3336 *J. Am. Chem. Soc.* **1989**, *111*, 3336-3346

Novel Bicyclization of Enynes and Diynes Promoted by Zirconocene Derivatives and Conversion of Zirconabicycles into Bicyclic Enones via Carbonylation[1]

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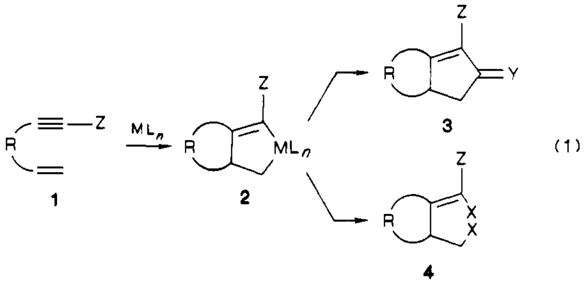
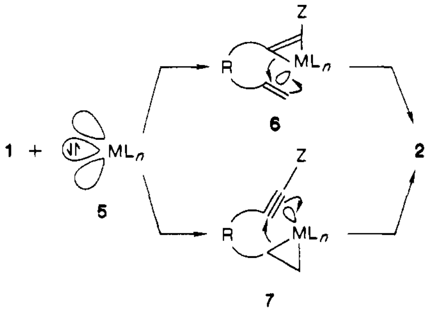
Abstract: Enynes and diynes react with "ZrCp$_2$" (where Cp = η^5-C$_5$H$_5$) generated by treating Cl$_2$ZrCp$_2$ with Mg and HgCl$_2$ or 2 equiv of an alkyllithium, such as *n*-BuLi, or a Grignard reagent, such as EtMgBr, and can produce in excellent yields zirconabicycles represented by **2** (M = Zr) and **8**, respectively. Their protonolysis can provide the corresponding exocyclic alkenes and conjugated dienes **9**, respectively. Iodinolysis of **2** (M = Zr) can give the corresponding diiodides in high yields, while carbonylation of **2** (M = Zr) can produce bicyclic enones **3** (Y = O) in moderate to good yields. Although the bicyclization reaction fails with terminal alkyne containing substrates, various types of substituents on the alkyne moiety, such as alkyl, alkenyl, aryl, trialkylsilyl, and trialkylstannyl groups, can be accommodated. Investigation of the *n*-BuLi–Cl$_2$ZrCp$_2$ reaction has revealed that it gives first (*n*-Bu)$_2$ZrCp$_2$ at −78 °C, which then decomposes to give Cp$_2$Zr(CH$_2$=CHEt), identified as its PMe$_3$ complex **11**. The PMe$_3$-stabilized complex reacts with diphenylacetylene to produce a crystalline compound which has been identified as a zirconacyclopropene, **36a**. This demonstrated, for the first time, the feasibility of converting alkynes into zirconacyclopropenes. The reaction of preformed, three-membered zirconacycles with alkynes gives five-membered zirconacycles. The reaction of diphenylacetylene is ca. 150 times as fast as that of (*E*)-stilbene. These results support a mechanism involving formation of a zirconacyclopropene intermediate followed by its intramolecular carbometalation with the alkene moiety of enynes for the Zr-promoted bicyclization of enynes.

Direct conversion of enynes into the corresponding metallabicycles followed by their conversion into bicyclic or even monocyclic organic compounds is, in principle, a synthetically attractive methodology[2] (eq 1). Consideration of molecular orbital interactions suggested to us that it would be desirable to generate a 14-electron species with at least one filled nonbonding orbital (**5**) or its equivalent containing a transition metal for facile conversion of **1** into **2** via a concerted process. Interaction of **1** with **5** can, in principle, lead to the formation of **6** or **7** through the use of a pair of orbitals: a filled nonbonding orbital (HOMO) and an empty orbital (LUMO). Intramolecular carbometalation involving the second empty orbital should lead to the formation of **2** (eq 2). Indeed, "ZrCp$_2$" equivalents, where Cp = η^5-C$_5$H$_5$, generated by two-electron reduction of Cp$_2$Zr(IV) derivatives were known to react with alkynes and alkenes to give zirconacyclopentadienes[3,4] and zirconacyclopentanes,[4] respectively. Related to these is the reaction of Cp$_2$ZrPh$_2$ with alkenes to give zirconaindan derivatives.[5] During the course of our investigation, a paper describing the reaction of (η^5-C$_5$Me$_5$)$_2$ZrH$_2$ with propyne leading to the formation of monocyclic zirconacyclopentenes was reported.[6] Also reported during this period was the conversion of diynes and one enyne into exocyclic alkenes promoted by "Cp$_2$Ti".[7]



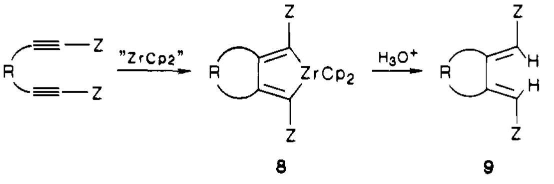
(1)

R = C and heteroatom-containing chain; X = H, halogen, etc.; Y = O, etc.; Z = H, C, Si, Ge, or Sn



(2)

In this paper we describe (i) full details of the bicyclization reactions of enynes and diynes with zirconium derivatives, i.e., "ZrCp$_2$", to produce zirconabicycles **2** and **8** reported first by us



(3)

R = C chain; Z = C or Si

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[1] Metal-Promoted Cyclization. 19. Part 18: Negishi, E.; Boardman, L. D.; Sawada, H.; Bagheri, V.; Tour, J. M.; Rand, C. L. *J. Am. Chem. Soc.* **1988**, *110*, 5383. Some preliminary results of the work have been communicated: (a) Neghish, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. (b) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (c) Negishi, E.; Zhang, Y.; Cederbaum, F. E.; Webb, M. B. *J. Org. Chem.* **1986**, *51*, 4080. (d) Negishi, E.; Swanson, D. R.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1987**, *28*, 917. (e) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987**, 623.

[2] A cobalt-promoted methodology for converting **1** into **3** was known at the outset of our investigation. (a) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1983**, 977. (b) Schore, N. E.; Croudace, M. C. *J. Org. Chem.* **1981**, *46*, 5436. (c) Croudace, M. C.; Schore, N. F. *J. Org. Chem.* **1981**, *46*, 5357. (d) Knudsen, M. J.; Schore, N. E. *J. Org. Chem.* **1984**, *49*, 5025. (e) Exon, C.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 2477. (f) Billington, D. C.; Willison, D. *Tetrahedron Lett.* **1984**, 4041.

[3] (a) Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1974**, *96*, 5936. (b) Demerseman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1977**, *132*, 223. (c) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 2687. (d) Thanedar, S.; Farona, M. F. *J. Organomet. Chem.* **1982**, *235*, 65.

[4] (a) Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 224; *J. Am. Chem. Soc.* **1981**, *103*, 2687.

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[6] McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281.

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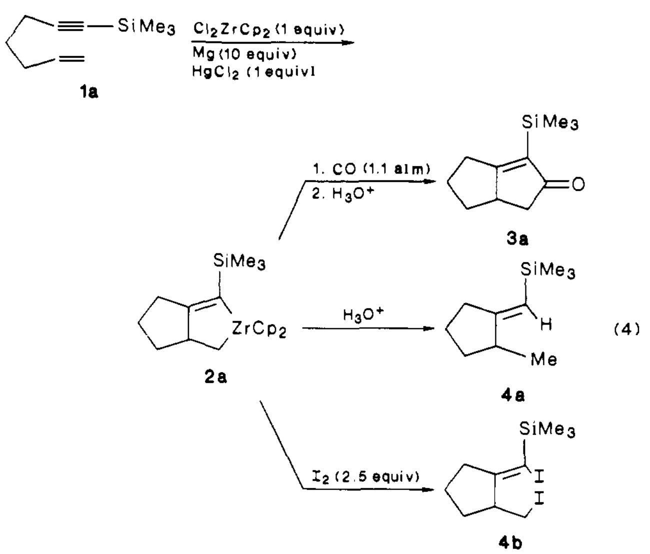
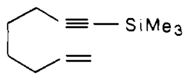
in preliminary communications,[1] (ii) the development of a convenient procedure for generating "ZrCp$_2$" from Cl$_2$ZrCp$_2$,[1b] (iii) conversion of **2** into **3** and **4** as well as that of **8** into **9**, and (iv) some mechanistic and structural aspects of the Zr promoted bicyclization reactions.

Results and Discussion

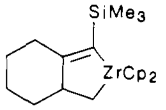
Enyne Bicyclization Using "ZrCp$_2$" Generated by the Treatment of Cl$_2$ZrCp$_2$ with Mg and HgCl$_2$ and Synthesis of Bicyclic Enones via Carbonylation. With the goal of developing a bicyclization reaction represented by eq 1, 7-(trimethylsilyl)-1-hepten-6-yne (**1a**) was first chosen as a test substrate. A 1:1 mixture of **1a** and Cl$_2$ZrCp$_2$ in THF was added at 0 °C under nitrogen to a mixture of 1 equiv of HgCl$_2$ and 10 equiv of Mg in THF.[3d] After 12 h at 25 °C, the yellow-brown supernatant liquid was siphoned into a separate flask, evaporated, extracted with hexane, filtered through Celite under nitrogen, and evaporated to provide 90–95% pure **2a** in a ca. 90% yield (eq 4). Although this compound was not further purified, its ^{1}H and ^{13}C NMR spectra were in agreement with the assigned structure. In toluene-d_8 two distinct singlets for the two Cp protons appeared at δ 5.78 and 5.82 ppm. The identity of **2a** was further supported by its conversion into 2-(trimethylsilyl)bicyclo[3.3.0]oct-1(2)-en-3-one (**3a**) in 55–65% isolated yield by treatment with CO (1.1 atm) for 2 h at 0 °C followed by quenching with 3 N HCl. Furthermore, protonolysis of **2a** produced **4a** in 90% yield based on **1a**, while its treatment with 2.5 equiv of I$_2$ (−78 to 25 °C) gave **4b** in 75% yield based on **1a**.



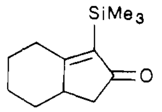
In a similar manner, 8-(trimethylsilyl)-1-octen-7-yne (**1b**) was converted into **2b**, **3b**, **4c**, and **4d**, in 90, 60, 87, and 76% yields, respectively. Although retention of the stereochemical identity was assumed in assigning the stereochemistry of **4b–d**, that of **4a** was clearly established by comparing its spectral data with an authentic sample prepared by an independent method.[8] Treatment of **4d** with 1 equiv of n-BuLi in ether at −78 °C[9] cleanly produced **10** in 70% yield, although the corresponding reaction of **4b** was complicated by some side reactions.



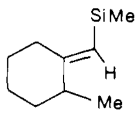
1b



2b



3b



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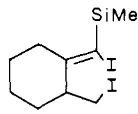

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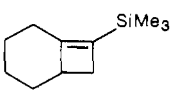

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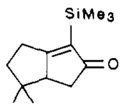
Table I. Zirconocene-Promoted Bicyclization–Carbonylation of Enynes Using the Cl$_2$ZrCp$_2$–Mg–HgCl$_2$ Procedure



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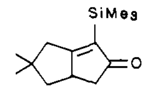
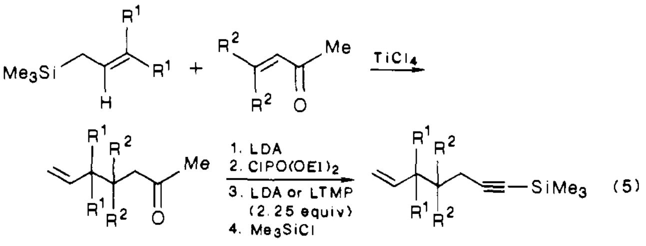


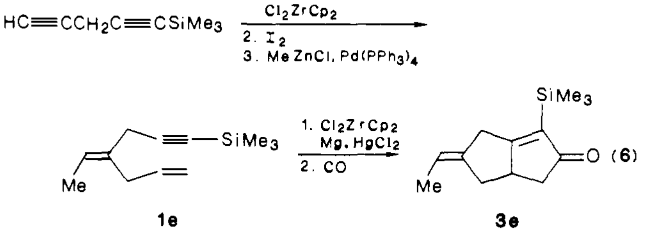
3d

enyne	product structure	product % isolated yield
1a	**3a**	55–65
1b	**3b**	62
1c	**3c**	50
1d	**3d**	60
1e	**3e**	55

The experimental results of the bicyclization–carbonylation reaction of several ω-(trimethylsilyl)-α,ω-enynes including **1a** and **1b** are summarized in Table I. Although the yields of bicyclic enones based on the starting enynes are 50–65% by isolation, the product region of the GLC trace in each case showed essentially one signal for the desired product. The preparation of **1a** and **1b** was carried out either by the reaction of [(trimethylsilyl)ethynyl]lithium with the corresponding ω-bromo- or ω-iodo-1-alkenes or by sequential treatment of ω-iodo-1-(trimethylsilyl)-1-alkynes with Mg in the presence of ZnCl$_2$ and vinyl bromide in the presence of Pd(PPh$_3$)$_4$ (5%).[10] The geminally dimethyl substituted derivatives **1c** and **1d** were conveniently prepared according to eq 5, involving the TiCl$_4$-promoted conjugate addition of allylsilanes[11] and a one-pot conversion of methyl ketones into silylated alkynes.[12] Finally, the preparation of **1e** required for the synthesis of **3e** was achieved via the Zr-promoted allylalumination[13] and the Pd-catalyzed methylation[10] using 1-(trimethylsilyl)-1,4-pentadiyne as the starting compound (eq 6).



1c: R^1 = Me, R^2 = H
1d: R^1 = H, R^2 = Me



An Alternate Procedure for Generation of "ZrCp$_2$" and the Scope of Enyne Bicyclization–Carbonylation. In search for more convenient and cleaner methods for generation of "ZrCp$_2$", we found

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(8) Miller, J. A.; Negishi, E. *Isr. J. Chem.* **1984**, *24*, 76.

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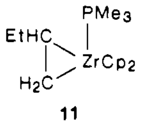
(13) Miller, J. A.; Negishi, E. *Tetrahedron Lett.* **1984**, *25*, 5863.

that treatment of Cl_2ZrCp_2 with alkylmetals containing Li or Mg was effective.[1b] Thus, treatment of Cl_2ZrCp_2 with 2 equiv of *n*-BuLi, *t*-BuLi, EtMgBr, and *t*-BuMgCl in THF at −78 °C for 1 h, addition of 1 equiv of **1a** at −78 °C, warming the mixture to 25 °C, stirring it for several additional hours at 25 °C, and quenching it with 3 M HCl produced **4a** in 95, 76, 83, and <5% yields, respectively. The yields of **2a** and **3a** using the *n*-BuLi–Cl_2ZrCp_2 procedure were comparable to those observed with the Cl_2ZrCp_2–Mg–$HgCl_2$ procedure. All subsequent experiments were run using the *n*-BuLi–Cl_2ZrCp procedure.

