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Hindered cyclopentadienyl rotation in hexakis(trimethylsilyl)metallocene dichlorides of zirconium and hafnium. Evidence for complete rotation of the tris(trimethylsilyl)cyclopentadienyl ligands

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Abstract

Reaction of tris(trimethylsilyl)cyclopentadienyllithium with zirconium and hafnium tetrachloride affords 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)zirconocene dichloride and 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)hafnocene dichloride. These complexes show hindered rotation of the cyclopentadienyl ligands, with barriers to rotation of 11.0 ± 0.02 kcal/mol and 11.3 ± 0.2 kcal/mol being found for the zirconium and hafnium complex, respectively. These values are compared with those of the corresponding 1,1′,3,3′-tetrakis(trimethylsilyl)metallocene dichlorides and a model is proposed to account for the large differences in rotational barriers.

Introduction

The barrier to rotation of η^5-cyclopentadienyl groups about the ring-transition metal axis has been examined by several different spectroscopic methods and has generally been found to be less than 13 kcal/mol [1–3]. Okuda has recently reported the cyclopentadienyl rotational barriers of a number of metallocene derivatives containing tris(trimethylsilyl)cyclopentadienyl and bis(trimethylsilyl)cyclopentadienyl ligands [3]. A significant result of these studies is the finding that metallocenes of iron and cobalt containing two bis(trimethylsilyl)cyclopentadienyl ligands have nearly identical cyclopentadienyl rotational barriers as the corresponding metallocenes that contain two tris(trimethylsilyl)cyclopentadienyl ligands. In order to account for this unusual observation, it was proposed that the metallocenes containing the bis(trimethylsilyl)cyclopentadienyl ligands are undergoing full rotation, while the metallocenes containing the tris(trimethylsilyl)cyclopentadienyl ligands only undergo a partial rotation. In connection with our studies concerning highly soluble organometallic Lewis acids [4], we were in a position to examine the

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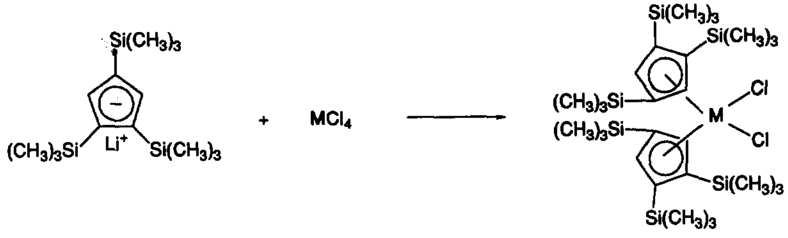
rotational processes in zirconocene and hafnocene dichlorides containing extremely bulky cyclopentadienyl substituents. We now wish to report the synthesis of the 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)metallocene dichlorides of zirconium and hafnium as well as the determination of their cyclopentadienyl rotational barriers. In addition, the rotational processes of the related 1,1′,3,3′-tetrakis(trimethylsilyl)metallocene dichlorides are described.

Results

Reaction of zirconium tetrachloride with two equivalents of 1,2,4-tris(trimethylsilyl)cyclopentadienyllithium [5] in refluxing toluene for 3–5 days affords 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)zirconocene dichloride (**1**, 53%; eq. 1). Complex **1** cannot be crystallized from hexane, even over extended periods (> 6 months) at −80 ° C, but can be conveniently isolated by column chromatography on silica gel using hexane as the eluant. Under these conditions, **1** has an R_f value of 0.9, which illustrates both the lipophilicity of the trimethylsilyl substituents and the extent to which the bulky groups protect the metal center from the reactive siloxy groups. In a similar manner, hafnium tetrachloride reacts with two equivalents of tris(trimethylsilyl)cyclopentadienyllithium in refluxing toluene over 3–5 days to afford 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)hafnocene dichloride (**2**, 35%; eq. 1). The properties of the hafnium complex are similar to its zirconium analog. The complexes 1,1′,3,3′-tetrakis(trimethylsilyl)zirconocene dichloride (**3**) and 1,1′,3,3′-tetrakis(trimethylsilyl)hafnocene dichloride (**4**) were prepared according to the literature procedure [6,7]



