Unsymmetrically substituted hafnacyclopentadiene compounds: synthesis and structure

Milind B. Sabade, Michael F. Farona*,

Department of Chemistry, The University of Akron, Akron, OH 44325 (U.S.A.)

Eugene A. Zarate and Wiley J. Youngs *

Department of Chemistry, Case Western Reserve University, Cleveland, OH 44106 (U.S.A.)

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Abstract

Hafnocene dichloride was reduced with amalgamated magnesium in the presence of asymmetric alkynes to give high yields of the corresponding bis(cyclopentadienyl)hafnacyclopentadiene compounds. An X-ray crystal structure has been performed on bis(η^5-cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-dimethylhafnacyclopentadiene (η^5-C$_5$H$_5$)$_2$Hf[C(SiMe$_3$)C(Me)C(Me)C(SiMe$_3$)] crystallized in the triclinic space group $P\bar{1}$ in a unit cell of dimensions a 9.067(3), b 10.421(3), c 12.296(4) Å, α 100.13(2), β 87.52(2), γ 105.07(2)° and V 1170.1(6) Å^3. The final agreement indices for 4719 reflections having $F_0^2 \geq 0$ are $R(F) = 0.047$.

Introduction

In an earlier paper, we reported the one-step synthesis of bis(η^5-cyclopentadienyl)hafnacyclopentadienes by reduction of Cp$_2$HfCl$_2$ with amalgamated magnesium in the presence of symmetrical alkynes [1]. In an effort to prepare unsymmetrically-substituted hafnacyclopentadienes, hafnocene dichloride was reduced in the presence of equimolar amounts of two symmetrical alkynes, e.g., diphenylacetylene and 3-hexyne. Surprisingly, very little, if any, of the diphenyldimethylhafnacyclopentadiene derivative was obtained. Instead, only the presence of the symmetrical compounds tetraphenyl- and tetramethylhafnacyclopentadienes were observed to a significant extent.

We have now extended the synthetic aspects of this work to include unsymmetrically-substituted derivatives of these metallacycles by the use of asymmetric alkynes.

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* Person to whom crystallographic questions should be directed.

Experimental

Starting materials and solvents

Hafnocene dichloride was purchased from Alfa and used as received. Phenylacetylene and 1-phenyl-1-propyne (Farchan) were purified by vacuum distillation, deoxygenated by purging with argon, and stored over 4 Å molecular sieves. 1-Trimethylsilyl-1-propyne (Aldrich) was used as received. Magnesium powder (70–80 mesh) and mercuric chloride were obtained from Fisher and used as received.

Ether and tetrahydrofuran were dried over the sodium ketyl of benzophenone and freshly distilled over lithium aluminum hydride.

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 4 Å molecular sieves before entering the glove box. Alumina (CAMAG, neutral grade) was predried by heating on a rotary evaporator with a heat gun. The alumina was deactivated with argon-saturated water (5% by weight) and stored under argon.

Physical methods

Proton NMR spectra were recorded on a Varian EM360 spectrometer and ^{13}C NMR spectra were taken on a Varian FT80A multinuclear NMR spectrometer. For both types of spectra, $CDCl_3$ was used as the solvent and TMS served as the internal standard. Infrared spectra were recorded on a Perkin–Elmer 597 spectrophotometer. Mass spectra were determined on a Finnigan 1015 mass spectrometer. Melting points were taken on a Thomas Hoover capillary apparatus and are uncorrected. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratory, Inc., Woodside, NY.

Preparation of the complexes

The experimental procedures for the synthesis of the hafnacycles are analogous; therefore, only one of these is described in detail. Differences in procedures are pointed out where appropriate.

