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Some metallabicyclo-octadienes and -nonadienes of dicyclopentadienyltitanium, -zirconium and -hafnium

Shahid M. Yousaf, Michael F. Farona *

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

Raymond J. Shively Jr. and Wiley J. Youngs *

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

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Abstract

Titanocene, zirconocene, and hafnocene dichlorides were reduced in the presence of terminally disubstituted 1,6-heptadiyne or 1,7-octadiyne to produce dicyclopentadienylmetallabicyclooctadienes and -nonadienes. The compounds were characterized by elemental analysis and ^1H and ^{13}C NMR spectrometry, and $(\text{C}_5\text{H}_5)_2\text{HfC}_7\text{H}_6[\text{Si}(\text{CH}_3)_3]_2$ was characterized by X-ray diffraction techniques. The compound crystallized in the triclinic space group $P\bar{1}$ in a unit cell of dimensions a 10.214(2), b 12.213(2), c 10.051(3) Å, α 79.53(2), β 105.25(2), γ 96.26(2)° and V 1187.2(5) Å³. Refinement was done to a final agreement for 3950 reflections with $F_0^2 \geq 3\sigma(F_0^2)$ of $R(F) = 0.042$

Introduction

Earlier papers reported the high yield synthesis of substituted dicyclopentadienylmetallacyclopentadiene complexes from Cp_2MCl_2 ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) and variously substituted alkynes [1–4]. Negishi et al. applied the synthetic technique to promote the bicyclization of enynes, in the process producing a zirconacyclopentene derivative [5].

In this paper, we report the bicyclization reactions of α,ω -bis(trimethylsilyl)-heptadiyne and -octadiyne.

Experimental

Starting materials and solvents

Titanocene dichloride was purchased from Strem Chemicals; zirconocene dichloride, hafnocene dichloride and *n*-butyllithium were obtained from Aldrich and used

* Person to whom crystallographic questions should be directed.

as received. Farchan supplied 1,6-heptadiyne and 1,7-octadiyne which were deoxygenated by purging with argon. Trimethylsilyl chloride (Aldrich) was distilled over calcium hydride. Magnesium (70–80 mesh, Fisher) and mercuric chloride (MCB) were used without further purification. Benzene and pentane were distilled over calcium hydride. Tetrahydrofuran and ether were distilled over sodium benzo-phenone immediately before use.

All manipulations of the air-sensitive metallacycles were performed in an argon-filled glove box. Column chromatography was carried out under argon using neutral grade alumina (Aldrich). The alumina was warmed with a heat gun on a rotary evaporator attached to a vacuum pump to remove water and oxygen, and then deactivated with argon-saturated water (5% by weight) and stored under argon.

The syntheses of 1,7-bis(trimethylsilyl)-1,6-heptadiyne and 1,8-bis(trimethylsilyl)-1,7-octadiyne were carried out according to literature methods, except that the original temperature was -78°C [6]. The compounds were characterized by elemental analysis, ^1H and ^{13}C NMR spectrometry. Found: C, 65.72; H, 10.24. $\text{C}_{13}\text{H}_{24}\text{Si}_2$ calc: C, 66.02; H, 10.23%. ^1H NMR (CDCl_3): δ 0.11 (s, 18H, $\text{Si}(\text{CH}_3)_3$), 1.69 (p, 2H, CH_2 , $J = 7.0$ Hz), 2.29 (t, 4H, CH_2 , $J = 7.0$ Hz). ^{13}C NMR (CDCl_3): δ (ppm) 85.02 (C(1)), 106.28 (C(2)), 19.03 (C(3)), 27.73 (C(4)), 0.12 ($\text{Si}(\text{CH}_3)_3$). Found: C, 67.84; H, 10.38. $\text{C}_{14}\text{H}_{26}\text{Si}_2$ calc: C, 67.14; H, 10.38%. ^1H NMR (CDCl_3): δ 0.12 (s, 18H, $\text{Si}(\text{CH}_3)_3$), 1.59 (m, 4H, CH_2), 2.27 (t, 4H, CH_2 , $J = 6.5$ Hz). ^{13}C NMR (CDCl_3): δ (ppm) 84.57 (C(1)), 106.91 (C(2)), 19.33 (C(3)), 27.60 (C(4)), 0.12 ($\text{Si}(\text{CH}_3)_3$).

