Zirconocene–Mediated Intramolecular Carbon–Carbon Bond Formation of Two Alkynyl Groups of Bis(alkynyl)silanes

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Zirconocene-Mediated Intramolecular Carbon−Carbon Bond Formation of Two Alkynyl Groups of Bis(alkynyl)silanes

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Received July 16, 1997[⊗]

Abstract: Treatment of bis(phenylethynyl)silane (PhC≡C)$_2$SiR$_2$ (R = Me (**2a**), Et (**2b**) or Ph (**2c**)) with Cp$_2$ZrEt$_2$ (**1**) (Cp = cyclopentadienyl) and H$_2$O/CuCl in this order afforded (1*E*,3*E*)-1,4-diphenyl-1,3-butadiene (**3**) in 56−88% yields after hydrolysis. On the other hand, hydrolysis of the reaction mixture of **2a**−**h** with Cp$_2$ZrEt$_2$ gave silacyclobutene derivatives **4a**−**h** in 61−87% yields. Zirconium-containing intermediate **7** was obtained as crystals suitable for X-ray analysis when *t*-BuC$_5$H$_4$ was used as the ligands of a zirconocene derivative. Structure of **7** showed that the intermediate contained the zirconacyclobutene−silacyclobutene fused ring system. Reaction of silacyclobutene **4a** with CuCl selectively opened the silacyclobutene ring. The further treatment of the reaction mixture with PhI in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ gave 1,3,4-triphenyl-1-silyl-1,3-butadiene compound **16**. Zirconacyclopentadienes with an alkynylsilyl group at the α-position afforded zirconacyclohexadiene derivatives **19** in 82−98% yields. When *t*-BuC$_5$H$_4$ was used as the ligands instead of two Cp, the structure was determined by X-ray analysis. The structure clearly showed that **19** had the zirconacyclohexadiene−silacyclobutene fused ring system.

Introduction

The coupling of two organic groups on metals is a basic reaction of organometallic compounds. It has been well investigated for transition metal complexes.[4] However, it is very rare for main group metal compounds such as organosilicon compounds.[5,6] We found when bis(alkynyl)silanes were treated with Cp$_2$ZrEt$_2$ (Cp = cyclopentadienyl) and iodine in this order, intramolecular coupling of the two alkynyl groups was observed.[7]

Further investigation revealed that the transformation proceeded via silacyclobutene ring formation. We found that this type of new rearrangement is general for the series of zirconacycles such as zirconacyclopropenes (**I**), zirconacyclopentenes (**II**), and zirconacyclopentadienes (**III**) (*vide infra*). In this paper, we describe the details of this novel type reaction of alkynylsilane groups.[7]
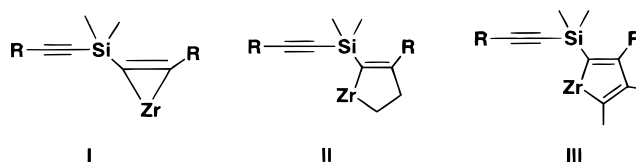
Results and Discussion

Intramolecular Coupling of Two Alkynyl Groups of Bis(alkynyl)silanes: Formation of Diene Derivatives. Recently, we have investigated the reactivity of Cp$_2$Zr(CH$_2$=CH$_2$)[8] which is quantitatively formed *in situ* from Cp$_2$ZrEt$_2$ (**1**). During the course of this study, we reported that the reaction of an alkynylsilane with **1** gave a zirconacyclopentene which was a coupling product of the alkyne with ethylene.[9] Iodination of such zirconacyclopentenes gives diiodobutene derivatives. However, unexpectedly, similar treatment of bis(phenylethynyl)-silanes (PhC≡C)$_2$SiR$_2$ (R = Me (**2a**), Et (**2b**), Ph (**2c**)) with 1 equiv of Cp$_2$ZrEt$_2$ and iodine in this order gave diphenyldiyne in high yields.[7]

A similar intramolecular carbon−carbon bond formation reaction was also observed when H$_2$O and CuCl instead of iodine was added to the reaction mixture of **2a**−**c** with **1**.

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[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1997.
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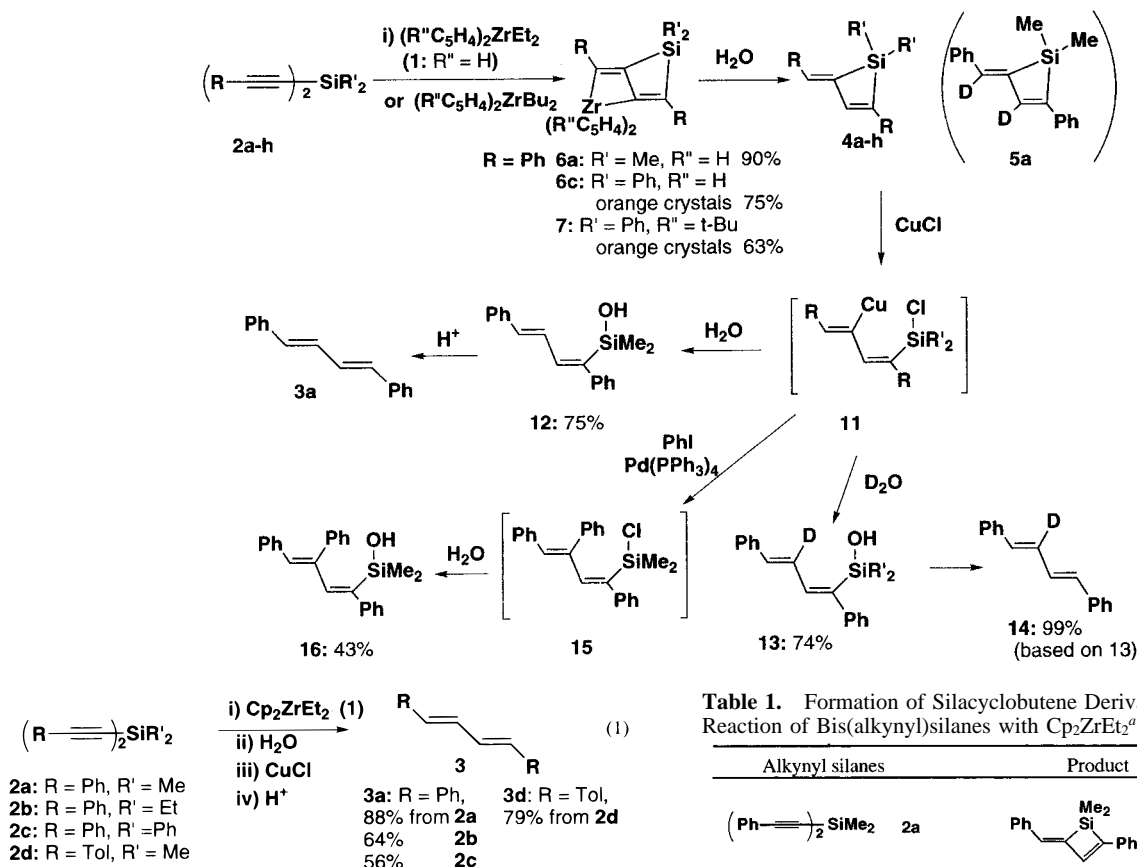(4) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987.
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Scheme 1

(1*E*,3*E*)-1,4-Diphenyl-1,3-butadiene (**3**) was obtained in good yields from **2a** (88%), **2b** (64%), and **2c** (56%) (eq 1).