Examination of the reaction of Cl_2ZrCp_2 with 2 equiv of *n*-BuLi by ^1H NMR at −78 °C revealed that the Cp singlet of Cl_2ZrCp_2 at δ 6.61 ppm shifted completely to δ 6.18 ppm within 30 min, indicating that Cl_2ZrCp_2 had been cleanly converted into $(n\text{-Bu})_2ZrCp_2$. The identity of the latter was confirmed by its treatment with 2 equiv of I_2 (−78 to 25 °C), which produced *n*-BuI (ca. 2 equiv) and I_2ZrCp_2 (0.8 equiv). Addition of **1a** to the mixture containing $(n\text{-Bu})_2ZrCp_2$ at −78 °C did not cause any immediate change in the Cp region of the ^1H NMR spectrum. At 20 °C, however, a new singlet at δ 6.21 ppm emerged and grew at the expense of that at δ 6.18 ppm. The new signal at δ 6.21 ppm has since been shown to correspond to the Cp group of **2a**. This change obeyed first-order kinetics, $k_1 = (4.2 \pm 0.3) \times 10^{-2}$ min^{-1} at 20 °C. In the absence of **1a**, decomposition of $(n\text{-Bu})_2ZrCp_2$ obeying first-order kinetics also displays a similar rate constant of $(4.6 \pm 0.4) \times 10^{-2}$ min^{-1} at 20 °C. These results clearly indicate that, under the above-described conditions, Cl_2ZrCp_2 is converted into $(n\text{-Bu})_2ZrCp_2$ before addition of **1a** and that decomposition of $(n\text{-Bu})_2ZrCp_2$ by some first-order process is the rate-determining step of the reaction of $(n\text{-Bu})_2ZrCp_2$ and **1a**. Treatment of $(n\text{-Bu})_2ZrCp_2$ with 2 equiv of PMe_3 gave a relatively stable product, which was erroneously identified as $Cp_2Zr(PMe_3)_2$ on the basis of a tripletlike ^1H NMR signal for the Cp group. Buchwald and his co-workers[14] recently suggested **11** as its structure. Reexamination by NMR including ^1H 2D NOESY NMR has now established that it is a ca. 90:10 mixture of **12** and **11**. It now is likely that "$ZrCp_2$" is **13**. Although this point needs to be further clarified, it is likely that $(n\text{-Bu})_2ZrCp_2$ directly decomposes to give **13** and *n*-butane (eq 7), and an alternate path involving the intermediacy of free $ZrCp_2$ (eq 8) is less likely.



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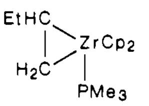

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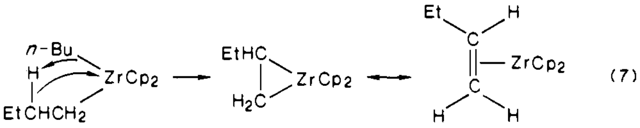
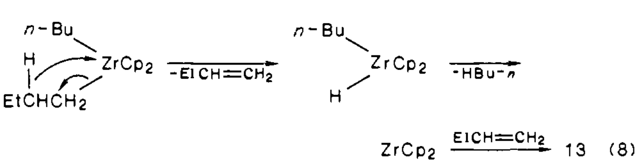
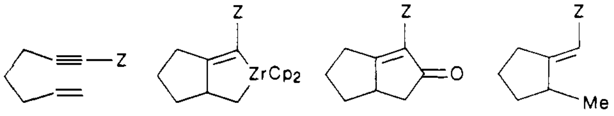


13a **13b**



To examine the effects of solvents, the bicyclization–carbonylation of **1a** was run in THF (73%), ether (62%), benzene (77%), toluene (74%) and hexane (66%). The yields of **3a** indicated in the parentheses were surprisingly insensitive to the nature of the solvents.

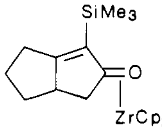
One of the difficulties encountered in the initial phase of our investigation was the inability of enynes containing a terminal alkyne group to undergo clean Zr-promoted bicyclization. Thus, the reaction of 1-hepten-6-yne itself with "$ZrCp_2$" led to products showing at least several ^1H NMR Cp signals. It is therefore necessary to use terminally substituted alkyne derivatives. To explore the scope with respect to the substituent (Z) of enynes represented by **1**, a series of 6-hepten-1-yne derivatives (**1a**, **1f–l**) containing a Si, Sn, alkyl, aryl, and alkenyl were prepared and reacted with "$ZrCp_2$". After 3 h at 22 °C, the reaction mixture was examined by ^1H NMR to estimate the yields of zirconabicycles, as described earlier. In some cases, a measured aliquot of the reaction mixture was quenched with 3 M HCl at 0 °C, and the protonolysis product was isolated and identified. Another aliquot was carbonylated at 1.1 atm to give the corresponding bicyclic ketone.



1 **2** **3** **4**

f, Z = $SnMe_3$; **g**, Z = Me; **h**, Z = $(CH_2)_2CH{=}CH_2$; **i**, Z = CH_2SiMe_3; **j**, Z = Ph; **k**, Z = $CH{=}CHHex\text{-}(E)$; **l**, Z = $CH{=}CHCH(OSiMe_2Bu\text{-}t)\text{-}C_5H_{11}\text{-}n\text{-}(E)$

The experimental results summarized in Table II show that, in all cases examined, the bicyclization yields estimated by ^1H NMR are ≥80%. The bicyclization products **2** were not isolated but directly converted into **3** and/or **4**. The bicyclization–carbonylation yields based on **1** were 55–65% by isolation. Full identification of the Zr-containing carbonylation products before quenching was hampered by the presence of byproducts. Nonetheless, the NMR spectral data of the concentrated reaction mixture were informative. The ^{13}C NMR spectrum indicated that the major product amounted to at least 80% of the total material and that it could not be **14**. Thus, in addition to the expected signals at 0.53 ($SiMe_3$) and 113.73 ppm (Cp), three aliphatic CH_2 signals at 23.58, 30.19, and 30.49 ppm, one aliphatic CH signal at 59.54 ppm, three low-field quaternary carbon signals at 109.25, 166.24, and 176.65 ppm as well as one CH signal at 107.91 ppm are attributable to the major product. Two likely candidates which are consistent with the ^{13}C NMR data are **15** and **16**. It is important from both mechanistic and synthetic viewpoints that, upon quenching the product with dry HCl in THF, Cl_2ZrCp_2 was regenerated in 97% yield by ^1H NMR along with **3a** and its desilylated parent bicyclic ketone in 60–70% combined yield. Significantly, little or no gas evolution (<1 mol %) occurred, strongly indicating that Z in **15** or **16** must not be H, even though a zirconium cyclopentenolate containing a Zr–H bond has previously been obtained in a similar carbonylation reaction.[15]



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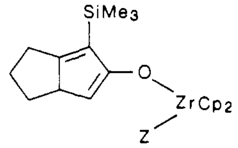

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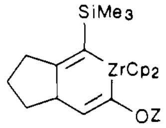

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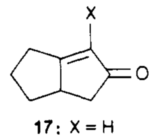
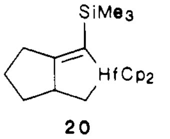


17: X = H
18: X = Br
19: X = I



20

The Me_3Sn-containing bicyclic ketone (**3f**) can be readily converted to its derivatives **17** (X = H, 82%), **18** (X = Br, 83%), and **19** (X = I, 91%) via treatment with HCl–MeOH, NBS, and I_2, respectively. Similarly, treatment of the Me_3Si-containing bicyclic ketone (**3a**) with NBS in DMF gave **18** in 75% yield.

To compare the ability of Zr to promote enyne bicyclization with that of Ti and Hf, the bicyclization reaction of **1a** with "$TiCp_2$" and "$HfCp_2$" generated by treating Cl_2TiCp_2 and

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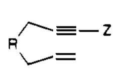
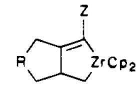
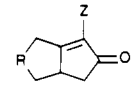
(14) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544.

(15) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716.

Table II. Zirconocene-Promoted Bicyclization–Carbonylation of Enynes Using the n-BuLi–Cl_2ZrCp_2 Procedure

 R	Z	 % yield[a]	 % yield[b]
CH_2	$SiMe_3$	95 (75)	65
CH_2	$SnMe_3$	92 (60)	63[c]
CH_2	Me	95 (65)	65 (70)
CH_2	$(CH_2)_2CH{=}CH_2$	80 (55)	
CH_2	CH_2SiMe_3	90	55[c]
CH_2	Ph	90 (70)	55[c]
CH_2	$CH{=}CHHex$-(E)	80 (75)	50
CH_2	$CH{=}CHCH(OSiMe_2Bu$-$t)C_5H_{11}$-n	(80)	
$PhCH_2N$	$SiMe_3$	85	66 (68)
21b			77

[a] By ^1H NMR. The numbers in parentheses are isolated yields of the protonolysis products. [b] Isolated yield. The numbers in parentheses are GLC yields. [c] The reaction was run in toluene. All the other reactions were run in THF.

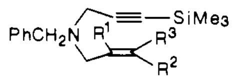
Table III. Reaction of Diynes with "Zirconocene" Generated by Treatment of Zirconocene Dichloride with n-Butyllithium[a]

$R^1C{\equiv}C(CH_2)_nC{\equiv}CR^2$			% yield of bis(alkylidene)-cycloalkane	
R^1	R^2	n	GLC	isolated
Me	n-Bu	2	76	67
Et	Et	3	85	80
Me	Me	4	84	55
Me_3Si	Me_3Si	4	97	89
n-Pr	Me_3Si	4		89
n-Pr	Ph	4		90
Me	Me	5	60	40

[a] Each reaction is carried out by treating Cl_2ZrCp_2 with 2 equiv of n-BuLi in hexane for 1 h at −78 °C in THF followed by addition of a diyne at −78 °C, warming the mixture to room temperature, and the standard workup with 3 N HCl, $NaHCO_3$, and brine.

Cl_2HfCp_2, respectively, with 2 equiv of n-BuLi was examined. The reaction with Cl_2TiCp_2 in either the presence or the absence of $PMePh_2$[7] did not give **3a** in any more than 5% yield. Treatment of Cl_2HfCp_2 with 2 equiv of n-BuLi in toluene at −78 °C produced $(n\text{-}Bu)_2HfCp_2$ (5.87 ppm for the ^1H NMR signal) in essentially quantitative yield. Its reaction with **1a** was considerably slower than that of $(n\text{-}Bu)_2ZrCp_2$, requiring 5 h at 100 °C for completion. The spectral data of the product (90%), especially its ^1H and ^{13}C NMR data, are in good agreement with **20**. The ^1H NMR Cp signals were at δ 5.90 and 5.94 ppm. Carbonylation of **20** with 1.1 atm of CO at 25 °C for 12 h produced **3a** in 80% GLC yield. At 3 atm, the reaction was complete within 2 h.

To test the effect of donor groups on the bicyclization–carbonylation reaction, a series of N-containing enynes represented by **21** were prepared by application of known methods. The bicyclization reaction in all four cases (**21a–d**) proceeded cleanly to give **22a–d** in 85, 95, 92, and 86% yields, respectively. No attempts were made to isolate **22a** and **22b**. To examine the stereochemistry of the bicyclization reaction, **22c** and **22d** were isolated as >95% pure substances (by ^{13}C NMR). Their ^1H and ^{13}C NMR spectra clearly indicated that they were stereoisomerically >98% pure and distinct from each other. Comparison of the ^1H and ^{13}C signals for the Me group on the ring as well as for the two methine protons, in particular the relative ^{13}C NMR chemical shift values for the Me group, led to the assigned stereochemistry, which in turn indicated that the bicyclization reaction proceeded with complete retention of the alkene stereochemistry. These zirconabicyclic compounds were directly converted into the corresponding protonolysis products **23a–c**. As expected, both **22c** and **22d** gave the identical product **23c**. Furthermore, carbonylation of **22a** and **22b** provided the corresponding bicyclic enones **24a** and **24b** in 66 and 77% yields, respectively.



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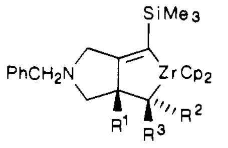

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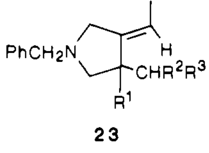

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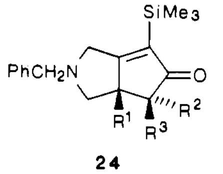
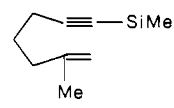


24

a, $R^1 = R^2 = R^3 = H$; **b**, $R^1 = Me$, $R^2 = R^3 = H$; **c**, $R^1 = R^2 = H$, $R^3 = Me$; **d**, $R^1 = R^3 = H$, $R^2 = Me$

In sharp contrast with the bicyclization reaction of **21b**, the corresponding reaction of **25** gave, after protonolysis, 0.32 equiv (64%) of a dimeric product, **26**, which must have been formed via **27**. There was no indication for the formation of the expected monomeric product **28**. The striking difference between the reaction of **21b** and that of **25** must be attributable to the amino group of **21b**, but its precise role remains unexplained. Unfortunately, addition of NEt_3, PMe_3, or $PMePh_2$ to "$ZrCp_2$" merely inhibited the formation of **27** without inducing the desired bicyclization reaction.



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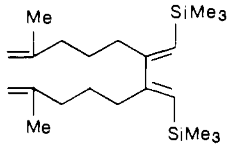

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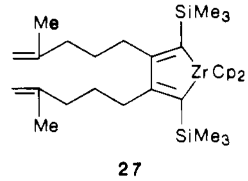
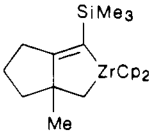


27

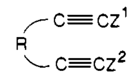


28

Diyne Bicyclization. Conversion of diynes into E,E-exocyclic dienes promoted by "$TiCp_2$" generated by treating Cl_2TiCp_2 with sodium amalgam in the presence of $PMePh_2$ was reported in 1984 by Nugent and Calabrese.[7] These authors stated in their report that the Ti reagent was uniquely effective among those containing the group 4A and 5A metals. However, no results pertaining to the use of Zr, Hf, or group 5A metals were presented at that time. In view of the favorable results obtained in the enyne bicyclization promoted by "$ZrCp_2$", the corresponding reaction of diynes was also examined.