Physical methods

^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer using CDCl_3 as the solvent. Infrared spectra were taken on a Perkin-Elmer 710B spectrophotometer. Melting points were measured on a Thomas-Hoover capillary apparatus, and are uncorrected. Elemental analyses were determined by Schwartzkopf Microanalytical Laboratory, Inc., Woodside, NY.

Preparation of the complexes

The experimental procedures for the synthesis of the metallacycles are analogous to those reported previously. A detailed procedure for the titanacycle and one zirconacycle are presented below.

Synthesis of dicyclopentadienyl-3-titanabicyclo[3.3.0]octadiene-1,4 (I)

A 250 ml, two-necked flask fitted with a gas adaptor and a rubber septum was evacuated and filled with argon several times. To the flask was added 0.06 g (2.5 mmol) of Mg powder and 0.62 g (2.5 mmol) of Cp_2TiCl_2 . The flask was flushed with argon for 15 min and 25 ml of freshly distilled THF was added, followed by 0.59 g (2.5 mmol) of 1,7-bis(trimethylsilyl)-1,6-heptadiyne. The gas inlet was closed and the mixture was stirred for 5 h at room temperature with a magnetic stirrer. The solvent was removed under vacuum and the flask was transferred to the glove box. The residue was dissolved in pentane and filtered through Celite packed on a fritted funnel. The pentane was removed under vacuum and the crude material was dissolved in a minimum amount of dry benzene and subjected to column chromatography. Elution with benzene brought down a dark orange band which, after the solvent was removed, yielded a red solid (0.55 g, 54% yield, m.p. $140\text{--}142^{\circ}\text{C}$).

The compound was purified further by recrystallization from pentane. Found: C, 66.50; H, 8.35. $C_{23}H_{34}Si_2Ti$ calc: C, 66.63; H, 8.26%.

Synthesis of dicyclopentadienyl-3-zirconabicyclo[3.3.0]octadiene-1,4 (II)

To a reaction flask prepared as described above was added 1.46 g (5.0 mmol) of Cp_2ZrCl_2 , 1.35 g (5.0 mmol) of $HgCl_2$, and 0.6 g (25 mmol) of Mg powder under argon. Then 1.18 g (5.0 mmol) of 1,7-bis(trimethylsilyl)-1,6-heptadiyne was added along with 40 ml of THF at 0 °C. The reaction mixture was allowed to reach room temperature and the mixture was stirred for 9 h, during which time the color changed to brown. The solvent was removed and the residue dried under vacuum. The crude product was dissolved in pentane and filtered through Celite in the glove box. An orange, crystalline product was obtained (1.97 g, 86% yield, m.p. 182–183 °C) from the pentane solution. Found: C, 59.84; H, 7.32. $C_{23}H_{34}Si_2Zr$ calc: C, 60.32; H, 7.48%.

Synthesis of dicyclopentadienyl-3-hafnabicyclo[3.3.0]octadiene-1,4 (III)

In this reaction, 1.89 g (5.0 mmol) of Cp_2HfCl_2 , 1.35 g (5.0 mmol) of $HgCl_2$, 0.6 g (25 mmol) of Mg and 1.18 g (5.0 mmol) of 1,7-bis(trimethylsilyl)-1,6-heptadiyne were used. The reaction time was 16 h and the weight of product was 2.21 g (81.5% yield, m.p. 192–193 °C). Found: C, 50.28; H, 6.24. $C_{23}H_{34}Si_2Hf$ calc: C, 50.67; H, 6.28%.

