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Stoichiometric Reactions of Nonconjugated Dienes with Zirconocene Derivatives. Further Delineation of the Scope of Bicyclization and Observation of Novel Multipositional Alkene Regioisomerization

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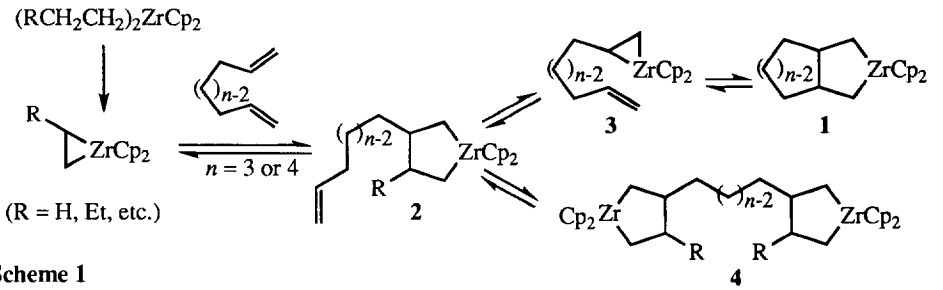
Abstract: The reaction of *n*-Bu_2ZrCp_2 with nonconjugated dienes containing substituted vinyl groups can lead to either bicyclization or the formation of conjugated diene-zirconocenes via multipositional regioisomerization.

INTRODUCTION

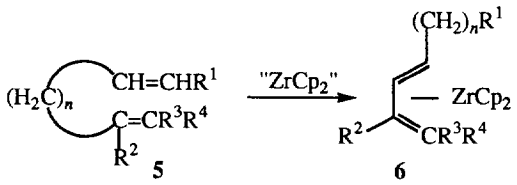
The reaction of nonconjugated dienes having two vinyl (-CH=CH_2) groups linked by a three- or four-atom tether with *n*-Bu_2ZrCp_2 (or other $ZrCp_2$ equivalents)[1] has been shown to give the corresponding zirconabicycles (**1**).[2-4] Although the mechanism of the reaction remains somewhat unclear, it likely involves intermediary formation of (alkene)zirconocenes,[1,5] zirconacyclopentanes (**2**),[6] and diene-zirconocene complexes (**3**)[7] (Scheme 1). If **2** is indeed an intermediate, the reaction can, in principle, produce **4** in cases where conversion of **2** into **3** is sufficiently slow.



Scheme 1

Unexpectedly, the same reaction of those dienes which contain one or two substituted vinyl groups has been shown to involve, in some cases, regioisomerization of the less-substituted double bond leading to the formation of conjugated diene-zirconocene complexes[8,9] (Eq. 1). This reaction is significant not only because it can compete with the diene bicyclization reaction (Scheme 1) and thereby limit the scope of the

bicyclization reaction but also because it provides a novel route to **6**. Only a limited number of methods for preparing conjugated diene-zirconocene complexes are known at present.[5e, 8-10]



R^1,R^3,R^4= H or C group
R^2= C group (1)

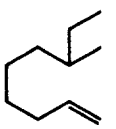
In this paper, we disclose details of the regioisomerization reaction shown in Eq. 1 and further delineate the scopes of competing paths that the reaction of nonconjugated dienes with $ZrCp_2$ derivatives can follow.

