78	6.57	0.65	8.67	0.300	0.420	0.440	0.470
(Hf)									

[a] T_1 values corresponding to $T_{1\,min}$ were measured at 198 K in $CD_3C_6D_5$.

Table 2
^{13}C chemical shifts [ppm] for complexes 1 and 2 in C_6D_6 at 298 K

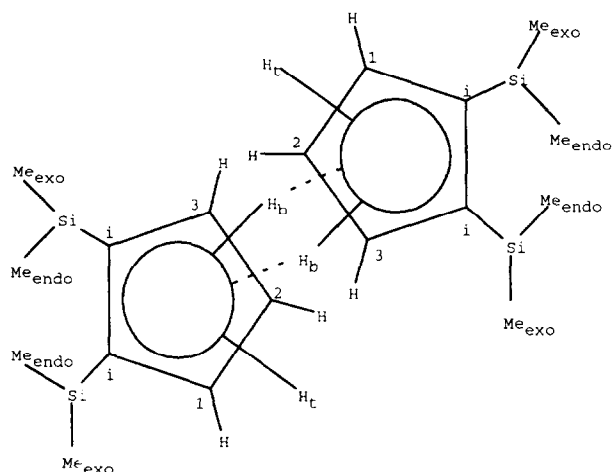| Complex	C_1	C_2	C_3	C_{ipso}	Me_{endo}	Me_{exo}
1	122.7	107.95	119.98	99.8	-3.1	2.35
(Zr)				102.6	-4.2	2.55
2	122.1	106.1	120.1	98.9	-3.05	2.37
(Hf)				102.1	-4.15	2.65

Fig. 1. View of the geometrical disposition of the hydrogen atoms in compounds 1 and 2.

multiplicity, spin-lattice relaxation times and spin–spin coupling constant of the H_1–H_3 and Me_{endo} and Me_{exo} signals allow their unequivocal assignment. The small difference in T_1 values for Me_{endo} and Me_{exo} makes it difficult to distinguish between the methyl groups bonded to Si_1 and Si_2. The spin–spin coupling constant $^2J_{H_1-H_t} = 0.5$ Hz and $^2J_{H_2-H_b} = 0.2$ Hz were observed.

No reaction occurs when the dihydrides 1–4 are treated with CO, NH_2^tBu, PhCOOEt, C_2H_2 or $C_2(SiMe_3)_2$ in THF or toluene. These results contrast with the reactivity shown by zirconocene hydrides with acetylenes [2]. However, compound 1 reacts overnight with CO_2 in toluene at room temperature to give a highly insoluble product whose IR spectrum shows the presence of the cyclopentadienyl ligand and two signals at 1585 and 1203 cm^{-1}, assignable to the $\nu(C=O)$ and $\nu(C-O)$ vibrations respectively. One strong signal at 762 cm^{-1}, owing to $\nu(Zr-O-Zr)$ stretching vibration, is also observed.

In contrast with the intramolecular hydride exchange H_t–H_b observed (60–70°C) for other related derivatives [3c,14], complex 1 shows a rigid behaviour in the NMR time scale between −80°C (500 MHz) and +80°C (300 MHz). This behaviour must be due to the presence of the double dimethylsilanodiyl bridged dicyclopentadienyl ligand, which prevents the H_t–H_b exchange through the participation of the cyclopentadienyl C–H bonds. C–H activation in the cyclopentadienyl ligand and the substituted R group bonded to the cyclopentadienyl ring in Ti and Zr(III) metallocene hydrides and cationic derivatives has been proposed [3c,7e].

When compound 1 is dissolved in THF-d_8 (sealed NMR tube), the initially colourless solution turns light blue. After 24 h the ^1H NMR spectrum of this sample shows the resonances assignable to 1 and the presence of new clear signals. The structure of this spectrum is maintained unchanged for months, even when the sample is heated under reflux. The ^1H NMR spectrum in THF-d_8 shows, along with the resonances for 1: three hydride signals, as dd at δ 3.56 for terminal Zr–H and δ −1.2 and −2.4 for bridged Zr–H (1 : 1 : 1 ratio); six resonances at δ 6.0, 6.2, 6.6, 6.7, 6.8 and 7.2 for the cyclopentadienyl ring protons; eight signals at δ 0.30, 0.34, 0.54, 0.57, 0.58, 0.74 and 0.81 which have been assigned to the methyl protons of the silanodiyl bridging groups. These spectral data are indicative of the formation of a new dinuclear zirconium species in which two non-equivalent bridging hydrides are maintained, whereas only one terminal hydride is present. Both zirconium centres show different coordination environments. This disposition makes the two metal atoms inequivalent, generating two sets of ABC spin system signals for the cyclopentadienyl protons and different resonances for the inequivalent eight methyl silanodiyl groups present. This behaviour is caused by the loss of the C_{2v} symmetry in the structural disposition of the final product.

All these data indicate that compound 1 reacts with traces of water (0.005%) present in THF-d_8, resulting in the selective hydrolysis of one of the terminal Zr–H bonds which is more reactive than the bridging hydrides. Addition of further amounts of H_2O or D_2O led to unidentifiable species.