Several diynes (**29**) in which the two alkyne groups are separated by two- to five-carbon chains were prepared by application of known methodologies. In cases where the two alkynyl groups are separated by three- to five-carbon chains, the reaction of alkynyllithiums with ω-bromo- or ω-iodoalkynes is a generally satisfactory method. On the other hand, this reaction mainly leads to β-elimination in cases where homopropargyl halides are used. The preparation of 2,6-undecadiyne (**29a**) was achieved by methylation of 1,5-decadiyne which, in turn, was prepared by the reaction of 2-heptynylmagnesium bromide with propargyl bromide.[16]

As the results summarized in Table III indicate, the reaction of all seven diynes **29a–g** with "$ZrCp_2$" generated by treating Cl_2ZrCp_2 with 2 equiv of *n*-BuLi at −78 to 25 °C followed by



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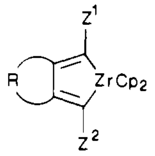

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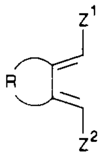

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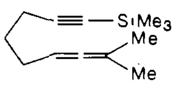

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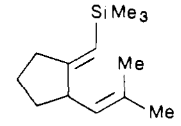


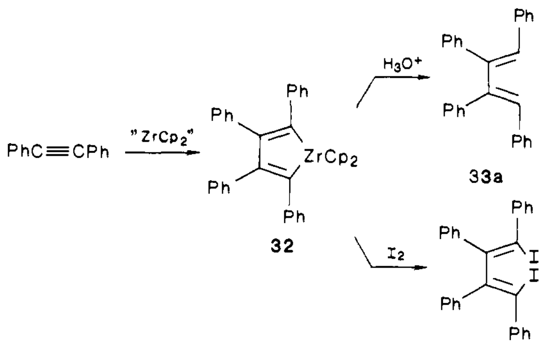
31

8, 9, 29	R	Z^1	Z^2
a	$(CH_2)_2$	Me	Bu-*n*
b	$(CH_2)_3$	Et	Et
c	$(CH_2)_4$	Me	Me
d	$(CH_2)_4$	$SiMe_3$	$SiMe_3$
e	$(CH_2)_4$	Pr-*n*	$SiMe_3$
f	$(CH_2)_4$	Pr-*n*	Ph
g	$(CH_2)_5$	Me	Me

quenching with 3 M HCl afforded *E,E*-exocyclic dienes containing four- through seven-membered rings in 60–97% GLC yields (40–89% by isolation). The following specific points are noteworthy. First, the Zr-promoted method readily accommodate both four- and seven-membered products in addition to five- and six-membered exocyclic dienes. A paper[17] published subsequent to our communication on the Zr-promoted diyne bicyclization[1b] compared the Zr-promoted reaction with the Ti-promoted reaction. The Ti-promoted method failed to produce four-membered exocyclic dienes, while the Zr-promoted method was highly satisfactory. The reported yields of a seven-membered exocyclic diene, (*E,E*)-1,2-bis(ethylidene)cycloheptane, were 24 and 45%, respectively, for the Ti- and Zr-promoted reactions. Moreover, 1,8-bis(trimethylsilyl)-1,7-octadiyne (**29d**) gave **9d** in excellent yield, whereas the Ti-promoted method reportedly failed to convert **29d** into **9d**.[7,17] That the Zr-containing bicyclization products are indeed **8** was demonstrated for the conversion of **29d** into **8d**, which was generated in 98% yield as determined by ^1H NMR and was characterized by ^1H and ^{13}C NMR as well as IR.

The *n*-BuLi–Cl_2ZrCp_2 procedure is also applicable to the bicyclization of allenynes, as indicated by the conversion of **30** into **31** in 45% yield.

Further Structural and Mechanistic Considerations. As discussed earlier, treatment of Cl_2ZrCp_2 with 2 equiv of *n*-BuLi at −78 °C produces $(n\text{-}Bu)_2ZrCp_2$. At higher temperatures, it decomposes to give a "$ZrCp_2$", which most likely is $Cp_2Zr(CH_2{=}CHC_2H_5)$ (**13**). The reaction of "$ZrCp_2$" with diphenylacetylene in a 1:2 ratio gave a known zirconacycle, **32**,[3] in essentially quantitative yield, from which **33a** and **33b** were obtained in 86 and 58% yields, respectively (eq 9). The zirconacycle **32** must have been formed via a 1:1 product, **34**. However, even when the reactant ratio was 1:1, the major products obtained after protonolysis were **33a** and bibenzyl. The ratio of **33a** to bibenzyl varied considerably from run to run. Interestingly, however, deuterolysis gave dideuterated **33a** and $\alpha,\alpha,\alpha',\alpha'$-tetradeuteriobibenzyl (92% D incorporation by ^1H NMR). We have so far failed to fully identify the Zr-containing precursor to the tetradeuterated product, although **35** is a likely candidate.



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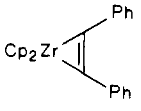

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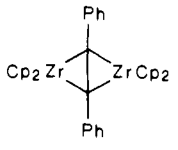

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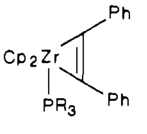
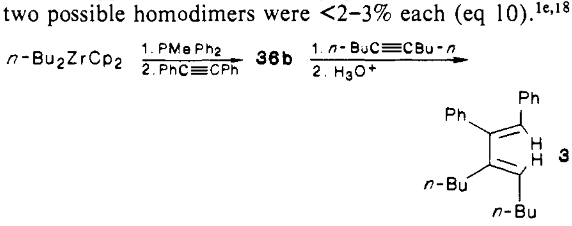


36a: R = Me
36b: R = $MePh_2$

In contrast with the above case, the reaction of $Cp_2Zr(CH_2{=}CHC_2H_5)(PMe_3)$ with 1 equiv of diphenylacetylene provided **36a** in 91% yield. The reaction was first order in each of the two reagents, and the second-order rate constant was $(2.1 \pm 0.2) \times 10^{-1}$ L mol^{-1} min^{-1} at 20 °C. Under the same conditions, (*E*)-stilbene also reacted with $Cp_2Zr(CH_2{=}CHC_2H_5)(PMe_3)$ with the second-order rate constant of $(1.4 \pm 0.3) \times 10^{-3}$ L mol^{-1} min^{-1}. These results indicate that diphenylacetylene is ca. 150 times as reactive as (*E*)-stilbene. A yellow crystalline sample of **36a**, mp 201–203 °C dec, obtained by recrystallization from THF–ether (1:2), yielded satisfactory elemental analytical data, IR, ^1H and ^{13}C NMR, and X-ray crystallographic data.[1e,14] Although not fully identified, the corresponding reaction of $Cp_2Zr(CH_2{=}CHEt)(PMePh_2)$ with 1 equiv of diphenylacetylene produced a compound to which **36b** has been tentatively assigned. Protonolysis of **36a** or **36b** with 3 M HCl gave essentially 100% pure (*Z*)-stilbene in 80–90% yield. The reaction of **36a** with 1 equiv of diphenylacetylene was very sluggish. On the other hand, the corresponding reaction of **36b** gave a 92% yield of **32**, identified by matching its spectral data with those of an authentic sample prepared above in the absence of a phosphine. The results indicate that a zirconacyclopropene, such as **34** and **36**, can be an intermediate for the formation of a five-membered zirconacycle.

The stepwise formation of **32** via **36** suggested the hitherto undeveloped synthetic possibility of selectively codimerizing two different acetylenes to produce mixed conjugated dienes. Indeed, the reaction of **36b** with 1 equiv of 5-decyne followed by protonolysis with 3 M HCl provided an 86% yield of **37**, which showed a clean ^1H NMR triplet at δ 5.50 ppm (J = 7 Hz) and a singlet at δ 6.82 ppm for the two alkenyl protons. The amounts of the two possible homodimers were <2–3% each (eq 10).[1e,18]



37 (10)

Treatment of **36a** with 4 equiv of acetone at room temperature for 1 h followed by protonolysis with 3 M HCl yielded **38** most probably via **39** (eq 11).[1e,18] The reactions of **36a** and **36b** with 5-decyne (eq 10) and acetone (eq 11) further justify the zirco-

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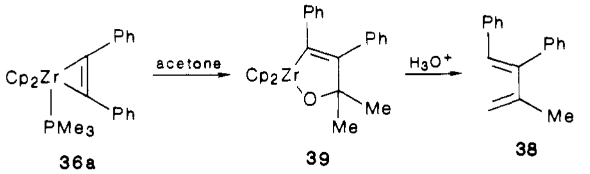
[16] Mori, K.; Tominaga, M.; Matsui, M. *Agric. Biol. Chem.* **1974**, *38*, 1551.

[17] Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788.

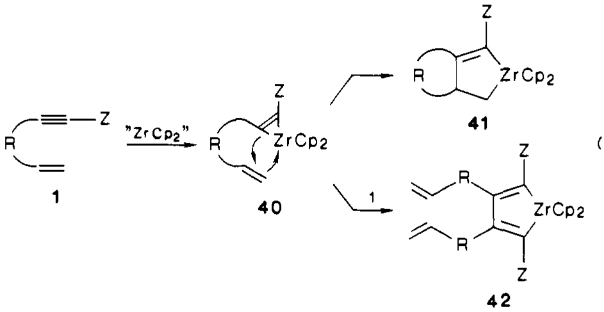
[18] (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (b) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7441. (c) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7137.

nacyclopropene or σ-bond formulation of **36**.

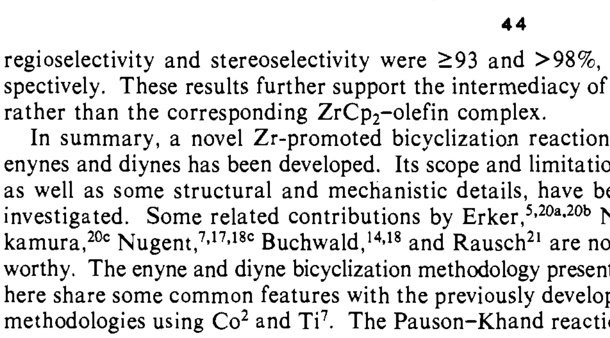


(11)

To further probe the mechanism of the "ZrCp$_2$"-promoted enyne bicyclization, **1a** was treated with 1 equiv of Cp$_2$Zr(CH$_2$=CHEt)(PMePh$_2$) at 20 °C. The reaction indeed gave **2a** in 90% yield, although ^{1}H NMR examination of the reaction mixture failed to detect any intermediate. The data presented in this and preceding sections support the following mechanism for the enyne bicyclization reaction. Enynes **1** react with a "ZrCp$_2$" to give first zirconacyclopropene intermediates represented by **40**, which then undergo intramolecular Zr–C bond addition to the alkene moiety to produce **41** (eq 12). If the second step is slower than the intermolecular reaction of **40** with another molecule of the enyne used, as might be the case with **25**, dimeric products represented by **42** are formed. We have further noted recently that formation of **41** from **40** must be reversible. Specifically, treatment of **2a** with MeCN[14,18,19] (1.1 equiv) in THF for 3 h at 25 °C produced **43** in 70% yield, which was hydrolyzed with 3 M HCl to give **44** in 60% yield based on **2a** (eq 13). The regioselectivity and stereoselectivity were ≥93 and >98%, respectively. These results further support the intermediacy of **40** rather than the corresponding ZrCp$_2$-olefin complex.



(12)



(13)

In summary, a novel Zr-promoted bicyclization reaction of enynes and diynes has been developed. Its scope and limitations, as well as some structural and mechanistic details, have been investigated. Some related contributions by Erker,[5,20a,20b] Nakamura,[20c] Nugent,[7,17,18c] Buchwald,[14,18] and Rausch[21] are noteworthy. The enyne and diyne bicyclization methodology presented here share some common features with the previously developed methodologies using Co[2] and Ti[7]. The Pauson–Khand reaction[2] using Co reagents can directly convert enynes into bicyclic enones under catalytic conditions. The reaction readily accommodates terminal alkynes and appears to be less sensitive to the steric hindrance about the alkyne moiety than the Zr-promoted reaction. The comparable data on the scope and limitations of the two reactions, however, are not yet well-documented. It should also be noted that the Zr-promoted bicyclization reaction proceeds at or below room temperature, whereas much higher temperatures (≥80 °C) seem to be required or desirable for the Pauson–Khand reaction. Furthermore, the Zr promoted bicyclization reaction produces zirconabicycles as discrete products which can be converted into other derivatives via protonolysis, iodinolysis, and so on. As far as bicyclization of enynes is concerned, the Zr procedure appears to be superior to the Ti procedure. Some comparative data[1b,7,17] also suggest that the Zr procedure may be superior to the Ti procedure in many cases of diyne bicyclization as well, although additional data are needed to further clarify this point.

It is worth noting that, over the past few years, a few other enyne bicyclization reactions involving Pd[22a–e] and Ni[22f,g] have also been reported. Although related, these methodologies are, at present, of much different synthetic value and are largely complementary with the others mentioned above. Development of additional related bicyclization reactions of enynes, diynes, and dienes involving other transition metals is likely.

Experimental Section

General Procedures. Manipulations involving organometallics were carried out under an atmosphere of N$_2$ or Ar. Flash chromatographic separations were carried out as described by Still[23] on 230–400-mesh silica gel 60. Alkyllithiums were titrated with either menthol–2,5′-bipyridyl or 2-butanol–1,10-phenanthroline.[24] Gas chromatographic measurements were performed on SE-30 (Chromosorb W) columns with appropriate saturated hydrocarbon standards. As needed, THF and diethyl ether were distilled from sodium benzophenone ketyl; CH$_2$Cl$_2$, (CH$_2$Cl)$_2$, and CCl$_4$ were distilled from P$_2$O$_5$; pentane, hexane, benzene, and toluene were distilled from LiAlH$_4$; HMPA was distilled from Ph$_3$CLi; ZnCl$_2$, LiCl, LiBr, and NaI were dried at 120 °C at ≤0.5 mm for 6–12 h. Other materials were purchased from appropriate sources and used as received. Zirconocene dichloride was purchased from Boulder Chemical Co. A cylinder of CO was obtained from Matheson Gas Products.

Bicyclization of Enynes with "ZrCp$_2$". The following procedures for the conversion of 7-(trimethylsilyl)-1-hepten-6-yne (**1a**) into **2a** are representative.