RESULTS AND DISCUSSION

Mechanism of Zirconocene-Promoted Bicyclization of Nonconjugated Dienes

In earlier studies[2,3] on the stoichiometric bicyclization of nonconjugated dienes using *n*-Bu_2ZrCp_2, there was no mention of a putative intermediate **2**, which might be converted to **1** via an unstable intermediate **3**. Examination by ^{1}H NMR spectroscopy of the reaction of 1,7-octadiene with 1 equiv of *n*-Bu_2ZrCp_2 at 23 °C indicated that the reaction was over within 1-2 h and that the only observable $ZrCp_2$-containing species were a 4:1 mixture of *cis*- and *trans*-8,8-bis(η^5-cyclopentadienyl)-8-zirconabicyclo[4.3.0]nonane (**1a**). To maximize the probability of obtaining and/or detecting **2**, we undertook to examine the reaction of 1,7-octadiene with Et_2ZrCp_2 by NMR spectroscopy and GLC analysis of hydrolysis and iodinolysis products. The reaction of 1,7-octadiene with Et_2ZrCp_2, generated *in situ* at -78 °C by treatment of 1 equiv (relative to the diene) of Cl_2ZrCp_2 with 2 equiv of EtMgBr, at 0 °C produced within 1 h, after protonolysis with 3 N HCl, 7-methyl-1-nonene (**7**) and 3,8-dimethyldecane (**8**) in 48 and 10% yields, respectively, along with 38% of 1,7-octadiene remaining unreacted. Examination of the reaction mixture, before quenching, by ^{1}H NMR spectroscopy indicated a somewhat broad singlet at δ 6.18 ppm assignable to all of the Cp groups of **2a** and **4a**. Its integration using naphthalene as an internal standard is consistent with the results of the GLC analysis. Significantly, only traces, if any, of other zirconacycles, such as **1a**, **9**, and **10**, were present. Upon standing at 23 °C for 10 h, however, both **2a** and **4a** were almost completely converted to a 4:1 mixture of the *cis* and *trans* isomers of **1a** (53% combined yield based on GLC analysis of protonolysis products). These transformations were also accompanied by the formation of **9** in 20-30% yield (NMR). To further establish the identity of **2a**, the initial reaction mixture was treated with CO (1.1 atm) at 0 °C for 7 h and I_2 (0 to 23 °C) to give **11** in 31% yield based on 1,7-octadiene. The cyclization reaction was also carried out using 2 and 3 equiv of Cl_2ZrCp_2 and the corresponding amounts of EtMgBr. With 2 equiv of Cl_2ZrCp_2 the initial cyclization products consisted of **2a** and **4a** formed in 42 and 39% yields, respectively. With 3 equiv of Cl_2ZrCp_2 the yields of **2a** and **4a** were 6 and 73%, respectively. Both of these initial reaction mixtures were converted to **1a** in 60-75% yields based on 1,7-octadiene. In these runs **4a** was also converted to the expected tetradeuterio derivative of **8** by treatment with DCl-D_2O. The results presented above and in Table I strongly support the associative mechanism involving the intermediary formation of monocyclic zirconacyclopentanes shown in Scheme 1. Other mechanisms involving dissociative formation of free $ZrCp_2$ and concerted alkene-alkene displacement without the intermediary formation of zirconacyclopentanes now appear to be much less

likely. The results also indicate that both **2a** and **4a** serve as intermediates and that they are converted to **1a** at roughly comparable rates. Although no rigorous kinetic studies were conducted, it is likely that **4a** can be rapidly converted to **2a** via expulsion of (ethylene)zirconocene and that **2a** is more slowly converted to **1a** via **3a**.



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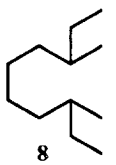

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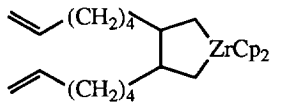

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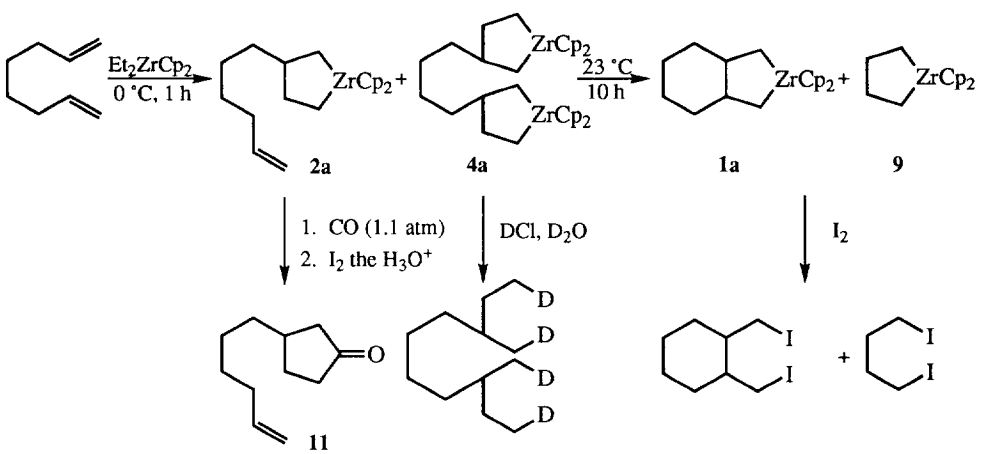
Table I. Reaction of 1,7-Octadiene with Et_2ZrCp_2 in THF

