A FACILE, HIGH-YIELD SYNTHESIS OF
DI-η^5-CYCLOPENTADIENYLHAFNACYCLOPENTADIENE COMPOUNDS

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(Received March 13th, 1986)

Summary

Hafnocene dichloride was reduced with amalgamated magnesium in the presence of alkynes giving high yields of di-η^5-cyclopentadienylhafnacyclopentadienes. Reaction with hydrochloric acid yields exclusively the corresponding (E,E)-butadiene derivatives.

Introduction

Earlier we reported the one-step synthesis of di-η^5-cyclopentadienylzirconacyclopentadienes by reduction of Cp_2ZrCl_2 with amalgamated magnesium in the presence of various alkynes [1]. An application of this synthetic method was reported by Negishi et al., to promote a bicyclization of enynes, thus preparing in situ a zirconacyclopentene derivative [2]. Rausch et al., have also used $Mg/HgCl_2$ as the reducing agent in the preparation of $[(CH_3)_5C_5]_2M(CO)_2$ (M = Ti, Zr, Hf) from $[(CH_3)_5C_5]_2MCl_2]$ [3].

More recently Sikora and Rausch prepared some hafnacyclopentadienes in 40–75% yields by treating $Cp_2Hf(CO)_2$ with alkynes under photolytic or thermolytic conditions [4]. Using methods analogous to those in the preparation of the zirconacyclopentadiene complexes, we report a high yield, one-step synthesis of di-η^5-cyclopentadienylhafnacyclopentadienes.

Experimental

Starting materials and solvents. Hafnocene dichloride was purchased from Alfa and used as received. Diphenylacetylene (Aldrich) was used without further purification while 2-butyne and 3-hexyne (Farchan) were deoxygenated by purging with argon and stored over 4Å molecular sieves. Magnesium powder (70–80 mesh) and mercuric chloride were obtained from Fisher and used as received.

Tetrahydrofuran and ether were dried over the sodium ketyl of benzophenone and freshly distilled under argon before use. Pentane and benzene were distilled over lithium aluminum hydride.

Physical methods. Proton NMR spectra were recorded on a Varian EM 360 spectrometer. ^{13}C NMR spectra were taken on a Varian FT80A multinuclear spectrometer. For both types of spectra $CDCl_3$ was used as the solvent and TMS served as the internal standard. Infrared spectra were obtained from a Perkin–Elmer 597 spectrophotometer. Mass spectra were taken on a Finnegan 1015 mass spectrometer and ultraviolet spectra were obtained from a Beckman Model 25 spectrophotometer. Melting points were determined on a Thomas Hoover capillary apparatus and are uncorrected. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratory Inc., Woodside, NY.

Preparation of the complexes. All manipulations of the air sensitive compounds were performed in an argon-filled glove box. The argon was dried with H_2SO_4, KOH and P_2O_5 and passed through 4Å molecular sieves before entering the glove box.

Synthesis of 1,1-di-η^5-cyclopentadienyl-2,3,4,5-tetramethylhafnacyclopentadiene. A 250 ml, 3-necked flask fitted with an argon inlet, a rubber septum and an outlet connected to an oil bubbler, was filled with argon by a series of evacuate/fill cycles. To the flask was added 1.896 g (5.0 mmol) of hafnocene dichloride, 0.607 g (25 mmol) of Mg powder, 1.354 g (5.0 mmol) of $HgCl_2$ and a magnetic stir bar. The flask was flushed with argon for 30 min, and 50 ml of freshly distilled THF was injected through the septum. The flask was cooled to $-78°C$ and 2.16 g (40 mmol) of 2-butyne was added through the septum. The flow of argon was stopped, and after the contents of the flask warmed to ambient temperatures, the reaction mixture was stirred magnetically for 30 h, during which time the color gradually changed to a greenish yellow. The solvent and unreacted 2-butyne were removed under vacuum and the flask was transferred to an argon-filled glove box. The residue was dissolved in a minimum amount of dry pentane and filtered over a pad of Celite packed on a fritted funnel. The Celite was washed several times with pentane, and the combined filtrate and washings were stripped to dryness by high vacuum, yielding 1.92 g (92.2%) of a yellowish-orange compound. This compound, which was obtained in reasonably analytically pure form without recrystallization, was characterized as 1,1-di-η^5-cyclopentadienyl-2,3,4,5-tetramethylhafnacyclopentadiene on the basis of elemental analysis, mass, NMR, and infrared spectra, and the spectral properties of the organic ligand obtained after reaction with HCl. Found: C, 51.10; H, 5.39. $C_{18}H_{22}Hf$ calcd.: C, 51.86, H, 5.28%. MS: m/e 418 (M^+), 364 ($M - CH_3C{\equiv}CCH_3$), 349 ($364 - CH_3^+$), 310 (Cp_2Hf^+). ^1H NMR ($CDCl_3$): δ 5.93 (s, 10H, C_5H_5), 1.60 ppm (broad s, 12H, CH_3). IR (KBr) 2900s, 2835s, 1690w, 1594w, 1420m, 1357w, 1015s, 800vs cm^{-1}.