(a) Representative Procedure Using Cl$_2$ZrCp$_2$, Mg, and HgCl$_2$.[3d] Into a 100-mL flask equipped with a magnetic stirring bar, a septum inlet, and a mercury bubbler were introduced 0.81 g (3.0 mmol) of HgCl$_2$ and 0.73 g (30.0 mmol) of Mg turnings. The metals were dried at 70 °C in vacuo (≤1 mmHg) for 2 h. After cooling to 0 °C, 30 mL of THF was added, followed by 0.50 g (3.0 mmol) of 7-(trimethylsilyl)-1-hepten-6-yne. Upon addition of 0.88 g (3.6 mmol) of Cp$_2$ZrCl$_2$, the reaction mixture was warmed to 25 °C and stirred for 12 h. The resulting yellow-brown supernatant liquid was siphoned into a separate flask, and the volatile compounds were removed in vacuo. The residue was extracted with hexane and filtered through Celite under a nitrogen atmosphere. The filtrate was concentrated to dryness to provide ca. 1.1 g (95%) of 3,3-bis(cyclopentadienyl)-2-(trimethylsilyl)-3-zirconabicyclo[3.3.0]oct-1(2)-ene (**2a**) (90–95% pure by ^{13}C NMR): IR (hexane) 1698 (w), 1591 (w), 1521 (m), 1244 (s), 1010 (s), 840 (s) cm^{-1}; ^{1}H NMR (toluene-d_8, Me$_4$Si) δ 0.11 (s, 9 H), 0.9–2.4 (m, 9 H), 5.78 (s, 5 H), 5.82 (s, 5 H); ^{13}C NMR (C$_6$D$_6$, Me$_4$Si) δ 1.27, 20.48, 33.33, 38.13, 41.13, 42.73, 109.15, 110.31, 152.23, 186.88. The crude product obtained above was used directly to prepare **3a**, **4a**, and **4b**. For synthetic purposes, the siphoned-out yellow-brown liquid may be used directly without further manipulation.

(b) Representative Procedure Using Cl$_2$ZrCp$_2$ and *n*-BuLi. To Cl$_2$ZrCp$_2$ (0.614 g, 2.1 mmol) in THF (7 mL) was added dropwise at

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−78 °C *n*-BuLi (1.6 M, 2.63 mL, 4.2 mmol). After stirring for 1 h at −78 °C, 7-(trimethylsilyl)-1-hepten-6-yne (0.332 g, 2.0 mmol) in THF (3 mL) was added. The mixture was warmed to 25 °C over 1–2 h and stirred for 3–6 h. ^{1}H NMR analysis of the signals due to the Cp (δ 6.17) and Me_3Si (δ 0.04) groups using benzene as an internal standard indicated the formation of **2a** in 95% yield. The reaction mixture obtained above was used directly for preparing **3a**, **4a**, and **4b**. The use of *t*-BuLi, EtMgBr, and *t*-BuMgCl in place of *n*-BuLi gave, after quenching with 3 M HCl, **4a** in 76, 83, and <5% yields. The preparation of **2a** and its conversion into **3a** and **4a** were also carried out in ether, benzene, toluene, and hexane. The yields of **3a** with these solvents were 62, 77, 74, and 66%, respectively.

8,8-Bis(cyclopentadienyl)-9-(trimethylsilyl)-8-zirconabicyclo[4.3.0]non-1(9)-ene (2b): 90% yield by ^{1}H NMR; IR (neat) 1790 (w), 1600 (w), 1515 (m), 1245 (s), 1010 (m), 830 (s) cm^{-1}; ^{1}H NMR (C_6D_6, Me_4Si) δ 0.12 (s, 9 H), 0.9–2.3 (m, 11 H), 5.96 (s, 5 H), 5.99 (s, 5 H); ^{13}C NMR (C_6D_6, Me_4Si) δ 2.59, 27.38, 28.26, 40.20, 41.55, 43.47, 47.15, 111.25, 111.93, 161.76, 188.84. This compound was converted into **3b**, **4c**, and **4d** without purification.

Representative Procedure for Carbonylation, Protonolysis, and Iodinolysis of Zirconabicycles. (a) **2-(Trimethylsilyl)bicyclo[3.3.0]oct-1(2)-en-3-one (3a).** A THF solution of **2a** (10-mmol scale) was cooled to 0 °C and evacuated (10–20 mmHg). To this was introduced CO. This process was repeated three times. The initial pressure of 1.1 atm was attained by having a 76-mmHg bubbler. The reaction mixture was stirred for 2 h at 0 °C, quenched with 3 M HCl and pentane, extracted, washed with aqueous $NaHCO_3$ and NaCl, dried over $MgSO_4$, and distilled to give 1.26 g (65%) of **3a**: IR (neat) 1790 (s), 1610 (s), 1250 (s), 830 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.18 (s, 9 H), 0.9–1.3 (m, 2 H), 1.9–2.4 (m, 4 H), 2.4–2.9 (m, 3 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.40, 25.53, 27.33, 30.79, 42.88, 48.31, 134.86, 198.79, 214.47. Anal. Calcd for $C_{11}H_{18}OSi$: C, 67.98; H, 9.34. Found: C, 67.72; H, 9.13.

(b) **(*E*)-1-[(Trimethylsilyl)methylene]-2-methylcyclopentane (4a).** A THF solution of **2a** (2-mmol scale) was quenched with 3 M HCl. The mixture was extracted with pentane, washed with $NaHCO_3$ and brine, dried over $MgSO_4$, concentrated, and distilled to provide 0.302 g (90%) of **4a**: IR (neat) 1640 (m), 1245 (s), 870 (s), 840 (s) cm^{-1}; ^{1}H NMR (CCl_4, C_6H_6) δ 0.15 (s, 9 H), 1.12 (d, *J* = 6 Hz, 3 H), 1.0–2.6 (m, 7 H), 5.3–5.4 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.26, 18.94, 24.28, 32.60, 34.79, 41.81, 116.27, 167.54. Anal. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.97. Found: C, 71.62; H, 12.02.

(c) **(*Z*)-1-[(Trimethylsilyl)iodomethylene]-2-(iodomethyl)cyclopentane (4b).** A THF solution containing **2a** (4-mmol scale) was treated at −78 °C with 3.00 g (11.8 mmol) of I_2 in 20 mL of THF. The reaction mixture was stirred for 1 h at −78 °C and warmed to 25 °C over 1 h. It was quenched with aqueous NH_4Cl, extracted with pentane, washed with $Na_2S_2O_3$ and $NaHCO_3$, dried over Na_2SO_4, concentrated, and column chromatographed (60–200-mesh silica gel, pentane) to afford 1.26 g (75%) of **4b**: IR (neat) 1590 (m), 1250 (s), 830 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.25 (s, 9 H), 1.8–1.9 (m, 4 H), 2.3–2.5 (m, 2 H), 3.0–3.2 (m, 2 H), 3.6–3.7 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.95, 9.46, 25.62, 31.34, 33.94, 56.83, 103.86, 163.42. Anal. Calcd for $C_{10}H_{18}I_2Si$: C, 28.59; H, 4.32. Found: C, 28.20; H, 4.07.

9-(Trimethylsilyl)bicyclo[4.3.0]non-1(9)-en-8-one (3b): 60% yield; IR (neat) 1690 (s), 1590 (s), 1245 (s), 830 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.18 (s, 9 H), 0.95–1.6 (m, 4 H), 1.7–2.25 (m, 4 H), 2.4–2.6 (m, 2 H), 2.9–3.05 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.22, 25.26, 27.35, 31.49, 35.45, 42.66, 43.40, 135.93, 191.38, 212.49. Anal. Calcd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.67. Found: C, 69.25; H, 10.02.

(*E*)-1-[(Trimethylsilyl)methylene]-2-methylcyclohexane (4c): 87% yield; IR (neat) 1610 (m), 1245 (s), 830 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.10 (s, 9 H), 1.00 (d, *J* = 9 Hz, 3 H), 1.3–1.5 (m, 4 H), 1.7–2.7 (m, 5 H), 5.10 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.44, 18.80, 25.82, 29.03, 34.94, 37.32, 40.78, 116.55, 163.87. Anal. Calcd for $C_{11}H_{22}Si$: C, 72.44; H, 12.16. Found: C, 72.02; H, 12.39.

(*Z*)-1-[(Trimethylsilyl)iodomethylene]-2-(iodomethyl)cyclohexane (4d): 76% yield; IR (neat) 1575 (m), 1250 (s), 1180 (s), 830 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.28 (s, 9 H), 1.0–2.3 (m, 8 H), 2.7–2.9 (m, 2 H), 3.2–3.5 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 2.29, 7.48, 19.72, 27.50, 31.06, 52.18, 106.98, 158.10. Anal. Calcd for $C_{11}H_{20}I_2Si$: C, 30.43; H, 4.64. Found: C, 30.59; H, 4.37.

8-(Trimethylsilyl)bicyclo[4.2.0]oct-1(8)-ene (10). To 2.30 g (5.3 mmol) of **4d** in 5 mL of ether was added at −78 °C 2.16 mL (5.3 mmol) of 2.45 M *n*-BuLi. The reaction mixture was stirred for 1 h at −78 °C and then warmed to 25 °C over 30 min. After quenching at 0 °C with water, the organic layer was separated and dried over Na_2SO_4. Distillation provided 0.69 g (72%) of **10**: IR (neat) 1620 (m), 1245 (s), 830 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.00 (s, 9 H), 0.9–2.6 (m, 10 H), 3.0–3.2 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −1.06, 25.02, 27.82, 29.06, 34.19, 36.54, 42.36, 136.67, 165.85. Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 72.96; H, 11.36.

ω-Substituted 1-Hepten-6-yne Derivatives. The following derivatives were prepared via 5-bromo-1-pentene as follows.

1-Hepten-6-yne. 5-Bromo-1-pentene[25] was preared in 60% yield by heating 1,5-dibromopentane (320 mmol) in HMPA (65 mL) first at 195 °C and then at 220 °C until no more product distilled. The product was redistilled: bp 126–128 °C; IR (neat) 1640 (s), 1245 (s), 990 (s), 910 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.8–2.4 (m, 4 H), 3.45 (t, *J* = 6 Hz, 2 H), 5.05–5.3 (m, 2 H), 5.65–6.1 (m, 1 H). To lithium acetylenide–ethylenediamine (18.4 g, 200 mmol) and DMSO (100 mL) was added at 0 °C 5-bromo-1-pentene (20.4 g, 136.8 mmol) in DMSO (10 mL) while maintaining the temperature below 8 °C.[26] After the mixture was stirred at 25 °C for 1 h, water (50 mL) was added slowly at or below 35 °C. The title compound was then distilled until only water was collected, with a Dean–Stark trap. The organic layer was separated and dried over $CaCl_2$. Distillation provided 9.0 g (70%) of the title compound: bp 96 °C; IR (neat) 3320 (s), 2120 (w), 1645 (m), 990 (m), 915 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.55–1.70 (m, 2 H), 1.95 (t, *J* = 1 Hz, 1 H), 2.10–2.25 (m, 4 H), 4.95–5.10 (m, 2 H), 5.70–5.90 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.69, 27.58, 32.57, 68.35, 84.11, 115.18, 137.59.

(a) **7-(Trimethylsilyl)-1-hepten-6-yne (1a).** This compound was prepared in 80–90% yield by successively treating 1-hepten-6-yne with *n*-BuLi (1 equiv) and Me_3SiCl (2–3 equiv): bp 66–68 °C (9 mmHg); IR (neat) 2175 (s), 1640 (m), 1245 (s), 1020 (m), 990 (m), 912 (s), 840 (s), 755 (s) cm^{-1}; ^{1}H NMR (CCl_4, C_6H_6) δ 0.27 (s, 9 H), 1.5–1.9 (m, 2 H), 2.1–2.4 (m, 4 H), 5.0–5.25 (m, 2 H), 5.6–6.05 (m, 1 H).

(b) **7-(Trimethylstannyl)-1-hepten-6-yne (1f).** This compund was prepared in 72% yield by successively treating 1-hepten-6-yne with *n*-BuLi (1 equiv) and Me_3SnCl (1.2 equiv): bp 113–115 °C (23 mmHg); IR (neat) 2153 (s), 1641 (m), 990 (m), 912 (s), 775 (s) cm^{-1}; ^{1}H NMR (CCl_4, Me_4Si) δ 0.35 (s, 9 H), 1.6–1.9 (m, 2 H), 2.1–2.45 (m, 4 H), 5.0–5.25 (m, 2 H), 5.6–6.1 (m, 1 H). The following compounds were prepared from 1-hepten-6-yne. The experimental details of their syntheses are presented as part of the supplemental material: **1-octen-6-yne (1g)**, **undeca-1,10-dien-5-yne (1h)**, **8-(trimethylsilyl)-1-octen-6-yne (1i)**, **7-phenyl-1-hepten-6-yne (1j)**, **pentadeca-1,8-dien-6-yne (1k)**, and **(*E*)-10-[(*tert*-butyldimethylsilyl)oxy]-1,8-pentadecadien-6-yne (1l)**. The preparation of **8-(trimethylsilyl)-1-octen-7-yne (1b)** and **2-methyl-7-(trimethylsilyl)-1-hepten-6-yne (25)** is also described in the supplemental material.

3,3-Dimethyl-7-(trimethylsilyl)-1-hepten-6-yne (1c). 5,5-Dimethyl-6-hepten-2-one was prepared in 59% yield by a literature procedure:[11] bp 78–80 °C (10 mmHg); IR (neat) 1715 (s), 1640 (w), 1360 (s), 1155 (m), 902 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.92 (s, 6 H), 1.48 (t, *J* = 9 Hz, 2 H), 1.99 (s, 3 H), 2.20 (t, *J* = 9 Hz, 2 H), 4.82 (m, 2 H), 5.65 (m, 1 H). This was converted into the title compound in 55% yield with lithium 2,2,6,6-tetramethylpiperidide (LTMP), $ClPO(OEt)_2$, and Me_3SiCl (2 equiv) by a literature procedure:[12] IR (neat) 2170 (s), 1245 (s), 830 s) cm^{-1}; ^{1}H NMR (CCl_4, C_6H_6) δ 0.26 (s, 9 H), 1.15 (s, 6 H), 1.69 (t, *J* = 9 Hz, 2 H), 2.23 (t, *J* = 9 Hz, 2 H), 4.9–5.15 (m, 2 H), 5.65–6.0 (m, 1 H). The preparation of **4,4-dimethyl-7-(trimethylsilyl)-1-hepten-6-yne (1d)** is described in the supplemental material.