Synthesis of 1,1-bis(η⁵-cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-dimethylhafnacyclopentadiene (I). A 250 ml, two-necked flask fitted with an argon inlet and a rubber septum was filled with argon by a series of evacuate-fill cycles. To the flask was added 0.948 g (2.5 mmol) of hafnocene dichloride, 0.303 g (12.5 mmol) of Mg powder, 0.677 g (2.5 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, followed by 1.12 g (10 mmol) of 1-trimethylsilyl-1-propyne. The flow of argon was stopped and the reaction mixture was stirred for 27 h at room temperature in a closed system, during which time the color gradually changed to brown. The volatiles 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 under high vacuum, yielding 1.21 g (90.9%) of a yellow compound. An analytically pure sample and crystals suitable for structure determination were grown from dry pentane by cooling the solution to 0°C for one

day. This product was characterized as a single stereoisomer, viz. 1,1-bis(η^5-cyclopentadienyl)-2,5-bis(trimethylsilyl)-3,4-dimethylhafnacyclopentadiene on the basis of its spectral properties, spectral properties of the organic ligand obtained after reaction with HCl, and its crystal structure determination (vide infra). Found: C, 50.08; H, 6.67. $C_{22}H_{34}Si_2Hf$ calc: C, 49.55; H, 6.38%.

Synthesis of 1,1-bis(η^5-cyclopentadienyl)dimethyldiphenylhafnacyclopentadiene (II). In this case, 0.580 g (5 mmol) of 1-phenyl-1-propyne was used, the reaction time was 27 h, and the yield of the final product was 1.22 g (90.7%). This yellowish-orange compound was characterized by elemental analysis, ^{1}H NMR and IR spectra, and study of the spectral properties of the organic product obtained after reaction with HCl. The proton NMR spectrum of the product indicated that it was an isomeric mixture of dimethyldiphenyl derivatives. The separation and study of the spectral properties of the substituted butadiene isomers obtained after reaction with HCl revealed that two isomers were present: the 2,4-dimethyl-3,5-diphenyl, and 3,4-dimethyl-2,5-diphenyl derivatives. Found: C, 61.87; H, 4.55. $C_{28}H_{26}$ Hf calc: C, 62.16: H, 4.81%.

Attempted synthesis of 1,1-bis(η^5-cyclopentadienyl)diphenylhafnacyclopentadiene (III). For the preparation of this compound, 0.51 g (5 mmol) of phenylacetylene was used, the reaction time was 6 h, and the yield of the product was 0.80 g (62.5%). Spectral data indicated that the yellow compound was an isomeric mixture, but attempted separation of the hafnacycles on neutral alumina led only to decomposition. Reaction with HCl did not yield a mixture of the diphenylbutadiene isomers, but rather a polymeric substance which has not been characterized.

Reaction of the hafnacyclopentadienes with HCl

The hafnacycles were all treated with HCl to release the butadiene ligand. Since all three reactions were carried out in the same manner, only that of compound I is described in detail.

Compound I (1 g, 1.9 mmol) was dissolved in 20 ml of ether and treated with 20 ml of 1.2 *M* HCl. The color of the reaction mixture instantly changed to pale yellow. The mixture was stirred for 15 min at room temperature, and the aqueous and organic layers were separated. The aqueous layer was extracted with three 15 ml portions of ether, which were combined with the organic fraction, washed with a saturated solution of sodium bicarbonate, and dried over anhydrous $MgSO_4$. The solvent was removed on a rotary evaporator leaving a yellow liquid which was purified by column chromatography on silica gel (100–200 mesh) to yield 0.34 g (83.5%) of a pure colorless liquid. This product was characterized as 1,4-bis(trimethylsilyl)-2,3-dimethyl-(1*E*,3*E*)-butadiene on the basis of its elemental analysis and spectral properties. Found: C, 64.34; H, 11.50. $C_{12}H_{26}Si_2$ calc: C, 63.66; H, 11.49%.

When 1 g (1.9 mmol) of II was treated with HCl for 3 h, the product was obtained as a semicrystalline solid (0.34 g, 79.6%). Spectral data indicated that the substituted butadiene was an isomeric mixture of 1,3-diphenyl-2-methyl-(1*E*,3*E*)-1,3-pentadiene (**a**) and 1,4-diphenyl-2,3-dimethyl-(1*E*,3*E*)-1,3-butadiene (**b**). Isomers **a** and **b** were separated by taking advantage of the insolubility of **b** in ethanol to yield 0.26 g (76.5%, based on the combined yield of the product) of **a** and 0.05 g (14.7%) of **b**. The spectral properties of **a** and **b** are identical to those of the same compounds reported by Eisch and Kaska [2].

In the case of compound III, 1 g (1.95 mmol) was treated with HCl for 1 h, but

only a yellow-colored, sticky substance was obtained after workup. The compound appears to be a polymer of diphenylbutadiene.