Synthesis of the other hafnacyclopentadienes. The tetraethyl derivative, obtained as a yellow solid in 91.0% yield showed spectral properties identical to those reported by Sikora and Rausch [4], as well as acceptable C–H analyses. The tetraphenyl derivative was prepared in a flask wrapped with black tape to exclude any light, since the final compound is light sensitive. The golden yellow solid was obtained in 82.2% yield, and was characterized by comparing its spectral properties to those of the same compound prepared by Sikora and Rausch [4].

Reaction of the hafnacyclopentadienes with HCl. The metallacyclopentadienes were all treated with HCl to release the organic ligand. Since all three were carried out in the same manner, only the reaction with the tetramethyl derivative is described in detail.

The tetramethylhafnacyclopentadiene derivative (1.0 g, 2.4 mmol) was dissolved in 25 ml of methylene chloride and treated with 25 ml of 1.2 M HCl. The color of the solution instantly changed from red to pale yellow. The reaction mixture was magnetically stirred for 1 h at room temperature, and the organic and aqueous layers were separated. The aqueous layer was extracted with three 15 ml portions of methylene chloride, which were combined with the CH_2Cl_2 fraction and dried over anhydrous $MgSO_4$. Distillation afforded 0.175 g (66.3% yield) of the pure 3,4-di-methyl-(2E,4E)-2,4-hexadiene (b.p. 132–134°C). The diene was identified as the single stereoisomer by comparison of its boiling point and spectral properties to those of an authentic compound [5].

The tetraethyl derivative reacted with HCl to yield 0.25 g (72.3%) of pure 4,5-diethyl-(3E,5E)-3,5-octadiene (b.p. 63°C, 750 Torr). This pure stereoisomer exhibited spectral properties identical to those reported for the same characterized compound [6].
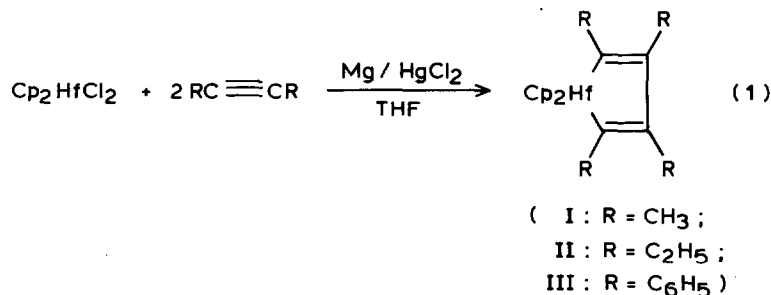
The tetraphenyl derivative yielded 0.383 g (71.3%) of a white compound after reaction with HCl. The melting point was 183°C (lit. [6,19] 182, 183°C).

Results and discussion

The one-step synthesis reported in this work for the substituted dicyclopentadienylhafnacyclopentadienes appears to give the highest yields of these compounds reported to date. Other than the synthesis using $Cp_2Hf(CO)_2$ as the starting material [4], other existing preparations of metallacyclopentadienes are lengthy, or result in low net yields [7–15].

