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Synthesis, Characterization, and Chemical Reactivity of Zirconium Dihydride $[(C_5H_4R)_2Zr(\mu\text{-}H)H]_2$ (R = $SiMe_3$, CMe_3). H/D Exchange Reactions of Anionic Species $[(C_5H_4R)_2ZrH_2]^-$. X-ray Crystal Structure of $[(C_5H_4SiMe_3)_2Zr(\mu\text{-}H)H]_2$

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The reaction of $(C_5H_4R)_2ZrCl_2$ with $LiAlH(OCMe_3)$ (or $NaAlH_2(OCH_2CH_2OCH_3)$) gives the dihydride complex $[(C_5H_4R)_2Zr(\mu\text{-}H)H]_2$ (R = $SiMe_3$ (**1**); R = CMe_3 (**2**)). The X-ray crystal structure of $[(C_5H_4SiMe_3)_2Zr(\mu\text{-}H)H]_2$, **1**, is described. The structure of the complex was resolved in the space group $Pn2_1a$ with a = 22.099(4) Å, b = 21.816(4) Å, c = 16.177(5) Å, and Z = 8. The structure was refined to R = 6.06 and R_w = 6.29. ESR studies were conducted to identify the paramagnetic Zr(III) species generated during the electrochemical or chemical reduction with various reductants (LiBu, LiMe, M(np) (M = Li, Na, K; np = naphthalenide)). The reduction process of **1** affords only one anionic paramagnetic species, $[(C_5H_4SiMe_3)_2ZrH_2]^-$, whereas two electrons are necessary to reduce the homodimetallic zirconium complex. H/D exchange is observed from $[(C_5H_4CMe_3)_2ZrD_2]^-$ *via* a C–H cyclopentadienyl activation process whereas, in the presence of H_2, $[(C_5H_4CMe_3)_2ZrH_2]^-$ is observed by EPR. Catalytic selective hydrogenation of 1,5- or 1,3-cyclooctadiene to cyclooctene is presented.

Introduction

Since its discovery in 1969, the chemistry of oligomeric $(Cp_2ZrHCl)_n$[1] has attracted a great deal of attention and has subsequently developed rapidly.[2] While a number of related metallocene dihydrides $[Cp'_2ZrH_2]_2$ (Cp′ = C_5H_4R) have been synthesized,[3,4] their chemistry remains less developed and mainly dimeric $[(C_5H_4Me)_2Zr(\mu\text{-}H)H]_2$ has been studied so far.[5,6]

The metal hydride chemistry is an attractive field of investigations, and we are interested in zirconium(III) hydride chemistry and in its application to hydrogenation catalysis. The replacement of a cyclopentadienyl ligand (C_5H_5) by a substituted cyclopentadienyl ligand (C_5H_4R) provides access to new physical properties in early transition metals and affords highly soluble products,[7] which are useful in homogeneous catalysis by comparison to insoluble $(Cp_2ZrHCl)_n$ or $[Cp_2ZrH(CH_2PPh_2)]_n$.[8]

A preliminary account of this work has been published,[9] and we now report the synthesis of zirconium hydrides $(Cp'_2ZrH_2)_2$ (Cp′ = $C_5H_4SiMe_3$ (**1**) or $C_5H_4CMe_3$ (**2**)) and the electrochemical and chemical reduction of **1** and **2** leading to Zr(III) anionic hydride species $(Cp'_2ZrH_2)^-$. The chemistry of these anionic species was monitored by ESR, and CH cyclopentadienyl activation and H/D exchange in Zr(III) species at the hydride position were observed. The catalytic selective hydrogenation of 1,5-COD (or 1,3-COD) to cyclooctene is presented. An X-ray crystal structure determination of **1** is given.

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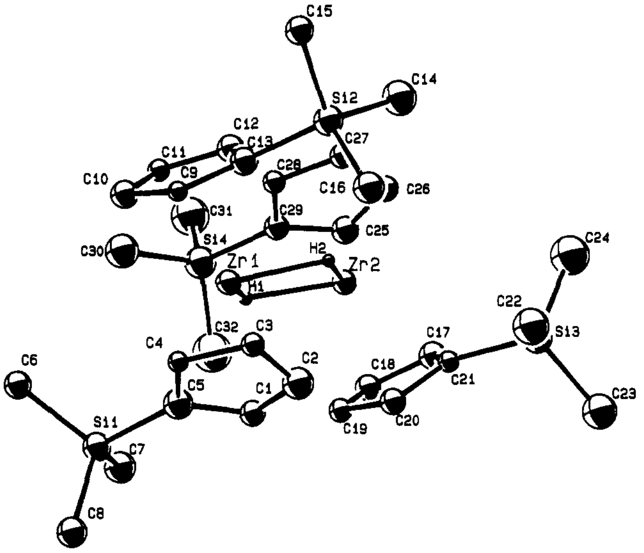

Figure 1. ORTEP drawing of a molecule of complex 1. Hydrogen atoms are omitted for clarity.

Results and Discussion

Synthesis, Spectroscopic Characterization, and Reactivity of $[(C_5H_4SiMe_3)_2Zr(\mu\text{-}H)H]_2$, 1, and $[(C_5H_4\text{-}CMe_3)_2Zr(\mu\text{-}H)H]_2$, 2. The basic synthetic methodology was used to prepare 1 and 2 from the corresponding zirconocene dichloride Cp'_2ZrCl_2 ($Cp' = C_5H_4SiMe_3$, $C_5H_4CMe_3$) and 2 equiv of $LiAlH(OCMe_3)_3$ in THF (or 2 equiv of $NaAlH_2(OCH_2CH_2OCH_3)_2$ in toluene). The presence of a substituted cyclopentadienyl ring allowed 1 and 2 to solubilize in hexane from which crystalline forms of both complexes were obtained.

^1H NMR resonance spectroscopy for 1 and 2 shows two sets of hydride peaks as a triplet for terminal (H_t) and bridged (H_b) hydrides (1 3.30 (H_t), −3.77 (H_b); 2 3.65 (H_t), −3.17 (H_b)), as already observed for the dimeric complex $[(C_5H_4Me)_2Zr(\mu\text{-}H)H]_2$.[6] Irradiation of one hydride site in 1 shows the expected formation of one singlet for the other hydride resonance at room temperature, but at 40 °C this signal begins to fade. The hydride exchange H_t–H_b is complete at 70 °C, as for the bis(indenyl) $[(C_9H_{11})_2Zr(\mu\text{-}H)H]_2$.[4a,b] The ^{13}C NMR spectra of 1 and 2 show the inequivalencies of the five cyclopentadienyl carbon atoms, and the withdrawing effect of the $SiMe_3$ substituent is observed.[10] No reaction occurs when 1 or 2 are under CO atmosphere at room temperature, as revealed by ^1H NMR spectra.

X-ray Crystal Structure of $[(C_5H_4SiMe_3)_2Zr(\mu\text{-}H)H]_2$. To ascertain the similarity between 1 and 2, since the X-ray structure of 2 had recently been published,[9] we have carried out the X-ray structure of 1. Details of the crystal structure determination are provided in the Experimental Data. The molecular structure of 1 shows two independent but very similar molecules in the unit cell, and Figure 1 is an ORTEP perspective view of one single molecule. Selected bond distances and bond angles are listed in Table I. The terminal hydrides were not located, but the dimeric structure with one bridging hydrogen atom between two zirconium atoms is confirmed. To minimize the steric hindrance, the Me_3Si groups have an eclipsed orientation. The presence of $SiMe_3$ or CMe_3 groups on the cyclopentadienyl rings has no significant effect on the structural parameters within the Zr_2H_2 core and can compare with the values observed in $[(C_5H_4Me)_2Zr(\mu\text{-}H)H]_2$[6] (Table II).