(1)

1 M = Zr 53%
2 M = Hf 35%

In order to obtain a quantitative measure of the bulkiness of the trimethylsilyl groups, the variable-temperature NMR behavior of **1** was examined in dichloromethane-d_2 (Fig. 1). The −80 ° C ^1H NMR spectrum showed two distinct singlets for the cyclopentadienyl hydrogens, while the trimethylsilyl groups showed three singlets of equal intensity. Upon warming, the cyclopentadienyl hydrogens coalesced to a single peak and the trimethylsilyl resonances coalesced to two singlets in a 2 : 1 ratio at 219 K. Application of standard dynamic NMR equations [8] to these processes affords a barrier to cyclopentadienyl rotation of $\Delta G^{\ddagger} = 11.0 \pm 0.2$ kcal/mol. The rotational barrier did not change upon doubling the concentration of **1**. Analysis of the rotational barrier of the trimethylsilyl carbons of **1** by $^{13}C\{^1H\}$ NMR afforded a value of 11.2 kcal/mol, although this number was not as precise as those derived from the ^1H NMR data, due to a small peak separation and lower signal to noise ratio. The dynamic NMR behavior of **2** (^1H NMR T_c(cyclopentadienyl hydrogens) = 223 K; T_c(trimethylsilyl methyls) = 221 K) was very similar to

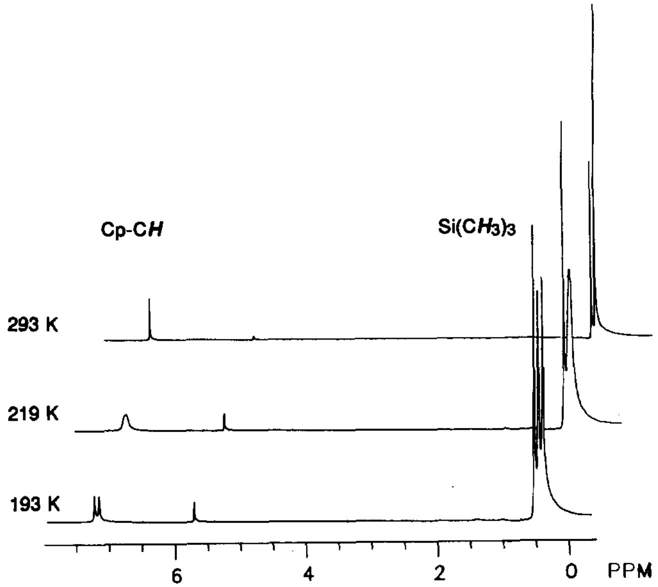


Fig. 1. Temperature-dependent ^{1}H NMR spectra of **1** (300 MHz, dichloromethane-d_2).

that of **1** and afforded a barrier to cyclopentadienyl rotation of $\Delta G^{\ddagger} = 11.3 \pm 0.2$ kcal/mol.

In order to have a basis for comparison, the cyclopentadienyl rotational barriers of 1,1′,3,3′-tetrakis(trimethylsilyl)zirconocene dichloride (**3**) and 1,1′,3,3′-tetrakis(trimethylsilyl)hafnocene dichloride (**4**) were examined in dichloromethane-d_2. Surprisingly, neither complex **3** nor **4** showed coalescence behavior in the ^{1}H and ^{13}C{^{1}H} NMR spectra down to −90 °C, although slight broadening of the cyclopentadienyl C–H resonances was apparent at −90 °C in the ^{1}H NMR. Using −90 °C as the upper limit of the coalescence temperature, we estimate that the barrier to cyclopentadienyl rotation in **3** and **4** is $\leqslant 9.2$ kcal/mol. The related complex 1,1′,3,3′-tetrakis(trimethylsilyl)titanocene dichloride has been reported to have a barrier to cyclopentadienyl rotation of 8.9 kcal/mol [3a].