Hydrolysis Product of the Intermediate: Formation of Silacyclobutene Compounds. Since this type of intramolecular carbon–carbon bond formation of two alkynyl groups of bis(alkynyl)silanes was quite unusual, we investigated the reaction mixture of **2a**–**c** with **1** (Scheme 1). Very interestingly, hydrolysis of the reaction mixture of **2a**–**c** with **1** afforded silacyclobutene derivatives **4a**–**c** in high yields as shown in Table 1.

Bis(anisylethynyl)silane **2e** and bis(tolylethynyl)silane **2h** also gave the similar silacyclobutenes **4e** and **4h**, respectively. It is noteworthy that not only aryl substituted bis(alkynyl)silanes such as **2a**–**c**, **2e**, and **2h** but also cyclohexenyl- and *tert*-butyl-substituted ones (**2f** and **2g**) gave similar types of silacyclobutene compounds, **4f** and **4g**, respectively, after hydrolysis of the reaction mixture with Cp$_2$ZrEt$_2$.

Preparative methods of silacyclobutenes are very limited.[10–13] *exo*-Alkylidenesilacyclobutenes have been prepared by Ishikawa by the reaction of silyl-substituted alkynes with polysilanes in the presence of an Ni(0) or Ni(II) species.[11b,c] Lukehart,

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Table 1. Formation of Silacyclobutene Derivatives by the Reaction of Bis(alkynyl)silanes with Cp$_2$ZrEt$_2$[a]

Alkynyl silanes	Product	Yield/%[b]
(Ph–≡–)$_2$SiMe$_2$　**2a**	**4a**	87 (65)
(Ph–≡–)$_2$SiEt$_2$　**2b**	**4b**	80 (67)
(Ph–≡–)$_2$SiPh$_2$　**2c**	**4c**	85 (70)
(MeO–C$_6$H$_4$–≡–)$_2$SiMe$_2$　**2e**	**4e**	87 (60)
(t-Bu–≡–)$_2$SiPh$_2$　**2f**	**4f**	76 (60)
(C$_6$H$_9$–≡–)$_2$SiPh$_2$　**2g**	**4g**	61 (52)
(Me–C$_6$H$_4$–≡–)$_2$SiPh$_2$　**2h**	**4h**	(66)

[a] Reaction time: 1 h. Reaction temperature: room temperature. Ratio of Cp$_2$ZrEt$_2$ to bis(alkynyl)silanes: 1.25:1. [b] GC yields. Isolated yields are given in parentheses.

McPhail, and co-workers have reported that 1,2-addition of Pt–H to one C–C triple bond of an bis(alkynyl)silane followed by an intramolecular insertion afforded *exo*-alkylidenesilacyclobutenyl ring compounds.[11d]

Formation of Zirconacyclobutene–Silacyclobutene Fused Complexes as an Intermediate. It is interesting that deu-

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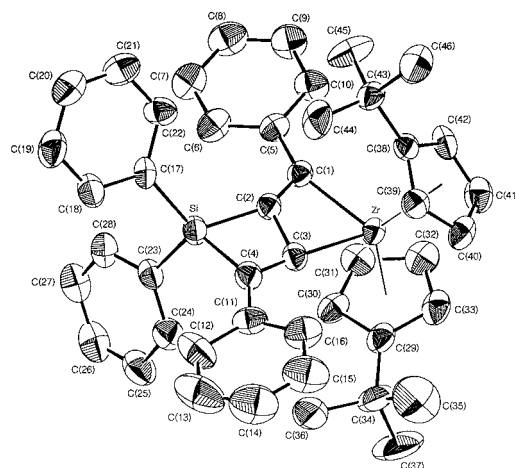
Figure 1. Perspective view of **7**.

terolysis instead of hydrolysis of the reaction mixture of **2a** with **1** afforded dideuterated compound **5a** in 86% yield with >99% of deuterium incorporation. This result suggested that the intermediate before hydrolysis has the zirconacyclobutene−silacyclobutene ring system. In fact, monitoring of the reaction mixture of **2a** with **1** showed the formation of **6a** in 90% NMR yield.

In the case of **2c**, the corresponding intermediate **6c** was obtained as orange crystals by the reaction of **2c** with Cp$_2$ZrBu$_2$ (Negishi reagent).[14] ^{1}H NMR spectrum of **6c** revealed one Cp signal at 5.58 ppm. Its ^{13}C NMR spectrum showed four olefinic carbons at 140.91, 142.33, 160.50, and 203.72 ppm. X-ray study of **6c**, unfortunately, resulted in the gradual loss of intensity during the measurement, and the final refinement led to a convergence with R_w of more than 10%.

In order to determine the structure of the zirconacyclobutene−silacyclobutene intermediate, a *t*-Bu group was introduced into cyclopentadienyl ligands as a substituent. Reaction of **2c** with (*t*-BuC$_5$H$_4$)$_2$ZrBu$_2$ gave the zirconacyclobutene−silacyclobutene complex **7** in 83% NMR yield. The ^{13}C NMR showed the characteristic four olefinic carbons at 140.87, 143.80, 161.79, and 202.90 ppm. Crystalization of **7** afforded orange crystals in 63% isolated yields.

The structure of **7** is shown in Figure 1. It clearly shows that a zirconacyclobutene−silacyclobutene fused ring system exists in the structure. Its structure reveals that the lengths of the Zr−C(sp^2) bonds, Zr−C1 2.202(4) Å and Zr−C3 2.180(4) Å, are slightly shorter than those for a 5-membered zirconacyclopentadiene[15] due to the strain of the 4-membered ring. Bond lengths for C1−C2, C2−C3, and C3−C4 are 1.322(6), 1.595-(6), and 1.348(6) Å, respectively. Compared with [(CH$_3$C$_5$H$_4$)$_2$-Ti]$_2$[C$_4$(C$_6$H$_5$)$_2$] which has a two-titanacyclobutene fused ring system, the bond length of C1−C2 of **7**, 1.322(6) Å, is not significantly different from the titanacyclobutene complex (1.325 Å), whereas the bond length of C2−C3 of **7**, 1.595(6) Å, is much longer than that of the titanacyclobutene complex (1.485 Å).[16] As for the structure of the silacyclobutene ring, the bond length of C3−C4 is 1.348(6) Å which is much shorter than the similar *exo*-alkylidene type of silacyclobutene ring system.[11d] Two Si−C bonds (1.883 (4) and 1.854 (5) Å) are consistent with the known *exo*-alkylidene silacyclobutene (1.88 and 1.86 Å).[11d] Crystallographic data for the X-ray structure analysis of