(*E*)-4-Ethylidene-7-(trimethylsilyl)-1-hepten-6-yne (1e). 1-(Trimethylsilyl)-1,4-pentadiyne (2.99 g, 22.0 mmol) was allylaluminated[13] with diisobutylallylalane (22.0 mmol) and Cl_2ZrCp_2 (6.38 g, 22 mmol) at room temperature for 1 h and iodinated with 3.36 g (13.2 mmol, 0.6 equiv) of iodine to provide 3.54 g (53%) of (*E*)-4-(iodomethylidene)-7-(trimethylsilyl)-1-hepten-6-yne after column chromatography (hexane, silica gel): IR (neat) 2175 (s), 1245 (s), 1015 (m), 835 (s), 755 (m) cm^{-1}; ^{1}H NMR (CCl_4, C_6H_6) δ 0.28 (s, 9 H), 2.1–3.2 (m, 4 H), 5.1–5.4 (m, 2 H), 5.6–6.1 (m, 1 H), 6.46 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.01, 27.65, 41.45, 78.42, 88.37, 102.00, 117.19, 132.87, 142.61. A solution of 1.09 g (8.0 mmol) of anhydrous $ZnCl_2$ in 4 mL of THF was treated at 0 °C with 4.62 mL (6.0 mmol) of a 1.30 M solution of methyllithium in ether. After stirring of the mixture at room temperature for 10 min, it was sequentially treated with 0.17 g (5 mol %) of $Pd(PPh_3)_4$ and 0.91 g (3.0 mmol) of (*E*)-4-(iodomethylene)-7-(trimethylsilyl)-1-hepten-6-yne and was stirred at 25 °C for 24 h.[10] The reaction mixture was quenched with saturated NH_4Cl and pentane, washed with saturated NaCl, and dried ($MgSO_4$). Kugelrohr distillation [80 °C (0.1 mm)] provided 0.48 g (83%) of the title compound, which was found to be isomerically pure and ≥98% regiochemically pure: IR (neat) 2180 (m), 1250 (s), 840 (s) cm^{-1}; ^{1}H NMR (CCl_4, C_6H_6) δ 0.23 (s, 9 H), 1.73 (d, *J* = 7 Hz, 3 H), 2.93 (m, 4 H), 5.0–5.25 (m, 2 H), 5.5–6.0 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$) δ 0.08, 13.10, 27.57, 34.28, 86.83, 104.53, 115.50, 121.44, 132.10, 135.15.

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Allylbenzyl[3-(trimethylsilyl)propynyl]amine Derivatives (21). (a) **Allylbenzyl[3-(trimethylsilyl)propynyl]amine (21a).** To a mixture of allylbenzylamine[27] (2.94 g, 20 mmol) and anhydrous Na_2CO_3 (4.0 g, 38 mmol) in absolute ethanol was added 3-(trimethylsilyl)propargyl bromide[28] (4.5 g, 23.6 mmol). The reaction mixture was stirred at room temperature for 6 h and poured onto 50 mL of 3 M HCl. The aqueous layer was brought to pH 12 with NaOH, and extracted with ether. The organic layers were washed with brine and dried over $MgSO_4$. Concentration followed by Kugelrohr distillation gave 4.01 g (78%) of **21a**: bp 100–110 °C (0.3 mmHg); IR (neat) 2170 (s), 1250 (s), 987 (s), 925 (m), 845 (s), 762 (s), 742 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$, CH_2Br_2) δ 0.20 (s, 9 H), 3.18 (d, J = 7 Hz, 2 H), 3.32 (s, 2 H), 3.65 (s, 2 H), 5.05–6.1 (m, 3 H), 7.2–7.5 (m, 5 H). The following compounds were similarly prepared, and their spectral data are summarized in the supplemental material: **benzyl(2-methylpropenyl)[3-(trimethylsilyl)propynyl]amine (21b)**, **(*E*)-benzyl-2-butenyl[3-(trimethylsilyl)propynyl]amine (21c), and (*Z*)-benzyl-2-butenyl[3-(trimethylsilyl)propynyl]amine (21d)**.

Bicyclo[3.3.0]oct-1(2)-en-3-ones. The representative procedures described for the synthesis of **3a** were used for the preparation of the following compounds. The Cl_2ZrCp_2-Mg-$HgCl_2$ procedure was used to convert **1c–e** to the corresponding zirconabicycles. In all of the other cases, the *n*-BuLi–Cl_2ZrCp_2 procedure was used.

(a) **2-(Trimethylsilyl)-6,6-dimethylbicyclo[3.3.0]oct-1(2)-en-3-one (3c)**: 62% yield; bp 65–70 °C (0.3 mmHg, Kugelrohr); IR (neat) 1690 (s), 1610 (s), 1245 (s), 830 (s) cm^{-1}; ^1H NMR (CCl_4, C_6H_6) δ 0.33 (s, 9 H), 0.9–1.5 (m with peaks at 0.84 and 1.30, 8 H), 1.9–3.0 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 1.21, 19.86, 27.10, 27.84, 37.50, 38.30, 41.29, 58.48, 136.00, 198.42, 214.59. Anal. Calcd for $C_{13}H_{22}OSi$: C, 70.20; H, 9.97. Found: C, 70.33; H, 9.78.

(b) **2-(Trimethylsilyl)-7,7-dimethylbicyclo[3.3.0]oct-1(2)-en-3-one (3d)**: 50% yield; bp 65–70 °C (0.4 mmHg, Kugelrohr); IR (neat) 1690 (s), 1600 (s), 1235 (s), 830 (s) cm^{-1}; ^1H NMR (CCl_4, C_6H_6) δ 0.30 (s, 9 H), 1.27 (s, 3 H), 1.34 (s, 3 H), 1.9–2.2 (m, 2 H), 2.5–2.8 (m with peaks at 2.49, 2.56, 2.67, and 2.75, 4 H), 3.0–3.4 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 1.24, 30.67, 40.43, 43.40, 43.66, 45.74, 135.09, 197.85, 213.83. Anal. Calcd for $C_{13}H_{22}OSi$: C, 70.20; H, 9.97. Found: C, 69.86; H, 9.78.

(c) **(*E*)-7-Ethylidene-2-(trimethylsilyl)bicyclo[3.3.0]oct-1(2)-en-3-one (3e)**: bp 95 °C (0.1 mmHg, Kugelrohr); 51% yield; IR (neat) 1680 (s), 1610 (s), 1240 (s), 830 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.10 (s, 9 H), 1.60 (d, J = 7 Hz, 3 H), 1.9–3.0 (m, 5 H), 3.26 (br s, 2 H), 5.42 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ −1.24, 14.28, 34.53, 35.51, 43.50, 46.68, 118.33, 135.13, 139.09, 195.25, 213.79. Anal. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15. Found: C, 70.75; H, 9.26.

(d) **2-(Trimethylstannyl)bicyclo[3.3.0]oct-1(2)-en-3-one (3f)**: 63% yield; IR (neat) 1680 (s), 1605 (s), 1230 (m), 775 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.25 (s, 9 H), 0.8–1.4 (m, 1 H), 1.8–2.4 (m, 4 H), 2.5–3.15 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −9.58, 25.48, 27.52, 31.22, 42.55, 49.40, 136.58, 200.30, 215.53; high-resolution MS calcd for $C_{11}H_{18}OSn$ 285.0452, found 285.0335.

(e) **2-Methylbicyclo[3.3.0]oct-1(2)-en-3-one (3g)**: 52% yield (70% GLC); IR (neat) 1705 (s), 1669 (s), 1378 (m), 1291 (m), 1048 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.7–1.0 (m, 2 H), 1.1–1.4 (m, 2 H), 1.74 (s, 3 H), 1.9–2.4 (m, 3 H), 2.4–2.9 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 22.50, 24.77, 25.43, 31.18, 41.43, 44.16, 131.76, 183.59, 210.67. Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.08; H, 9.16.

(f) **2-[(Trimethylsilyl)methyl]bicyclo[3.3.0]oct-1(2)-en-3-one (3i).** 55% yield; IR (neat) 1708 (s), 1652 (s), 1250 (s), 860 (s), 840 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.06 (s, 9 H), 0.8–1.7 (m, 4 H), 1.45–2.2 (m, 4 H), 2.3–2.9 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ −1.28, 13.88, 25.29, 25.58, 31.50, 41.37, 43.96, 134.35, 179.62, 210.12; high-resolution MS calcd for $C_{12}H_{20}OSi$ 208.1284, found 208.1282.

(g) **2-Phenylbicyclo[3.3.0]oct-1(2)-en-3-one (3j)**: 55% yield; IR (neat) 1700 (s), 765 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.75–1.5 (m, 3 H), 1.5–2.5 (m, 4 H), 2.5–3.1 (m, 2 H), 7.4–7.9 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 25.78, 27.18, 30.84, 42.78, 44.51, 127.56, 128.12, 131.65, 134.34, 185.27, 208.56; high-resolution MS calcd for $C_{14}H_{14}O$ 198.1045, found 198.1027.

(h) **(*E*)-2-(1′-Octenyl)bicyclo[3.3.0]oct-1(2)-en-3-one (3k)**: 50% yield; IR (neat) 1704 (s), 971 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.7–1.1 (m, 3 H), 1.1–1.6 (m, 13 H), 1.8–2.4 (m, 4 H), 1.5–2.9 (m, 2 H), 5.9–6.6 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.91, 22.49, 26.14, 26.34, 28.81, 29.16, 31.22, 31.62, 33.66, 41.08, 44.49, 119.00, 131.59, 136.03, 182.35, 208.88; high-resolution MS calcd for $C_{16}H_{24}O$ 232.1828, found 232.1839.

(i) **3-Benzyl-8-(trimethylsilyl)-3-azabicyclo[3.3.0]oct-1(8)-en-7-one (24a)**: 66% yield; IR (neat) 1697 (s), 1617 (s), 1248 (s), 1234 (s), 841 (s) cm^{-1}; ^1H NMR ($CDCl_3$, CH_2Cl_2) δ 0.15 (s, 9 H), 1.9–2.2 (m, 2 H), 2.54 (dd, J = 6 and 18 Hz, 1 H), 3.15 (d, J = 18 Hz, 1 H), 3.33 (dd, J = 12 and 18 Hz, 2 H), 3.80 (dd, J = 24 and 12 Hz, 2 H), 4.04 (d, J = 18 Hz, 1 H), 7.2–7.7 (m, 5 H); ^{13}C NMR ($CDCl_3$, CH_2Cl_2) δ −1.47, 41.21, 47.37, 54.67, 57.90, 60.07, 127.22, 128.43, 128.58, 135.31, 131.38, 193.55, 213.12; high-resolution MS calcd for $C_{10}H_{25}NOSi$ 285.4650, found 285.4662.

(j) **3-Benzyl-8-(trimethylsilyl)-5-methyl-3-azabicyclo[3.3.0]oct-1(8)-en-7-one (24b)**: 77% yield: IR (neat) 1697 (s), 1618 (s), 1247 (s), 840 (s), 745 (s) cm^{-1}; ^1H NMR ($CDCl_3$, CH_2Cl_2) δ 0.10 and 0.19 (s, 9 H), 1.30 and 1.35 (s, 3 H), 2.32 (s, 2 H), 2.9–3.1 (m, 2 H), 3.19 (d, J = 18 Hz, 1 H), 3.7–4.0 (m, 2 H), 4.08 (d, J = 18 Hz, 1 H), 7.1–7.6 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −1.45, 26.40, 50.37, 51.19, 53.41, 59.73, 63.13, 127.04, 128.33, 128.70, 138.83, 197.11, 212.87; high-resolution MS calcd for $C_{17}H_{28}NOSi$ 299.4921, found 299.4907.

Characterization of the Carbonylation Product Obtained from 2a. A 1.1-mmol aliquot of **2a** prepared as described earlier was evaporated. The resulting yellow solid was redissolved in C_6D_6 and carbonylated at 1.1 atm first at 0 °C for 2 h and then at 25 °C for 24 h. The mixture yielded the following spectral data: IR (C_6D_6) 2950 (s), 2860 (m), 1495 (s), 1240 (s), 1010 (s) cm^{-1}; ^1H NMR (C_6D_6, Me_4Si) δ 0.37 (s, 9 H), 1.9–2.7 (m, 6 H), 3.1–3.3 (m, 1 H), 5.7–6.3 (m with sharp signals at 5.72 and 6.18, 11 H); ^{13}C NMR (C_6D_6, Me_4Si) δ 0.53 (q), 23.58 (s), 30.19 (s), 30.49 (s), 59.55 (t), 107.9 (t) 109.25 (q), 113.73 (Cp), 123.58 (t), 166.24 (q), 176.65 (q). Methyl iodide (1 equiv) was added to an aliquot of the carbonylated mixture. After 1 h, the ^1H NMR spectrum indicated no changes in the original signals. Another aliquot was quenched with anhydrous HCl in THF (2 equiv). Virtually no gas (<1 mol %) was evolved. Examination by ^1H NMR indicated the regeneration of Cl_2ZrCp_2 in 97% yield.

Conversion of 3a or 3f into 17–19. (a) **Bicyclo[3.3.0]oct-1(2)-en-3-one (17).** To a solution of concentrated HCl (2 mL) and MeOH (20 mL) was added **3f** (0.285 g, 1 mmol) at 25 °C. After the mixture was stirred for 1 h, it was poured into water and ether, extracted with ether, washed with aqueous $NaHCO_3$ and brine, and dried over $MgSO_4$. Concentration and purification by column chromatography (silica gel, 5:1 hexane–ethyl acetate) provided 0.10 g (82%) of the title compound.[29] IR (neat) 2960 (s), 2875 (m), 1705 (s), 1625 (s), 1255 (m), 1175 (m), 870 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.5–1.4 (m, 1 H), 1.9–2.4 (m, 4 H), 2.5–3.1 (m, 4 H), 5.97 (br s, 1 H).

(b) **Conversion of 3a into 2-Bromobicyclo[3.3.0]oct-1(2)-en-3-one (18).** Treatment of **3a** (1.94 g, 10 mmol) in 35 mL of DMF with NBS (4.45 g, 25 mmol) at 25 °C in the dark for 6 h followed by quenching with 3 N HCl, the usual workup, and column chromatography (silica gel, 9:1 hexane–EtOAc) provided 1.50 g (75%) of **18**: IR (neat) 1715 (s), 1640 (s), 1240 (m), 925 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.8–1.5 (m, 1 H), 2.0–2.4 (m, 4 H), 2.55–3.15 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.08, 26.83, 31.58, 40.65, 46.06, 116.87, 187.09, 202.56; high-resolution MS calcd for C_8H_9BrO 199.9837, found 199.9841.

(c) **Conversion of 3f into 18.** Treatment of **3f** (0.285 g, 1 mmol) in 3 mL of CCl_4 with bromine (0.19 g, 1.2 mmol) in 2 mL of CCl_4 in the dark at 0 °C for 30 min or with NBS in THF at −20 °C for 2 h followed by quenching with $NaHCO_3$ provided 0.17 g (85%) of **18**.