Molar equiv of Et_2ZrCp_2	Conditions[a]	Diene (%)	Product yield (%)			
			2a[b]	**4a**[b]	**1a**[b]	**9**[c]
1	A	38	49	10	trace	trace
1	A + B	31	8	trace	53[d]	24
2	A	5	42	39	trace	trace
2	A + B	0	trace	trace	75[d]	47
3	A	trace	6	73	trace	trace
3	A + B	trace	trace	4	60[d]	[e]

[a] A = 1 h at 0 °C. B = 10 h at 23 °C. [b] Based on 1,7-octadiene and determined by GLC analysis of protonolysis products. [c] By NMR spectroscopy. [d] *Cis/trans* = 4. [e] Not determined.

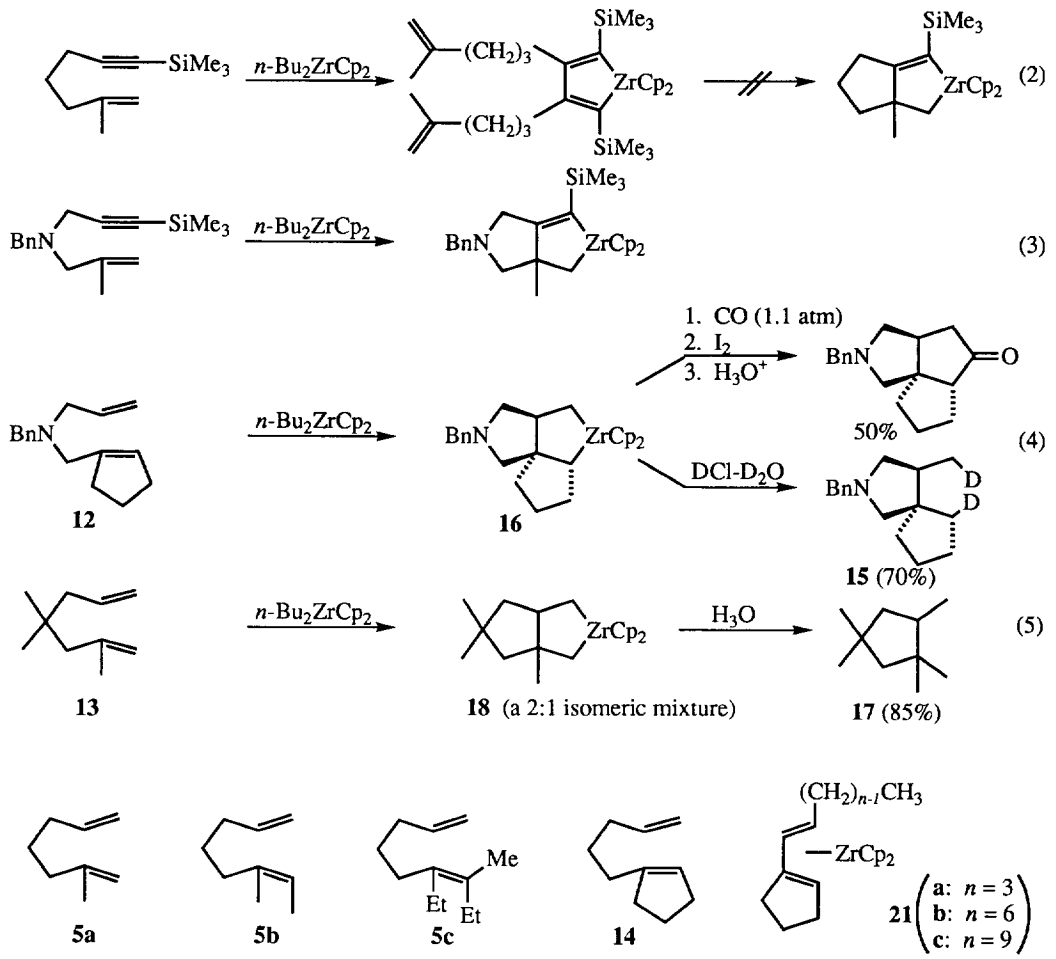


Zirconocene-Promoted Bicyclization of Nonconjugated Dienes Containing Substituted Vinyl Groups

For the $ZrCp_2$-promoted bicyclization reaction to be of high synthetic utility, it is desirable that the reaction can accommodate various substitutents, especially at the eventual bridgehead positions. In our earlier study of the corresponding reaction of enynes we noted contrasting results (shown in Eqs. 2 and 3) which, perhaps for the first time, revealed favorable effects of appropriately placed amino groups.[1b,11]

To probe the effects of substituents we prepared **5a-5c** and **12-14** and examined their reaction with *n*-

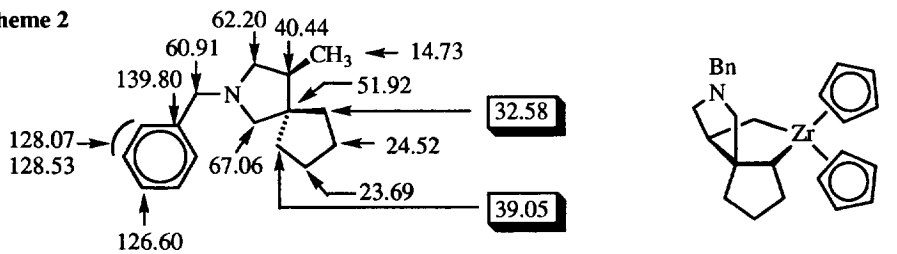
Bu_2ZrCp_2 generated *in situ* in THF.[12,13] Of the six dienes mentioned above only **12** and **13** gave the expected cyclization products in good yields (Eqs. 4 and 5). In the other cases an unexpected isomerization shown in Eq. 1 took place (*vide infra*). Thus, under the conditions used, the bicyclization reaction with *n*-Bu_2ZrCp_2 is feasible only with those dienes having amine-containing or alkyl-substituted tethers.