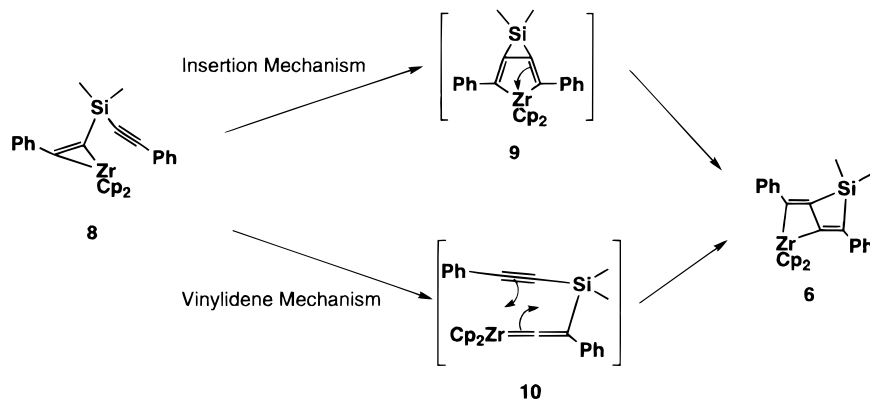(14) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829−2832.

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Table 2. Crystal Data and Refinement for Compounds **7** and **19c**

	7	**19c**[a]
formula	C$_{46}$H$_{46}$SiZr	C$_{55}$H$_{63}$SiZr
fw	718.18	843.4
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
a, Å	11.461(2)	31.268(3)
b, Å	15.245(2)	13.434(3)
c, Å	22.038(4)	22.733(4)
β, deg	95.43(1)	102.28(1)
Z	4	8
V, Å^3	3833.4(9)	9330(3)
μ(Mo Kα), cm^{-1}	3.41	2.89
cryst color	orange	yellow
cryst habit	prismatic	prismatic
cryst size, mm^3	0.2 × 0.3 × 0.4	0.2 × 0.3 × 0.3
d_{calcd}, (g/cm^3)	1.24	1.20
R	0.051	0.056
R_w	0.046	0.051

^{a} This contains 0.5C$_6$H$_{14}$ as a solvent. $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$, $w = [\sigma^2(F_o) + \{0.015(F_o)\}^2]^{-1}$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **7**

Zr−C(1)	2.202(4)	C(1)−Zr−C(3)	72.7(2)
Zr−C(3)	2.180(4)	Zr−C(1)−C2	83.1(3)
C(1)−C(5)	1.488(6)	C(1)−C(2)−C(3)	125.6(4)
C(1)−C(2)	1.322(6)	C(2)−C(3)−Zr	78.4(2)
C(2)−C(3)	1.595(6)	C(2)−C(3)−C(4)	105.0(3)
C(3)−C(4)	1.348(6)	C(3)−C(4)−Si	92.6(3)
C(4)−C(11)	1.466(7)	C(4)−Si−C(2)	77.5(2)
Si−C(2)	1.883(4)	Si−C(2)−C(3)	84.2(3)
Si−C(4)	1.854(5)	C(17)−Si−C(23)	108.8(2)
Si−C(17)	1.876(4)		
Si−C(23)	1.878(5)		

Table 4. Selected Bond Distances (Å) and Angles (deg) for **19c**

Zr−C(1)	2.304(6)	C(1)−Zr−C(5)	93.9(2)
Zr−C(5)	2.250(5)	Zr−C(1)−C(2)	121.5(4)
C(1)−C(2)	1.362(7)	C(1)−C(2)−C(3)	124.8(5)
C(2)−C(3)	1.492(7)	C(2)−C(3)−C(4)	127.9(5)
C(3)−C(4)	1.367(9)	C(3)−C(4)−C(5)	132.6(5)
C(4)−C(5)	1.513(8)	C(4)−C(5)−Zr	109.2(4)
C(5)−C(6)	1.367(8)	C(5)−C(6)−Si	93.2(4)
Si−C(4)	1.861(6)	C(4)−Si−C(6)	74.9(3)
Si−C(6)	1.846(6)	C(5)−C(4)−Si	88.1(4)
Si−C(11)	1.863(5)		
Si−C(17)	1.875(7)		

7 and selected structural data in **7** are given in Table 2 and 3, respectively.

Mechanism of the Formation of Silacyclobutene Derivatives from Bis(alkynyl)silanes. A plausible mechanism involves (i) a replacement of an ethylene ligand of Cp$_2$Zr-(CH$_2$=CH$_2$) by an alkynyl group of **2a−c** to form a zirconacyclopropene compound **8** and (ii) transformation from **8** to **6**. There are two possible mechanisms from **8** to **6**, namely, an insertion mechanism and a vinylidene mechanism (Scheme 2). Formation of zirconacyclopentadienes by intermolecular or intramolecular coupling of two alkyne moieties is well-known.[17]

The latter mechanism consists of a migration of the silyl group forming zirconocene-vinylidene species **10**.[18] Vinylidene formation from disubstituted alkynes is rare, and formation of zirconocene−vinylidene species is not yet reported, although many examples are well-known for the formation of zirconocene−alkyne complexes. Therefore, the former insertion path is more likely over the vinylidene path which, however, can not be ruled out for this reaction.
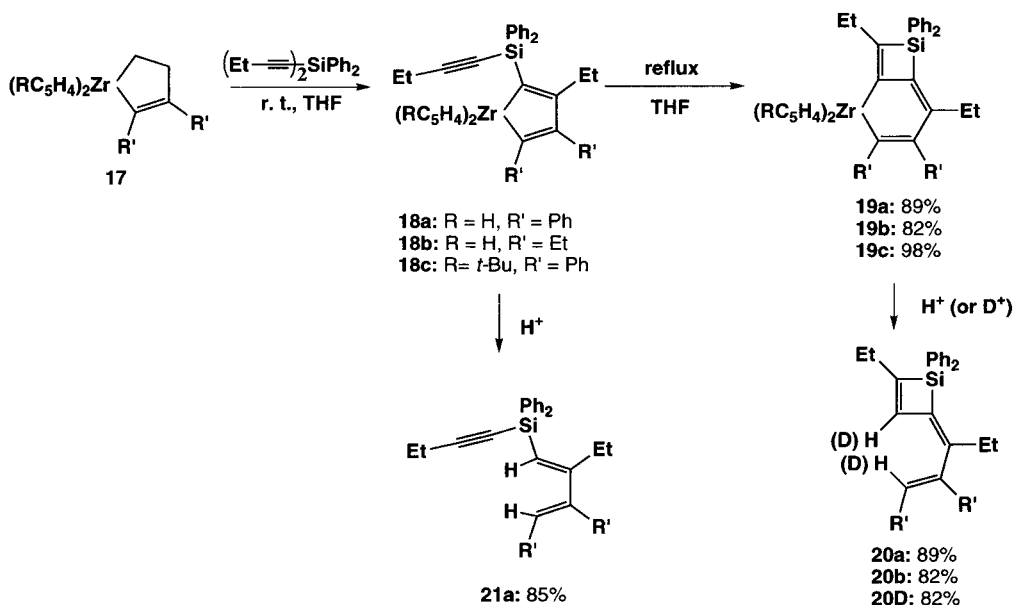
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Scheme 2