Synthesis of dicyclopentadienyl-8-zirconabicyclo[4.3.0]nonadiene-6,9 (IV)

For the preparation of this compound, 0.73 g (2.5 mmol) of Cp_2ZrCl_2 , 0.67 g (2.5 mmol) of $HgCl_2$, 0.3 g (12.5 mmol) Mg and 0.63 g (2.5 mmol) of 1,8-bis(trimethylsilyl)-1,7-octadiyne were added to 50 ml of THF. An orange, crystalline compound was obtained (0.9 g, 74% yield, m.p. 175–176 °C). Found: C, 61.87; H, 7.69. $C_{24}H_{36}Si_2Zr$ calc: C, 61.10; H, 7.69%.

Synthesis of dicyclopentadienyl-8-hafnabicyclo[4.3.0]nonadiene-6,9 (V)

In this reaction, 1.89 g (5.0 mmol) of Cp_2HfCl_2 , 1.35 g (5.0 mmol) of $HgCl_2$, 0.6 g (25 mmol) of Mg and 1.25 g (5.0 mmol) of 1,8-bis(trimethylsilyl)-1,7-octadiyne and 50 ml of THF were added to the reaction flask, and the mixture was stirred for 24 h at room temperature. A yellow, crystalline product was obtained (2.0 g, 76% yield, m.p. 177–178 °C). Found: C, 50.83; H, 6.42. $C_{24}H_{36}Si_2Hf$ calc: C, 51.54; H, 6.48%.

Reaction of the metallacycles with HCl

The complexes were allowed to react with HCl in a manner described previously [4] to release the organic ligand and produce the metallocene dichloride. The bicyclooctadienes yielded 1,2-bis(trimethylsilylmethylene)cyclopentane while the bicyclononadienes gave 1,2-bis(trimethylsilylmethylene)cyclohexane. The organic ligands were obtained in 77–81% yield and were characterized by elemental analysis and 1H and ^{13}C NMR spectrometry.

Collection of X-ray diffraction data

A single yellow crystal of compound III was selected for X-ray analysis and was fixed on the end of a glass fiber with epoxy. The crystal was aligned and data

Table 1

Experimental data for the X-ray diffraction study of $\text{Hf}(\text{C}_5\text{H}_5)_2\text{C}_7\text{H}_6(\text{Si}(\text{CH}_3)_3)_2$

formula	$\text{HfSi}_2\text{C}_{23}\text{H}_{34}$
formula weight	545.19 amu
crystal class	triclinic
space group	$P\bar{1}$
<i>a</i>	10.214(2) Å
<i>b</i>	12.213(2) Å
<i>c</i>	10.051(3) Å
α	79.53(2)°
β	105.25(2)°
γ	96.26(2)°
volume	1187.2(5) Å ³
<i>Z</i>	2
ρ (calc)	1.53 g/cc
crystal dimensions	0.36 × 0.32 × 0.14
crystal faces	{1 0 0}, {0 1 0}, {0 0 1}, {−1 0 0}, {0 −1 0}, {0 0 −1}, {0 1 1}, {−1 1 1}, {−2 2 −1}
crystal volume	3.04 × 10 ^{−3} mm ³
diffractometer	Syntex P2 ₁
radiation	Mo- K_α (0.71073 Å)
monochromator	graphite crystal
linear absorption coefficient	44.584 cm ^{−1}
transmission factors	0.2703–0.3618
temperature	22° C
scan type	2 θ – θ
scan speed	3.91° min ^{−1}
scan range	1.0° below $K_{\alpha 1}$ to 1.0° above $K_{\alpha 2}$
standard reflections	3 per 100 reflections
indices	{1 8 1}, {7 2 −1}, {1 5 4}
crystal stability	Some decay of the standard reflections was observed.
total reflections scanned	4600 (141 were standards)
unique data $F_0^2 \geq 3\sigma(F_0^2)$	3950
average absorption correction	0.5645
final number of variables	235
$R(F)$ $F_0^2 \geq 3\sigma(F_0^2)$	0.042
$R_w(F)$ $F_0^2 \geq 3\sigma(F_0^2)$	0.052

collected on a Syntex P2₁ automated diffractometer with the use of methods described previously [4]. Crystal parameters are given in Table 1.