The stereochemistry of the bicyclization reactions shown in Eqs. 4 and 5 is worth noting. Conversion of **12** into **15** via **16** proceeded in a nearly completely stereoselective manner. The terminal methyl group and one of the CH_2 groups of the cyclopentane moiety corresponding to the ^{13}C NMR signal at δ 32.58 ppm were cleanly monodeuterated (≥95%) upon treatment of **16** with DCl-D_2O. The assignment of the two ^{13}C NMR signals at δ 23.69 and 24.52 ppm and those two at δ 32.58 and 39.05 ppm as the β and α methylene groups relative to the quaternary C atom of the cyclopentane ring has been unequivocally established by ^{13}C–^{13}C 2D INADEQUATE NMR technique.[15] The distinctly higher chemical shift of the methylene C atom (32.58 ppm), which is monodeuterated upon deuterolysis of **16**, relative to the other α-methylene C signal (39.05 ppm) is a clear indication that the former is *cis* to CH_3, thereby establishing the *cis* fusion between the pyrrolidine and zirconacyclopentane rings. The stereochemistry of the other ring fusion, *i.e.*, fusion between the

zirconacyclopentane and cyclopentane rings, has not been rigorously established. However, the *cis* fusion is very likely on the following grounds. In the doubly *cis*-fused isomer the steric requirements of the two rings fused to the zirconacyclopentane ring are more or less evenly distributed above and below the zirconacyclopentane ring (Scheme 2). It is reasonable to assume that this mode of fusion is more favorable than either the doubly *trans*-fused or *cis*, *trans*-fused mode in terms of minimization of both strains due to fusions and steric interactions between the ring substituents, *i.e.*, pyrrolidine and cyclopentane, and the two Cp rings. The discussion presented above also provides a ready explanation for the complete reversal of the commonly encountered *trans* fusion in the reaction of **12**.