Discussion

In contrast to the situation found in silylated ferrocenes and cobaltocenes [3], the hexakis(trimethylsilyl) complexes **1** and **2** have substantially higher rotational barriers than the tetrakis(trimethylsilyl) analogs **3** and **4**. This can be rationalized by examining the conformation of the trimethylsilyl groups found in the crystal structure of **3** [7]. In this case (**I**), the trimethylsilyl groups are arranged so as to minimize steric interactions. The longer metal–cyclopentadienyl distances found in the early transition metals should allow a facile "gear mesh" rotational mechanism in **3** and **4**. A model for the structure of **1** and **2** can be obtained by adding 2 trimethylsilyl groups to **I**. As can be seen by inspecting the model (**II**), substantial steric interactions are introduced in **1** and **2** relative to **3** and **4**. A ring rotation in **1** and **2** now involves the eclipsing of two trimethylsilyl groups and a gear mesh

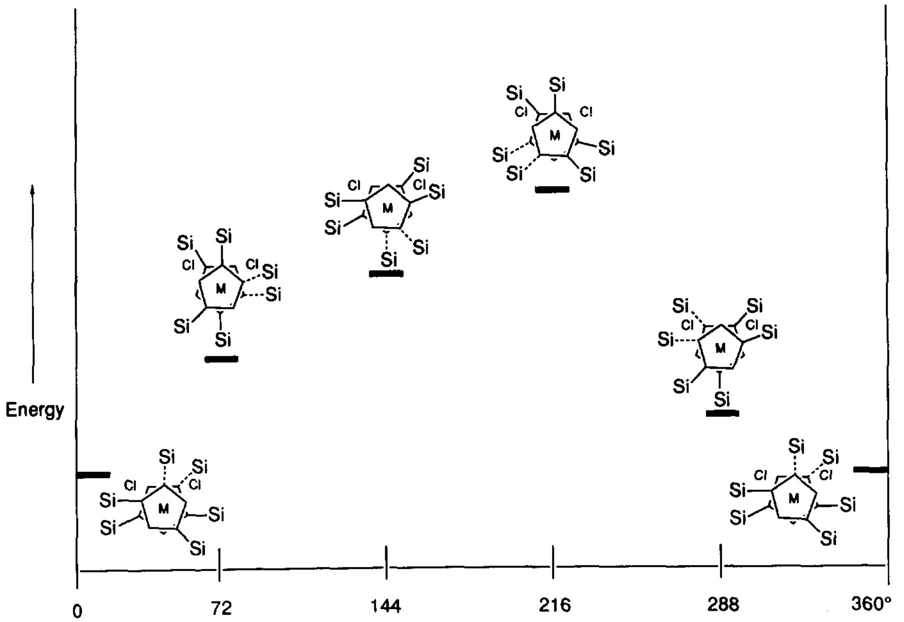
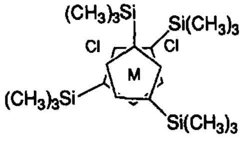
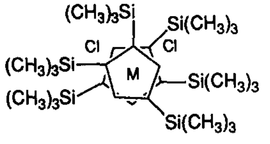


Fig. 2. Qualitative energy diagram for cyclopentadienyl rotation in **1** and **2**.

mechanism should be energetically less favorable. Hence, the barrier to cyclopentadienyl rotation in **1** and **2** should be higher than in **3** and **4**, as is observed.



I



II

A significant question that remains is whether complete or partial ring rotation is required to account for the dynamic behavior of the bent metallocene dichlorides **1** and **2**. Figure 2 shows a qualitative energy diagram for a gear mesh rotation of the cyclopentadienyl ligands along the metal–cyclopentadienyl vector. It has been assumed that eclipsing of trimethylsilyl groups is a high energy process and that placement of trimethylsilyl groups in the region opposite of the metal–chlorine bonds is also a high energy process. From this analysis, it is clear that the cyclopentadienyl hydrogens (and trimethylsilyl hydrogens and carbons) can become equivalent only with full rotation of the cyclopentadienyl ligands. A partial rotation mechanism, similar to one proposed for the silylated ferrocenes and cobaltocenes [3], would place the bulky trimethylsilyl groups directly in the interannular region of the bent metallocene dihalide. Such an arrangement of the trimethylsilyl groups would be energetically prohibitive.

