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Preparation and reactions of Cp_2HfRCl, Cp_2HfRR' and hafnacyclopent-2-enes

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Abstract

Reaction of Cp_2HfCl_2 with R_3Al (R = Et, *n*-Pr, or *n*-Bu) in hexane selectively produced monoalkylhafnocene complexes, Cp_2HfRCl (**1**), in high yields. $Cp_2HfMeCl$ (**1a**) was prepared by the reaction of oxo-bridged hafnocene complex $(Cp_2HfCl)_2(\mu\text{-}O)$ with Me_3Al. The treatment of **1** with alkylating reagents such as R'Li or EtMgBr afforded unsymmetrical dialkylhafnocene complexes Cp_2HfRR' (**3**) in good to excellent yields. The kinetic study of thermolysis of Cp_2HfEtR (R = Me, Et, *n*-Bu, *sec*-Bu, *t*-Bu or Ph) suggested that decomposition of $Cp_2HfEt(sec\text{-}Bu)$ was much faster than the others. $Cp_2Hf(sec\text{-}Bu)_2$ (**2e**) can be used as a good precursor of $Cp_2Hf(II)$ species. Hafnacyclopent-2-enes (**4**) were prepared in good yields by the reaction of Cp_2HfEt_2 (**2b**) with alkynes. © 1997 Elsevier Science S.A.

Keywords: Alkylhafnocene chloride; Dialkylhafnocene; Hafnacyclopent-2-ene; Hafnacyclopentadiene

1. Introduction

In comparison with the chemistry of zirconocene and titanocene derivatives which has been extensively studied over the past two decades, the corresponding hafnocene chemistry has remained undeveloped [1,2]. One of the reason is that the chemistry of hafnium seems to be very similar to zirconium chemistry. And that organohafnium compounds are less reactive compared with organozirconium. In addition, it may be more important that hafnium compounds are not inexpensive.

Dialkylzirconocene compounds play an important role in the zirconium(II) chemistry [3] but they are not stable at room temperature when alkyl groups have a β-hydrogen. In order to investigate the reaction mechanism of such zirconium chemistry, there are some difficulties due to the instability of dialkylzirconocenes.

On the other hand, the corresponding hafnocene derivatives are stable at room temperature. Unfortunately, however, practical and convenient preparative methods of dialkylhafnocene with, especially, two different alkyl groups have not been developed yet.

In this paper, we would like to report a systematic study on preparation of monoalkylhafnocene chlorides, unsymmetrical dialkylhafnocenes and hafnacyclopent-2-enes [4].

2. Results and discussion

2.1. Practical method for preparation of Cp_2HfRCl (1) (R = Me (1a), Et (1b), n-Pr (1c), n-Bu (1d)) and Cp_2HfRR' (3) (R = Me, Et, n-Bu, R' = Me, Et, Pr, n-Bu, sec-Bu, t-Bu and Ph)

Although hydrohafnation reaction of alkenes and the subsequent functionalization of organic moiety have been reported, monoalkylhafnocene compounds have not been isolated and characterized as pure compounds [5]. It is

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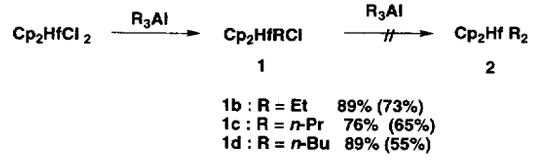
known that hydrohafnation reaction sometimes gives a mixture of several hafnocene complexes. In fact, as Erker et al. [6] reported, hydrohafnation reaction of ethylene by $(MeCp)_2HfHCl$ afforded a mixture of monoethylhafnium and diethylhafnium compounds.

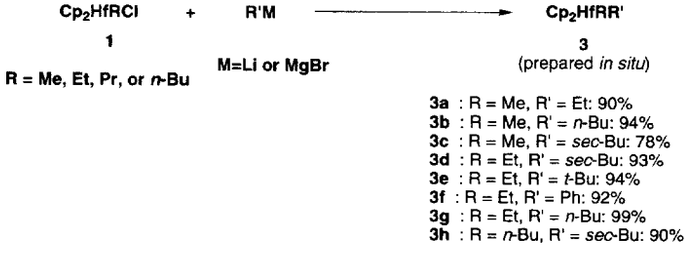
Direct alkylation of Cp_2HfCl_2 by RLi or RMgX is the most attractive method to prepare monoalkylated hafnocenes, Cp_2HfRCl. However, such a method did not give the desired monoalkylated compounds selectively. Only in the case of a bulky *t*-butyllithium, the formation of monoalkylated hafnocene complex, $Cp_2Hf(t\text{-Bu})Cl$, was reported [7,8].