Two of the compounds prepared in this work, the tetraethyl and tetraphenyl derivatives, have been synthesized and characterized previously. The tetraphenyl-hafnacyclopentadiene was prepared by the photolysis of $Cp_2Hf(CH_3)_2$, with diphenylacetylene [11,16]. As previously mentioned, both the tetraphenyl and tetraethyl derivatives can be obtained from $Cp_2Hf(CO)_2$ with the appropriate alkynes [4,17]. Attempts to prepare dicyclopentadienyl-2,3,4,5-tetramethylzirconacyclopentadiene from $Cp_2Zr(CO)_2$ failed; no attempt to prepare the analogous hafnium derivative was reported. However, our method produces both the zirconium and hafnium derivatives in high yields.

The use of mercuric chloride is necessary in the reduction of Cp_2HfCl_2 as with the analogous Cp_2ZrCl_2 [1]; without it, reductions are slow and reactions are incomplete. Apparently, magnesium reduces $HgCl_2$ to metallic mercury, which forms an amalgam with the excess magnesium powder. The amalgamated magnesium is, therefore, the principal reducing agent. This contention is supported by the fact that the use of an equivalent amount of metallic Hg in place of $HgCl_2$ gives the same results as described above.

$$Cp_2HfCl_2 + 2\,RC\equiv CR \xrightarrow[\text{THF}]{\text{Mg / HgCl}_2} \quad \begin{array}{c} R \quad R \\ \diagdown \diagup \\ Cp_2Hf \\ \diagup \diagdown \\ R \qquad R \end{array} \qquad (1)$$

(I : R = CH_3 ;
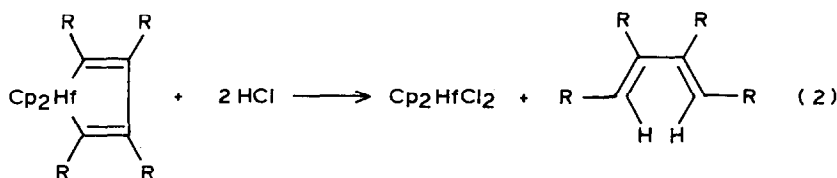II : R = C_2H_5 ;
III : R = C_6H_5)

The general reaction carried out in this work is shown in eq. 1.

The new tetramethylhafnacyclopentadiene (compound I) was characterized by elemental analysis, mass, infrared, ^{1}H and ^{13}C NMR spectral studies, and also by its degradation product after reaction with HCl. The yellow-orange crystalline product exhibits a sharp singlet at δ 5.93 ppm, assignable to the ten equivalent cyclopentadienyl protons. The inequivalent methyl protons are observed as overlapping singlets at δ 1.60 ppm. The mass spectrum shows a parent ion peak at m/e 418 together with fragments at m/e 349 and 310 from successive loss of 2-butyne. The structurally significant bands in the infrared spectrum appear at 3100 (CH stretching, Cp), 2900, 2835 (CH stretching), 1594 (C=C stretching), 1440 (CC stretching), 1015 (CH in-plane deformation) and 798 cm^{-1} (CH out-of-plane deformation). These bands are characteristic of metallocene-type structures [18].

The spectral properties of the tetraphenyl and tetraethyl derivatives, compounds II and III, are in good agreement with those reported elsewhere for the characterized products.

The metallacycles were treated with aqueous HCl in a manner similar to that reported by Freedman [19]. The general reaction is shown in eq. 2. Because of the

$$
\begin{array}{ccc}
\text{Cp}_2\text{Hf} \left[\begin{array}{c} R \quad R \\ \diagdown \diagup \\ \diagup \\ \diagdown \diagup \\ R \quad R \end{array} \right] + 2\,\text{HCl} \longrightarrow \text{Cp}_2\text{HfCl}_2 + R-\!\!\left[\begin{array}{c} R \quad R \\ \diagdown \diagup \\ \diagdown \\ H \quad H \end{array} \right]\!\!-R & (2)
\end{array}
$$

solubility of Cp$_2$HfCl$_2$ in water, the yield of recovery was low in the methylene chloride extract. However, its identity was determined by its melting point (230–233°C), and ^{1}H NMR spectrum. Also isolated from all these reactions was the stereospecific E,E-isomer of the substituted 1,3-butadiene. The tetramethyl derivative led to specifically 3,4-dimethyl-($2E,4E$)-2,4-hexadiene (b.p. 134°C), and compared identically to that of an authentic sample in terms of spectral properties (UV, IR, NMR) [5].