Scheme 3

18a: R = H, R' = Ph
18b: R = H, R' = Et
18c: R = *t*-Bu, R' = Ph

19a: 89%
19b: 82%
19c: 98%

21a: 85%

20a: 89%
20b: 82%
20D: 82%

Formation of Butadiene Derivatives. When the reaction mixture of **2a−d** with **1** was treated with a mixture of 1 equiv of CuCl and an excess of water, diphenyl- or ditolyldiene was formed in good yields. A plausible mechanism is shown in Scheme 1 which involves the selective cleavage of Si−C bond of **4** and the formation of alkenylcopper species **11**. Hydrolysis of alkenylcopper species **11** affords **12**. Desilylation from **12** with concentrated hydrochloric acid gives butadiene derivatives **3**. In fact, compound **12** (R = Ph, R′ = Me) has been isolated (75% yield). In order to obtain evidence for the formation of **11**, two reactions were carried out. One is deuterolysis of **11** instead of hydrolysis. This reaction selectively gave monodeuterated compound **13** in 74% isolated yield with >98% of deuterium incorporation. Desilylation with hydrochloric acid (35%) produced monodeuterated diene **14** in 99% yield based on **13**. The other is a carbon−carbon bond formation reaction using PhI and a catalytic amount of palladium. As expected, selective phenylation occurred at the C3 carbon of the diene to give **16** in 43% isolated yield as shown in Scheme 1. All of these observations indicate that the cleavage reaction of the Si−C bond of the silacyclobutene moiety by CuCl proceeded with high selectivity.

Intramolecular Insertion of a Carbon−Carbon Triple Bond into Zirconacyclopentadienes: Formation of Zircona-cyclohexadiene Derivatives. As an extension of the same type of reaction of the silylalkynyl group with zirconacycles, we investigated the reaction of zirconacyclopentadienes.

Zirconacyclopentadienes **18**,[9a,19,20] prepared from zirconacyclopentenes **17** and an alkyne, were treated at reflux for 3 h to afford 1-zirconacyclohexa-2,4-diene fused with a silacyclobutene ring **19** in high yields (82−98%). Their ^{1}H NMR spectra showed one Cp signal at 5.92 ppm for **19a** and at 5.96 ppm for **19b**. ^{13}C NMR spectra revealed two sp[2] carbons attached to Zr at 199.82 and 231.30 ppm for **19a**, 196.47 and 230.81 ppm for **19b**, and 200.61 and 234.43 ppm for **19c**. Hydrolysis of **19** produced silacyclobutene derivatives **20** in high yields (89% for **20a**, 82% for **20b**). Deuterolysis of **19b** afforded dideuterated compound **20D** in 82% yield with >99% of deuterium incorporation (Scheme 3).

The zirconacyclohexadiene **19c** with a *t*-Bu group in each Cp ring was structurally characterized by X-ray study. The structure of **19c** is shown in Figure 2. This clearly shows the compound **19c** has the 6,4 fused ring system. The zirconium containing a 6-membered ring is a zirconacyclohexadiene moiety. It is interesting since only several examples of metallacyclohexadienes are known.[21] This structure shows that the bond lengths of two Zr−C(sp[2]) are 2.304(6) Å and 2.250-

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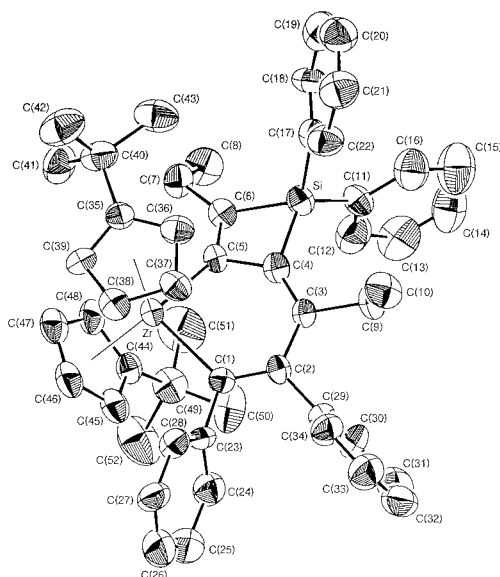
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Figure 2. Perspective view of **19c**. Solvent ($0.5C_6H_{14}$) was omitted for clarity.

(5) Å for Zr–C1 and Zr–C5, respectively, which are comparable to those for zirconacyclopentadienes.[15] Bond lengths of C1–C2, C2–C3, C3–C4, and C4–C5 are 1.362(7), 1.492(7), 1.367(9), and 1.513(8) Å, respectively. The bond length of C5–C6 in a silacyclobutene ring is 1.367 (8) Å which is slightly longer than that of **7**.

A proposed mechanism for the formation of complex **19** from zirconacyclopentadiene **18** is shown in Scheme 4. This mechanism involves an intramolecular insertion reaction of a C–C triple bond into zirconacyclopentadiene **18** providing zirconacycloheptatriene **22** with a silacyclopropane side ring and then 1,2-migration of the silyl group to form **19** in a similar way to the insertion mechanism described for a zirconacyclopropene and a zirconacyclopentene.[7] For this reaction, the alternative vinylidene mechanism can be ruled out, since zirconacyclopentadiene **18b** does not show the β,β-bond cleavage reaction, although some zirconacyclopentadienes with a trimethylsilyl group at the α-position undergo β,β-bond cleavage.[22] It is consistent with the observation of platinum-mediated silacyclobutene formation via silacyclopropane ring.[11d] Since the same mechanism is expected for the formation of silacyclobutene rings for zirconacyclopropenes, zirconacyclopentenes, and zirconacyclopentadienes, the insertion mechanism is plausible. The vinylidene mechanism is not likely.

Conclusion

Treatment of bis(phenylalkynyl)silanes with Cp_2ZrEt_2 followed by the reaction with a mixture of H_2O and CuCl gave 1,4-diphenyldiene. Bis(phenylalkynyl)silane shows unusual intramolecular coupling of two alkynyl groups when it reacted with Cp_2ZrEt_2. In this paper, we clearly indicated that these reactions proceeded via zirconacyclobutene-silacyclobutene fused ring intermediates. The same type of transformation was also observed for zirconacyclopentenes and zirconacyclopen-

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tadienes which have a silylalkynyl group at the α-position of those zirconacycles. Two possible mechanisms can be considered which are an insertion mechanism and a vinylidene mechanism. However, since the vinylidene mechanism cannot be considered for the transformation of zirconacyclopentadiene **18b** and the zirconocene–vinylidene complex has not been reported yet, the insertion mechanism is plausible for all cases.