In summary, we have found that the rotational barrier in bent metallocene dichlorides containing six trimethylsilyl cyclopentadienyl substituents is substantially higher than in metallocene dichlorides containing four trimethylsilyl groups.

This difference arises from the steric consequences that occur upon the addition of more bulky groups to the bent metallocene dichloride skeleton.

Experimental

General considerations

All organometallic manipulations were performed under an atmosphere of argon or nitrogen using glovebox or Schlenk techniques. Toluene was distilled from a purple solution of sodium/benzophenone. Hexane was distilled from sodium. NMR solvents were purified by vacuum transfer from activated 4 Å molecular sieves. Tris(trimethylsilyl)cyclopentadiene was prepared according to the literature procedure [5]. Zirconium and hafnium tetrachloride were used as received from Aldrich. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were obtained on a General Electric QE-300 or GN-300 spectrometer. Infrared spectra were obtained on a Nicolet DX20 spectrophotometer. Mass spectra were obtained on Kratos MS-50 or MS-80 spectrometers in the electron impact mode. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Haake Buchler HBI digital melting point apparatus and are uncorrected.

Preparation of 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)zirconocene dichloride (1)

A 200-mL Schlenk flask was charged with tris(trimethylsilyl)cyclopentadiene (7.91 g, 28.0 mmol), toluene (10 mL) and a stir bar and was fitted with a reflux condenser. A solution of n-butyllithium in hexane (10.0 *M*, 2.8 mL, 28.0 mmol) was added via syringe and the mixture was refluxed for 2 h. After cooling to room temperature, zirconium tetrachloride (3.94 g, 16.9 mmol) was added under flow of argon, and the mixture was refluxed for 4 days. The volatiles were removed under reduced pressure and the residue was extracted with hexane (100 mL). The colorless hexane extract was applied to a 5-cm pad of silica gel on a coarse glass frit and was eluted with hexane (100 mL). Removal of the solvent under reduced pressure and vacuum drying afforded analytically pure **1** as an off-white crystalline solid (5.33 g, 53%): m.p. 161–164 °C; IR (cm^{-1}, KBr) 2955 (s), 2901 (s), 1431 (m), 1408 (m), 1384 (m), 1250 (vs), 1095 (s), 992 (s), 932 (s), 837 (vs), 754 (vs), 692 (s), 635 (s); ^1H NMR (C_6D_6, δ) 7.07 (s, $C_5H_2(Si(CH_3)_3)_3$), 0.46 (s, 2 $Si(CH_3)_3$), 0.31 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR 143.87 (s, $CSi(CH_3)_3$), 134.79 (s, $CSi(CH_3)_3$), 126.94 (s, Cp–CH), 1.92 (s, 2 $Si(CH_3)_3$), 1.51 (s, $Si(CH_3)_3$); HRMS: Calcd for $C_{28}H_{58}Cl_2Si_6Zr$, 722.15473. Found: 722.1581.

Anal.: Calcd for $C_{28}H_{58}Cl_2Si_6Zr$: C, 46.36; H, 8.06. Found: C, 46.18; H, 7.90%.