Table I. Bond Lengths (Å) and Angles (deg)[a]

molecule 1		molecule 2	
Zr(1)-H(1)	1.95	Zr(3)-H(3)	2.40
Zr(1)-H(2)	2.02	Zr(3)-H(4)	1.97
Zr(2)-H(1)	2.05	Zr(4)-H(3)	2.35
Zr(2)-H(2)	2.00	Zr(4)-H(4)	1.91
H(1)-H(2)	2.08	H(3)-H(4)	2.43
Zr(1)···Zr(2)	3.44	Zr(3)···Zr(4)	3.44
Cp-Zr(av)	2.21	Cp-Zr(av)	2.21
Zr(1)-H(1)-Zr(2)	118	Zr(3)-H(3)-Zr(4)	92
Zr(1)-H(2)-Zr(2)	117	Zr(3)-H(4)-Zr(4)	127
H(1)-Zr(1)-H(2)	62	H(3)-Zr(3)-H(4)	67
H(1)-Zr(2)-H(2)	62	H(3)-Zr(4)-H(4)	68
Cp(1)-Zr(1)-Cp(2)	128	Cp(3)-Zr(3)-Cp(4)	129
Cp(1)-Zr(1)-H(1)	115	Cp(3)-Zr(3)-H(3)	105
Cp(1)-Zr(1)-(H2)	109	Cp(3)-Zr(3)-H(4)	103
Cp(2)-Zr(1)-H(1)	115	Cp(4)-Zr(3)-H(3)	123
Cp(2)-Zr(1)-(H2)	102	Cp(4)-Zr(3)-H(4)	108

[a] Cp(1), Cp(2), Cp(3), and Cp(4) are the centroids of the C_5H_4 rings C(1)–C(5), C(9)–C(13), C(33)–C(37), and C(41)–C(45), respectively.

Table II. Interatomic Distances (Å) and Bond Angles (deg) for Dinuclear Zirconium Dihydride Complexes $[(C_5H_4R)_2Zr(\mu\text{-}H)H]_2$

compd	Zr-Ht	Zr-Hb	Zr-Hb-Zr'	HbZrHb'
1	*a*	2.00	118	62
2	1.82	2.00	121	59
$[(C_5H_4Me)_2Zr(\mu\text{-}H)H]_2$[b]	1.78	1.94 2.05	120	60

[a] Not located. [b] Reference 6a.

Electrochemical and Chemical Reduction of 1 and 2. Reduction potential data are obtained by cyclic voltammetry for 1 and 2 in THF solution at a Pt electrode in 10^{-2} M (NBu_4BF_4) with Cp_2Fe as standard. 1 and 2 reduce in a reversible diffusion-controlled two-electron process at −2.8 V (I_e/I_p = 145 mV) and −2.5 V (I_e/I_p = 100 mV) for 1 and 2, respectively. Another minor unidentified peak was observed at −2.5 V for 1 in the reductive wave. Oxidative voltammograms of 1 and 2 show an anodic peak at −0.65 and −0.4 V, respectively. Addition of $LiC_5H_4SiMe_3$ to a solution of 1 does not increase the intensity of the wave at −0.65 V but gives a new peak at +0.5 V. This experiment seems to prove that $(C_5H_4R)^0$ is not involved in the reductive process of 1 (or 2). As a reminder, $(C_5H_5)^0$ was identified as an oxidation wave at −0.2 V.[11]

In order to determine the nature of the reduced species, electrolysis of 1 was performed in an EPR cavity with a steady current flow of 20 μA. As previously published for 2 (g = 1.996; $a(^1H)$ = 8.4 G; $a(^{91}Zr)$ = 16.2 G),[9] 1 affords the same EPR signal, stable for several minutes, *i.e.* a 1:2:1 triplet attributed to the coupling of the unpaired electron with two magnetically equivalent hydrogen atoms as $[Cp'_2ZrH_2]^-$ (g = 1.996; $a(^1H)$ = 8.0 G; $a(^{91}Zr)$ = 17.6 G; Figure 2). Supplementary evidence for this anionic species comes from the electrochemical reduction of $[(C_5H_4\text{-}t\text{-}Bu)_2Zr(\mu\text{-}D)D]_2$ in the ESR tube.[9] The chemical reduction of 1 or 2 with sodium, potassium, or lithium naphthalenide M(np) (M = Li, Na, or K) exhibits an intense ESR spectra consisting of a quartet of triplets due to interaction of an unpaired electron with two hydrogen atoms and with the nuclear spin of the alkali metal (I = $^3/_2$) (Figures 3–5). Complete chemical reduction of 1 and

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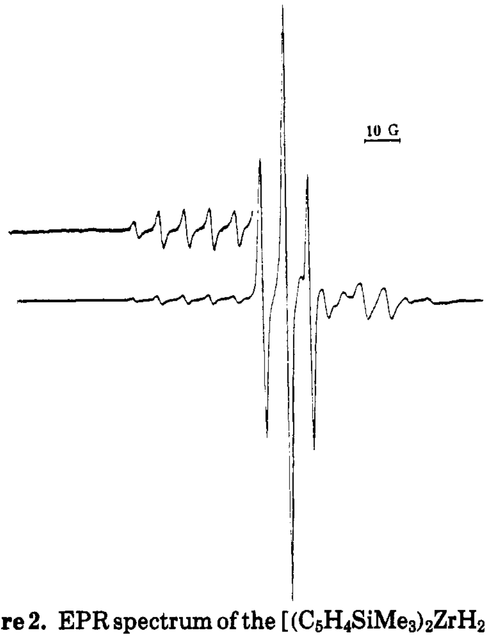

Figure 2. EPR spectrum of the $[(C_5H_4SiMe_3)_2ZrH_2]^-$ radical anion at 283 K produced by electrochemical reduction of **1** in THF inside the cavity of the EPR spectrometer and expanded view (×10) for a portion of the Zr hyperfine signals (^{91}Zr, 11.3% natural abundance, $I = {}^5/_2$).

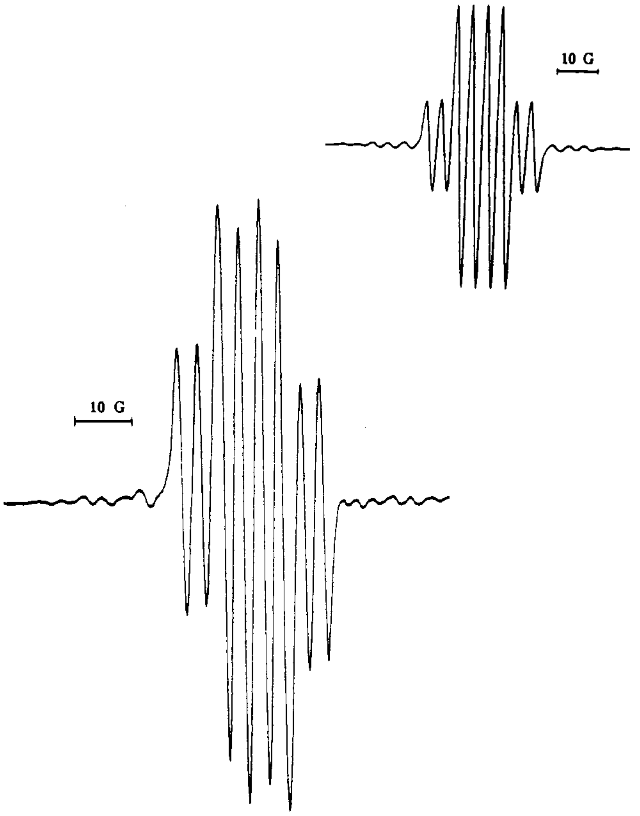

Figure 3. EPR spectra of $[(C_5H_4SiMe_3)_2ZrH_2]^-Li^+$ at room temperature produced by chemical reduction of **1** with Li(np) in THF: (a) experimental; (b) computer simulation assuming electron interaction with one lithium nucleus ($I = {}^3/_2$, 100%).

2 with Na(np) was assumed with paramagnetic moment measurements by Evans' method[14] (1.7 μ_B is closely obtained for $[\mathbf{1}]^-$ and $[\mathbf{2}]^-$, respectively). The simulation of experimental spectra leads to calculated $a(^1H)$, $a(^{91}Zr)$, and $a(^{3/2}M)$ (M = Li, Na, or K) values (Table III) in agreement with the formation of $[(C_5H_4R)_2ZrH_2]^-M^+$ paramagnetic species.