Interestingly, treatment of hafnocene dichloride with 1 equiv. of Et_3Al in hexane afforded monoethylated product, $Cp_2HfEtCl$ (**1b**), cleanly in 89% yield. No formation of diethylhafnocene was detected. This is in sharp contrast to the zirconium case in which an ethylene bridged dizirconium complex was produced upon treatment of Cp_2ZrCl_2 with Et_3Al [9]. Other monoalkylhafnocene chlorides with *n*-Pr or *n*-Bu group (**1c–d**) were similarly obtained in good yields as pure compounds. It is noteworthy that Cp_2HfRCl (**1**) were inert towards another equiv. of R_3Al. This is the most important factor which accounts for the selective formation of monoalkylation products.



(1)

Exceptionally, $Cp_2HfMeCl$ (**1a**) was not cleanly formed by this method using Me_3Al. It could be prepared as a pure compound in 76% isolated yield by the reaction of oxo-bridged complex (**5**) with Me_3Al as reported in the case of $Cp_2ZrMeCl$ [10]. Surprisingly, however, the treatment of the oxo-bridged complex (**5**) with other trialkylaluminum compounds, such as Et_3Al, $(n\text{-Pr})_3Al$ and $(n\text{-Bu})_3Al$ did not give **1b–1d** cleanly.



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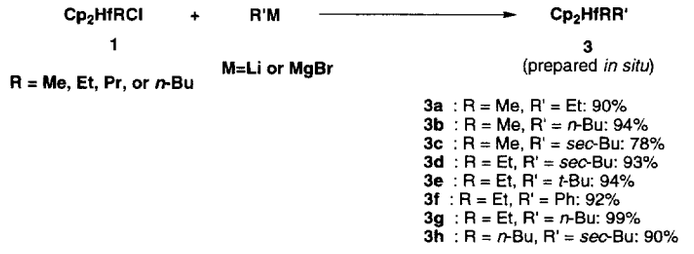
Symmetrical dialkylhafnocene complexes Cp_2HfR_2 (R = Et (**2b**), *n*-Bu (**2d**), *sec*-Bu (**2e**)), were easily prepared in excellent yields by simple addition of 2 equiv. of RLi reagents to the solution of Cp_2HfCl_2 in ether as already known [1,2].

Selective preparation of unsymmetrical dialkylhafnocene complexes, Cp_2HfRR' (**3**), is more attractive. From the pure monoalkylhafnocene chlorides **1** obtained above, unsymmetrical dialkylhafnocene compounds were cleanly formed. The reaction of Cp_2HfRCl (**1**) with 1 equiv. of R'M (R' = alkyl or aryl groups; M = Li or MgX) proceeded to yield Cp_2HfRR' selectively in excellent yields. These dialkylhafnocene compounds prepared in situ can be used for further reactions without isolation. Dialkylhafnocene compounds were characterized by NMR without isolation. The ^{13}C NMR spectrum of $Cp_2HfEt(n\text{-Bu})$ **3g**



(3)

showed that the complex prepared by this method was very pure as shown in Fig. 1, and it was stable in THF at room temperature. Disproportionation of **3g** to produce $Cp_2Hf(n\text{-Bu})_2$ and Cp_2HfEt_2 was not observed (Eq. (4)). In some

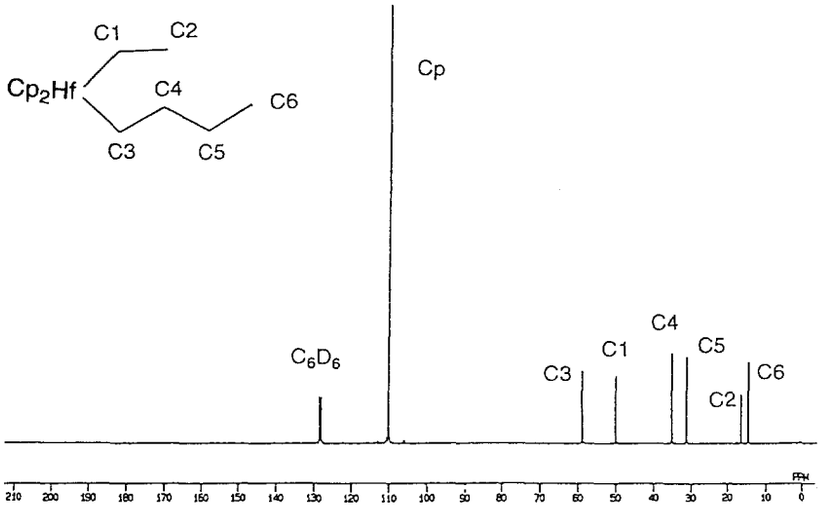


Fig. 1. ^{13}C NMR spectrum of $Cp_2HfEt(n\text{-Bu})$ (**3g**) in C_6D_6.