3. Experimental section

All manipulations were performed under an inert atmosphere (dinitrogen or argon) using Schlenk and high vacuum line techniques or a VAC glove box Model HE 63P. Solvents were purified by distillation from an appropriate drying/deoxygenated agent (sodium for toluene and sodium/potassium alloy for hexane). LiBHEt$_3$ and LiBDEt$_3$ (Aldrich) were purchased and used without further purification. Zr(CpSi$_2$Cp)Cl$_2$ and Hf(CpSi$_2$Cp)Cl$_2$ [11c] were prepared according to literature procedures. NMR spectra were recorded on Varian Unity 300 and Varian Unity 500 Plus instruments (^1H, ^2H and ^{13}C chemical shifts were referenced to SiMe$_4$, $\delta = 0$ ppm). IR spectra were performed (Nujol mulls) on an 883 Perkin-Elmer spectrophotometer. Mass spectra were recorded on a Hewlett Packard 5890 spectrometer. Elemental C, H analyses were carried out on a Perkin-Elmer 240B microanalyzer.

3.1. Synthesis of [Zr(CpSi$_2$Cp)H(μ-H)]$_2$ (1)

A 1 M solution of LiBHEt$_3$ in THF (6.42 ml) was added dropwise to a toluene solution (50 ml) containing Zr(CpSi$_2$Cp)Cl$_2$ (1.36 g, 3.22 mmol), at −78°C. The reaction mixture was slowly warmed to room temperature and then stirred for 12 h. The colour of the solution turned dark blue-green. After filtration and evaporation

to dryness a solid was obtained, which was recrystallized from toluene/hexane at $-78°C$ giving compound **1** as brown–white crystals (yield 0.49 g, 46%).

Anal. Found: C, 49.56; H, 5.46. $C_{28}H_{44}Si_4Zr_2$. Calc.: C, 50.11; H, 5.96%. IR (Nujol mull cm^{-1}) $\nu(Zr-Hb) = 996$. Electron impact mass spectrum (70 eV) $m/z = 666$ (100%) $[M-2H_t]^+$.

3.2. Synthesis of [Hf(CpSi₂Cp)H(μ-H)]₂ (2)

The same procedure (Section 3.1) used to synthesize **1** from $Hf(CpSi_2Cp)Cl_2$ (1.22 g, 2.5 mmol) and 5 ml of a 1 M solution of LiBHEt₃ in THF gave 0.43 g (43% yield) of **2** as a brown–white solid.

The high instability made it impossible to obtain a reliable elemental analysis. IR (Nujol mull cm^{-1}) $\nu(Hf-H_t) = 1552$; $\nu(Hf-H_b) = 1070$. Electron impact mass spectrum (70 eV) $m/z = 840$ (50%) $[M-2H_t]^+$.

3.3. Synthesis of [M(CpSi₂Cp)D(μ-D)]₂ [M = Zr (3); Hf (4)]

The same procedure (Section 3.1) used to synthesize **1** and **2** using a 1 M solution of LiBDEt₃ in THF gave 0.32 g (50% yield) of **3** and 0.30 g (51% yield) of **4** as brown–white solids.

(3) ^1H NMR (C_6D_6, 300 MHz, 25°C): δ 0.30 (s, 6H, Si–CH₃), 0.51 (s, 6H, Si–CH₃), 0.53 (s, 6H, Si–CH₃), 0.54 (s, 6H, Si–CH₃), 6.04 (t, 4H, C_5H_3), 6.82 (t, 4H, C_5H_3), 7.32 (t, 4H, C_5H_3). ^2D NMR (C_7D_8, 46 MHz, 25°C): δ -3.41 (D$_b$), 3.21 (D$_t$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz., 25°C): δ -4.2, -3.1, 2.4, 2.6 (Si–CH₃), 99.8, 102.7 (C_{ipso} Cp), 108.0, 120.0, 122.7 (C_{1-3}, Cp). Electron impact mass spectrum (70 eV) $m/z = 668$ (20%)$^-[M-2H_t]^+$.

(4) ^1H NMR (C_6D_6, 300 MHz, 25°C): δ 0.030 (s, 6H, Si–CH₃), 0.42 (s, 6H, Si–CH₃), 0.44 (s, 6H, Si–CH₃), 0.47 (s, 6H, Si–CH₃), 5.78 (t, 4H, C_5H_3), 6.57 (t, 4H, C_5H_3), 7.19 (t, 4H, C_5H_3). ^2D NMR (C_7D_8, 46 MHz, 25°C): δ 1.04 (D$_b$), 8.17 (D$_t$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 25°C): δ -4.1, -3.1, 2.4, 2.6 (Si–CH₃), 98.9, 102.1 (C_{ipso} Cp), 106.1, 120.1, 122.1 (C_{1-3}, Cp). Electron impact mass spectrum (70 eV) $m/z = 842$ (5%) $[M-2H_t]^+$.

Acknowledgment

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