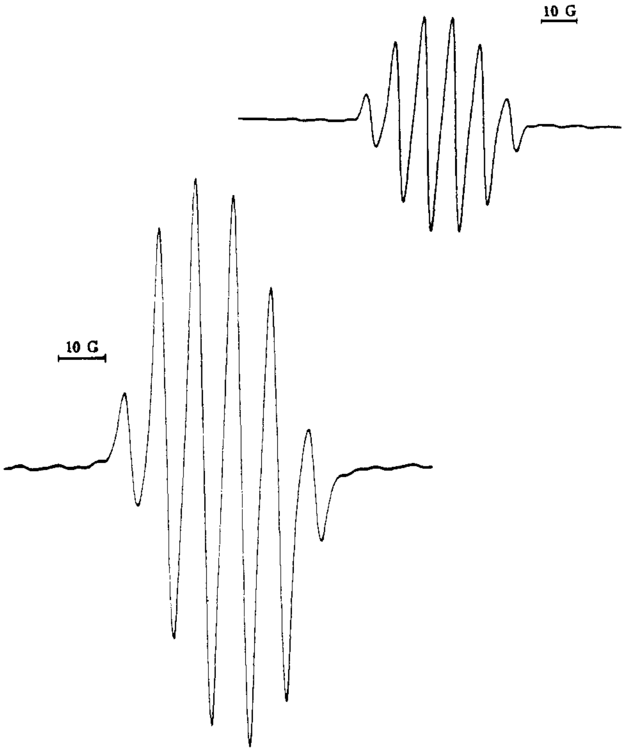

Figure 4. EPR spectra of $[(C_5H_4SiMe_3)_2ZrH_2]^-Na^+$ at room temperature produced by the chemical reduction of **1** with Na(np) in THF: (a) experimental; (b) computer simulation assuming electron interaction with one sodium nucleus ($I = {}^3/_2$, 100%).

In attempts to determine the different steps of the overall phenomenon, observed by cyclic voltammetry and combined with electrochemical reduction in the EPR cavity, the ferrocene/ferrocenium couple was used as an internal standard in the cyclic voltammetry of **1** at 0.01 V/s and a two-electron reduction was involved in the electrochemical reduction process. Still, only one EPR signal was detected in our experimental reductions and it was not possible to predict the mechanism of dissociation of **1** and **2** to the anionic $[(C_5H_4R)_2ZrH_2]^-$. Reasonable postulated EC mechanisms are shown in Scheme I, and the formation of the dimeric anionic species $[(C_5H_4R)_2ZrH_2]_2^-$ or $[(C_5H_4R)_2ZrH_2]_2^{2-}$ is suggested prior to the formation of the monomeric anionic species $[(C_5H_4R)_2ZrH_2]^-$.

Treatment of a THF solution of **1** or **2** with LiMe or LiBu as a reductant revealed by EPR that anionic $[(C_5H_4R]_2ZrH_2]^-Li^+$ was formed. Attempts to isolate Zr(III) hydride anionic species with crown ethers[12] (benzo-15-crown-5, 18-crown-6, 12-crown-4) or *via* cation exchange reactions (PPN^+Cl^-, $N(hexyl)_4BF_4$, $Rh(COD)(PPh_3)_2BPh_4$) have failed.

CH Cyclopentadienyl Activation, H/D Exchange with Molecular H_2. The chemistry of Zr(III) hydride species[13] has drawn little attention in comparison with

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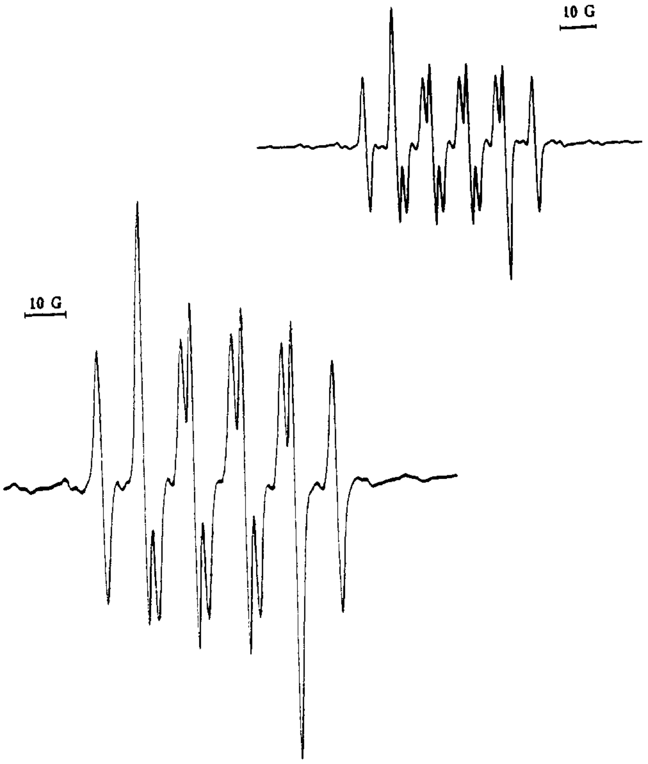

Figure 5. EPR spectra of $[(C_5H_4CMe_3)_2ZrH_2]^-Na^+$ at room temperature produced by the chemical reduction of 1 with Na(np) in THF: (a) experimental; (b) computer simulation assuming electron interaction with one sodium nucleus ($I = {}^3/_2$, 100%).

Table III. EPR Parameters of Anionic $[(C_5H_4R)_2ZrH_2]^-M^+$ Compounds Characterized in Solution

compd	M	g	$A(^{91}Zr)$ (G)	$a(^1H)$ (G)	a(M) (G)
$[1]^-M^+$	Li	1.994	8.1	7.3	3.6
	Na	1.995	12.8	8.9	8.9
	K	1.996	14.7	8.2	1.8
$[2]^-M^+$	Li	1.993	*a*	7.8	3.9
	Na	1.992	10.4	8.3	10.1
	K	1.994	14.4	8.5	2.0

[a] Unobserved experimentally.

Scheme I

a) $[Cp'_2Zr(\mu\text{-}H)H]_2 + e^- \Leftrightarrow [Cp'_2Zr(\mu\text{-}H)H]_2^-$

$[Cp'_2Zr(\mu\text{-}H)H]_2^- \Leftrightarrow [Cp'_2ZrH_2]^- + [Cp'_2ZrH_2]$

$[Cp_2ZrH_2] + e^- \Leftrightarrow [Cp'_2ZrH_2]^-$

$2[Cp'_2ZrH_2] \Leftrightarrow [Cp'_2Zr(\mu\text{-}H)H]_2$

b) $[Cp'_2Zr(\mu\text{-}H)H]_2 + e^- \Leftrightarrow [Cp'_2Zr(\mu\text{-}H)H]^-_2$

$[Cp'_2Zr(\mu\text{-}H)H]^-_2 + e^- \Leftrightarrow [Cp'_2Zr(\mu\text{-}H)H]^{2-}_2$

$[Cp'_2Zr(\mu\text{-}H)H]^{2-}_2 \Leftrightarrow 2[Cp'_2ZrH_2]^-$

the analogous Zr(IV) hydride systems.[2,15] Regarding this point, our initial report on the formation of the anionic Zr(III) species $[Cp'_2ZrH_2^-]$ and $[Cp'_2ZrD_2]^-$, generated by