cases, the signals assigned to Cp carbons or alkyl carbons for Cp_2HfRR' were similar to those for Cp_2HfR_2 or $Cp_2HfR'_2$ in their ^{13}C NMR spectra. However, their ^1H NMR spectra were quite different.

$$\underset{\textbf{3g}}{Cp_2HfEt(n\text{-Bu})} \xrightarrow[//]{\text{THF, r.t.}} \underset{\textbf{2b}}{Cp_2HfEt_2} + \underset{\textbf{2d}}{Cp_2Hf(n\text{-Bu})_2} \quad (4)$$

2.2. Thermal stability of Cp_2HfEtR (R = Me (**3a**), Et (**2b**), n-Bu (**3g**), sec-Bu (**3d**), t-Bu (**3e**) and Ph (**3f**))

In order to probe the synthetic potential of these dialkylhafnocene complexes, information about thermal stability of these complexes is necessary. It is well accepted that dialkylzirconocenes easily decompose via β-hydrogen abstraction to produce alkene complexes which are useful reagents for organic synthesis.

Thermal decomposition reaction rate was measured for Cp_2HfEtR (**2b**, **3a**, **3d–g**) at 60°C using ^1H NMR spectroscopy. The decomposition obviously obeyed first order rule and the rate constants were determined by decrease of the Cp signals of Cp_2HfEtR. The results are shown in Table 1. The thermal stability increased in the order of R groups *sec*-Bu < *t*-Bu, Et < *n*-Bu ≪ Me, Ph for Cp_2HfEtR. This order is the same as obtained for β-hydrogen abstraction of Cp_2ZrMeR [11]. The complexes $Cp_2HfEtMe$ and $Cp_2HfEtPh$ were very stable. It is noteworthy that $Cp_2HfEt(sec\text{-Bu})$ decomposed much faster than the others.

2.3. Formation of hafnacyclopent-2-enes (**4a–g**) and hafnacyclopentadiene (**6**)

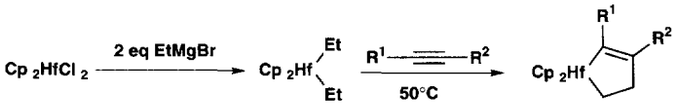
The first full characterization of hafnacyclopent-2-ene $Cp_2\overline{Hf(CH_2CH_2CPh=CPh)}$ was reported by Erker et al. [12] and it was prepared by the reaction of hafnacyclopentane with diphenylacetylene (yield 38%). Recently, we have

Table 1
The first order rate constants for thermolysis of Cp_2HfEtR[a]

R group	Rate constant ($10^{-2} \times k$) min^{-1}
sec-Bu	5.2
t-Bu	1.6
Et	1.6
n-Bu	0.5
Me	[b]0.09
Ph	[c]

[a]Reaction conditions: temperature 60°C.
[b]88% of unreacted $Cp_2Hf(Et)Me$ was remained even after 12 h.
[c]Not determined because it was very slow.

developed a preparative method of zirconacyclopentenes from Cp_2ZrEt_2 and alkynes [13]. We used our method for preparation of hafnacyclopent-2-enes, since **2b** decomposes at 60°C with a rate of 1.6×10^{-2} min^{-1}. The reaction of **2b** prepared in situ with diphenylacetylene proceeded smoothly at 50°C to yield hafnacyclopent-2-ene **4d** in 77% yield. The ^{13}C NMR spectrum of **4d** showed characteristic signals at 31.66, 44.81, 111.44, 150.62 and 191.82 ppm in addition to signals of phenyl carbons. Its ^1H NMR spectrum indicated two triplets at 1.22 and 3.03 ppm assignable to two CH_2 groups and a singlet at 5.86 ppm assigned to Cp protons. These NMR data were the same as reported for $Cp_2Hf(CH_2CH_2CPh{=}CPh)$ whose structure was determined by X-ray analysis [13]. Hydrolysis of **4d** gave (*Z*)-1,2-diphenyl-1-butene in 77% yield. Other hafnacyclopent-2-enes were obtained in a similar way in good to high yields as shown in Table 2.