Experimental Section

General. Unless otherwise noted, all starting materials were commercially available and were used without further purification. All reactions involving organometallic compounds were carried out under a positive pressure of dry N_2 using standard Schlenk techniques. THF was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Zirconocene dichloride was purchased from Aldrich Chemical Company, Inc. *n*-BuLi (1.6 M, hexane solution), EtMgBr (1.0 M, THF solution), and (*t*-BuC_5H_4)$_2ZrCl_2$ were obtained from Kanto Chemicals Co. Ltd. Copper(I) chloride was purchased from Wako Pure Chemical Industries Ltd. All of the Si-bridged diynes were prepared by the reaction of lithium acetylide (2 equiv) with dichlorodialkylsilane (or dichlorodiarylsilane) (1 equiv).

GC analysis was performed on a gas chromatograph (SHIMADZU GC-14A) equipped with a flame ionization detector using a fused silica capillary column (CBP1-M25–025) and SHIMADZU CR6A-Chromatopac integrator. GC yields were determined using suitable hydrocarbons as internal standards. ^{1}H NMR (270 MHz) and ^{13}C NMR (67.5 MHz) spectra were recorded on a JOEL EX-270 FT NMR spectrometer, GC-MS were on SHIMADZU GCMS-QP 1000EX, and high-resolution MS were on SHIMADZU Krotos CONCEPT IS.

Formation of 1,3-Butadiene 3 by the Reaction of 2a–d with Cp_2ZrEt_2, H_2O, CuCl, and Aqueous HCl in This Order: A Representative Procedure for Formation of 3a from 2a. To a THF (10 mL) solution of Cp_2ZrCl_2 (1.25 mmol, 0.365 g) at −78 °C (dry-ice/methanol bath) in a 20 mL Schlenk tube was added dropwise EtMgBr (2.5 mmol, 0.90 M THF solution, 2.78 mL) with a syringe. After the addition was complete, the reaction mixture was stirred at −78 °C for 1 h. To the reaction mixture was then added 1 mmol of bis(phenylethynyl)dimethylsilane (**2a**), and the mixture was allowed to warm up gradually to room temperature. After the reaction mixture was stirred at room temperature for 1 h, water (0.10 mL) and CuCl (1.2 mmol) were added, and the reaction mixture was then heated at 50 °C for 12 h. Hydrolysis of the reaction mixture with concentrated HCl (35%) afforded (1*E*,3*E*)-1,4-diphenyl-1,3-butadiene (**3a**) in 88% isolated yield.

Similarly, (1*E*,3*E*)-1,4-diphenyl-1,3-butadiene (**3a**) was obtained in 64% yield from **2b** and 56% yield from **2c**, respectively.

When **2d** was applied, (1*E*,3*E*)-1,4-ditolyl-1,3-butadiene (**3d**) was isolated in 79% yield: ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 2.34 (s, 6H), 6.59–6.63 (m, 2H), 6.87–6.91 (m, 2H), 7.13 (d, *J* = 7.9 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 4H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 21.22, 126.25, 128.52, 129.35, 132.26, 134.74, 137.33.
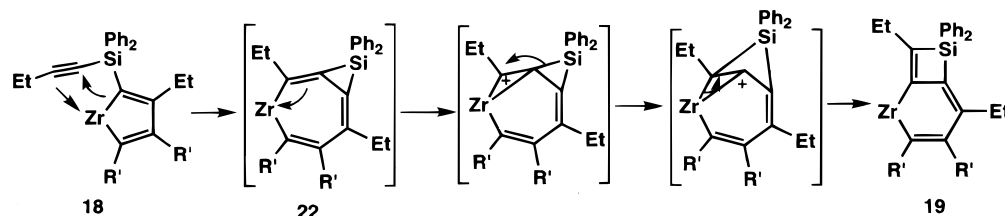
Formation of Silacyclobutene Derivatives 4a–h: A Representative Procedure for 4a from 2a. The procedure used here was exactly the same as that described above for the formation of **3**. However, instead of treatment with I_2, water, and CuCl, the reaction was quenched with 3 N HCl, and the resulting mixture was extracted with diethyl ether (3 × 70 mL) and washed with water and brine. The extract was dried over MgSO$_4$. The solvent was then evaporated *in vacuo* to give light-brown solids. Recrystalization from ethanol at room temperature yielded colorless crystals of **4a**: GC yield 87%, isolated yield 65%; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.51 (s, 6H), 6.70 (s, 1H), 7.25–7.35 (m, 10H), 7.70 (s, 1H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ −0.68, 125.92, 126.74, 126.87, 127.88, 128.75, 128.86, 137.13, 139.41, 146.15, 149.02, 158.51; HRMS calcd for $C_{18}H_{18}Si$ 262.1178, found 262.1181.

For **4b**: GC yield 80%; recrystalization from ethanol at room temperature yielded colorless crystals in 67% isolated yield; ^{1}H NMR(CDCl$_3$, Me$_4$Si) δ 1.20–1.32 (m, 10H), 7.03 (s, 1H), 7.33–7.60 (m, 10H), 8.04 (s, 1H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 6.18, 7.51, 126.00, 126.60, 126.90, 127.64, 128.55, 129.22, 137.47, 139.55, 143.79, 150.12, 156.10; HRMS calcd for $C_{20}H_{22}Si$ 290.1491, found 290.1498.

Scheme 4

Cp ligands were omitted for clarity.

For **4c**: GC yield 85%; recrystalization from a mixture of hexane and ether (70:30) afforded colorless crystals in 70% isolated yield; mp 158−159 °C; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 7.09 (s, 1H), 7.18−7.57 (m, 16H), 7.83−7.88 (m, 4H), 8.22 (s, 1H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 126.66, 126.69, 126.95, 127.17, 128.03, 128.35, 128.44, 128.66, 129.63, 130.56, 132.54, 135.60, 136.53, 138.81, 143.54, 152.65, 157.21; HRMS calcd for C$_{28}$H$_{22}$Si 386.1491, found 386.1505. Anal. Calcd for C$_{28}$H$_{22}$Si: C, 87.24; H, 5.94. Found C, 87.01; H, 5.74.

For **4e**: GC yield 87%; recrystalization from ethanol afforded colorless crystals in 60% isolated yield; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.51 (s, 6H), 3.72 (s, 6H), 6.60 (s, 1H), 6.76−6.81 (m, 4H), 7.13−7.25 (m, 4H), 7.56 (s, 1H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ −0.58, 55.32, 114.15, 126.98, 127.07, 128.12, 130.24, 132.63, 143.84, 147.07, 156.58, 158.56, 159.36; HRMS calcd for C$_{20}$H$_{22}$O$_2$Si 322.1389, found 322.1386.