(d) **2-Iodobicyclo[3.3.0]oct-1(2)-en-3-one (19).** Treatment of **3f** (0.56 g, 1.96 mmol) in THF (10 mL) with iodine (0.635 g, 2.5 mmol) in THF (3 mL) at −78 to 25 °C followed by the same workup as in the preparation of **17** provided 0.44 g (91%) of **19**: mp 80–82 °C; IR (film) 1710 (s), 1625 (s), 1220 (s), 915 (s), 885 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.8–1.5 (m, 1 H), 1.4–2.4 (m, 4 H), 2.4–3.15 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 24.60, 28.76, 31.69, 40.09, 48.36, 93.77, 194.31, 204.64; high-resolution MS calcd for C_8H_9IO 247.9698, found 247.9699.

3,3-Bis(cyclopentadienyl)-3-zirconabicyclo[3.3.0]oct-1(2)-ene Derivatives. In most cases, the enyne bicyclization products were neither isolated nor fully characterized, but their yields were estimated by quantitative analysis of the Cp signals using an appropriate standard, e.g., benzene. The results are summarized in Table II. In addition to **2a** and **2b**, the following zirconabicycles were more extensively characterized, but no attempts were made to purify them.

(a) ***cis*-3-Benzyl-6-methyl-7,7-bis(cyclopentadienyl)-8-(trimethylsilyl)-3-aza-7-zirconabicyclo[3.3.0]oct-1(8)-ene (22c)**: 92% yield by ^1H NMR; ^1H NMR (benzene-d_6, benzene) δ 0.17 (s, 9 H), 1.45 (d, J = 7 Hz, 3 H), 1.71 (q, J = 7 Hz, 1 H), 2.25–2.35 (m, 1 H), 2.65 (d, J = 14 Hz, 1 H), 3.15 (s, 1 H), 3.3–3.7 (m, 3 H), 3.83 (d, J = 14 Hz, 1 H), 5.65 (s, 5 H), 5.77 (s, 5 H), 7.0–7.5 (m, 5 H); ^{13}C NMR (benzene-d_6, benzene) δ 1.47, 22.95, 31.28, 38.46, 60.72, 64.86, 109.17, 110.54, 127.51, 128.00, 128.30, 128.49, 140.35, 143.48.

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(27) Prepared by an application of a literature method (Lustenberger, N.; Lange, H. W.; Hempel, K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 227).

(28) Miller, R. B. *Synth. Commun.* **1972**, *2*, 267.

(29) Davidson, S. K.; Heathcock, C. H. *Synthesis* **1986**, 897.

(b) The trans isomer of 22c (22d): 95% yield by ^1H NMR; ^1H NMR (benzene-d_6, benzene) δ 0.11 (s, 9 H), 1.29 (d, *J* = 7 Hz, 3 H), 1.46 (dq, *J* = 11 and 7 Hz, 1 H), 1.69 (dd, *J* = 10 and 8 Hz, 1 H), 2.02 (dddd, *J* = 11, 10, 6, and 3 Hz, 1 H), 2.70 (dd, *J* = 14 and 3 Hz, 1 H), 3.4–3.65 (m, 3 H), 3.85 (d, *J* = 14 Hz, 1 H), 5.73 (s, 5 H), 5.77 (s, 5 H), 7.0–7.5 (m, 5 H); ^{13}C NMR (benzene-d_6, benzene) δ 1.44, 23.10, 40.86, 51.08, 60.60, 63.95, 65.28, 109.57, 110.45, 127.12, 127.51, 128.00, 128.49, 140.32, 148.10.

1-Alkylidene-2-methylcyclopentane Derivatives. The following compounds were obtained by treatment of the corresponding zirconabicyclic intermediates with 3 M HCl.

(a) (*E*)-1-[(Trimethylstannyl)methylene]-2-methylcyclopentane (4f): 60% yield; ^1H NMR (CCl_4, Me_4Si) δ –0.09 (s, 9 H), 0.84 (d, *J* = 7 Hz, 3 H), 1.2–2.3 (m, 1 H), 5.38 (br s, 1 H).

(b) (*E*)-1-Ethylidene-2-methylcyclopentane (4g): 65% yield; IR (neat) 1450 (s), 1390 (m), 820 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.02 (d, *J* = 7 Hz, 3 H), 1.2–1.4 (m, 2 H), 1.60 (d, *J* = 7 Hz, 3 H), 1.7–2.05 (m, 2 H), 2.05–2.5 (m, 3 H), 5.0–5.4 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.48, 19.00, 23.92, 28.88, 35.65, 38.92, 113.14, 148.64. Anal. Calcd for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 86.82, H, 12.97.

(c) (*E*)-1-(4′-Pentenylidene)-2-methylcyclopentane (4h): 55% yield; bp 70–75 °C (5 mmHg, Kugelrohr); IR (neat) 1635 (w), 905 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.75–1.45 (m, 4 H), 1.05 (d, *J* = 4 Hz, 3 H), 1.5–2.6 (m, 7 H), 4.85–5.2 (m, 3 H), 5.6–6.05 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.03, 23.96, 28.82, 29.03, 33.84, 35.48, 38.83, 114.23, 118.43, 138.77, 148.20; high-resolution MS calcd for $C_{11}H_{18}$ 150.1409, found 150.1381.

(d) (*E*)-1-(Benzylidene)-2-methylcyclopentane (4j): 70% yield; bp 60 °C (0.05 mmHg); IR (neat) 1650 (w), 1597 (w), 1490 (m), 1442 (m), 910 (m), 860 (m), 745 (m), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.4–2.1 (m, 4 H), 1.16 (d, *J* = 4 Hz, 3 H), 2.5–2.8 (m, 3 H), 6.17–6.30 (m, 1 H), 7.0–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.37, 24.66, 31.44, 34.56, 40.87, 120.20, 125.57, 128.07, 138.96, 151.46; high-resolution MS calcd for $C_{13}H_{16}$ 172.1252, found 172.1251.

(e) (*E*,*E*)-1-(2′-Nonenylidene)-2-methylcyclopentane (4k): 75% yield; bp 70–80 °C (0.15 mmHg); IR (neat) 1720 (s), 1685 (w), 1625 (w), 1455 (s), 1375 (m), 1285 (w), 1150 (w), 966 (s), 870 (w), 722 (w) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.7–1.0 (m, 3 H), 1.07 (d, *J* = 6 Hz, 3 H), 1.15–1.5 (m, 12 H), 1.5–2.6 (m, 4 H), 5.2–6.3 (m, 3 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.00, 18.00, 22.62, 24.08, 28.94, 29.57, 29.65, 31.79, 32.94, 35.33, 39.23, 119.57, 128.11, 131.64, 149.25; high-resolution MS calcd for $C_{15}H_{26}$ 206.2072, found 206.2053.

(f) (*E*,*E*)-1-[4′-(*tert*-Butyldimethylsiloxy)-2′-nonenylidene)-2-methylcyclopentane (4l): 80% yield (a 1:1 mixture of two diastereomers); IR (neat) 1655 (w), 1250 (s), 1070 (s), 970 (s), 830 (s), 770 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.035 (s, 3 H), 0.05 (s, 3 H), 0.89 (m, 3 H), 0.9 (s, 9 H), 1.08 (d, *J* = 7 Hz, 3 H), 1.2–2.0 (m, 13 H), 2.3–2.5 (m, 2 H), 4.1–4.2 (m, 1 H), 5.52 (dd, *J* = 6 and 15 Hz, 1 H), 5.82 (dd, *J* = 2 and 11 Hz, 1 H), 6.15–6.35 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si, two diastereomers) δ –4.79, –4.25, 14.09, 18.31, 18.72, 22.70, 24.12, 25.12, 25.99, 29.70, 31.97, 35.40, 38.73, 39.48, 73.56, 73.71, 112.62, 119.26, 127.33, 127.42, 134.21, 134.27, 151.72, 151.78; high-resolution MS calcd for $C_{21}H_{40}OSi$ 336.2848, found 336.2848.

(g) (*Z*)-*N*-Benzyl-3-[(trimethylsilyl)methylene]-4-methylpyrrolidine (23a): 69% yield; bp 85–95 °C (5 mmHg); IR (neat) 1632 (s), 1245 (s), 865 (s), 840 (s), 740 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.08 (s, 9 H), 1.08 (d, *J* = 7 Hz, 3 H), 1.95–2.15 (m, 1 H), 2.4–3.5 (m, 4 H), 3.67 (s, 2 H), 5.2–5.4 (m, 1 H), 7.38 (s, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.48, 17.44, 40.38, 59.38, 60.75, 61.31, 116.75, 126.92, 128.22, 128.79, 138.92, 162.84; high-resolution MS calcd for $C_{16}H_{25}NSi$ 259.1756, found 259.1748.

(h) (*Z*)-*N*-Benzyl-3-[(trimethylsilyl)methylene]-4,4-dimethylpyrrolidine (23b): 72% yield; bp 90–95 °C (0.15 mmHg); IR (neat) 1618 (s), 1487 (m), 1442 (s), 1349 (s), 1235 (s), 870 (s), 830 (s), 730 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, CH_2Br_2) δ 0.08 (s, 9 H), 1.00 (s, 6 H), 2.30 (s, 2 H), 3.77 (d, *J* = 2 Hz, 2 H), 3.58 (s, 2 H), 5.2–5.3 (m, 1 H), 7.2–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ –0.04, 28.01, 43.80, 59.66, 60.49, 67.47, 114.60, 126.78, 128.56, 139.39, 167.37; high-resolution MS calcd for $C_{17}H_{27}NSi$ 273.1952, found 273.1978.

(i) (*Z*)-*N*-Benzyl-3-[(trimethylsilyl)methylene]-4-ethylpyrrolidine (23c): 62% yield; bp 105–115 °C (0.20 mmHg); IR (neat) 1633 (s), 1498 (s), 1455 (s), 1250 (s), 870 (s), 840 (s), 745 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$, CH_2Br_2) δ 0.05 (s, 9 H), 0.81 (t, 3 H), 0.9–1.7 (m, 2 H), 1.83–2.1 (m, 1 H), 2.1–2.6 (m, 1 H), 2.7–3.1 (m, 2 H), 3.28–3.52 (m, 1 H), 3.55 (s, 2 H), 5.25–5.40 (m, 1 H), 7.30–7.55 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ –0.41, 12.11, 26.23, 47.33, 58.99, 59.71, 60.84, 117.23, 126.93, 128.24, 128.78, 138.92, 161.39; high-resolution MS calcd for $C_{17}H_{27}N_1Si$ 273.1952, found 273.1936.

(*E*,*E*)-2,11-Dimethyl-6,7-bis[(trimethylsilyl)methylene]-1,11-dodecadiene (26). The reaction of 2-methyl-7-(trimethylsilyl)-1-hepten-6-yne (**25**) (0.36 g, 2.0 mmol) with Cl_2ZrCp_2 and *n*-BuLi was carried out as in the reaction of **1a**. After the same workup, distillation afforded 0.23 g (63%) of **26**: bp 90–100 °C (0.01 mmHg, Kugelrohr); IR (neat) 1645 (s), 1590 (s), 1555 (m), 1245 (s), 885 (s), 840 (s), 770 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.21 (s, 18 H), 1.0–1.6 (m, 4 H), 1.71 (s, 6 H), 1.85–2.4 (m, 8 H), 4.69 (br s, 4 H), 5.48 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.36, 22.28, 27.52, 33.66, 38.00, 110.14, 125.73, 145.58, 160.57; high-resolution MS calcd for $C_{22}H_{42}Si_2$ 362.2827, found 362.2826.

Reaction of 25 with Zirconocene Derivatives. Treatment of Cl_2ZrCp_2 with 2 equiv of *n*-BuLi at –78 °C in the presence of 2 equiv of NEt_3, PMe_3, or PMePh followed by warming the mixture to 25 °C and addition of **25** led to the formation of **26**, in 15, <1, and 10% yield, respectively.

Reaction of 1a with Cl_2HfCp_2 and *n*-BuLi. (a) 3,3-Bis(cyclopentadienyl)-2-(trimethylsilyl)-3-hafnabicyclo[3.3.0]oct-1(2)-ene (20). To a mixture of Cl_2HfCp_2 (380 mg, 1.0 mmol) in 3 mL of toluene cooled at –78 °C was added *n*-BuLi (2.43 M, 0.88 mL, 2.0 mmol). The mixture was stirred at –78 °C for 30 min and warmed to 25 °C. The ^1H NMR spectrum of the mixture indicated a Cp singlet at 5.87 for $(n\text{-}Bu)_2HfCp_2$. To this mixture was added **1a** in 2 mL of toluene. The mixture was heated at 100 °C for 5 h. The ^1H NMR spectrum of the mixture indicated two Cp singlet at δ 5.90 and δ 5.94 for the zirconabicycle (90% yield). The volatiles were evaporated and the yellow solid was dissolved in C_6D_6 to give the following spectral data: IR (neat) 1520 (m), 1434 (m), 1232 (s), 1009 (s), 792 (s) cm^{-1}; ^1H NMR (C_6D_6, Me_4Si) δ 0.16 (s, 9 H), 0.2–0.4 (m, 1 H), 0.85–1.5 (m, 4 H), 1.85–2.0 (m, 1 H), 2.0–2.15 (m, 2 H), 2.3–2.5 (m, 1 H), 5.75 (s, 5 H), 5.81 (s, 5 H); ^{13}C NMR (C_6D_6, Me_4Si) δ 1.90, 21.37, 36.61, 38.32, 43.07, 45.49, 109.23, 110.39, 156.92, 187.18.

(b) Conversion of 20 into 3a. Carbonylation of an aliquot containing **16** with 1.1 atm of CO at 25 °C for 12 h produced **3a** in 80% GLC yield. At 3 atm, the reaction was complete within 2 h.

Reaction of 1a with Titanocene Derivatives. Treatment of Cl_2TiCp_2 with 2 equiv of *n*-BuLi at –78 °C followed by addition of 2 equiv of $PMePh_2$ and **1a** and warming the mixture to 25 °C over 1–2 h did not give, after protonolysis, a detectable amount of **4a**, with 90% of **1a** remaining unreacted. Omission of $PMePh_2$ did not improve the yield of **4a**.

Diynes 29. (a) 2,8-Decadiyne (29c). Representative Procedure. To 1.06 g (10 mmol) of 1,7-octadiyne in THF (20 mL) was added at –78 °C 8 mL (20 mmol) of a 2.5 M solution of *n*-BuLi in hexane. After stirring for 1 h, MeI (2.84 g, 20 mmol) in HMPA (30 mL) was added. The reaction mixture was warmed to room temperature, stirred for 30 min, poured into water, extracted with pentane, washed with brine, dried ($MgSO_4$), and distilled to provide 1.2 g (90%) of **29c**: bp 55–60 °C (6 mmHg, Kugelrohr); IR (neat) 2920 (s), 2860 (m), 1440 (m, cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.45–1.65 (m, 4 H), 1.75 (s, 6 H), 2.05–2.25 (m, 4 H; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 1.45–1.65 (m, 4 H), 1.75 (s, 6 H), 2.05–2.25 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 3.17, 18.18, 28.03, 75.36, 78.66.