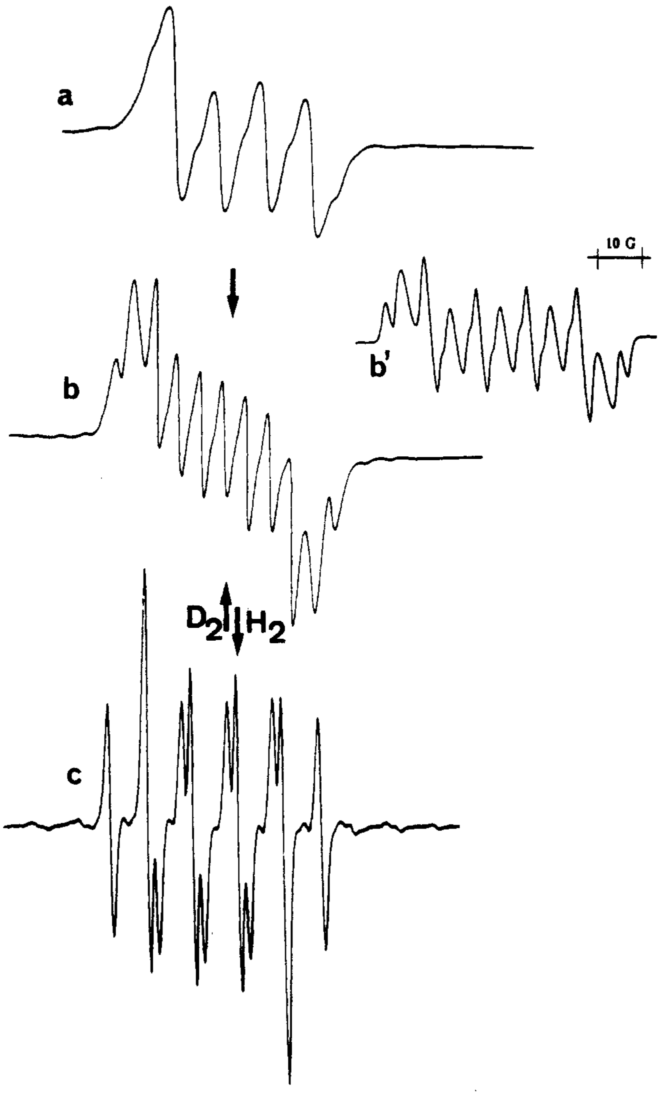

Figure 6. EPR spectra of H/D exchange with anionic Zr(III) species. (a) EPR spectrum of $[(C_5H_4CMe_3)_2ZrD_2]^-Na^+$ at room temperature produced by chemical reduction of **2d** with Na(np) in THF. (b) and (b′) Evolution of EPR spectrum of $[(C_5H_4CMe_3)_2ZrD_2]^-Na^+$ (a) at room temperature after a few minutes, analyzed by computer simulation as a mixture of $[(C_5H_4CMe_3)_2ZrD_2]^-Na^+$, $[(C_5H_4CMe_3)_2ZrHD]^-Na^+$, and $[(C_5H_4CMe_3)_2ZrH_2]^-Na^+$ (36%, 55%, and 9%, respectively. (c) Evolution of (b) under H_2 atmosphere leading to $[(C_5H_4CMe_3)_2ZrH_2]^-Na^+$.

electrolysis of **2** or $[(C_5H_4CMe_3)_2Zr(\mu\text{-}D)D]_2$, **2d**, respectively, could provide a direct EPR test to explore the H_2 molecular activation with Zr(III) hydride complexes.

The reaction of **1** and **2** with D_2 (1 atm) or labeled complexes $[(C_5H_4R)_2Zr(\mu\text{-}D)D]_2$, **1d** (R = SiMe$_3$), **2d** (R = CMe$_3$), with H_2 (1 atm) was monitored by ^{1}H NMR for 2 weeks at room temperature, and during this time no H/D exchange was observed at the hydride sites.

In contrast, exchange processes occurred rapidly with Zr(III) hydride species. Chemical reduction of **2d** with sodium naphthalenide Na(np) in THF gave the characteristic EPR spectrum of $[(C_5H_4CMe_3)_2ZrD_2]^-Na^+$ (g = 1.995; ΔB = 2 G; $a(^{23}Na)$ = 8.9 G; $a(^2D) = {}^1/_6 a^1(H)$ which is small enough to prevent resolution of the ^{2}D hyperfine coupling; Figure 6a). This species is transformed within a few minutes into another complicated stable EPR signal (Figure 6b) analyzed by computer simulation as a mixture of $[(C_5H_4CMe_3)_2ZrD_2]^-Na^+$ (36%), $[(C_5H_4CMe_3)_2ZrHD]^-Na^+$ (55%), and $[(C_5H_4CMe_3)_2ZrH_2]^-Na^+$ (9%) (Figure 6b′). When the reaction is performed with **2d**, deuterated

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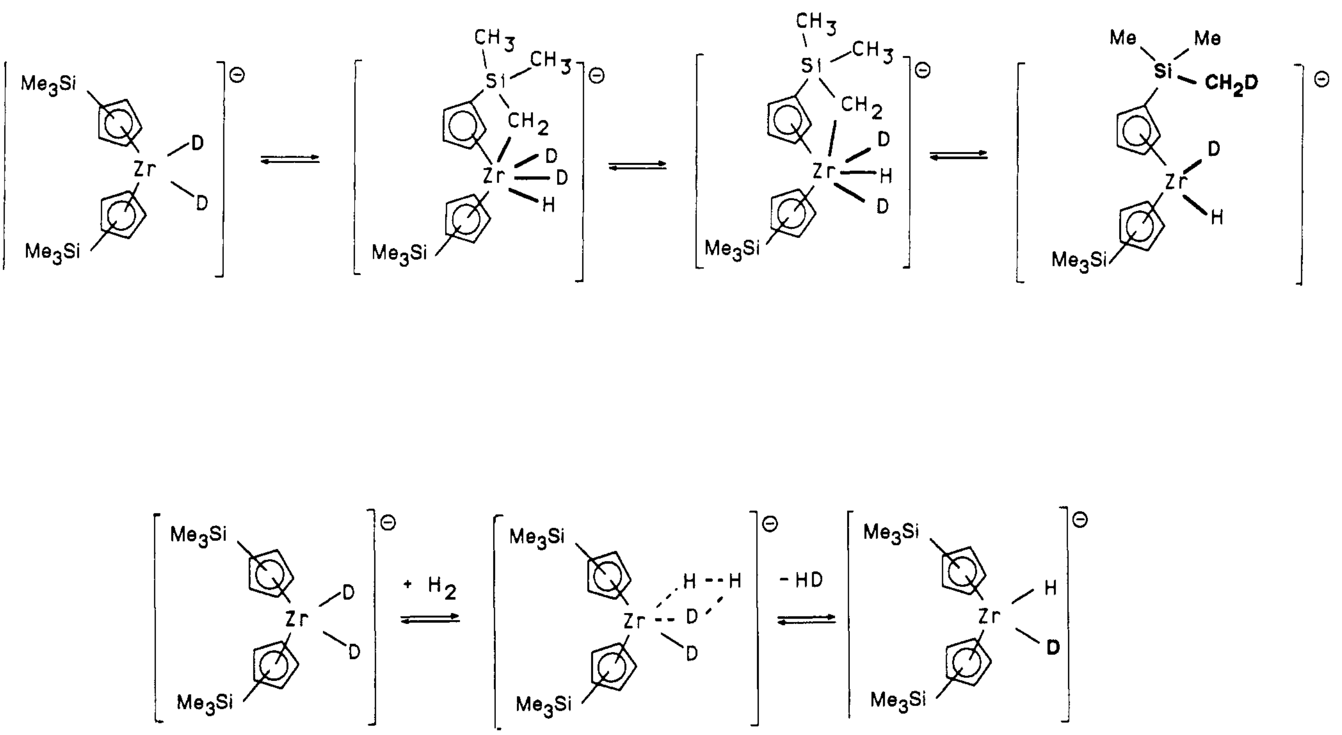
Scheme II



THF, and deuterated naphthalene, a similar EPR evolution is observed which precludes the H/D exchange at the hydride sites between $[(C_5H_4CMe_3)_2ZrD_2]^-$ species and one hydrogen from the solvent or the naphthalene. Investigations in order to improve mechanisms by which Zr(III) hydride exchanges H/D were difficult to operate under EPR techniques. An applicable method is the conversion of Zr(III) hydride species as their diamagnetic dichloride analogues[15] to test the presence of D on the cyclopentadienyl ring. EPR solutions of the mixture $[[Zr]D_2]^-$, $[[Zr]HD]^-$, and $[[Zr]H_2]^-$ prepared from **1d** or **2d** and Na(np) were oxidized with HCl to $(C_5H_4CMe_3)_2ZrCl_2$ and $[(C_5H_4SiMe_3)_2ZrCl_2$, respectively (identified by $^1H^{10}$). In this dichloride series, ^2H NMR spectra show evidence of incorporation of D mainly in CMe_3 or $SiMe_3$ sites but also to a lesser extent in the C_5H_4R ring (we are unable to distinguish the incorporation of D between the α or β sites of the C_5H_4R ring[19]). The EPR solution of the mixture $[[Zr]D_2]^-$, $[[Zr]HD]^-$, and $[[Zr]H_2]^-$ under H_2 atmosphere at room temperature affords the characteristic spectrum of anionic dihydride $[(C_5H_4CMe_3)_2ZrH_2]^-Na^+$ within 2 h, showing that the H_2 activation process is complete (Figure 6c to be compared to Figure 5). Mass spectral analysis of the gas above the THF solution shows the presence of HD in the gas phase. Reversibility of this H/D exchange process is operating when H_2 is replaced by D_2 atmosphere to give the EPR spectrum of the mixture described above. This EPR spectral feature is not modified under a slight pressure of D_2 in the EPR tube.