Solution and refinement of the structure

The analytical forms of the scattering factors for neutral hafnium, silicon and carbon were used throughout the analysis [7a]. The contributions of all non-hydrogen atoms were corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion [7b]. Interpretation of the MULTAN solution led to the location of the hafnium atom, both silicons and several of the cyclopentadienyl and butadiene ring carbon atoms [8]. The remaining carbon atoms were located by a difference-Fourier synthesis. All hydrogen atoms were placed in idealized positions (C–H = 0.95 Å with $B = 1.0 \text{ \AA}^2$ greater than the equivalent B of the carbon to

Table 2

¹H NMR data for the bicyclic compounds

Compound	¹ H NMR signals and assignments, δ ^a
I	5.91 (s, 10H, Cp), 2.02 (t, 4H, CH ₂ , <i>J</i> = 7.0 Hz), 1.36 (p, 2H, CH ₂ , <i>J</i> = 7.0 Hz), 0.07 (s, 18H, Si(CH ₃) ₃).
II	5.85 (s, 10H, Cp), 2.38 (t, 4H, CH ₂ , <i>J</i> = 7.0 Hz) 1.30 (p, 2H, CH ₂ , <i>J</i> = 7.0 Hz), 0.16 (s, 18H, Si(CH ₃) ₃).
III	5.93 (s, 10H, Cp), 2.27 (t, 4H, CH ₂ , <i>J</i> = 7.0 Hz), 1.28 (p, 2H, CH ₂ , <i>J</i> = 7.0 Hz), 0.12 (s, 18H, Si(CH ₃) ₃).
IV	6.10 (s, 10H, Cp), 2.07 (m, 4H, CH ₂) 1.47 (m, 4H, CH ₂), 0.04 (s, 18H, Si(CH ₃) ₃).
V	6.05 (s, 10H, Cp), 2.13 (m, 4H, CH ₂), 1.5 (m, 4H, CH ₂), 0.05 (s, 18H, Si(CH ₃) ₃).

^a CDCl₃ solvent.

which it is bonded) [9]. A numerical absorption correction was based on the indexed and measured faces of the crystal and the contents of the unit cell. Full-matrix least-squares refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms led to final convergence with $R(F) = 0.042$, $R_w(F) = 0.052$ and $GOF = 2.02$ for 235 variables and 3950 reflections with $I \geq 3\sigma$.

Results and discussion

Metallacyclopentadienes with fused five- or six-membered rings were prepared in this work according to procedures developed in our laboratory for the synthesis of various metallacyclopentadienes [2,3,4]. In this case, α,ω -diynes were employed to give bicyclic compounds, according to the following general equation.

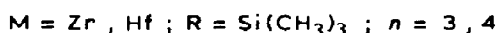
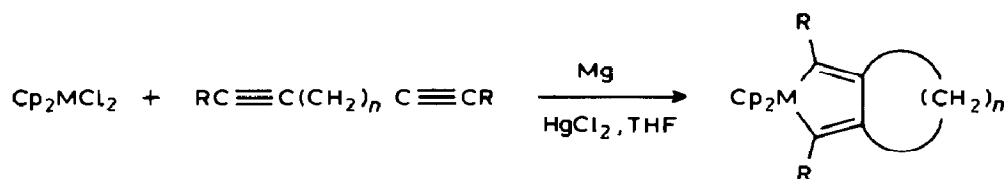


Table 2 shows the ¹H NMR signals obtained for compounds I–V.

¹³C NMR signals were also assigned with the aid of distortionless enhancement by polarization transfer (DEPT) spectra, and also by comparing the present data with similar systems already assigned in the literature [3,10,11]. These are shown in Table 3. Assignments are made based on the numbering systems as shown:

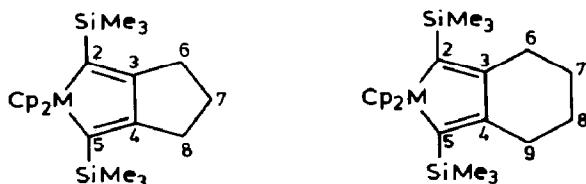


Table 3

 ^{13}C NMR data for the bicyclic compounds, $\delta(\text{ppm})^a$

Assignment	Compound			Assignment	Compound	
	I	II	III		IV	V
Cp	111.34	108.63	108.87	Cp	110.23	109.76
C(2),C(5)	204.18	189.98	189.84	C(2),C(5)	197.71	196.38
C(3),C(4)	131.80	132.55	139.23	C(3),C(4)	144.77	145.41
C(6),C(8)	36.29	40.02	38.88	C(6),C(9)	33.75	33.81
C(7)	22.90	20.61	21.77	C(7),C(8)	21.20	21.41
$\text{Si}(\text{CH}_3)_3$	1.65	1.27	1.55	$\text{Si}(\text{CH}_3)_3$	2.27	2.51

^a CDCl_3 solvent.

The proton decoupled ^{13}C NMR spectrum of I shows a total of six signals; the DEPT spectrum exhibits only four, since the signals arising C(2), C(5), and C(3), C(4) disappear in the DEPT spectrum. Therefore, the signals at 204.18 and 131.80 are attributed to these quaternary carbons, and those attached directly to the metal (C(2), C(5)) are shifted downfield with respect to C(3) and C(4). This shift is diagnostic of a metallacyclopentadiene system and has been observed in compounds of similar structure [11]. Ten (10) equivalent carbons of the Cp ring resonate at 111.34 ppm, and the aliphatic signals at 36.29 and 22.90 ppm are assigned as indicated in Table 3; C(6) and C(8) are downfield from C(7) since they are attached to olefinic carbons. The assignments of compounds II–V (Table 3) were made by similar reasoning.

The compounds were treated with HCl to release the organic ligands as shown in the following equations.

Compounds VI and VII appear to be specifically the *E,E* isomers. This is expected since reactions of a variety of metallacyclopentadienes with HCl led to the recovery of exclusively *E,E* isomers [2,3,4]. Also, molecular models of VI and VII

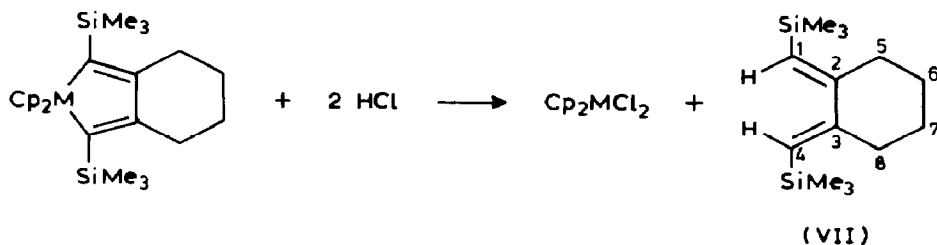
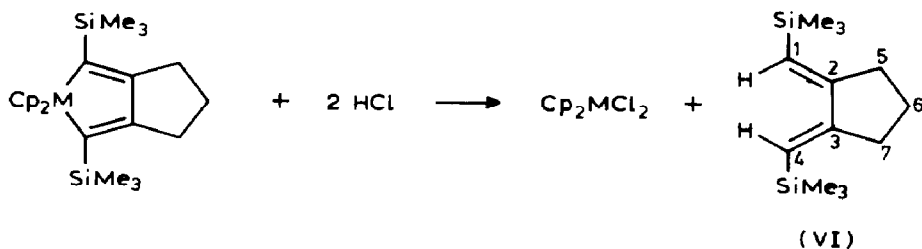


Table 4

Selected interatomic distances (Å) and angles (°) with standard deviations for $\text{Hf}(\text{C}_5\text{H}_5)_2\text{C}_7\text{H}_6(\text{Si}(\text{CH}_3)_3)_2$