(b) 2,6-Undecadiyne (29a). 1,5-Decadiyne was prepared as described in the literature.[16] Its methylation as above afforded **29a** in 70% yield: bp 60–65 °C (6.5 mmHg, Kugelrohr); IR (neat) 2980 (s), 2870 (m) cm^{-1}; ^1H NMR ($CDCl_3$, C_6H_6) δ 0.91 (t, *J* = 2.5 Hz, 3 H), 1.3–1.5 (m, 4 H), 1.77 (s, 3 H), 2.1–2.2 (m, 2 H), 2.31 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 3.25, 13.46, 18.34, 19.37, 19.45, 21.81, 31.08, 76.15, 77.81, 78.64, 81.00. The preparation of the following diynes are described in the supplemental material: **3,8-undecadiyne (29b)**, **1,8-bis(trimethylsilyl)-1,7-octadiyne (29d)**, **1-(trimethylsilyl)-1,7-undecadiyne (29e)**, **1-phenyl-1,7-undecadiyne (29f)**, and **2,9-undecadiyne (29g)**.

1,2-Bis(alkylidene)cycloalkanes. (a) (*E*,*E*)-1,2-Bis[(trimethylsilyl)-methylene]cyclohexane (9d). Representative Procedure. Zirconocene dichloride (0.614 g, 2.1 mmol) in THF (7 mL) was treated at –78 °C with *n*-BuLi in hexane (2.6 M, 1.62 mL, 4.2 mmol). The mixture was stirred for 1 h, and 1,8-bis(trimethylsilyl)-1,7-octadiyne (0.5 g, 2.0 mmol) in THF (3 mL) was added. The reaction mixture was allowed to warm to room temperature and was stirred for 4 h. Examination of the mixture by ^1H NMR (δ 5.95) indicated the formation of **8d** in 98% yield. The mixture was poured into 3 N HCl and pentane, extracted with pentane, washed with aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, concentrated, and chromatographed (silica gel, pentane) to provide 0.45 g (89%) of **9d**: IR (neat) 1600 (s), 1245 (s), 920 (s), 840 (s), 762 (s), 735 (s), 710 (s), 690 (s), 630 (s); cm^{-1}; ^1H NMR (CCl_4, C_6H_6) δ 0.27 (s, 18 H), 1.7–1.9 (m, 4 H), 2.35–2.6 (m, 4 H), 5.53 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.19, 26.75, 34.58, 122.01, 161.66; high-resolution MS calcd for $C_{14}H_{28}Si_2$ 252.1729, found 252.1727.

8,8-Bis(cyclopentadienyl)-7,9-bis(trimethylsilyl)-8-zirconabicyclo-[4.3.0]nona-1(9),6(7)-diene (8d). In another run, the cyclization reaction mixture was evaporated in vacuo. The residue was extracted with hexane, filtered through Celite under nitrogen, and dried at 50 °C and 0.5

mmHg to give **8d**: IR (C_6D_6) 1260 (m), 1245 (s), 1015 (s), 950 (s), 840 (s), 795 (s) cm^{-1}; ^{1}H NMR (C_6D_6, Me_4Si) δ 0.14 (s, 18 H), 1.45–1.55 (m, 4 H), 2.1–2.2 (m, 4 H), 5.95 (s, 10 H); ^{13}C NMR (C_6D_6) δ 2.62, 21.55, 34.19, 110.58, 145.64, 198.02.

(b) (*E*,*E*)-1-Ethylidene-2-pentylidenecyclobutane (9a): 67% yield; IR (neat) 1665 (w), 1070 (m), 810 (m), 730 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.75–1.0 (m, 3 H), 1.2–1.5 (m, 4 H), 2.08 (d, J = 6 Hz, 3 H), 1.5–2.65 (m, 4 H), 5.35–5.65 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.07, 13.85, 22.31, 25.04, 25.17, 27.72, 31.71, 111.41, 117.13, 140.75, 141.74; high-resolution MS calcd for $C_{11}H_{18}$ 150.1408, found 150.1395.

(c) (*E*,*E*)-1,2-Bis(propylidene)cyclopentane (9b): 80% yield; IR (neat) 1660 (w), 1030 (m), 890 (w), 835 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.97 (t, J = 5 Hz, 6 H), 1.2–2.5 (m, 10 H), 5.6–5.85 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.99, 22.78, 23.82, 30.02, 119.31, 140.21; high-resolution MS calcd for $C_{11}H_{18}$ 150.1408, found 150.1398.

(d) (*E*,*E*)-1,2-Bis(ethylidene)cyclohexane (9c):[7] 55% yield; IR (neat) 1650 (w), 910 (w), 805 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.56 (d, J = 8 Hz, 6 H), 1.4–2.3 (m, 8 H), 5.2–5.5 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.01, 26.51, 28.22, 116.05, 142.47.

(e) (*E*,*E*)-1-Butylidene-2-[(trimethylsilyl)methylene]cyclohexane (9e): 89% yield; IR (neat) 1598 (m), 1250 (s), 850 (s), 840 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, C_6H_6) δ 0.13 (s, 9 H), 0.92 (t, J = 7.3 Hz, 3 H), 1.35–1.5 (m, 2 H), 1.55–1.7 (m, 4 H), 1.95–2.05 (m, 2 H), 2.2–2.3 (m, 2 H), 2.3–2.4 (m, 2 H), 5.37 (s, 1 H), 5.47 (t, J = 7.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.25, 13.86, 23.02, 26.30, 27.18, 28.72, 29.57, 34.62, 120.83, 123.46, 143.60, 160.42; high-resolution MS calcd for $C_{14}H_{26}Si$ 222.1805, found 222.1809.

(f) (*E*,*E*)-1-Benzylidene-2-butylidenecyclohexane (9f): 90% yield; IR (neat) 1601 (w), 1495 (m), 920 (m), 700 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.93 (t, J = 7.3 Hz, 3 H), 1.35–1.5 (m, 2 H), 1.5–1.65 (m, 4 H), 2.0–2.1 (m, 2 H), 2.25–2.35 (m, 2 H), 2.45–2.55 (m, 2 H), 5.52 (t, J = 7.3 Hz, 1 H), 6.44 (s, 1 H), 7.05–7.3 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.82, 23.04, 26.36, 26.71, 28.70, 29.74, 29.88, 122.40, 124.25, 125.93, 127.87, 129.30, 138.24, 141.79, 144.63; high-resolution MS calcd for $C_{17}H_{22}$ 226.1722, found 226.1721.

(g) (*E*,*E*)-1,2-Bis(ethylidene)cycloheptane (9g):[7] 40% yield; IR (neat) 1645 (w), 840 (m), 805 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.7–1.8 (m, 6 H), 1.57 (d, J = 7 Hz, 6 H), 2.1–2.4 (m, 4 H), 5.25–5.6 (m, 2 H); ^{13}C NMR ($CDCl_3$ δ 13.11, 27.75, 29.45, 31.79, 117.39, 146.06.

2-Methyl-9-(trimethylsilyl)-2,3-nonadien-8-yne (30). To 1-bromo-3-methyl-1,2-butadiene (4.41 g, 30 mmol), prepared from 2-methyl-3-butyn-2-ol by a literature procedure,[30] in ether (30 mL) at −78 °C was added dropwise *n*-BuLi in hexane (2.4 M, 12.5 mL, 30 mmol). The reaction mixture was stirred for 1 h, and 1-(trimethylsilyl)-5-iodo-1-pentyne (6.65 g, 25 mmol) in THF (40 mL) was added.[31] The reaction mixture was first stirred for 1 h at −78 °C and then for 2 h at room temperature. It was quenched with saturated aqueous NH_4Cl, extracted with pentane, washed with saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated. Flash chromatography (silica gel, pentane) afforded 4.12 g (80%) of the title compound: IR (neat) 2175 (s), 1975 (w), 1250 (s), 1050 (m), 850 (s), 760 (s), 640 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, C_6H_6) δ 0.15 (s, 9 H), 1.55–1.65 (m, 2 H), 1.67 (d, J = 1.4 Hz, 6 H), 2.0–2.1 (m, 2 H), 2.25 (t, J = 7.2 Hz, 2 H), 4.85–4.95 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.14, 19.11, 20.64, 28.06, 28.24, 84.34, 87.78, 95.05, 107.31, 201.95.

(*E*)-1-[(Trimethylsilyl)methylene]-2-(2′-methylpropenyl)cyclopentane (31). The title compound was prepared in a manner analogous to the preparation of (*E*)-1-[(trimethylsilyl)methylene]-2-methylcyclopentane using Cl_2ZrCp_2 (0.614 g, 2.1 mmol), *n*-BuLi in hexane (2.4 M, 1.75 mL, 4.2 mmol), and 2-methyl-9-(trimethylsilyl)-2,3-nonadien-8-yne (0.412 g, 2.0 mmol) in THF (10 mL). Flash chromatography (silica gel, pentane) afforded (0.187 g (45%) of the title compound: IR (neat) 1620 (s), 1245 (s), 870 (s), 840 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, C_6H_6) δ 0.10 (s, 9 H), 1.2–1.3 (m, 2 H), 1.5–1.65 (m, 1 H), 1.66 (s, 3 H), 1.76 (s, 3 H), 1.75–1.95 (m, 1 H), 2.25–2.35 (m, 1 H), 2.4–2.5 (m, 1 H), 3.1–3.2 (m, 1 H), 4.9–5.0 (m, 1 H), 5.15–5.2 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ −0.24, 18.02, 24.92, 25.84, 32.27, 33.82, 47.44, 117.97, 127.83, 132.11, 165.14; high-resolution MS calcd for $C_{13}H_{24}Si$ 208.1647, found 208.1645.

Reaction of Cl_2ZrCp_2 with *n*-BuLi and Further Transformations of (*n*-Bu)$_2$ZrCp. (a) (*n*-Bu)$_2$ZrCp$_2$. To 2.92 g (10 mmol) of Cl_2ZrCp_2 in 40 mL of THF was added 12.3 mL (1.63 M, 20 mmol) of *n*-BuLi at −78 °C, and the mixture was stirred for 1 h. An aliquot was quickly transferred to an NMR tube cooled at −78 °C. Its ^{1}H NMR spectrum taken after 30 min at −78 °C indicated the Cp singlet at δ 6.61 had completely shifted to δ 6.18. The yield of the product by ^{1}H NMR was essentially 100%. The mixture was warmed to 20 °C, and its decomposition was monitored by ^{1}H NMR. The first-order rate constant for this reaction was $(4.6 \pm 0.4) \times 10^{-2}$ min^{-1} at 20 °C. The product was not identified. Another aliquot of the *n*-BuLi–Cl_2ZrCp_2 reaction mixture was treated with 2 equiv of I_2 in THF (−78 to 25 °C). Examination by ^{1}H NMR indicated the formation of I_2ZrCp_2 (δ 6.63) in 80% yield, and GLC analysis of the mixture, after hydrolytic workup, indicated the formation of 2 equiv of *n*-BuI (ca. 100%), whose signal was discrete from that of *n*-octane present as a byproduct.

(b) Bis(cyclopentadienyl)(η^2-1-butenyl)(trimethylphosphine)zirconium (12). To a 2.0-mmol aliquot of (*n*-Bu)$_2$ZrCp$_2$ in THF was added PMe_3 (0.4 mL, 300 mg, 4 mmol). This mixture was warmed to 25 °C and stirred for 1 h. The ^{1}H NMR spectrum of the mixture indicated a signal at δ 5.29 appearing as an apparent triplet in 98% yield relative to benzene as an internal standard. Evaporation of the volatiles followed by dissolving the residue in C_6D_6 gave a sample which yielded the following spectral data: IR (Nujol) 1280 (m), 1143 (m), 1010 (m), 950 (m), 793 (s), 770 (s) cm^{-1}; ^{1}H NMR (C_6D_6, Me_4Si) δ −0.21 (ddd, J = 11, 6, and 6 Hz, 1 H), 0.44 (ddd, J = 11, 9, and 6 Hz, 1 H), 0.84 (d, J = 6 Hz, 9 H), 0.95–1.2 (m, 1 H), 1.4–1.7 (m, 4 H), 1.9–2.3 (m, 1 H), 5.01 (d, J = 2 Hz, 5 H), 5.02 (d, J = 2 Hz, 5 H); ^{13}C NMR (C_6D_6, Me_4Si) δ 17.18 (d, J = 16.2 Hz), 20.98, 21.37, 35.38 (d, J = 1.6 Hz), 39.27 (d, J = 3.3 Hz), 99.725 (d, J = 0.64 Hz), 99.925 (J = 0.60 Hz). The ^{1}H 2D NOESY NMR spectrum indicates that the protons of PMe_3 are proximal to one of the terminal protons of 1-butene at δ −0.21. In addition, the ^{1}H NMR spectrum indicates some signals for an apparent isomer including the following: 0.90 (d, J = 6 Hz), 4.99 (d, J = 2 Hz), 5.03 (d, J = 2 Hz). The ^{13}C NMR spectrum also shows the following signals: δ 18.04 (d, J = 14.6 Hz), 99.6 (d, J = 0.69 Hz), 100.83 (d, J = 0.62 Hz). The major-to-minor isomer ratio is 90:10.

(c) Reaction of (*n*-Bu)$_2$ZrCp$_2$ with Diphenylacetylene. Synthesis of 32, 33a, and 33b. Treatment of (*n*-Bu)$_2$ZrCp$_2$ generated in THF with 2 equiv of diphenylacetylene (−78 to 25 °C) produced a 94% yield (^{1}H NMR) of **32**,[3] which showed a singlet for the Cp group at δ 6.49. Protonolysis of **32** provided an 86% yield of **33a**:[32] ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.46 (s, 2 H) 6.8–7.9 (m, 20 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 126.59, 127.33, 127.77, 128.79, 129.47, 130.37, 131.65, 137.23, 139.74, 145.58. Treatment of **32** with 2 equiv of I_2 afforded a 58% yield of **33b**:[33] ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.9–7.5 (m, 20 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 127.41, 127.85, 127.94, 130.05, 136.87, 144.01, 156.10. The reaction of (*n*-Bu)$_2$ZrCp$_2$ with 1 equiv of diphenylacetylene under the same condition as above produced a variable amount of **32** along with another Cp_2Zr derivative which showed a ^{1}H NMR singlet at δ 5.47. In one run, the yield of **33a** obtained after protonolysis was 8%. The major protonolysis product was bibenzyl (88%). Deuterolysis with D_2O led to the formation of $\alpha,\alpha,\alpha',\alpha'$-tetradeuteriobibenzyl (92% D incorporation).