From the literature[8b,16–19] and from our studies, it is clear that two independent mechanisms are operative in the H/D exchange process in anionic zirconium hydride: (i) the H/D exchange observed in the chemical reduction of **2d** (or **1d**) as well as the presence of deuterated sites on the C_5H_4 ring and CMe_3 or $SiMe_3$ substituents confirm the participation of the cyclopentadienyl ring and the substituted R group bonded to the cyclopentadienyl ring[17] (CH cyclopentadienyl activation was recently demonstrated in Ti(III)[18] and cationic Zr(IV)[19] chemistry; (ii) the presence of HD above the THF EPR solution indicates a heterolytic cleavage of H_2 (or D_2), previously postulated in zirconium(IV). Activation of the alkyl substituent as the most important process in the H/D exchange chemistry of anionic Zr(III) and as a simple explanation of our observations is summarized in Scheme II and consistent with previous works on pentamethylcyclopentadienyl ligand activation. To take into account the presence of D on the cyclopentadienyl ring, a reversible metal-to-ring hydride transfer is assumed to involve an apparent intramolecular Zr(I)–Zr(III) pathway capable of exchange with D_2 according to a four-center mechanism (Scheme III).

Anionic Zirconium(III) Hydrides as Olefin Hydrogenation Catalysts. An extension of the chemistry described above is the application of Zr(III) species to catalytic hydrogenation purposes. Selective hydrogenation of 1,3- or 1,5-cyclooctadiene (COD) to selective cyclooctene was recently achieved with $[Cp_2ZrH(CH_2PPh_2)]_n$ as catalyst.[8a] Complex **2** had already been tested in the hydrogenation of some alkenes, and total conversion to their corresponding alkanes was observed.[8c] In our experimental conditions, *i.e.* 80 °C, 40 bars of H_2, THF as solvant, [substrate]/[catalyst] = 300, **1** and **2** as well as anionic $[Cp'_2ZrH_2]^-M^+$ ($Cp' = C_5H_4SiMe_3$, C_5H_4-*t*-Bu; M = Li, Na, K) were used with 1,3- or 1,5-COD as substrates and the catalytic reaction was monitored by GC analysis.

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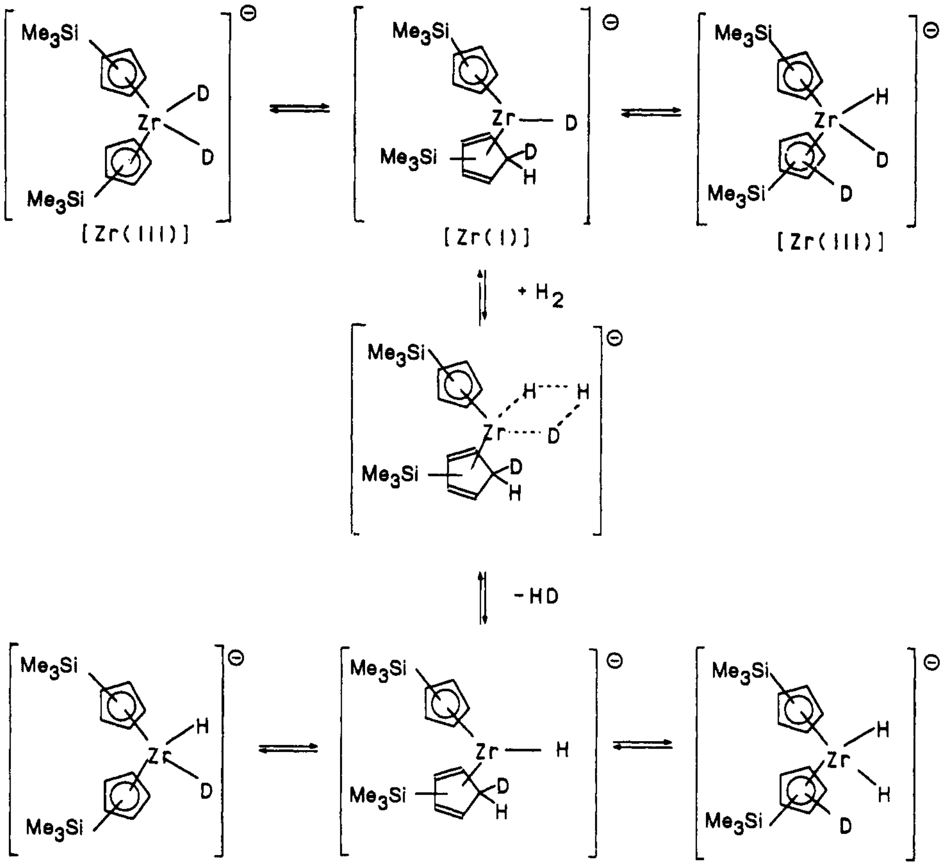
[19] Guo, Z.; Bradley, P. K.; Jordan, R. F. *Organometallics* **1992**, *11*, 2690 and references therein.

Scheme III



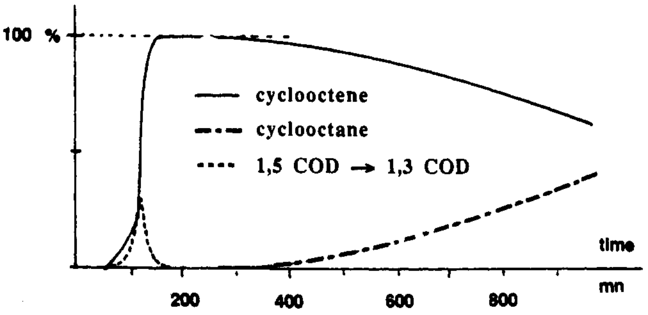


Figure 7. Plot of the conversion of 1,5-COD to cycloctene, cyclooctane, and 1,3-COD versus time (min) with 2.

Table IV. Catalytic Hydrogenation of 1,5-COD by 1, 2, and Anionic [(C$_5$H$_4$R)$_2$ZrH$_2$]$^-$M$^+$ Compounds

compd	conversion time of 1,5-COD to cyclooctene (min)	conversion time of 1,5-COD to 50% cyclooctane (h)
1	80	5
[1]$^-$M$^+$		
M = Li	50	7
Na	55	7
K	65	7
2	180	7.5
[2]$^-$Na$^+$	80	7

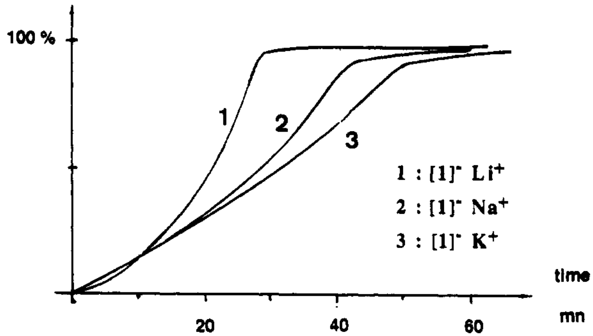


Figure 8. Plot of the conversion of 1,5-COD to cyclooctene versus time (min), with [(C$_5$H$_4$SiMe$_3$)$_2$ZrH$_2$]$^-$Li$^+$, [(C$_5$H$_4$SiMe$_3$)$_2$ZrH$_2$]$^-$Na$^+$, and [(C$_5$H$_4$SiMe$_3$)$_2$ZrH$_2$]$^-$K$^+$ (curves 1–3, respectively).