Collection of the X-ray diffraction data

A yellow single crystal (dimensions 0.34 × 0.26 × 0.30 mm) suitable for examination by X-ray diffraction procedures was sealed in a thin-walled glass capillary in an argon filled drybox. The crystal was mounted for data collection on a Syntex P2$_1$ automated four-circle diffractometer. The compound was found to be triclinic and no systematic absences were observed suggesting the space group $P\bar{1}$. Unit cell parameters and the orientation matrix were obtained and data collection was carried

Table 1

Experimental data for the X-ray diffraction study of Hf(C$_5$H$_5$)$_2$C$_4$(Si(CH$_3$)$_3$)$_2$(CH$_3$)$_2$

Formula	HfSi$_2$C$_{22}$H$_{34}$
Formula weight	533.18 amu
Space group	$P\bar{1}$
a	9.067(3) Å
b	10.421(3) Å
c	12.296(4) Å
α	100.13(2)°
β	87.52(2)°
γ	105.07(2)°
V	1170.1(6) Å^3
Z	2
ρ(calc)	1.51 g/cc
Crystal dimensions	0.34 × 0.30 × 0.26 mm
Crystal faces	{1 0 0}, {−1 0 0}, {0 0 1},
	{0 0 −1}, {0 −2 2}, {0 2 −2}
Crystal volume	3.16 × 10^{-3} mm^3
Diffractometer	Syntex P2$_1$
Radiation	Mo-K_α (0.71073 Å)
Monochromator	graphite crystal
Linear absorption coefficient	45.214 cm^{-1}
Transmission factors	0.2876–0.4282
Temperature	23°C
Scan type	$2\theta-\theta$
Scan speed	3.91° min^{-1}
Scan range	1.0° below K_{α_1} to 1.0° above K_{α_2}
2θ scan limits	3.0–50.0°
Standard reflections	3 per 100 reflections
Indices	{1 2 −8}, {2 −7 1}, {6 −1 1}
Crystal stability	No indication of standard reflection decay during data collection
Total reflections scanned	5344 (165 were standards)
Unique data $F_0^2 \geq 0\sigma(F_0^2)$	4719
Average absorption correction	0.6149
Final number of variables	226
$R(F)$ ($F_0^2 \geq 0\sigma F_0^2$)	0.047
$R_w(F)$ ($F_0^2 \geq 0\sigma F_0^2$)	0.047
$R(F)$ ($F_0^2 \geq 3\sigma F_0^2$)	0.038
$R_w(F)$ ($F_0^2 \geq 3\sigma F_0^2$)	0.045

out using a $2\theta-\theta$ scan. Details relevant to the structure appear in Table 1. Data were corrected for Lorentz and polarization factors and were reduced to $|F_0|$ values.

Solution and refinement of the structure

The analytical form of the scattering factors for neutral hafnium, silicon and carbon were used throughout the analysis [3a]. The contributions of all non-hydrogen atoms were corrected for both the real $(\Delta f')$ and imaginary $(\Delta f'')$ components of anomalous dispersion [3b]. The positions of the non-hydrogen atoms were found by direct methods [4]. Interpretation of the MULTAN solution led to the location of the hafnium atom, both silicons and several of the cyclopentadienyl and butadiene carbon atoms. The remaining carbon atoms were located via a series of difference-Fourier syntheses, each being phased by an increasing number of atoms. All hydrogen atoms whose approximate positions could be obtained from the electron density map were placed in idealized positions, those remaining were included by calculation (all were based upon C–H 0.95 Å, tetrahedral and trigonal angles and idealized thermal parameters with B 1.0 Å^2 greater than the equivalent B of the atom to which it is attached) [5]. A numerical absorption correction was performed based on the indexed and measured faces of the crystal and the contents of the unit cell. Refinement was based on F and involved only those reflections having $F_0^2 \geq 0$. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms led to final convergence with $R(F) = 0.047$, $R_w(F) = 0.047$ and $GOF = 1.52$ for 226 variables and 4719 reflections.

Results and discussion

The one-step syntheses of the compounds reported herein, like those of the symmetrically-substituted metallacycles [1], also affords very high yields of products. To the best of our knowledge, none of the compounds in this work have been reported previously.