For **4f**: GC yield 76%; distillation afforded the compound in 60% isolated yield; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.90 (s, 9H), 1.00 (s, 9H), 5.96 (s, 1H), 7.29−7.38 (m, 7H), 7.75−7.79 (m, 4H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 29.87, 30.17, 34.41, 34.52, 127.89, 129.85, 134.05, 135.54, 136.89, 139.78, 151.57, 170.38; HRMS calcd for C$_{24}$H$_{30}$Si 346.2115, found 346.2110.

For **4g**: this compound was obtained when the reaction was carried out at 50 °C; GC yield 61%; distillation afforded the compound in 52% isolated yield; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.45−1.65 (m, 8H), 1.90−2.26 (m, 8H), 5.65−5.70 (m, 2H), 6.55 (s, 1H), 7.3−7.78 (m, 11H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 22.19, 22.37, 24.82, 25.61, 26.09, 26.17, 128.01, 129.02, 130.06, 131.57, 132.33, 133.75, 135.26, 135.67, 137.90, 140.14, 149.74, 158.56; HRMS calcd for C$_{28}$H$_{30}$Si 394.2115, found 394.2121.

For **4h**: recrystalization from a mixture of hexane and ether (70:30) yielded colorless crystals in 66% isolated yield; ^{1}H NMR (CDCl$_3$, Me$_4$-Si) δ 2.22 (s, 3H), 2.28 (s, 3H), 6.94 (s, 1H), 6.96 (d, J = 7.8 Hz, 2H), 7.07 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 7.31−7.41 (m, 8H), 7.73−7.76 (m, 4H), 8.06 (s, 1H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 21.11, 21.33, 126.54, 128.30, 129.02, 129.16, 129.36, 130.44, 132.83, 133.89, 135.60, 136.17, 136.66, 137.93, 142.46, 151.86, 156.37. Anal. Calcd for C$_{30}$H$_{26}$Si: C, 86.91; H, 6.32. Found: C, 87.09; H, 6.49.

Reaction of 2a with Cp$_2$ZrEt$_2$: Formation of the Zirconium-Containing Intermediate 6a. The reaction mixture of **2a** with Cp$_2$-ZrEt$_2$ was investigated before hydrolysis. Zirconium-containing intermediate **6a** was formed and detected by NMR (90% yield by ^{1}H NMR based on a Cp signal). Its ^{1}H NMR (THF−C$_6$D$_6$, Me$_4$Si) showed one Cp signal at 5.74 ppm. For **6a**: ^{13}C NMR (THF−C$_6$D$_6$, Me$_4$Si) δ −0.01, 106.72, 127.29, 128.80, 129.01, 130.21, 132.01, 141.26, 143.00, 162.41, 203.46.

Deuterolysis of **6a** followed by usual workup afforded dideuterated compound **5a** in 86% yield with >99% deuterium incorporation. For **5a**: ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.63 (s, 6H), 7.25−7.40 (m, 10H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ −0.70, 126.22, 126.79, 126.93, 127.87, 128.21 (t, J = 23.0 Hz), 128.86, 137.16, 139.45, 145.96, 148.70 (t, J = 22.3 Hz), 158.56; HRMS calcd for C$_{18}$H$_{16}$D$_2$Si 264.1301, found 264.1312.

Isolation of 6c. To a suspension of 0.58 g (2.0 mmol) of Cp$_2$ZrCl$_2$ in 20 mL hexane was added 2.4 mL (1.6 M, 4.0 mmol) of n-BuLi in hexane at −78 °C. The reaction mixture was stirred for 1 h at −78 °C and then slowly warmed to 0 °C. The precipitated LiCl was separated using a frit. After 20 mL of THF was added at −20 °C, bis-(phenylethynyl)diphenylsilane **2c** (2.0 mmol) was added. The reaction mixture was allowed to warm to room temperature for 3 h. ^{1}H NMR measurement showed **6c** was formed in 85% yield. From the clear filtrate, **6c** was crystallized at −40 °C as orange crystals (isolated yield

75%); ^{1}H NMR (C$_6$D$_6$, Me$_4$Si) δ 5.58 (s, 10H), 7.08−8.10 (m, 20H); ^{13}C NMR (C$_6$D$_6$, Me$_4$Si) δ 96.69, 106.70, 127.54, 127.81, 128.49, 128.60, 128.70, 128.83, 129.12, 130.58, 134.29, 135.63, 140.91, 142.33, 160.50, 203.72. Anal. Calcd for C$_{38}$H$_{30}$SiZr: C, 75.32; H, 4.99; Si, 4.63. Found: C, 74.98; H, 5.12; Si, 4.47.

Isolation of 7. To a suspension of 0.80 g (2.0 mmol) of (t-BuC$_5$H$_4$)$_2$-ZrCl$_2$ in 20 mL of hexane was added 2.4 mL (1.6 M, 4.0 mmol) of n-BuLi in hexane at −78 °C. The reaction mixture was stirred for 1 h at −78 °C and then slowly warmed to 0 °C. The precipitated LiCl was separated using a frit. After 20 mL of THF was added at −20 °C, bis(phenylethynyl)diphenylsilane **2c** (2.0 mmol) was added. The reaction mixture was allowed to warm to room temperature for 3 h. ^{1}H NMR measurement showed **7** was formed in 83% yield. From the clear filtrate, **7** was crystallized at −40 °C as orange crystals (isolated yield 63%): ^{1}H NMR (C$_6$D$_6$, Me$_4$Si) δ 1.08 (s, 18H), 5.48−5.51 (m, 2H), 5.52−5.54 (m, 2H), 5.83−5.86 (m, 2H), 5.90−5.92 (m, 2H), 7.08−8.02 (m, 20H); ^{13}C NMR (C$_6$D$_6$, Me$_4$Si) δ 31.91 (6 CH$_3$), 34.39 (2C), 102.01, 104.41, 104.59, 105.00, 106.22, 127.30, 127.52, 128.00, 128.18, 128.59, 128.83, 129.80, 130.49, 134.62, 135.78, 140.03, 140.87, 143.80, 161.79, 202.90. The structure of the title complex was confirmed by X-ray crystallography.