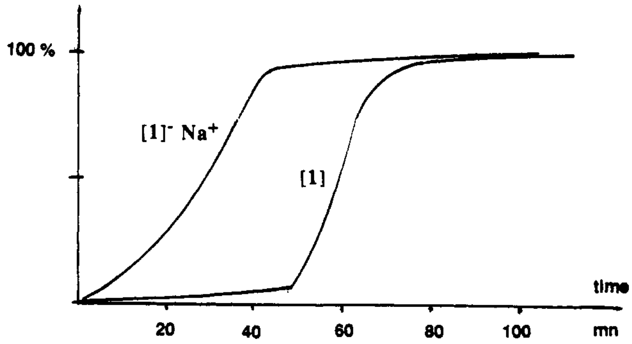


Figure 9. Plot of the conversion of 1,5-COD to cyclooctene versus time (min) with [(C$_5$H$_4$SiMe$_3$)$_2$ZrH$_2$]$^-$Na$^+$ and 1.

Whatever the catalyst, the catalytic hydrogenation of 1,3- or 1,5-COD to selective cyclooctene was complete within a few hours whereas the formation of cyclooctane appeared after a longer reaction time (50% cyclooctane is formed after 7 h of reaction) (Table IV; Figure 7). It was found that 1 and anionic species originating from 1 are more active than 2 and its related anionic species and that a slight difference in the hydrogenation rate is observed depending on the counteranion used, Li > Na > K (Table IV; Figure 8), presumably related to the ion-pairing of the couple [Zr]$^-$M$^+$. If we focus on the first step of the catalytic reaction, the hydrogenation rate of neutral and anionic species is different and an inductive period of 1–2 h is observed for 1 and 2 (Figure 9). During this inductive period, 1,5-COD does not isomerize into 1,3-COD and no change is observed by GC in the catalytic mixture. In order to understand the beginning of the catalytic reaction between 1 or 2 and their anionic species, we investigated the stoichiometric reaction at 80 °C under an H_2 atmosphere of these zirconium hydride complexes in the presence of 1,3-COD using the EPR technique (1,3-COD was chosen preferentially to 1,5-COD to avoid an isomerization process). A Zr(III) hydride species ($g = 1.988$; $a(^1H) = 6.3$ G) is observed in low yield (paramagnetic moment measurements by Evans' method reveal that no more than 10–20% Zr(III) hydride species is obtained) after 15 min of heating at 80 °C with 1 or immediately at room temperature with $[1]^-Na^+$. This Zr(III) hydride species was also obtained for 20 h at 80 °C by thermolysis of 1 or 2, but during this period other unidentified paramagnetic species are observed. Thermolysis of $[(C_5H_4Me)_2Zr(\mu\text{-}H)H]_2$ led to the only hydride species $(C_5H_4Me)_2ZrH$ ($g = 1.985$; $a(^1H) = 6.8$ G) within a few minutes.[17b] The ^1H NMR spectrum of $[1]^-Na^+$ in deuterated THF with 1,3-COD could not be registered due to the strong paramagnetism of the solution. The ^1H NMR spectrum of 1 in the presence of 1,3-COD after 1 h of thermolysis at 80 °C showed the disappearance of 1,3-COD, the formation of cyclooctene, the absence of the hydride signals of the starting material, and the formation of new $C_5H_4SiMe_3$ resonances which are not readily interpretable. On the other hand, the inductive period observed for 1 and 2 and the thermolytic experiments made in the presence of 1,3-COD provide significant evidence that this period is necessary in order to prepare potentially active Zr(III) or other reduced species valuable for hydrogenation catalysis. Although the hydrogenation rates of 2 and $[2]^-Na^+$ are quite similar, not considering the inductive period, we cannot conclude that they have the same hydrogenation rate due to the restricted experiments performed. But the main feature remains the selective formation of cyclooctene in the first step of the catalysis where only cyclooctene was detected as the sole organic compound after the total consumption of 1,5- or 1,3-COD within 30–60 min according to the catalyst, if we abstract the inductive period observed for 1 and 2. At this stage, an additional charge of 1,5- or 1,3-COD could be done without loss of selectivity toward cyclooctene and with approximately the same hydrogenation rate (no cyclooctane was detected by GC analysis; at least three additional charges of 1,3-COD were successively added with $[Cp'_2ZrH_2]^-M^+$ ($Cp' = C_5H_4SiMe_3$; M = Na) as catalyst).

It was also found that the isomerization process from 1,5- to 1,3-COD occurred with 1 and 2 in the absence of hydrogen after an inductive period of 1 h at 80 °C and was completed within 2 h whereas no inductive period was required with anionic species and complete isomerization occurred in 1 h at 80 °C (at 20 °C, 75% 1,3-COD is recovered and 90% after 24 h).

Concluding Remarks

From these studies it is clear that the R substituent on the cyclopentadienyl ring does not change fundamentally the structure of the bimetallic Zr hydride but enhances the solubility in organic solvants such as hexane or pentane. The Zr(III) hydride anionic species exchange easily molecular H_2 at the hydride sites, but also participation of the cyclopentadienyl ring (*via* CH activation of the cycle and R substituent) is fast when Zr(IV) is reduced to Zr(III) species, as demonstrated by EPR. Selective formation of cyclooctene is obtained in the catalytic hydrogenation of 1,3- or 1,5-COD with anionic Zr(III) species, and the participation of a mononuclear Zr species is usually suggested for the hydrogenation of olefins.[8a] Due to the facile H/D exchange observed in anionic Zr(III) hydride species, it is conceivable that Zr atoms at different oxidation states could potentially provide several pathways in the catalytic cycle. Further efforts on the characterization of such species will be carried out.

Experimental Data

All manipulations were carried out under inert atmosphere (argon) by conventional Schlenk tube techniques or using a drybox (Vacuum Atmosphere Dri-Lab) filled with nitrogen. Liquids were transferred *via* syringe or cannula. All solvents were dried and distilled under argon and degassed before use. ^1H, ^2H, and ^{13}C NMR spectra were recorded on a Bruker WH 90 or WM 250 spectrometer. ESR spectra were recorded on a Bruker ER 200 T spectrometer. Elemental analyses were performed by the Service Central de Microanalyse du CNRS. A "homemade microcomputer-controlled instrument" with ohmic resistance compensation was used for cyclic voltammetry studies. A platinum auxiliary electrode and a SCE reference electrode were used in conjunction with a platinum disk electrode as the working electrode. NBu_4PF_6 was used as the supporting electrolyte for cyclic voltammetry studies. It was melted under vacuum before use to ensure efficient dehydration. GC analyses were performed on an Intersmat IGC 121 apparatus. Cp'_2ZrCl_2 ($Cp' = C_5H_4SiMe_3$, $C_5H_4CMe_3$) was prepared by published procedures.[10] M(np) (M = Li, Na, K) was prepared from a mixture of a known weight of naphthalene and an excess of freshly cut M in 0.5 mL of THF with stirring for 2 h.

Preparation of $[(C_5H_4SiMe_3)_2Zr(\mu\text{-}H)H]_2$, 1. To a solution of $(C_5H_4SiMe_3)_2ZrCl_2$ (5.5 g, 12.6 mmol) in 30 mL of THF was added a slight excess of $LiAlH(OCMe_3)_3$ (7.8 g, 30.26 mmol) in THF (or 4.3 mL of $NaAlH_2(OCH_2CH_2OCH_3)_2$ (70% in toluene)). The mixture was stirred for 1 day at room temperature and evaporated to dryness. Hexane (100 mL) was then added and the solution filtered on Celite to remove LiCl (or NaCl). The resulting solution was concentrated to 20 mL and left overnight at −30 °C to give colorless crystals suitable for X-ray analysis. Microcrystals of 1 were separated by filtration. ^1H NMR (C_6D_6), δ (ppm): 6.10, 5.73, 5.39, 5.29 (m, C_5H_4); 0.32 (s, $SiMe_3$); 3.30 (t, $J_{HH} = 7.4$ Hz, H_t); −3.77 (t, $J_{HH} = 7.4$ Hz, H_b). ^{13}C NMR (C_6D_6), δ (ppm): 113.30 (s, substituted C, C_5H_4); 110.1, 109.1, 105.7, 104.7 (m, C_5H_4); 1.2 (q, $J_{CH} = 120$ Hz, $SiMe_3$). Yield: 3.2 g (70%). Anal. Calcd for $C_{16}H_{28}Si_2Zr$: C, 52.29; H, 7.60; Zr, 24.79. Found: C, 52.17; H, 7.84; Zr, 24.70.