Preparation of 1,1′,2,2′,4,4′-Hexakis(trimethylsilyl)hafnocene dichloride (2)

In a fashion similar to the preparation of **1**, tris(trimethylsilyl)cyclopentadiene (1.460 g, 5.16 mmol), n-butyllithium in hexane (10.0 *M*, 0.53 mL, 5.3 mmol), and hafnium tetrachloride (0.750 g, 2.34 mmol) were reacted in toluene (10 mL) to afford **2** as an off-white crystalline solid (0.675 g, 35%): m.p. 152–155 °C; IR (cm^{-1}, KBr) 2954 (s), 2897 (s), 1435 (m), 1407 (m), 1384 (m), 1250 (vs), 1092 (s), 994 (s), 935 (s), 840 (vs), 758 (vs), 694 (s), 638 (s); ^1H NMR (C_6D_6, δ) 6.98 (s, $C_5H_2(Si(CH_3)_3)_3$), 0.45 (s, 2 $Si(CH_3)_3$), 0.32 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR 142.03 (s, $CSi(CH_3)_3$), 133.77 (s, $CSi(CH_3)_3$), 125.49 (s, Cp–CH), 1.97 (s, 2 $Si(CH_3)_3$), 1.62 (s, $Si(CH_3)_3$); HRMS: Calcd for $C_{28}H_{58}Cl_2HfSi_6$, 812.19992. Found: 812.2007.

Anal.: Calcd for $C_{28}H_{58}Cl_2HfSi_6$: C, 41.38; H, 7.19. Found: C, 40.85; H, 7.13%.

Determination of the rotational barrier for 1

A 5-mm NMR tube was charged with **1** (13.6 mg, 0.0187 mmol) and dichloromethane-d_2 (0.75 mL) and was fitted with a rubber septum. The tube was transferred to a 193 K NMR probe. At this temperature, the trimethylsilyl protons existed as 1 : 1 : 1 singlets in the ^{1}H NMR, with the two peaks that coalesced into a singlet at higher temperatures having a peak separation ($\Delta\nu$) of 19.5 Hz. The cyclopentadienyl hydrogens existed as two singlets ($\Delta\nu = 20.1$ Hz). The cyclopentadienyl hydrogens coalesced to a single peak and the trimethylsilyl resonances coalesced to two singlets in a 2 : 1 ratio at 219 K. Application of standard dynamic NMR equations to these processes afforded rotational barriers of 11.0 ± 0.2 kcal/mol for both the trimethylsilyl and cyclopentadienyl protons. The rotational barrier remained the same upon doubling the concentration of **1**. A determination of the coalescence behavior of the trimethylsilyl carbons of **1** at 212 K yielded a rotational barrier of 11.2 kcal/mol, although this data was not as precise as the ^{1}H NMR determinations, due to the small peak separation ($\Delta\nu = 6.1$ Hz) and the poorer signal-to-noise ratio in the ^{13}C spectra.

Determination of the rotational barrier for 2

In a fashion similar to **1**, complex **2** (11.6 mg, 0.0143 mmol) in dichloromethane-d_2 (0.70 mL) was subjected to variable-temperature ^{1}H NMR analysis. At 193 K, the trimethylsilyl protons existed as 1 : 1 : 1 singlets in the ^{1}H NMR, with the two peaks that coalesced into a singlet at higher temperatures having a peak separation ($\Delta\nu$) of 18.9 Hz. The cyclopentadienyl hydrogens existed as two singlets ($\Delta\nu = 12.9$ Hz). The cyclopentadienyl hydrogens coalesced to a single peak at 221 K and the trimethylsilyl resonances coalesced to two singlets in a 2 : 1 ratio at 223 K. Application of standard dynamic NMR equations to these processes afforded rotational barriers of 11.3 ± 0.2 kcal/mol for both the trimethylsilyl and cyclopentadienyl protons.

Determination of the upper limit of the rotational barriers for 3 and 4

The following experimental procedure is representative: complex **4** (12.6 mg, 0.0188 mmol) in dichloromethane-d_2 (0.71 mL) was transferred to a 183 K NMR probe. At this temperature, no coalescence behavior was observed for any of the proton or carbon resonances. Using 183 K as the upper limit of the coalescence temperature and an estimated proton peak separation of 19 Hz, the barrier to cyclopentadienyl rotation must be $\geqslant 9.2$ kcal/mol. Essentially identical behavior was found for **3**, which also leads to an upper limit of $\geqslant 9.2$ kcal/mol for the barrier to cyclopentadienyl rotation.

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