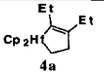
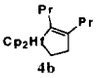
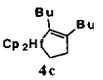
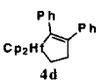
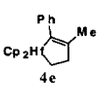
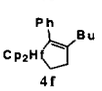
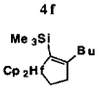


4a : R^1, R^2 = Et: 87%
4b : R^1, R^2 = Pr: 80%
4c : R^1, R^2 = Bu: 92%
4d : R^1, R^2 = Ph: 77%
4e : R^1 = Ph, R^2 = Me: 68%
4f : R^1 = Ph, R^2 = Bu: 71%
4g : R^1 = Me_3Si, R^2 = Bu: 68%

(5)

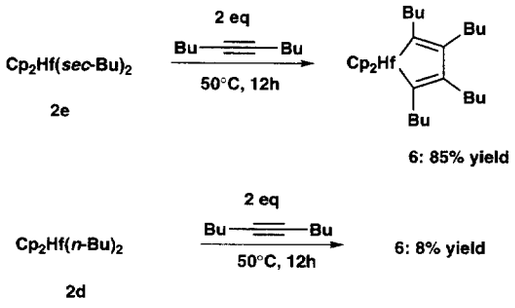
For preparation of hafnacyclopentadienes [7,12], $Cp_2Hf(n\text{-}Bu)_2$ (**2d**) has been used [14]. However, high temperature (above 80°C) and a long reaction time was required [14]. Our kinetic data (Table 1) showed that the decomposition reaction from *sec*-Bu group was much faster than *n*-Bu group. Kinetic study showed that the first order rate constant for thermolysis of $Cp_2Hf(sec\text{-}Bu)_2$ (**2e**) was about 90 times as large as that of **2d**. It is thus expected that conversion of **2e** to hafnacyclopentadienes would be much easier than that of **2d**. Actually, the reaction of **2e** with 2 equiv. of 5-decyne in THF at 50°C after 1, 3, and 12 h gave hafnacyclopentadiene **6** in 58%, 73%, and 85% yields, respectively. However, **2d** with 2 equiv. of 5-decyne under the same conditions gave **6** only in 1%, 3%,

Table 2
Formation of hafnacyclopent-2-ene compounds from Cp_2HfCl_2, EtMgBr and alkynes[a]

Run	Alkyne	Time/h	Hafnacyclopent-2-ene	Yield/%[b]	Hydrolysis	Yield/%[c]
1	Et—≡—Et	3	 4a	87		86
2	Pr—≡—Pr	3	 4b	80		82
3	Bu—≡—Bu	3	 4c	92		95
4	Ph—≡—Ph	6	 4d	77		77
5	Ph—≡—Me	6	 4e	68		73
6	Ph—≡—Bu	6	 4f	71		70
7	Me_3Si—≡—Bu	6	 4g	68		65

[a]All reactions were carried out at 50°C.
[b]Yields were determined by NMR.
[c]Yields were determined by GC.

and 8% yields, respectively. Obviously, $Cp_2Hf(sec\text{-}Bu)_2$ can be used as a good source of $Cp_2Hf(II)$ species.



(6)

3. Experimental

3.1. General procedures

All reactions were carried out under nitrogen atmosphere using standard Schlenk tube techniques. THF (tetrahydrofuran), diethyl ether and hexane were distilled over sodium and benzophenone. Hafnocene dichloride, diphenylacetylene, 1-trimethylsilyl-1-hexyne were purchased from Aldrich Chemical. Ethylmagnesium bromide (THF solution), methyllithium (ether solution), *n*-butyllithium (hexane solution), *sec*-butyllithium (cyclohexane solution), *t*-butyllithium (hexane solution), phenyllithium (cyclohexane–ether solution) were purchased from Kanto Chemicals. 3-Hexyne, 4-octyne, 5-decyne, 1-phenyl-1-propyne, 1-phenyl-1-hexyne and 3,5-octadiyne were purchased from Tokyo Chemical. $(Cp_2HfCl)_2(\mu\text{-O})$ was prepared as reported in the literature [10].

NMR spectra were recorded on a JEOL EX-270 FT NMR spectrometer. Tetramethylsilane (TMS) was used as the reference for ^1H and ^{13}C NMR. The NMR yields were determined using mesitylene as an internal standards. GC analyses were performed on a Shimadzu GC-14A equipped with a flame ionization detector using Shimadzu Capillary Column (CBPI-M25-025). The GC yields were determined using suitable hydrocarbon internal standards. Mass spectra were obtained on JEOL JMS-AX505HA mass spectrometer.