Preparation of $[(C_5H_4CMe_3)_2Zr(\mu\text{-}H)H]_2$, 2. The same procedure as above was used. Starting from $(C_5H_4\text{-}t\text{-}Bu)_2ZrCl_2$ (5.0 g, 12.37 mmol) and $LiAlH(OCMe_3)_3$ (7.66 g, 29.7 mmol) in THF, microcrystalline 2 was obtained (2.0 g, 50%). ^1H NMR (C_6D_6), δ (ppm): 5.90, 5.50, 5.14, 4.98 (m, C_5H_4); 1.33 (s, CMe_3); 3.65 (t, $J_{HH} = 7.2$ Hz, H_t); −3.17 (t, $J_{HH} = 7.2$ Hz, H_b). ^{13}C NMR (C_6D_6), δ (ppm): 140.50 (s, substituted C, C_5H_4); 101.66, 101.19, 99.56, 98.0 (m, C_5H_4); 32.68 (q, $J_{CH} = 125$ Hz, CMe_3); 32.19 (s, CMe_3). Yield: 3.5 g (50%). Anal. Calcd for $C_{18}H_{28}Zr$: C, 64.48; H, 8.36; Zr, 27.16. Found: C, 64.60; H, 8.47; Zr, 26.90.

Chemical Reduction of 1 (or 2) with M(np). In a typical procedure, 1 (100 mg, 0.135 mmol) in 0.5 mL of THF was treated with 1.1 equiv of a THF solution of sodium naphthalenide per Zr atom (prepared from a mixture of naphthalene (40 mg, 0.312 mmol) and excess sodium in 0.5 mL of THF with stirring for 2 h). The brown, dark solution was stirred for 5 min and placed in ESR tubes with or without substrate (TMEDA, benzo-15-crown-5, 18-crown-6, and 12-crown-4). The tubes were sealed and the solutions monitored by ESR as well as ^1H NMR techniques. ESR THF solutions of $[1]^-Na$ with 1 or 2 equiv or excess of TMEDA or benzo-15-crown-5 were unchanged; $[1]^-Na$ with 1 or 2 equiv of 18-crown-6 immedialy afforded a new ESR spectrum [one singlet ($g = 1.987$) and one doublet ($g = 1.993$; $a(^1H) = 6.6$ G)]; $[1]^-Li^+$ and 12-crown-4 also gave one doublet ($g = 1.991$; $a(^1H) = 8.2$ G). These results show that a monohydride Zr(III) species is formed by adding crown ethers and that the

Table V. Crystallographic Data for $[(C_5H_4SiMe_3)_2Zr(\mu\text{-}H)H]_2$, 1, and Structure Determination Details

formula	$C_{48}H_{84}Si_6Zr_3$
fw	1103
system	orthorhombic
space group	$Pn2_1a$
a, Å	22.099(9)
b, Å	21.816(8)
c, Å	16.177(7)
V, Å^3	7799(2)
Z	8
d_{calc}, g cm^{-3}	2.41
μ(Mo Kα), cm^{-1}	12.78
2θ range, deg	$3 < 2\theta < 60$
scan type	$\omega/2\theta$
scan width, deg	$0.9 + 0.347 \tan\theta$
scan speed, deg min^{-1}	variable
diffractometer	Enraf-Nonius CAD4
no. of unique reflctns	11 580
no. of reflctns with $I < 3\sigma(I)$	4074
no. of refined params	630 (refined in two independent blocks)
R^a	0.0606
$R_w{}^b$	0.0629

[a] $R = \sum||F_o| - k|F_c||/S|F_o|$. [b] $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w F_o{}^2]^{1/2}$.

dihydride species disappeared and were not trapped. Reaction of $[1]^-Na$ with PPN^+Cl^-, $N(Hexyl)_4BF_4$, and $Rh(COD)(PPh_3)_2$-BPh_4 led to decoloration of the solution with evolution of H_2 (identified by MS).

Chemical Reduction of 1 (or 2) with LiR (R = Me, Bu). To 1 (0.10 g, 0.135 mmol) in 10 mL of THF was added 1.2 equiv of LiR per Zr atom (LiMe, 5% in hexane; LiBu, 15% in hexane), and the mixture was stirred for 15 min. The final red-brown solution was transferred to an ESR tube with or without substrate (TMEDA, 1, 2, or 10 equiv), which was sealed and monitored by ESR.

Thermolytic Experiments. An NMR tube (or a quartz ESR tube) containing a weighted amount of 1 with or without substrate was filled with deuterated or undeuterated solvent. The NMR tube was sealed and heated with a sand bath at 80 °C. ^1H and ESR spectra were monitored from time to time to follow the evolution of the reaction.

H/D Exchange with Anionic Zr(III) Species. The glass reaction vessel was composed of an ESR tube sealed to a Schlenk tube (20 mL), allowing the zirconium complex to separate from the reductant before EPR analysis. **1d** (0.1 g, 0.135 mmol) in the ESR tube and 2.2 equiv of Na(np) in THF (1 mL) in a 20-mL Schlenk tube were mixed just before ESR measurement to follow the evolution of the spectra. The resulting solution was then cooled with liquid nitrogen and the volume of the reaction vessel evacuated and filled with H_2 or D_2. The reaction solution was warmed to room temperature, and ESR spectra were registered. In an another experiment, the EPR solution of **1d** and 2.2 equiv of Na(np) is oxidized at −30 °C with HCl (prepared from an excess of Me_3SiCl and 2.2 equiv of MeOH) to give partially deuterated $(C_5H_4SiMe_3)_2ZrCl_2$ analyzed by ^1H and ^2H NMR. The same reaction was performed with **2d** to give partially deuterated $(C_5H_4\text{-}t\text{-}Bu)_2ZrCl_2$. An approximate ratio of 4:1 is observed by ^2H NMR in the incorporation of D between $SiMe_3$ or CMe_3 sites and the C_5H_4 ring according to different experiments.

General Procedure for Catalytic Experiments. Catalytic tests were carried out in a 75-mL capacity autoclave. The temperature was maintained at 80 °C through oil circulation in a double jacket. The gas was admitted from a 125-mL gas tank, and the fall in pressure in the tank was followed with a pressure gauge connected to an electronic measurement and recording

Table VI. Fractional Atomic Coordinates and Isotropic Thermal Parameters (Å^2) with Estimated Standard Deviations in Parentheses for the Non-Hydrogen Atoms of 1