Scheme 2

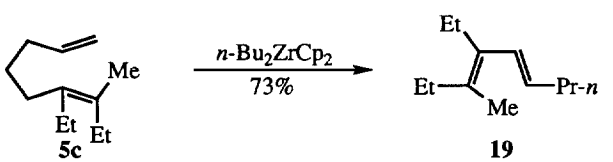


The reaction of **13** produced, after protonolysis, **17** in 85% yield as a reasonably pure compound. However, examination of the reaction mixture, before protonolysis, by ^{1}H NMR spectroscopy indicated the formation of two isomers exhibiting two sets of Cp signals at δ 6.09 and 6.12 as well as δ 6.00 and 6.06 ppm in a 2:1 ratio, which corresponded to a combined NMR yield of 88%. Although no further identification was performed, the formation of a 2:1 stereoisomeric mixture further supports the stereochemical arguments presented above. With an angular methyl group the thermodynamic advantage of *trans* ring fusion in the bicyclization reaction is at least partially lost, leading to a lower stereoselectivity.

On the basis of all currently available results obtained by us[2] and others[3,13] the following tentative summary may be presented. The stereochemistry of ring fusion in the $ZrCp_2$-promoted bicyclization of dienes is, in most cases, dictated by the relative thermodynamic stability of the two possible stereoisomeric zirconacycles. Two significant factors among others are (i) steric interactions between the two Cp rings and the rest of the molecule, which usually favor *trans* fusion, and (ii) strain due to ring fusion.

Zirconocene-Induced Conversion of Nonconjugated Dienes into Conjugated Diene-Zirconocenes via Multipositional Regiosomerization

The reaction of **5a**, **5b**, and **14** with *n*-Bu_2ZrCp_2 produced the corresponding conjugated diene-zirconocenes as represented by Eq. 1, rather than the initially expected bicyclization products. In the reaction of **5c** a similar alkene regioisomerization did take place, but the product was a free conjugated diene **19** (Eq. 6).



5c **19** (6)

The diene isomerization reaction is not limited to those dienes with a three-carbon tether. Thus, **20a** and **20b** also underwent this reaction, although the product yield appeared to decrease as the tether length

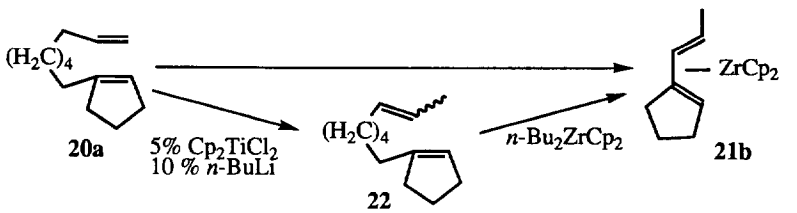
increased. The experimental results including pertinent NMR spectral data are summarized in Table II. In each case, the conjugated diene-zirconocene product is *s-cis*[7,16] and the diene moiety is ≥95% regio- and stereochemically pure, the stereochemistry of 1,2-disubstituted alkene moiety being *E*. The $ZrCp_2$-containing products were treated with I_2 to give the corresponding free conjugated dienes. We have previously reported[17] that the reaction of certain conjugated dienes, such as 1-vinylcyclohexene, with *n*-Bu_2ZrCp_2 gives the corresponding 1-butene-diene coupling products. Since one of the byproducts in the reaction shown in Eq. 1 is 1-butene, the diene-zirconocene complexes can, in principle, react further with 1-butene to give similar coupling products. While such products may have been formed in minor quantitites, their amounts are <5%. These seemingly contradictory results may be attributable to the fact that all of the conjugated dienes used in the previous study[17] contained the parent vinyl group, *i.e.*, CH_2=CH-, while the conjugated diene moiety in **6** and **21** does not. The higher degree of substitution in the dienes in these complexes must hinder their coupling with 1-butene. This interpretation has been supported by the reaction of (*E*, *E*)-3-methyl-2,4-octadiene, prepared from **5b** as described above, with *n*-Bu_2ZrCp_2, which gave **6b** in 88% yield without producing the 1-butene-diene coupling product. The direct conversion of certain conjugated dienes into the corresponding diene-zirconocene complexes by treatment with *n*-Bu_2ZrCp_2 represents yet another convenient route to conjugated diene-zirconocenes.