Hf–C(1)	2.485(9)	Si(1)–C(11)	1.852(8)
Hf–C(2)	2.465(9)	Si(1)–C(15)	1.873(12)
Hf–C(3)	2.482(11)	Si(1)–C(16)	1.876(14)
Hf–C(4)	2.467(10)	Si(1)–C(17)	1.875(15)
Hf–C(5)	2.468(9)	Si(2)–C(14)	1.861(8)
Hf–C(6)	2.488(9)	Si(2)–C(21)	1.876(13)
Hf–C(7)	2.511(10)	Si(2)–C(22)	1.865(14)
Hf–C(8)	2.491(9)	Si(2)–C(23)	1.870(14)
Hf–C(9)	2.456(9)	C(11)–C(12)	1.355(11)
Hf–C(10)	2.453(9)	C(12)–C(13)	1.499(12)
Hf–C(Cp) avg.	2.477(18)	C(12)–C(18)	1.522(11)
Hf–Cent	2.194	C(13)–C(14)	1.342(12)
Hf–Cent'	2.196	C(13)–C(20)	1.516(11)
Hf–C(11)	2.233(7)	C(18)–C(19)	1.503(17)
Hf–C(14)	2.240(7)	C(19)–C(20)	1.460(17)
C(11)–Hf–C(14)	86.5(3)	Si(2)–C(14)–C(13)	124.4(6)
Cent–Hf–Cent'	131.3	C(11)–C(12)–C(13)	125.6(7)
Cent–Hf–C(11)	108.7	C(11)–C(12)–C(18)	127.7(8)
Cent–Hf–C(14)	107.9	C(13)–C(12)–C(18)	106.8(7)
Cent'–Hf–C(11)	105.6	C(12)–C(13)–C(14)	125.4(7)
Cent'–Hf–C(14)	107.7	C(14)–C(13)–C(20)	126.8(8)
Hf–C(11)–Si(1)	134.6(4)	C(12)–C(13)–C(20)	107.8(7)
Hf–C(14)–Si(2)	134.2(4)	C(12)–C(18)–C(19)	105.2(8)
Hf–C(11)–C(12)	101.1(5)	C(18)–C(19)–C(20)	108.3(8)
Hf–C(14)–C(13)	101.4(6)	C(13)–C(20)–C(19)	105.8(8)
Si(1)–C(11)–C(12)	124.1(6)		

show that considerable steric problems exist with *E,Z* or *Z,Z* structures. Some direct experimental evidence has also been obtained. The ^1H NMR signal of the olefinic protons of VI occurs as a triplet at δ 5.9 (2H) with $J = 1.9$ Hz due to long range allylic coupling. For *trans* coupling, J is in the 1.6–3.0 Hz range while *cis* splitting leads to $J = 0$ –1.5 Hz [13]. A doublet of triplets at δ 2.44 (4H, $J = 7.0$ and 2.0 Hz) is assigned to the CH_2 protons attached to C(5) and C(7), whereas a pentet at δ 1.70 (2H, $J = 7.0$) arises from the methylene protons on C(6). The methyl signals appear at δ 0.14 (s, 18H). The ^{13}C resonances for C(1) and C(4) appear at 116.88, C(2) and C(3) resonate at 157.72, C(5) and C(7) show a signal at 32.95, C(6) is at 23.9 and the methyl resonances appear at 0.43 ppm. The fact that the ^{13}C signal of the methyl groups is shifted upfield also supports the *E,E* conformation of VI. *E* isomers show trimethylsilyl ^{13}C signals around -1 ppm while those of *Z* isomers appear at δ 0.4–0.6 [14].

Description of the structure

Shown in Table 4 are selected interatomic distances and angles. Figure 1 illustrates the molecular structure and atom numbering scheme. Direct comparisons may be drawn between this structure, $\text{Hf}(\text{C}_5\text{H}_5)_2\text{C}_7\text{H}_6(\text{Si}(\text{CH}_3)_3)_2$ (III), and both $\text{Hf}(\text{C}_5\text{H}_5)_2\text{C}_4(\text{Si}(\text{CH}_3)_3)_2(\text{CH}_3)_2$ (VIII) [4] and $\text{Hf}(\text{C}_5\text{H}_5)_2\text{C}_4(\text{C}_6\text{H}_5)_4$ (IX) [12]. Bond lengths are nearly identical within the ranges of the e.s.d.'s along the