For compound I, which is a yellow, crystalline material, the structurally-significant bands in the infrared spectrum appear at 2950 (CH aliphatic stretching), 1590 (C=C stretching), 1435 (CC stretching), 1020 (CH in-plane deformation) and 790 (CH out-of-plane deformation) cm^{-1}. These bands are characteristic of metallocene-type structures [6].

Compound I exhibits a sharp singlet at δ 6.1 ppm, assignable to the ten equivalent cyclopentadienyl protons. Eighteen equivalent methyl resonances of the trimethylsilyl group appear at δ 0.16 ppm as a singlet. The singlet at δ 1.86 ppm is attributable to the six equivalent protons of the two methyl groups on the ring.

The proton decoupled ^{13}C NMR spectrum of I shows the Cp carbons as a singlet at δ 109.91 ppm. The quaternary carbons at positions 2 and 5 in the metallacyclic ring which are bonded directly to hafnium are substantially shifted downfield (δ 200.32 ppm) from carbon atoms 3 and 4 (δ 144.75 ppm). This shift is diagnostic of a metallacyclopentadiene ring system and has been observed previously [1,7]. The aliphatic region exhibits two signals at δ 25.47 and 2.47 ppm, which are assigned to the carbon atoms of the methyl groups, and the carbon atoms of the trimethylsilyl group, respectively.

Compound I is clearly a single geometric isomer, based on the data above. Two structures are possible which satisfy the spectral data, compounds **A** and **B** shown below.

(A)   (B)
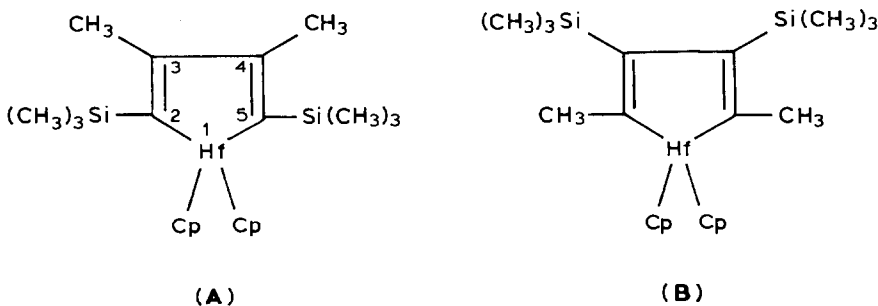
Compound I was treated with HCl, releasing the organic ligand:
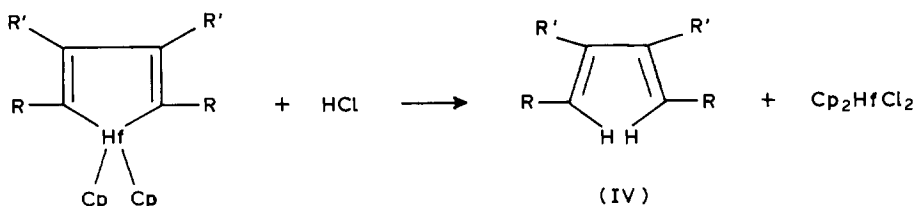
Compound IV, obtained after purification by column chromatography, exhibited a sharp singlet at δ 0.16 ppm (Si(CH$_3$)$_3$, 18H) a sharp singlet at δ 1.80 ppm (CH$_3$, 6H), and a sharp singlet at δ 5.4 ppm, (olefinic, 2H) in the ^{1}H NMR spectrum. These data clearly rule out structure (**B**) as a possibility; the structure of **A** was confirmed by a crystal structure determination, presented later in this work.

The ^{1}H NMR spectrum of II indicated that it was an isomeric mixture of the dimethyldiphenylhafnacyclopentadiene structure. Two signals are observed at δ 6.00 and δ 6.09 ppm (10H), which are attributable to two sets of equivalent cyclopentadienyl protons, whereas a broad multiplet at δ 6.8–7.2 ppm is assigned to the aromatic protons. Three singlets at δ 1.26, 1.66, and 2.00 ppm are observed with an intensity ratio of 2/1/1, respectively. These signals are assigned to the three sets of nonequivalent methyl protons.

After reaction of II with HCl, the two organic ligands were separated, purified by column chromatography, and identified as 1,3-diphenyl-2-methyl-(1E,3E)-1,3-pentadiene and 1,4-diphenyl-2,3-dimethyl-(1E,3E)-butadiene by comparison of physical and spectral properties with those reported for the same compounds elsewhere [2].