atom	x/a	y/b	z/c	U(iso)	atom	x/a	y/b	z/c	U(iso)
Zr(1)	0.30062(6)	0.2490(1)	0.1208(1)	0.0435	Zr(3)	0.12447(9)	0.83041(7)	0.1228(1)	0.0421
Zr(2)	0.45606(6)	0.2537(1)	0.1208(1)	0.0438	Zr(4)	0.12171(9)	0.67243(8)	0.1214(1)	0.0470
C(1)	0.3035(6)	0.2345(6)	0.271(1)	0.0514	C(33)	0.1384(6)	0.8292(6)	−0.033(1)	0.0602
C(2)	0.2896(8)	0.2980(5)	0.266(1)	0.0665	C(34)	0.0752(5)	0.8384(6)	−0.019(1)	0.0438
C(3)	0.2354(8)	0.3038(5)	0.222(1)	0.0426	C(35)	0.0675(6)	0.8947(6)	0.022(1)	0.0524
C(4)	0.2096(5)	0.2447(6)	0.215(1)	0.0454	C(36)	0.1258(7)	0.9207(5)	0.033(1)	0.0392
C(5)	0.2515(7)	0.2011(3)	0.246(1)	0.0571	C(37)	0.1700(4)	0.8809(7)	−0.001(1)	0.0576
C(6)	0.1948(8)	0.0877(8)	0.165(1)	0.0727	Si(5)	0.2517(3)	0.8988(3)	−0.0158(4)	0.0617
Si(1)	0.2374(3)	0.1164(2)	0.2560(4)	0.0560	C(38)	0.2585(9)	0.9499(7)	−0.1078(9)	0.0651
C(7)	0.3115(6)	0.0757(7)	0.266(1)	0.0711	C(39)	0.282(1)	0.9386(9)	0.077(1)	0.0980
C(8)	0.1907(9)	0.103(1)	0.3504(9)	0.0817	C(40)	0.2940(9)	0.8259(7)	−0.034(1)	0.1146
C(9)	0.2149(6)	0.2884(7)	0.034(1)	0.0410	C(41)	0.0802(8)	0.9132(6)	0.214(1)	0.0581
C(10)	0.2238(8)	0.2272(6)	0.006(1)	0.0561	C(42)	0.1403(7)	0.9032(6)	0.240(1)	0.0505
C(11)	0.2827(8)	0.2231(5)	−0.029(1)	0.0696	C(43)	0.1429(8)	0.8441(7)	0.278(1)	0.0575
C(12)	0.3094(7)	0.2825(7)	−0.027(1)	0.0546	C(44)	0.0861(9)	0.8160(5)	0.266(1)	0.0555
C(13)	0.2674(7)	0.3231(3)	0.012(1)	0.0590	C(45)	0.0466(5)	0.8595(8)	0.230(1)	0.0562
Si(2)	0.2789(3)	0.4078(2)	0.0086(4)	0.0666	C(49)	0.1200(7)	0.5819(5)	0.022(1)	0.0576
C(14)	0.3601(5)	0.4260(8)	−0.013(1)	0.0698	C(50)	0.1777(5)	0.6110(6)	0.015(1)	0.0513
C(15)	0.2303(8)	0.4386(9)	−0.076(1)	0.0638	C(51)	0.1681(6)	0.6695(5)	−0.020(1)	0.0476
C(16)	0.255(1)	0.4443(9)	0.108(1)	0.1012	C(52)	0.1042(6)	0.6775(5)	−0.032(1)	0.0431
C(17)	0.5460(6)	0.2602(6)	0.216(1)	0.0551	C(53)	0.0742(4)	0.6240(6)	−0.003(1)	0.0464
C(18)	0.5215(8)	0.2009(5)	0.229(1)	0.0497	Si(7)	−0.0088(3)	0.6090(3)	−0.0166(4)	0.0680
C(19)	0.4629(7)	0.2079(5)	0.260(1)	0.0346	C(54)	−0.0188(9)	0.5660(8)	−0.1156(9)	0.0828
C(20)	0.4540(6)	0.2707(5)	0.278(1)	0.0475	C(55)	−0.0392(8)	0.5617(8)	0.070(1)	0.0796
C(21)	0.5033(6)	0.3040(3)	0.2437(9)	0.0328	C(56)	−0.0494(8)	0.6838(6)	−0.023(1)	0.0815
Si(3)	0.5193(3)	0.3877(2)	0.2544(4)	0.0714	C(57)	0.1685(7)	0.5878(6)	0.209(1)	0.060(6)
C(22)	0.4470(6)	0.4315(8)	0.261(1)	0.0889	C(58)	0.1078(6)	0.5933(6)	0.236(1)	0.058(5)
C(23)	0.5639(8)	0.3995(9)	0.351(1)	0.0783	C(59)	0.1001(6)	0.6524(7)	0.270(1)	0.058(5)
C(24)	0.5654(9)	0.4152(9)	0.166(1)	0.0991	C(60)	0.1575(7)	0.6817(6)	0.270(1)	0.058(5)
C(25)	0.5404(6)	0.2098(7)	0.029(1)	0.0558	C(61)	0.1983(5)	0.6440(7)	0.224(1)	0.067(6)
C(26)	0.5313(7)	0.2720(6)	0.007(1)	0.0523	Si(8)	0.2809(3)	0.6625(3)	0.2244(5)	0.105(3)
C(27)	0.4737(7)	0.2768(5)	−0.030(1)	0.0479	C(62)	0.290(1)	0.7454(6)	0.256(1)	0.13(1)
C(28)	0.4459(5)	0.2180(6)	−0.026(1)	0.0371	C(63)	0.316(1)	0.655(1)	0.120(1)	0.14(1)
C(29)	0.4875(6)	0.1763(3)	0.010(1)	0.0493	C(64)	0.320(1)	0.614(1)	0.303(1)	0.17(2)
Si(4)	0.4789(3)	0.0910(2)	0.0135(5)	0.0776	Si(6)	−0.0346(4)	0.8374(4)	0.2265(6)	0.127(3)
C(30)	0.3982(6)	0.0697(8)	−0.008(1)	0.0963	C(47)	−0.064(1)	0.839(1)	0.12291)	0.13(1)
C(31)	0.5275(9)	0.057(1)	−0.069(1)	0.1101	C(46)	−0.078(1)	0.886(1)	0.295(2)	0.17(2)
C(32)	0.502(1)	0.0602(9)	0.1166(9)	0.1233	C(48)	−0.041(1)	0.7581(7)	0.262(2)	0.22(2)

[a] $U(iso) = [U(11)U(22)U(33)]^{1/3}$.

unit. Samples for GC analysis were syringed off during the course of the catalytic reaction. In a typical experiment, a mixture of 1 (80 mg, 0.22 mmol), 1,3-COD (7.14 g, 66 mmol), *n*-hexane (1 mL), and THF (the total volume of the solution being 25 mL) was syringed into the preheated (80 °C) autoclave and the gas was immediately admitted (40 bars of H_2). Each run was repeated at least three times to confirm the validity of the experimental results.

Isomerization. Samples for isomerization were prepared from a stock solution of 1 or $[1]^-Na^+$ in THF with 1,5-COD. A typical solution of 1 (0.1 g, 0.135 mmol) and 300 equiv of 1,5-COD per Zr atom in 20 mL of THF was transferred by portions of 1 mL to 20 glass tubes which were sealed. The tubes were heated in a sand bath at 80 °C and broken from time to time to follow the isomerization process by GC analysis.

X-ray Crystal Structure Determination for $[(C_5H_4SiMe_3)_2Zr(\mu\text{-}H)H)]_2$, 1. Collection and Reduction of X-ray Data. Data were collected on an Enraf-Nonius CAD 4 four-circle diffractometer with graphite monochromated Mo Kα radiation at room temperature. Unit cell parameters and basic informations about data collection and structure refinement are given in Table V. Accurate lattice parameters and the orientation matrix were obtained from least-squares refinement of the setting angles of 25 well centered reflections found by an automated search routine. The systematic abscences indicated the space group to be either *Pnma* or *Pn*2$_1$*a*. During data collections, no deorientation or decay was detected. The intensity data were corrected for Lorentz and polarization effects. The structure was solved using SHELX86[20] for the localization of the Zr atoms; the refinement was performed on an ALLIANT VFX-80 computer using CRYSTALS,[21] examination of the structure was done using PLATON,[22] and illustration was by means of ORTEP.[23] From Patterson maps, the Zr atom positions were determined in the *Pnma* space group. However, this group does not give reasonable solutions for the other atoms. The space group *Pn*2$_1$*a* was then adopted and allowed to realize the refinement with a good convergence. The first chemical set around Zr(1) and Zr(2) was refined correctly with satisfactory thermic agitation parameters. Concerning the second independent molecule, around the Zr(3) and Zr(4) atoms, the thermic agitation of two substituted rings ($C_5H_4Si(8)$ and $C_5H_4Si(6)$) is anomalously high. If the substituted ring $C_5H_4Si(8)$ is actually well localized, the isotropic thermic agitation for the second ring Si(6), C(46), C(47), and C(48) is really too big. A rotation around the C(45) Si(6) direction leads to disordered positions of these four atoms. It is worth noting this disorder is mainly responsible for the absence of a symmetric center in the structure. At this stage of the refinement, the X-ray diffraction was undertaken at −150 °C without further satisfactory results in the localization of both cyclopentadienyl rings bearing Si(6) and Si(8). Although the reliable factor is $R = 0.0637$, we are aware of the fact that these results give a mediated structure for molecule 2, the H(3) and H(4) positions not being so precise. Anomalous dispersion terms were applied. Final positional and equivalent or isotropic temperature factors are listed in Table VI.

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Supplementary Material Available: An ORTEP diagram of a molecule of 1 and listings of fractional atomic parameters, bond lengths and angles, and thermal parameters (18 pages). Ordering information is given on any current masthead page.

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