3.2. Preparation of monoalkylhafnocene complexes

3.2.1. Preparation of $Cp_2HfMeCl$ (**1a**)

To a solution of $Cp_2HfCl(O)ClHfCp_2$ (3 g, 4.2 mmol) in 20 ml of CH_2Cl_2, were added excess of Me_3Al (25 ml, 1.02 M, 25.5 mmol) at room temperature. This mixture was stirred for 1 h. To this mixture was added 5 ml of ether and solvents were evaporated under vacuum to give a white solid. The white residue was dissolved in 25 ml of hexane and filtrated. Crystallization in hexane at −40°C gave the title complex, 1,1-Bis(η^5-cyclopentadienyl)chloromethylhafnium (**1a**) in 76% isolated yield. M.p.: 120–122°C. ^1H NMR (C_6D_6, Me_4Si): δ 0.26 (s, 3H), 5.68 (s, 10H); ^{13}C NMR (C_6D_6, Me_4Si): δ 33.84, 111.70. Anal. Calc. for $C_{11}H_{13}ClHf$: C: 36.78; H: 3.66; Cl: 9.87. Found: C: 36.70; H: 3.69; Cl: 9.79.

3.2.2. $Cp_2HfEtCl$ (**1b**)

To a solution of Cp_2HfCl_2 (5.7 g, 15 mmol) in 15 ml of hexane, was added 1 equiv. of Et_3Al (16.1 ml, 0.92 M, 15 mmol) at room temperature. This mixture was stirred for 1 h at room temperature. Solvents were evaporated under vacuum to give a white solid. The white residue was dissolved in 20 ml of hexane and filtrated. Crystallization in hexane at 8–10°C gave the title complex, 1,1-Bis(η^5-cyclopentadienyl)chloroethylhafnium (**1b**) in 73% isolated yield. NMR yield 89%. M.p.: 70–72°C. ^1H NMR (C_6D_6, Me_4Si): δ 0.86 (q, $J = 8$ Hz, 2H), 1.64 (t, $J = 8$ Hz, 3H), 5.74 (s, 10H); ^{13}C NMR (C_6D_6, Me_4Si): δ 17.90, 46.68, 111.66. Anal. Calc. for $C_{12}H_{15}ClHf$: C: 38.62; H: 4.06; Cl: 9.50. Found: C: 38.28; H: 3.90; Cl: 9.68.

3.2.3. $Cp_2Hf(n\text{-}Pr)Cl$ (**1c**)

Instead of Et_3Al, $(n\text{-}Pr)_3Al$ was used. NMR yield 76%. Isolated yield 65%. M.p.: 52–53°C. ^1H NMR (C_6D_6, Me_4Si): δ 0.79–0.82 (m, 2H), 1.11 (t, $J = 7$ Hz, 3H), 1.59–1.73 (m, 2H), 5.73 (s, 10H); ^{13}C NMR (C_6D_6, Me_4Si): δ 22.66, 27.51, 58.71, 111.61. Anal. Calc. for $C_{13}H_{17}ClHf$: C: 40.32; H: 4.43; Cl: 9.15. Found: C: 40.25; H: 4.38; Cl: 9.00.

*3.2.4. $Cp_2Hf(n\text{-}Bu)Cl$ (**1d**)*

Instead of Et_3Al, $(n\text{-}Bu)_3Al$ was used. NMR yield 89%. Isolated yield 55%. M.p.: 55–57°C. ^1H NMR (C_6D_6, Me_4Si): δ 0.81–0.87 (m, 2H), 1.04 (t, $J = 7$ Hz, 3H), 1.41 (tq, $J = 7$ Hz, 7 Hz, 2H), 1.57–1.69 (m, 2H), 5.73 (s, 10H); ^{13}C NMR (C_6D_6, Me_4Si): δ 14.20, 30.76, 36.42, 55.35, 111.64. Anal. Calc. for $C_{14}H_{19}ClHf$: C: 41.90; H: 4.78; Cl: 8.83. Found: C: 41.73; H: 4.67; Cl: 8.98.