Table II. Reaction of Nonconjugated Dienes with *n*-Bu_2ZrCp_2 in THF to Give Conjugated Diene-Zirconocenes

Nonconjugated diene	Product	Yield (%)[a]	– NMR Cp signals (ppm) – ^1H[b]	^{13}C[c]
$CH_2=C(CH_3)(CH_2)_3CH=CH_2$ (**5a**)	**6a**	59	5.11 and 5.58	100.60 and 103.85
$CH(CH_3)=C(CH_3)(CH_2)_3CH=CH_2$ (**5b**)	**6b**	78	5.01 and 5.55	100.50 and 103.64
 (**14**)	**21a**	73	5.02 and 5.51	101.00 and 103.81
 (**20a**)	**21b**	66	5.06 and 5.55	100.93 and 103.73
 (**21b**)	**21c**	51	5.04 and 5.54	100.71 and 103.51

[a] By ^1H NMR. [b] In THF-hexane-*p*-xylene-Me_4Si. [c] In C_6D_6-*p*-xylene-Me_4Si.

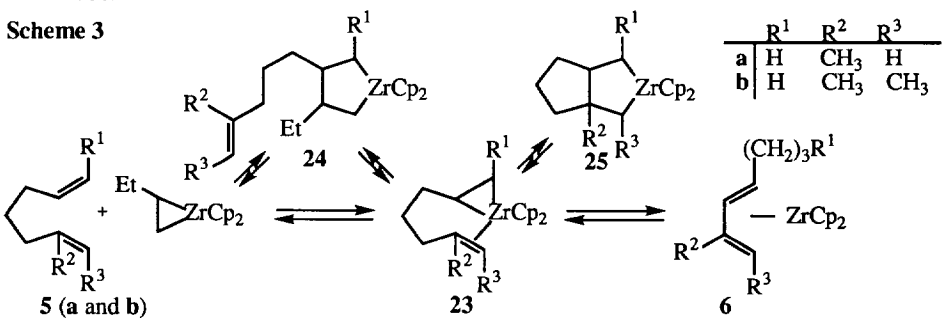
Some other noteworthy aspects of the reaction are as follows. The migrating group can be either the parent vinyl or a 1,2-disubstituted alkenyl group. Thus, for example, both **20a** and its double bond isomer **22**, prepared from **20a** by its treatment with 5% Cp_2TiCl_2 and 10% *n*-BuLi,[18] were converted to **21b** at comparable rates in comparable yields (Eq. 7). The results also suggest that the double bond migration must proceed along the chain and that **22** must represent the diene moiety of intermediary diene-zirconocene complexes.



(7)

The alkene group at the migration terminus must be either 1,1-di or trisubstituted for the formation of a single predominant diene-zirconocene. Although trisubstituted alkenes may be either proximally or distally disubstituted relative to the other alkene moiety, all of those that have been tested thus far, such as **5b**, **14**, and **20**, are proximally disubstituted, and no information about distally disubstituted alkenes is available at this time. Formation of free conjugated diene **19** from a diene containing a tetrasubstituted alkene (**5c**) was described earlier (Eq. 6). A more subtle effect of the degree of substitution at the migrating terminus has been observed in the comparison of the reaction of **5a** and **5b** with n-Bu_2ZrCp_2. Both gave the expected diene-zirconocenes **6a** and **6b** in 59 and 78% yields, respectively. However, the rate of formation of **6b** was considerably higher (complete in 15 h at 25 °C) than that of **6a**, which required 70 h under the same conditions. We suggest that, like the diene bicyclization reaction, the double bond migration reaction also proceeds via **23** and that, the less substituted the second double bond is, the more stable is **23**, which leads to slower isomerization. Furthermore, examination of the reaction of **5a** within the first few hours revealed the formation of **24a** in up to 60% yield, as judged by quantitative analysis of ^{1}H NMR Cp signals at δ 6.11 and 6.17 ppm as well as by GLC analysis of the protonolysis product of **24a**, *i.e.*, 2,6,7-trimethyl-1-nonene. Taken together with the mechanism of the bicyclization reaction discussed earlier, the overall mechanism for both bicyclization and double bond migration may be unified as shown in Scheme 3 featuring the intermediary of **23** and **24**. In view of the known instability of zirconacyclopentanes to ring contraction,[7] **25** could possibly revert back to **23** which could then be converted to **6**. However, no attempts to observe this possibility have as yet been made.