Compound II, after reaction with HCl, gave 4,5-diethyl-($3E,5E$)-3,5-octadiene (b.p. 63°C), and was identical in spectral properties to those reported for this compound [6]. The HCl degradation product of III yielded 1,2,3,4-tetraphenyl-($1E,3E$)-1,3-butadiene (m.p. 183°C), which is identical in various spectral properties reported earlier [6,19].

Whereas Rausch et al. have assigned ^{13}C NMR signals to some titanacyclopentadiene systems [20], and Jones and Peterson have performed analogous assignments to zirconacyclopentadienes [14] as did Thanedar and Farona [1], ^{13}C NMR assignments have not yet been made for the corresponding hafnium compounds. We have investigated the ^{13}C spectra of the three compounds prepared in this work; data are shown in Table 1.

For compound I, proton-decoupled and off-resonance decoupled (ORD) ^{13}C NMR spectra were obtained. The singlet at δ 109.19 ppm is split into a doublet in the ORD spectrum; hence, this peak is assigned to the equivalent carbon atoms of the Cp rings. The signals in the aliphatic region at δ 20.31 and 14.95 ppm are split into quartets in the ORD spectrum, and are attributable to C(6)–C(9). The quaternary carbon atoms, C(2) and C(5) in the metallacyclic ring are bonded

TABLE 1

¹³C NMR DATA OF SUBSTITUTED HAFNACYCLOPENTADIENES [a]

¹³C NMR DATA OF SUBSTITUTED HAFNACYCLOPENTADIENES [a]

δ (ppm)	δ (ppm)	δ (ppm)
Cp: 109.19	Cp: 109.03	Cp: 110.92
C(2,5): 184.97	C(2,5): 192.77	C(2,5): 196.82
C(3,4): 131.99	C(3,4): 134.22	C(3,4): 148.73
C(6,7): 20.31	C(6,8): 29.21	C(6): 141.65
C(8,9); 14.95	C(7,9): 21.14	C(7): 139.94
	C(10,12): 14.25	C(8–13): 130.84, 127.52
	C(11,13): 14.01	127.32, 126.34
		124.28, 122.89

[a] $CDCl_3$ was the solvent. TMS was the internal standard.

directly to hafnium and are substantially shifted downfield from the other two ring carbons (C(3) and C(4)). This shift is diagnostic of a metallacyclopentadiene system and has been observed previously [20]. As expected, the signals at δ 184.97 and 131.99 ppm remain unchanged in the ORD spectrum.

In order to assign the signals in the ¹³C spectrum of compound II, proton-decoupled and attached proton test (APT) ¹³C spectra were obtained. The Cp carbons are assigned to the signal at δ 109.03 ppm. The aliphatic region exhibits four peaks at δ 14.01, 14.25, 21.14 and 29.21 ppm. When subjected to APT, the signals at 21.14 and 29.21 ppm are inverted, whereas the other two are not. Consequently, those which are inverted correspond to the secondary methylene carbons (C(6), C(8), C(10), C(12)) while the others are attributed to the methyl carbon signals. The carbon atoms of the CH_2 and CH_3 groups closest to the metal (C(6), C(8), C(7), C(9)) are more strongly deshielded than the groups away from hafnium. Hence, the signals at δ 29.21 and 21.14 ppm are assigned to the C(6), C(8) and C(10), C(12) atoms, respectively. The signals at 14.25 and 14.01 ppm, therefore, arise from C(7), C(9) and C(11), C(13), respectively. Finally, the signals at δ 192.77 ppm are assigned to C(2), C(5), whereas the δ 134.42 ppm peak is due to C(3), C(4). This is further confirmed in the APT spectrum, where both signals are inverted.

The ¹³C chemical shift values for compound III are in good agreement with those of the titanium analogue, reported by Rausch et al. [20], and are assigned accordingly, as shown in Table 1.

Acknowledgment

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