3.3. Preparation of unsymmetrical dialkylhafnocene complexes

*3.3.1. Preparation of $Cp_2HfMeEt$ (**3a**)*

To a solution of 359 mg (1.0 mmol) of $Cp_2HfMeCl$ in 5 ml of ether, were added 1 equiv. of EtMgBr (1.2 mmol, 0.99 M, 1.21 ml) at −78°C. This mixture was warmed up to room temperature, stirred for 1 h and filtrated through a frit. The title complex **3a** was formed in 90% yield. The solution was concentrated to a volume of 2 ml under vacuum. To this was added 5 ml of hexane and the mixture was cooled to −40°C. After 12 h at −40°C, the title complex **3a** was obtained in 74% yield as white powder. ^1H NMR (C_6D_6, Me_4Si): δ −0.32 (s, 3H), 0.13 (q, $J = 8$ Hz, 2H), 1.46 (t, $J = 8$ Hz, 3H), 5.65 (s, 10H); ^{13}C NMR (C_6D_6, Me_4Si): δ 16.15, 36.89, 49.18, 109.86.

*3.3.2. $Cp_2HfMe(n\text{-}Bu)$ (**3b**)*

Yield 94% (by NMR). ^1H NMR (C_6D_6, Me_4Si): δ −0.34 (s, 3H), 0.12–0.17 (m, 2H), 1.01 (t, $J = 7$ Hz, 3H), 1.29–1.37 (m, 2H), 1.40–1.50 (m, 2H), 5.66 (s, 10H); ^{13}C NMR (C_6D_6, Me_4Si): δ 14.20, 30.91, 34.86, 36.93, 58.11, 109.79.

*3.3.3. $Cp_2HfMe(sec\text{-}Bu)$ (**3c**)*

Yield 78% (by NMR). ^1H NMR (C_6D_6, Me_4Si): δ −0.31 (s, 3H), 0.61–0.66 (m, 1H), 0.98 (t, $J = 7$ Hz, 3H), 1.18 (d, $J = 7$ Hz, 3H), 1.21–1.34 (m, 2H), 5.65 (s, 5H), 5.66 (s, 5H); ^{13}C NMR (C_6D_6, Me_4Si): δ 16.46, 19.69, 30.78, 37.36, 62.57, 109.88, 109.92.

*3.3.4. $Cp_2HfEt(sec\text{-}Bu)$ (**3d**)*

Yield 93% (by NMR). ^1H NMR (C_6D_6, Me_4Si): δ 0.16 (q, $J = 7.7$ Hz, 2H), 0.52–0.57 (m, 1H), 0.98 (t, $J = 7.2$ Hz, 3H), 1.18 (d, $J = 7.1$ Hz, 3H), 1.13–1.25 (m, 2H), 1.43 (t, $J = 7.7$ Hz, 3H), 5.66 (s, 5H), 5.67 (s, 5H); ^{13}C NMR (C_6D_6, Me_4Si): δ 15.95, 16.56, 19.52, 30.63, 49.96, 62.89, 109.93, 109.96.

*3.3.5. $Cp_2HfEt(t\text{-}Bu)$ (**3e**)*

Yield 94% (by NMR). ^1H NMR (C_6D_6, Me_4Si): δ 0.55 (q, $J = 7.6$ Hz, 2H), 1.17 (s, 9H), 1.48 (t, $J = 7.7$ Hz, 3H), 5.69 (s, 10H); ^{13}C NMR (C_6D_6, Me_4Si): δ 16.46, 35.12, 53.88, 57.62, 110.60.

*3.3.6. $Cp_2HfEtPh$ (**3f**)*

Yield 92% (by NMR). ^1H NMR (C_6D_6, Me_4Si): δ 0.61 (q, $J = 7.6$ Hz, 3H), 1.50 (t, $J = 7.7$ Hz, 3H), 5.70 (s, 10H), 7.03–7.27 (m, 5H); ^{13}C NMR (C_6D_6, Me_4Si): δ 15.99, 53.09, 110.98, 124.94, 127.50, 136.56, 193.24.

*3.3.7. $Cp_2Hf(n\text{-}Bu)Et$ (**3g**)*

Yield 99% (by NMR). ^1H NMR (C_6D_6, Me_4Si): δ 0.10–0.18 (m, 4H), 1.03 (t, $J = 7$ Hz, 3H), 1.46 (t, $J = 8$ Hz, 3H), 1.34–1.49 (m, 4H), 5.66 (s, 10H); ^{13}C NMR (C_6D_6, Me_4Si): δ 14.20, 16.06, 31.07, 34.82, 49.76, 58.69, 109.88.