1,2-Diphenyl-3,3-bis(cyclopentadienyl)-3-(trimethylphosphine)-3-zirconacyclopropene (36a). To (*n*-Bu)$_2$ZrCp$_2$ in THF generated at −78 °C by treating Cl_2ZrCp_2 (2 mmol) with *n*-BuLi (4 mmol) was added 356 mg (2 mmol) of diphenylacetylene at −78 °C. After stirring the reaction mixture at 25 °C for 3 h, **36a** was formed in 91% yield (^{1}H NMR). The mixture was evaporated until a yellow solid started precipitating. A small amount of THF was added to dissolve the yellow solid. To this solution was added 15 mL of ether, which induced precipitation of a white solid. After filtering off the white solid, the resultant orange solution was kept at −10 °C overnight to give 524 mg (55%) of yellow crystals of **36a**: mp 201–203 °C dec; IR (Nujol) 1660 (s), 1582 (s), 1280 (m), 1010 (m), 950 (s), 790 (s), 780 (s), 770 (s), 720 (m), 700 (m), 690 (m) cm^{-1}; ^{1}H NMR (benzene-d_6, Me_4Si) δ 0.83 (d, J = 7 Hz, 9 H), 5.47 (s, 5 H), 5.49 (s, 5 H), 6.8–7.9 (m, 10 H); ^{13}C NMR (THF, Me_4Si) δ 16.02, 16.35, 102.63, 120.63, 120.75, 122.78, 124.57, 127.31, 128.97, 141.61, 156.42. Anal. Calcd for $C_{27}H_{29}PZr$: C, 68.17; H, 6.14. Found: C, 68.02; H, 6.30. The X-ray crystallographic data are presented in the supplemental material. In another experiment, the reaction of the $Cp_2Zr(CH_2{=}CHEt)(PMe_3)$ with diphenylacetylene was monitored by ^{1}H NMR at 20 °C. It displayed second-order kinetics, and the second-order rate constant was $(2.1 \pm 0.2) \times 10^{-1}$ L mol^{-1} min^{-1}. The second-order rate constant for the corresponding reaction of (*E*)-stilbene was $(1.40 \pm 0.3) \times 10^{-3}$ L mol^{-1} min^{-1} at 20 °C. Treatment of **36a** with 3 M HCl gave a 90% yield of (*Z*)-stilbene (≥98% *Z*).

Generation of 1,2-Diphenyl-3,3-bis(cyclopentadienyl)-3-(methyldiphenylphosphine)-3-zirconacyclopropene (36b) and Its Reaction with

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(34) **Note Added in Proof**: After submission of this manuscript, a paper describing enyne bicyclization mediated by titanocene and zirconocene derivatives has been published (RajanBabu, T. V.; Nugent, W. A.; Taber, D. F.; Fagan, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7128).

Diphenylacetylene and 5-Decyne. Generation of **36b** was achieved in 90% yield (^{1}H NMR) as in the case of ^{3}6a with $PMePh_2$ in place of PMe_3. Treatment of **36b** with 3 M HCl afforded (*Z*)-stilbene in 80% yield (≥98% *Z*). To **36b** (2 mmol) in THF was added 356 mg (2 mmol) of diphenylacetylene at 25 °C. After stirring of the mixture for 1 h at 25 °C, ^{1}H NMR analysis indicated that the mixture contained a 92% yield of **32**. In another experiment, **36b** (10 mmol) was sequentially treated with 5-decyne (10 mmol, 25 °C, 3 h) and 3 M HCl to give an 86% yield of **37**: IR (neat) 1580 (w), 1480 (m), 1430 (m), 685 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.92 (t, J = 7 Hz, 6 H), 1.1–1.6 (m, 8 H), 2.0–2.5 (m, 4 H), 5.50 (t, J = 7 Hz, 1 H), 6.82 (s, 1 H), 6.82 (s, 1 H), 7.0–7.7 (10 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.10, 22.53, 22.83, 27.82, 28.37, 31.19, 31.32, 32.02, 125.30, 126.06, 126.85, 127.73, 128.31, 129.44, 130.04, 132.20, 137.86, 140.32, 142.67, 144.86. Anal. Calcd for $C_{24}H_{30}$: C, 90.50; H, 9.50. Found: C, 90.17; H, 9.45.

Reaction of 36b with Diphenylacetylene. To **36b** (2 mmol) in THF was added 0.356 g (2 mmol) of diphenylacetylene at room temperature. After stirring of the mixture for 1 h at 25 °C, ^{1}H NMR analysis indicated that the mixture contained a 92% yield of **31**.

Reaction of 36 with Acetone. (*Z*)-1,2-Diphenyl-3-methyl-1,3-butadiene (38). Acetone was added to **36a** in THF, and the reaction mixture was monitored by ^{1}H NMR. With 1 equiv of acetone, the reaction was very slow. After stirring for 6 h at 25 °C only a 21% yield (based on analysis of the ^{1}H NMR Cp signals) of a new Zr-containing product exhibiting a Cp signal at δ 5.99 was formed along with 54% of **36a** remaining unreacted. With 4 equiv of acetone, the same Zr-containing compound was formed in 93% yield after 1 h at 25 °C. After hydrolysis of this compound, **38** was obtained in 44% yield: IR (neat) 1680 (s), 1670 (s), 1595 (s), 1490 (s), 1446 (s), 1440 (s), 1209 (s), 755 (s), 690 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.16 (s, 3 H), 4.80 (s, 1 H), 5.21 (s, 1 H), 6.87 (s, 1 H), 6.9–7.2 (m, 10 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.08, 117.44, 126.57, 126.99, 127.09, 127.83, 128.24, 128.47, 129.01, 129.52, 129.96, 131.61. Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.59; H, 7.62.

Reaction of 1a with the Reagent Generated by Treatment of (n-Bu)$_2$ZrCp$_2$ with 2 equiv of PMePh$_2$. Treatment of (n-Bu)$_2$ZrCp$_2$ (1-mmol scale) with $PMePh_2$ (2 equiv) first at −78 °C and then at 25 °C (1 h) followed by addition of **1a** (1 mmol) produced a 91% yield of **2a**. The second-order rate constant measured by ^{1}H NMR at 20 °C was (2.9 ± 0.4) × 10^{-1} L mol^{-1} min^{-1}.

1,1-Bis(cyclopentadienyl)-3-methyl-4-(4′-pentenyl)-5-(trimethylsilyl)-1-zircona-2-azacyclopentadiene (43). To **2a** (0.102 g, 0.263 mmol) in benzene-d_6 (0.5 mL) in a 5-mm NMR tube was added MeCN (10 L, 0.289 mmol) at 25 °C. The reaction monitored by ^{1}H NMR and ^{13}C NMR was complete in 3 h and produced a 70% yield of **43**: ^{1}H NMR (C_6H_6, C_6H_6) δ 0.48 (s, 9 H), 1.5–1.65 (m, 2 H), 2.12 (s, 3 H), 2.15–2.25 (m, 2 H), 2.5–2.6 (m, 2 H), 5.0–5.2 (m, 2 H), 5.74 (s, 10 H), 5.85–6.05 (m, 1 H); ^{13}C NMR (C_6H_6) δ 5.47, 26.67, 31.15, 34.91, 37.59, 109.31, 115.25, 138.66, 152.46, 188.87, 215.48.

1-(Trimethylsilyl)-2-(4′-pentenyl)-3-buten-2-one (44). To Cl_2ZrCp_2 (0.92 g, 3.15 mmol) in THF (11 mL) was added at −78 °C n-BuLi in hexane (2.4 M, 2.63 mL, 6.3 mmol). After stirring of the mixture for 1 h at −78 °C, 7-(trimethylsilyl)-1-hepten-6-yne (0.498 g, 3 mmol) in THF (4 mL) was added. The mixture was warmed to 25 °C and stirred for 3 h. Acetonitrile (0.136 g, 3.3 mmol) was then added, and the reaction mixture was stirred for an additional 3 h. It was quenched with 3 M HCl (5 mL) and stirred at 25 °C for 3 h. Extraction with ether, washing with aqueous $NaHCO_3$ and brine, drying ($MgSO_4$), concentration, and flash chromatography (95:5 pentane–ether) provided 0.378 g (60%) of the title compound: IR (neat) 3090 (w), 2960 (s), 1755 (s), 1595 (w), 1250 (m), 1212 (m), 912 (m), 855 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, C_6H_6) δ 0.21 (s, 9 H), 1.4–1.5 (m, 2 H), 2.05–2.15 (m, 2 H), 2.3–2.4 (m, 2 H), 2.33 (s, 3 H), 4.95–5.05 (m, 2 H), 5.75–5.9 (m, 1 H), 6.61 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −0.45, 25.71, 29.19, 30.40, 33.98, 114.60, 138.17, 140.76, 156.48, 200.02; high-resolution MS calcd for $C_{12}H_{22}OSi$ 210.1439, found 210.1440.

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Registry No. 1a, 94012-65-4; **1b**, 91657-05-5; **1c**, 95978-63-5; **1d**, 95978-64-6; **1e**, 95978-74-8; **1f**, 109828-43-5; **1g**, 109828-40-2; **1h**, 109828-41-3; **1i**, 119639-62-2; **1j**, 19016-85-4; **1k**, 109828-42-4; **1l**, 109852-99-5; **2a**, 95978-77-1; **2b**, 95978-78-2; **2c**, 119656-16-5; **2d**, 119656-17-6; **2e**, 119656-18-7; **2f**, 109799-96-4; **2g**, 109799-91-9; **2h**, 109799-92-0; **2i**, 119679-39-9; **2j**, 109799-93-1; **2k**, 109799-94-2; **2l**, 109799-95-3; **3a**, 95978-79-3; **3b**, 95978-65-7; **3c**, 95978-66-8; **3d**, 95978-67-9; **3e**, 95978-75-9; **3f**, 109828-49-1; **3g**, 24730-96-9; **3i**, 119639-63-3; **3j**, 119639-64-4; **3k**, 119639-65-5; **4a**, 94012-72-3; **4b**, 95978-69-1; **4c**, 95978-68-0; **4d**, 95978-70-4; **4f**, 119639-66-6; **4g**, 119639-67-7; **4h**, 119639-68-8; **4j**, 119639-69-9; **4k**, 119639-70-2; (*R**,*R**)-**4l**, 119717-79-2; (*R**,*S**)-**4l**, 119717-80-5; **8d**, 119693-82-2; **9a**, 106449-83-6; **9b**, 106449-84-7; **9c**, 92013-62-2; **9d**, 106449-85-8; **9e**, 119639-79-1; **9f**, 119639-80-4; **9g**, 92013-64-4; **10**, 95978-71-5; **11**, 119477-24-6; **12**, 119390-11-3; **17**, 72200-41-0; **18**, 119639-72-4; **19**, 109828-50-4; **20**, 119656-14-3; **21a**, 109828-51-5; **21b**, 109828-52-6; **21c**, 109828-53-7; **21d**, 109828-54-8; **22a**, 109799-97-5; **22b**, 109834-18-6; **22c**, 109958-00-1; **22d**, 109799-98-6; **23a**, 119639-73-5; **23b**, 119639-74-6; **23c**, 119639-75-7; **24a**, 118235-53-3; **24b**, 119639-71-3; **25**, 109828-55-9; **26**, 119639-76-8; **29a**, 106449-81-4; **29b**, 106449-82-5; **29c**, 4116-93-2; **29d**, 63873-32-5; **29e**, 119639-77-9; **29f**, 119639-78-0; **29g**, 1785-53-1; **30**, 119639-81-5; **31**, 119639-82-6; **32**, 53433-58-2; **33a**, 1608-10-2; **33b**, 78479-61-5; **36a**, 113177-54-1; **36b**, 113192-49-7; **37**, 119639-85-9; **38**, 50555-63-0; 43, 119656-15-4; **44**, 119639-83-7; Cp_2ZrCl_2, 1291-32-3; $HC{\equiv}CCH_2C{\equiv}CSiMe_3$, 71789-10-1; $H_2C{=}CHCH_2Al(Bu\text{-}i)_2$, 102859-51-8; $Pd(PPh_3)_4$, 14221-01-3; $PhCH_2NHCH_2C(CH_3){=}CH_2$, 52853-55-1; (*E*)-$PhCH_2NHCH_2CH{=}CHCH_3$, 107733-62-0; (*Z*)-$PhCH_2NHCH_2CH{=}CHCH_3$, 119639-84-8; Cl_2HfCp_2, 12116-66-4; (n-Bu)$_2$HfCp$_2$, 80005-42-1; (n-Bu)$_2$ZrCp$_2$, 80005-41-0; I_2ZrCp_2, 1298-41-5; 1-hepten-6-yne, 65939-59-5; 5-bromo-1-pentene, 1119-51-3; 1,5-dibromopentane, 111-24-0; lithium acetylenide, 1111-64-4; (*E*)-4-(iodomethylidene)-7-(trimethylsilyl)-1-hepten-6-yne, 96156-86-4; allylbenzylamine, 4383-22-6; 3-(trimethylsilyl)propargyl bromide, 38002-45-8; 1,5-decadiyne, 53963-03-4; 1-bromo-3-methyl-1,2-butadiene, 6214-32-0; 1-(trimethylsilyl)-5-iodo-1-pentyne, 35761-91-2; diphenylacetylene, 501-65-5; (*Z*)-stilbene, 645-49-8; 5-decyne, 1942-46-7; acetone, 67-64-1; 1,7-octadiyne, 871-84-1; propynyllithium, 4529-04-8; 2-chloro-1,5-hexadiene, 101933-88-4; diisopropylamine, 108-18-9; (trimethylsilyl)methyl trifluoromethanesulfonate, 64035-64-9; phenylacetylene, 536-74-3; (*E*)-1-iodo-1-octene, 42599-17-7; (*E*)-3-*tert*-butyldimethylsilyloxy-1-iodo-1-octene, 39178-66-0; (trimethylsilyl)ethynyllithium, 54655-07-1; 5-bromo-2-methyl-1-pentene, 41182-50-7; 4,4-dimethyl-6-hepten-2-one, 17123-68-1; 1,6-heptadiyne, 2396-63-6; 1-bromo-5-nonyne, 81168-90-3; 1,7-undecadiyne, 91428-14-7; 1,8-nonadiyne, 2396-65-8.

Supplementary Material Available: Synthetic procedures for various compounds, tables of crystal data and parameters, and an ORTEP drawing of **36a** (16 pages). Ordering information is given on any current masthead page.