The ^{1}H NMR spectrum of III indicated that it was an isomeric mixture of a diphenylhafnacyclopentadiene compound. Two sharp signals at δ 6.00 and δ 6.03 ppm (Cp, 10H), a broad multiplet at δ 6.73–7.03 ppm (aromatic, 10H) and a broad multiplet at δ 5.73–5.86 (olefinic, 2H) are observed. The mass spectrum showed a parent ion peak at m/e 512.5 (M^+) together with fragments at m/e 435 ($M - C_6H_5^+$), and m/e 358 (435 − C$_6$H$_5$). The fragment at 310 corresponds to Cp$_2$Hf$^+$. Attempts to separate these hafnacycles by column chromatography on neutral alumina led to decomposition, and reaction with HCl yielded a sticky, polymeric

Table 2

Selected interatomic distances (Å) and angles (°) with standard deviations for Hf(C$_5$H$_5$)$_2$C$_4$(Si-(CH$_3$)$_3$)$_2$(CH$_3$)$_2$

Hf–C(1)	2.486(9)	Hf–C(14)	2.215(6)
Hf–C(2)	2.521(9)	Si(1)–C(11)	1.861(6)
Hf–C(3)	2.505(9)	Si(1)–C(15)	1.861(11)
Hf–C(4)	2.494(9)	Si(1)–C(16)	1.850(10)
Hf–C(5)	2.480(9)	Si(1)–C(17)	1.866(10)
Hf–C(6)	2.501(8)	Si(2)–C(14)	1.879(6)
Hf–C(7)	2.480(9)	Si(2)–C(20)	1.847(12)
Hf–C(8)	2.463(10)	Si(2)–C(21)	1.889(11)
Hf–C(9)	2.474(9)	Si(2)–C(22)	1.866(13)
Hf–C(10)	2.477(8)	Si–C avg.	1.865(29)
Hf–C(Cp)avg.	2.488(28)	C(11)–C(12)	1.370(8)
Hf–Cent	2.218	C(12)–C(13)	1.503(9)
Hf–Cent′	2.208	C(13)–C(14)	1.346(9)
Hf–C(11)	2.230(5)		
C(11)–Hf–C(14)	82.7(2)	Hf–C(14)–C(13)	107.9(4)
Cent–Hf–Cent′	133.12	Si(1)–C(11)–C(12)	123.5(4)
Cent–Hf–C(11)	106.68	Si(2)–C(14)–C(13)	122.7(5)
Cent–Hf–C(14)	108.21	C(11)–C(12)–C(13)	122.8(5)
Cent′–Hf–C(11)	106.83	C(11)–C(12)–C(18)	121.0(6)
Cent′–Hf–C(14)	107.73	C(13)–C(12)–C(18)	116.2(5)
Hf–C(11)–Si(1)	130.9(3)	C(12)–C(13)–C(14)	120.9(5)
Hf–C(14)–Si(2)	129.2(3)	C(12)–C(13)–C(19)	115.6(6)
Hf–C(11)–C(12)	105.6(4)	C(14)–C(13)–C(19)	123.5(6)

compound. It is known that 1,3-diphenyl-1,3-butadiene dimerizes at room temperature [8].

Description of the structure

Important interatomic distances and angles and their standard deviations (e.s.d.'s) are shown in Table 2. The molecular structure and atom numbering scheme of Hf(C$_5$H$_5$)$_2$C$_4$(Si(CH$_3$)$_3$)$_2$(CH$_3$)$_2$ are shown in Fig. 1. The configuration of the complex is clearly that of a metallocycle with the four butadiene carbons being coplanar with the hafnium atom as opposed to a η^4-metal-coordinated butadiene [9].

The hafnium-butadiene-bis-cyclopentadienyl portion of the molecule is nearly identical to the analogous portion of 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylhafnole (V) [10]. The cyclopentadienyl rings exhibit a staggered conformation with the Hf–C(cyclopentadienyl) bond lengths ranging from 2.463(10) to 2.521(9) Å. The distances from the hafnium to the ring centers are 2.208 and 2.218 Å. The Cent–Hf–Cent′ angle [11*], at 133.12°, is greater than the expected tetrahedral angle of 109°, presumably due to steric interactions between cyclopentadienyl rings, but comparable to that of its analog V. The centroid-Hf-C(α carbon of the butadiene) angles average 107.36°. The C(11)–Hf–C(14) bond angle is 82.7(2)°, four degrees greater than the comparable angle of V at 78.7(8)°, but is considerably less than the expected tetrahedral angle.