*3.3.8. $Cp_2Hf(n\text{-}Bu)(sec\text{-}Bu)$ (**3h**)*

Yield 90% (by NMR). ^1H NMR (C_6D_6, Me_4Si): δ 0.12–0.17 (m, 2H), 0.48–0.62 (m, 1H), 0.97 (t, $J = 7$ Hz, 3H), 1.00 (t, $J = 7$ Hz, 3H), 1.17 (d, $J = 7$ Hz, 3H), 1.23–1.43 (m, 6H), 5.66 (s, 5H), 5.67 (s, 5H); ^{13}C NMR (C_6D_6, Me_4Si): δ 14.18, 16.56, 19.66, 30.64, 31.04, 34.74, 58.82, 62.92, 109.87, 109.92.

*3.4. Kinetic studies for the thermal decomposition of Cp_2HfEtR (R = Me (**3a**), Et (**2b**), n-Bu (**3g**), sec-Bu (**3d**), t-Bu (**3e**) and Ph (**3f**))*

3.4.1. Representative procedure

To a solution of $Cp_2HfEtCl$ (186 mg, 0.5 mmol) in 2.5 ml of THF, was added 1 equiv. of *sec*-BuLi (0.48 ml, 1.04 M, 0.5 ml) at −78°C. The reaction mixture was warmed to room temperature and stirred for 1 h at room temperature. A reaction mixture (0.25 ml) was transferred into a NMR tube with 0.25 ml of C_6D_6. Thermal decomposition reaction

was carried out at 60°C. The reaction was monitored by ^{1}H NMR. The Cp signal assigned to $Cp_2HfEt(sec\text{-}Bu)$ gradually decreased. After 3 h, it completely disappeared. The rate constant was determined using the decrease of intensity of the Cp signal; $k = 5.16 \times 10^{-2}$ (min^{-1}).

3.5. Preparation of hafnacyclopent-2-enes

3.5.1. $Cp_2Hf(CH_2CH_2CEt{=}CEt)$ (4a)

To a solution of 1.42 g (3.75 mmol) of Cp_2HfCl_2 in 15 ml of THF, were added 2 equiv. of EtMgBr (7.5 mmol, 0.99 M, 7.58 ml) at −78°C. This mixture was warmed to room temperature and stirred for 1 h. To this mixture was added 1 equiv. of 3-hexyne (342 μl, 3.0 mmol) at room temperature. The reaction mixture was stirred at 50°C for 3 h. The complex **4a** was formed in 87% yield. Hydrolysis of the mixture gave 3-ethyl-3-hexene in 86% yield [13]. The solution containing **4a** obtained above was concentrated to a volume of 3 ml under vacuum. To this was added 15 ml of hexane and the solution was cooled to −40°C. After 12 h at −40°C, crude **4a** was obtained in 71% as yellow powder. Attempts to obtain crystals were not successful. M.p.: > 135°C (decomp). ^{1}H NMR (C_6D_6, Me_4Si): δ 0.87 (t, J = 8 Hz, 3H), 1.01 (t, J = 8 Hz, 3H), 1.02 (t, J = 7 Hz, 2H, α-CH_2), 1.09 (q, J = 8 Hz, 2H), 2.28 (q, J = 8 Hz, 2H), 2.47 (t, J = 7 Hz, 2H, β-CH_2), 5.84 (s, 10H); ^{13}C NMR (C_6D_6, Me_4Si): δ 13.30, 15.91, 26.37 (C4), 28.89, 29.01, 43.10 (C5), 110.18 (Cp), 141.77 (C3), 189.02 (C2).

3.5.2. $Cp_2Hf(CH_2CH_2CPr{=}CPr)$ (4b)

Yield 80% (by NMR). ^{1}H NMR (C_6D_6, Me_4Si): δ 0.96 (t, J = 7 Hz, 3H), 0.97 (t, J = 7 Hz, 3H), 1.02 (t, J = 7 Hz, 2H, α-CH_2), 1.11–1.19 (m, 2H), 1.41–1.47 (m, 2H), 1.91 (t, J = 7 Hz, 2H), 2.47 (t, J = 7 Hz, 2H, β-CH_2), 5.85 (s, 10H); ^{13}C NMR (C_6D_6, Me_4Si): δ 14.60, 15.44, 21.89, 24.75, 26.79 (C4), 38.16, 39.87, 43.32 (C5), 110.16 (Cp), 140.53 (C3), 188.89 (C2). After hydrolysis, (*Z*)-4-ethyl-4-octene was obtained in 82% yield [13].