1,4-Diphenyl-1-(dimethylhydroxysilyl)-1,3-butadiene (12). A mixture of **4a** (260 mg, 1.0 mmol), CuCl (119 mg, 1.2 mmol), and H$_2$O (50 μL) in 10 mL of THF was stirred at 50 °C for 3 h. The reaction mixture was then hydrolyzed with 3 N HCl and extracted with ether. The organic layer was washed successively with water and brine and then dried over MgSO$_4$. After evaporation of the solvent, column chromatography (silica gel, hexane/ether = 95:5) afforded 1,4-diphenyl-1-(dimethylhydroxylsilyl)-1,3-butadiene (**12**) as a colorless oil in 75% isolated yield: ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.42 (s, 6H), 2.45 (br, 1H), 6.67 (d, J = 15.3 Hz, 1H), 6.91 (d, J = 11.4 Hz, 1H), 7.22−7.54 (m, 11H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 2.20, 126.11, 126.63, 127.31, 127.85, 127.87, 128.17, 128.67, 135.90, 137.19, 144.76, 145.44, 145.63; HRMS calcd for C$_{18}$H$_{20}$OSi 280.1283, found 280.1254.

Hydrolysis of the above reaction mixture with concentrated HCl (35%) instead of 3 N HCl afforded **3a** (GC yield 96%, isolated yield 83%). Desilylation of **12** by using concentrated HCl (35%) also generated **3a** in 77% isolated yield.

13. Instead of H$_2$O, D$_2$O was used in the procedure for **12**. Deteurated compound **13** was thus isolated in 74% isolated yield with D incorporation > 98%. For **13**: ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.38 (s, 6H), 2.10 (br, 1H), 6.62 (s, 1H), 6.87 (s, 1H), 7.16−7.44 (m, 10H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 2.24, 126.11, 126.63, 127.31, 127.80 (t, J = 22.5 Hz), 127.86, 128.17, 128.65, 135.79, 137.18, 144.69, 145.44, 145.60.

For **14**: treatment of **13** with concentrated HCl (35%) afforded **14** in 99% yield; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 6.60−6.63 (m, 2H), 6.88−6.92 (m, 1H), 7.16−7.39 (m, 10H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 126.26, 127.55, 128.72, 129.06 (t, J = 23.0 Hz), 129.21, 133.11, 133.18, 137.40.

16. A mixture of **4a** (260 mg, 1.0 mmol), CuCl (119 mg, 1.2 mmol), Pd(PPh$_3$)$_4$ (55 mg, 0.05 mmol), and iodobenzene (135 μL, 1.2 mmol) in 10 mL of THF was stirred at 50 °C for 6 h. The resulting solution was then hydrolyzed with 3 N HCl and extracted with ether. The extract was washed successively with water and brine and then dried over MgSO$_4$. After the solvent was evaporated, column chromatography (silica gel, hexane/ether = 95:5) afforded **16** in 43% isolated yield. For **16**: ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.34 (s, 6H), 1.88 (br, 1H), 6.85 (s, 1H), 7.06−7.32 (m, 16H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 2.42, 126.17, 127.25, 127.78, 128.20, 128.25, 128.57, 129.05, 129.41, 136.40, 138.75,

141.50, 145.35, 145.79, 148.13; HRMS calcd for $C_{24}H_{24}OSi$ 356.1596, found 356.1588.

Formation of 21a. To a THF solution of zirconacyclopentene **17a** (1 equiv) was added bis(1-butynyl)diphenylsilane (1 equiv) at 0 °C. The reaction was complete after 12 h at room temperature forming zirconacyclopentadiene **18a** in 85% NMR yield. NMR data for **18a**: ^1H NMR (C_6D_6, Me_4Si) δ 0.63 (t, $J = 7.3$ Hz, 3H), 0.91 (t, $J = 7.6$ Hz, 3H), 1.94 (q, $J = 7.6$ Hz, 2H), 2.40 (q, $J = 7.3$ Hz, 2H), 6.21 (s, 10H), 6.71−8.01 (m, 20H); ^{13}C NMR (C_6D_6, Me_4Si) δ 13.71, 14.00, 14.04, 34.62, 84.76, 111.51, 112.58, 123.13, 126.29, 127.31, 127.84, 128.58, 129.28, 129.30, 130.5, 136.03, 138.67, 142.20, 142.81, 149.21, 161.72, 185.41, 200.33. Hydrolysis of the reaction mixture followed by normal workup provided **21a**, which was obtained as a pure compound (sticky oil) by means of column chromatography (hexane/ ether = 95:5). For **21a**: NMR yield 85%; isolated yield 77%; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.96 (t, $J = 7.4$ Hz, 3H), 1.21 (t, $J = 7.4$ Hz, 3H), 2.52 (q, $J = 7.4$ Hz, 2H), 2.35 (q, $J = 7.4$ Hz, 2H), 5.75 (s, 1H), 6.81 (s, 1H), 6.88−7.68 (m, 20H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.50, 13.68, 13.89, 27.31, 79.55, 112.77, 122.62, 126.72, 127.17, 127.74, 127.83, 128.09, 128.50, 129.38, 129.68, 129.95, 134.84, 137.23, 138.80, 139.59, 145.05, 165.55; HRMS calcd for $C_{34}H_{32}Si$ 468.2273, found 468.2299.

Formation of 19 and 20. A General Procedure. After the formation of zirconacyclopentadiene **18** was complete, the reaction mixture was heated up to reflux in THF for 3 h. Zirconacyclohexadiene **19** was thus formed and obtained as solids or crystals after recrystalization from hexane at low temperature (0 °C). Hydrolysis of the reaction mixture with 3 N HCl and followed by usual workup afforded **20**.

For **19a**: NMR yield 89%; isolated yield 83%; ^1H NMR (C_6D_6, Me_4-Si) δ 0.89 (t, $J = 7.3$ Hz, 3H), 1.15 (t, $J = 7.6$ Hz, 3H), 2.22 (q, $J = 7.6$ Hz, 2H), 2.41 (q, $J = 7.3$ Hz, 2H), 5.92 (s, 10H), 6.49−7.93 (m, 20H); ^{13}C NMR (C_6D_6, Me_4Si) δ 15.44, 15.80, 28.86, 33.55, 110.85, 122.71, 125.17, 127.04, 127.67, 127.90, 128.39, 129.90, 130.78, 135.70, 137.09, 141.13, 144.85, 147.90, 151.37, 152.56, 176.13, 199.82, 231.30.

For **19b**: NMR yield 82%; isolated yield 57%; ^1H NMR (C_6D_6, Me_4Si) δ 0.93 (t, $J = 7.3$ Hz, 6H), 1.08 (t, $J = 7.4$ Hz, 3H), 1.10 (t, $J = 7.6$ Hz, 3H), 1.31 (q, $J = 7.3$ Hz, 2H), 2.12 (q, $J = 7.6$ Hz, 2H), 2.22 (q, $J = 7.4$ Hz, 2H), 2.24 (q, $J = 7.3$ Hz, 2H), 5.96 (s, 10H), 7.16−7.94 (m, 10H); ^{13}C NMR (C_6D_6, Me_4Si) δ 15.22, 15.39, 15.80, 16.71, 17.68, 24.40, 28.81, 32.79, 110.11, 128.31, 129.70, 135.72, 137.70, 141.79, 145.50, 152.08, 172.92, 196.47, 230.81.