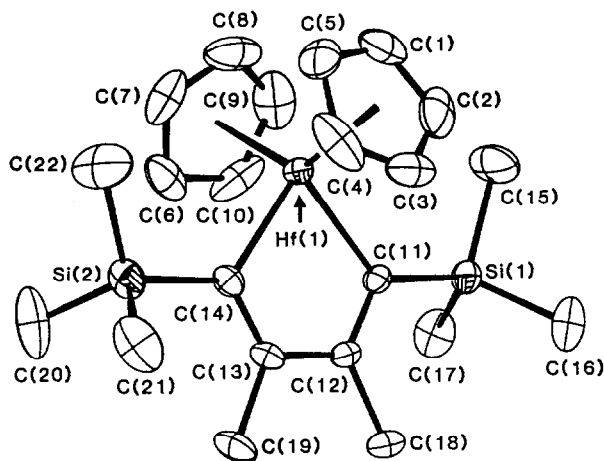* Reference number with asterisk indicates a note in the list of references.

Fig. 1. ORTEP labeling diagram for Hf(C$_5$H$_5$)$_2$C$_4$(Si(CH$_3$)$_3$)$_2$(CH$_3$)$_2$. The thermal ellipsoids are drawn at the 20% probability level. The hydrogens have been omitted for clarity.

The geometry of the five-membered heterocyclic ring system in Hf(C$_5$H$_5$)$_2$C$_4$(Si-(CH$_3$)$_3$)$_2$(CH$_3$)$_2$ shows equivalent bond distances, within e.s.d.'s, to those of Hf(C$_5$H$_5$)$_2$C$_4$(C$_6$H$_5$)$_4$ and are listed in Table 2. The bond angles, however, vary slightly with Hf–C(α-carbon)–C(β-carbon) bond angles being 105.6(4) and 107.9(4)° and the C(α-carbon)–C(β-carbon)–C(β-carbon)' bond angles at 122.8(5) and 120.9(5)°, compared to the α carbon angles of V at 114.1(8) and 113.1(8)° and the β carbons of V at 114(2) and 120(2)°. The Hf–C(α-carbon–Si angles at 130.9(3) and 129.2(3)° are greater than the ideal value of 120° for an sp^2 carbon atom. The other silicon–carbon and carbon–carbon distances and angles are unremarkable.

In our original attempts to synthesize unsymmetrically-substituted hafnacyclopentadienes, the approach was to add equimolar amounts of two symmetrically-substituted acetylenes, such as diphenylacetylene and 3-hexyne, or 2-butyne and 3-hexyne, and the like. However, this approach, somewhat surprisingly, led only to the isolation and/or spectral identification of symmetrically-substituted hafnacyclopentadienes. Little, if any, of the mixed compounds could be detected.

Another approach would be to assume a stepwise coordination of the alkyne to "Cp$_2$Hf", analogous to that of the synthesis of titanacyclopentadienes [12] and add the various acetylenes individually at certain times during the reaction. The problem with this approach is the rather lengthy reaction time to obtain high yields of the hafnacycles. It is difficult to estimate the time of addition of the second alkyne.

Furthermore, in our attempts to synthesize unsymmetrically-substituted titanacyclopentadienes by stepwise addition of two different alkynes, starting from both Cp$_2$Ti(CO)$_2$ and Cp$_2$TiCl$_2$/Mg, only the symmetrically-substituted final compounds were observed as the major products [13]. Shur et al. have had success in synthesizing unsymmetrical titanacyclopentadienes by stepwise addition of two different symmetrical acetylenes [14]. However, this approach, in our hands, did not lead to the desired materials as major products of the reactions.

Acknowledgment

Supplementary material available: Atomic positional parameters, thermal parameters, complete tables of bond lengths and angles and tables of indices with F(obs) vs. F(calcd) (26 pages) are available from W.J.Y.

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