3.5.3. $Cp_2Hf(CH_2CH_2CBu{=}CBu)$ (4c)

Yield 92% (by NMR). ^{1}H NMR (C_6D_6, Me_4Si): δ 0.97 (t, J = 7 Hz, 3H), 0.99 (t, J = 7 Hz, 3H), 1.03 (t, J = 7 Hz, 2H, α-CH_2), 1.13–1.22 (m, 2H), 1.30–1.46 (m, 6H), 1.93 (t, J = 7 Hz, 2H), 2.34 (t, J = 8 Hz, 2H), 2.49 (t, J = 7 Hz, 2H, β-CH_2), 5.87 (s, 10H); ^{13}C NMR (C_6D_6, Me_4Si): δ 14.44, 14.50, 23.44, 24.04, 26.89 (C4), 31.10, 33.86, 35.89, 36.88, 43.35 (C5), 110.17 (Cp), 140.79 (C3), 188.51 (C2). After hydrolysis, (*Z*)-5-ethyl-5-decene was obtained in 95% yield [15].

3.5.4. $Cp_2Hf(CH_2CH_2CPh{=}CPh)$ (4d)

Yield 77% (by NMR). ^{1}H NMR (C_6D_6, Me_4Si): δ 1.22 (t, J = 7 Hz, 2H, α-CH_2), 3.03 (t, J = 7 Hz, 2H, β-CH_2), 5.86 (s, 10H), 6.64–7.16 (m, 10H); ^{13}C NMR (C_6D_6, Me_4Si): δ 31.66 (C4), 44.81 (C5), 111.44 (Cp), 122.96, 125.57, 127.16, 127.60, 127.97, 128.94, 144.45, 146.10, 150.6 2 (C3), 191.82 (C2). After hydrolysis, (*Z*)-1,2-diphenyl-1-butene was obtained in 77% yield [15].

3.5.5. $Cp_2Hf(CH_2CH_2CPh{=}CMe)$ (4e)

Yield 68% (by NMR). ^{1}H NMR (C_6D_6, Me_4Si): δ 1.11 (t, J = 7 Hz, 2H, α-CH_2), 1.49 (s, 3H), 2.60 (t, J = 7 Hz, 2H, β-CH_2), 5.82 (s, 10H), 6.81–7.29 (m, 5H); ^{13}C NMR (C_6D_6, Me_4Si): δ 23.27, 30.88 (C4), 43.35 (C5), 110.91 (Cp), 123.13, 126.44, 128.22, 139.19, 151.59 (C3), 189.23 (C2). After hydrolysis, (*E*)-2-methyl-1-phenyl-1-butene was obtained in 73% yield [16].

3.5.6. $Cp_2Hf(CH_2CH_2CPh{=}CBu)$ (4f)

Yield 71% (by NMR). ^{1}H NMR (C_6D_6, Me_4Si): 80.81 (t, J = 7 Hz, 3H), 1.11 (t, J = 7 Hz, 2H, α-CH_2), 1.10–1.22 (m, 2H), 1.33–1.39 (m, 2H), 1.84 (t, J = 8 Hz, 2H), 2.65 (t, J = 7 Hz, 2H, β-CH_2), 5.83 (s, 10H), 6.81–7.26 (m, 5H); ^{13}C NMR (C_6D_6, Me_4Si): δ 14.31, 23.06, 28.41 (C4), 31.05, 36.64, 43.95 (C5), 110.93 (Cp), 122.97, 126.31, 128.11, 143.66, 151.29 (C3), 189.68 (C2). After hydrolysis, 1-phenyl-2-ethyl-1-hexene was obtained in 70% yield [17].

3.5.7. $Cp_2Hf(CH_2CH_2C(SiMe_3){=}CBu)$ (4g)

Yield 68% (by NMR). ^{1}H NMR (C_6D_6, Me_4Si): δ 0.18 (s, 9H), 1.02 (t, J = 7 Hz, 3H), 1.11 (t, J = 7 Hz, 2H, α-CH_2), 1.27–1.45 (m, 4H), 1.92 (t, J = 8 Hz, 2H), 2.46 (t, J = 7 Hz, 2H, β-CH_2), 5.86 (s, 10H); ^{3}C NMR (C_6D_6, Me_4Si): δ 3.38, 14.49, 23.63, 29.26 (C4), 31.62, 41.52 (C5), 45.28, 110.44 (Cp), 148.74 (C3), 190.54 (C2). After hydrolysis, (*E*)-2-butyl-1-(trimethylsilyl)-1-butene was obtained in 65% yield [15].

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