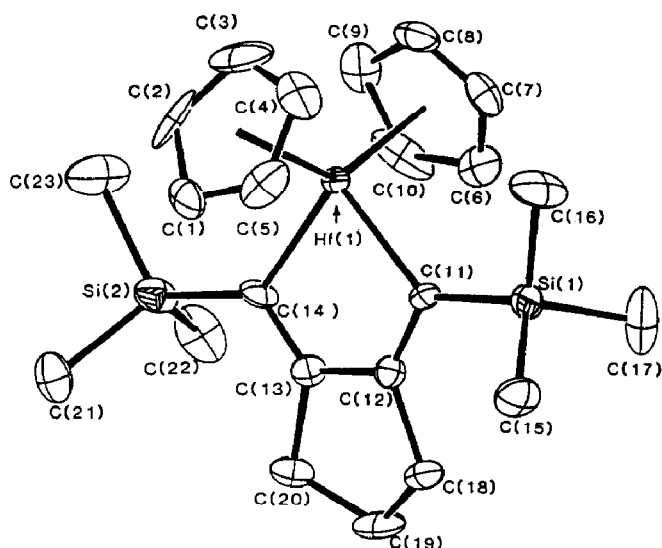


Fig. 1. ORTEP labeling diagram for $\text{Hf}(\text{C}_3\text{H}_5)_2\text{C}_7\text{H}_8(\text{Si}(\text{CH}_3)_3)_2$. The thermal ellipsoids are drawn at a 20% probability level. The hydrogens have been omitted for clarity.

biscyclopentadienyl–hafnium–butadiene portion of the molecules. Also, carbon–silicon bond distances in III and VIII are similar and not unusual.

The geometry around the hafnium can be roughly described as tetrahedral, with a centroid–Hf–centroid' angle of 131.3° , a $\text{C}(\alpha)\text{–Hf–C}(\alpha')$ angle of $86.5(3)^\circ$, and a centroid–Hf– $\text{C}(\alpha)$ average angle of 107.5° . (For convenience C(11) and C(14) are referred to as $\text{C}(\alpha)$, while C(12) and C(13) are referred to as $\text{C}(\beta)$). The closing of the second ring, as in III, is shown to impose steric requirements that distort the trigonal geometry of the butadiene carbons. Comparison of the $\text{C}(\alpha)\text{–Hf–C}(\alpha')$ angles in the three compounds shows that the angle is largest in III, $86.5(3)^\circ$, smaller in VIII, $82.7(2)^\circ$, and smaller yet in IX, $80.3(2)^\circ$. Similar shifts in bond angles are observed around the hafnium–butadiene ring systems. In VIII, the average hafnium– $\text{C}(\alpha)\text{–C}(\beta)$ angle is $105.6(4)^\circ$ versus $101.3(6)^\circ$ in III. Similarly, the $\text{C}(\alpha)\text{–C}(\beta)\text{–C}(\beta')$ angle is $122.8(5)^\circ$ in VIII as compared to $125.5(7)^\circ$ in III.

The synthesis of these bicyclic metallacycles provides a convenient method of making 1,2-dimethylenecycloalkanes in high yields. The trimethylsilyl groups function as protective species both in the synthesis of the metallacycles and the dimethylenecycloalkanes. When the synthesis of the metallacycle was attempted with 1,7-octadiyne, the bicyclic product was formed (according to NMR studies), but the product is difficult to purify and is obtained only in low yields. It was noted that considerable oligomerization of the monomer occurs with the unprotected diyne.

Therefore, it appears that the trimethylsilyl group (or some other protective entity which can sterically hinder oligomerization) is necessary to achieve high yields of the desired product. A wealth of chemistry is known to remove the silyl group and replace it with hydrogen or other functional groups.

Supplementary material available

Atomic positional parameters, thermal parameters, complete tables of bond lengths and angles and tables of indices with $F(\text{obs})$ vs. $F(\text{calcd})$ (24 pages) are available from W.J.Y.

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