19c. Recrystalization from cold hexane (0°C) afforded crystals suitable for X-ray analysis. X-ray analysis showed this complex contained $0.5C_6H_{14}$ in the crystal. For **19c**: NMR yield 98%; isolated yield 79%; ^1H NMR (C_6D_6, Me_4Si) δ 0.85 (t, $J = 7.3$ Hz, 3H), 1.18 (t, $J = 7.6$ Hz, 3H), 1.27 (s, 18H), 2.37 (q, $J = 7.3$ Hz, 2H), 2.38 (q, $J = 7.6$ Hz, 2H), 6.04 (m, 2H), 6.08 (m, 4H), 6.13 (m, 2H), 6.69−7.94 (m, 20H); ^{13}C NMR (C_6D_6, Me_4Si) δ 15.08, 15.67, 30.31, 31.72, 33.32, 34.41, 107.02, 107.82, 108.80, 112.51, 122.86, 125.05, 126.93, 127.24, 127.85, 128.37, 129.80, 130.76, 135.81, 136.80, 141.04, 142.68, 145.62, 149.34, 151.17, 152.88, 176.55, 200.61, 234.43.

20a. Hydrolysis of the reaction mixture containing **19a** with 3 N HCl, followed by normal workup, provided **20a**, which was then purified by means of flash chromatography (hexane/ether = 95:5). For **20a**: NMR yield 89%; isolated yield 54%; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.85 (t, $J = 7.4$ Hz, 3H), 0.99 (t, $J = 7.4$ Hz, 3H), 2.08 (q, $J = 7.4$ Hz, 2H), 2.40 (qd, $J = 7.4$ Hz, 1.3 Hz, 2H), 6.63 (s, 1H), 7.01−7.72 (m, 21H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.50, 13.64, 25.35, 30.10, 126.32, 127.02, 127.85, 128.07, 128.41, 128.66, 129.52, 129.67, 130.01, 134.34, 135.24, 137.57, 140.23, 140.75, 141.11, 141.85, 152.72, 162.75; HRMS calcd for $C_{34}H_{32}Si$ 468.2273, found 468.2281.

20b. Hydrolysis of the reaction mixture containing **19b** with 3 N HCl, followed by normal workup, provided **19b**, which was then purified by means of flash chromatography (hexane/ether = 95:5). For **20b**: NMR yield 82%; isolated yield 61%; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.83 (t, $J = 7.4$ Hz, 3H), 0.95 (t, $J = 7.6$ Hz, 3H), 1.02 (t, $J = 7.4$Hz, 6H), 2.11 (q, $J = 7.4$ Hz, 2H), 2.12 (q, $J = 7.4$ Hz, 2H), 2.16 (q, $J = 7.4$ Hz, 2H), 2.40 (qd, $J = 7.6$ Hz, 1.3 Hz, 2H), 5.28 (t, $J = 7.3$ Hz, 1H), 7.31−7.39 (m, 6H), 7.54 (t, $J = 1.3$ Hz, 1H), 7.65−7.70 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.41, 13.50, 13.66, 14.90, 21.10, 21.98, 25.30, 29.90, 127.98, 129.81, 129.94, 134.82, 135.24, 137.03,

139.66, 142.01, 152.86, 160.32; HRMS calcd for $C_{26}H_{32}Si$ 372.2273, found 372.2259.

20D. The reaction mixture containing **19b** was hydrolyzed with DCl/D_2O instead of 3 N HCl. Normal workup provided **20D**, which was then purified by means of flash chromatography (hexane/ether = 95:5). For **20D**: NMR yield 82%; isolated yield (220 mg) 59%; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.81 (t, $J = 7.4$ Hz, 3H), 0.94 (t, $J = 7.6$ Hz, 3H), 1.02 (t, $J = 7.4$Hz, 6H), 2.11 (q, $J = 7.4$ Hz, 2H), 2.13 (q, $J = 7.4$ Hz, 2H), 2.16 (q, $J = 7.6$ Hz, 2H), 2.40 (q, $J = 7.4$ Hz, 2H), 7.34− 7.69 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.40, 13.53, 13.67, 14.94, 21.10, 21.98, 25.36, 29.90, 127.93, 129.81, 129.53 (t, $J = 23.8$ Hz), 134.80, 135.22, 137.14, 139.61, 142.10, 152.80 (t, $J = 23.5$ Hz), 160.35; HRMS calcd for $C_{26}D_2H_{30}Si$ 374.2397, found 374.2422.

X-ray Crystallographic Analysis of 7. An orange prismatic crystal of approximate dimensions $0.2 \times 0.3 \times 0.4$ mm^3 was sealed in a capillary tube and mounted on an Enraf-Nonius CAD4 X-ray diffractometer. Intensity data were collected at room temperature with monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The cell constants and orientation matrices for data collection were obtained from a least-squares refinement using the setting angles of carefully centered 25 reflections. Crystallographic data are given in Table 2. The data were collected in $\omega - 2\theta$ mode. The intensities of three standard reflections were checked every 2 h to ascertain crystal integrity, and the intensities were corrected for the decay (16%). A total of 12189 reflections were measured ($2\theta_{max} = 60°$), of which 4616 unique reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the solution and refinement of the structure.The structure was solved by direct methods (SHELXS-86)[23] and the following conventional Fourier techniques. Refinement was carried out by full-matrix least-squares using Xtal3.2 software.[24] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed to the calculated positions with isotropic thermal parameters equal to those of parent carbon atoms. Refinement of positional and thermal parameters led to a convergence with $R = 0.051$, $R_w = 0.046$, and GOF = 1.33. The maximum and minimum peaks on the final difference Fourier map correspond to 0.57 and -0.43 e/Å^3, respectively.

X-ray Crystallographic Analysis of 19c. A crystal of approximate dimensions $0.2 \times 0.3 \times 0.3$ mm^3 was sealed in a capillary tube and mounted on an Enraf-Nonius CAD4 X-ray diffractometer. Unit cell parameters were determined by least-squares refinement of the angular positions of 25 well-centered reflections. Crystallographic data are listed in Table 2. Diffraction data were collected at room temperature by using graphite-monochromated Mo Kα radiation and an ω scan technique. The intensities of three standard reflections were checked every 2 h, and no significant loss of intensity was observed. A total of 11 934 reflections were measured, of which 4320 reflections were unique with $|F_o| > 3\sigma(|F_o|)$. The position of zirconium atom was determined from a Patterson map and used as the initial phasing model for difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically, and a subsequent difference Fourier synthesis revealed the positions of hydrogen atoms. Data reduction and structure refinment were performed using Xtal3.2 software.[24] Refinement of positional and thermal parameters led to a convergence with $R = 0.056$, $R_w = 0.051$, and GOF = 1.43.

Supporting Information Available: Crystallographic data, positional and thermal parameters and lists of bond lengths and angles for **7** and **19c** (17 pages). See any current masthead page for ordering and Internet access instructions.

JA972381V

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