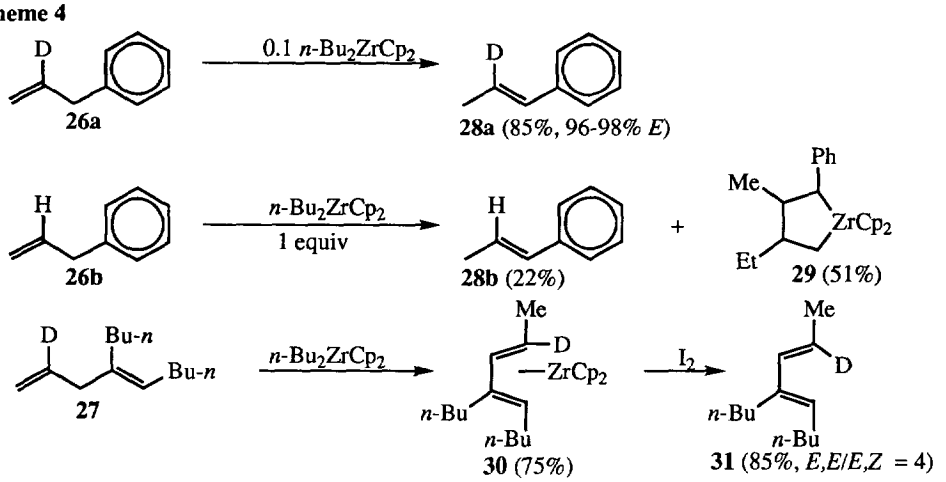
Scheme 3



Finally, two likely mechanisms for double bond migration along the tether are (i) β-dehydrometallation-rehydrometallation via 1,2-hydrogen shift and (ii) 1,3-hydrogen shift via allylic organometals.[18] The former process involving dehydrozirconation-rehydrozirconation is a well-established reaction.[19] The latter process has been implicated for the $TiCp_2$-catalyzed isomerization of monosubstituted 1-alkenes.[18] However, no firm data appear to have been reported on the $ZrCp_2$ catalyzed or promoted 1,3-hydrogen shift. One clear-cut difference between the two processes is that, whereas the 1,2-hydrogen shift process would scramble and place

any given hydrogen initially located between the migration origin and teminus on all carbons along the chain, the 1,3-hydrogen shift process would place any given hydrogen only on alternating carbons. With this prediction in mind we prepared (2-deuterioallyl)benzene (**26a**) (≥94% D) by deuteriozirconation of propargylbenzene with $Cp_2Zr(D)Cl$, generated *in situ* by treating Cp_2ZrCl_2 with $LiAlD_4$, and 2-deuterio-4-(*n*-butyl)-1,4-nonadiene (**27**) (≥92% D) by the reaction of allylzirconation of 5-decyne with 2-deuterioallyl phenyl ether.[20] The reaction of **26a** with 10 mol % of *n*-Bu_2ZrCp_2 in THF at 60 °C for 2 h gave (*E*)-(2-deuteriopropenyl)benzene (**28a**) (96-98% *E*, >91% D on C-2) in 85% yield. Significantly, the amounts of the 1- and 3-deuterio derivatives were less than the noise level (3-4%). Using the stoichiometric amount of *n*-Bu_2ZrCp_2 **26b** was converted to a mixture of **28b** (22%) and 1,1,-bis(η^5-cyclopentadienyl)-2-phenyl-3-methyl-4-ethyl-1-zirconacyclopentane (**29**) in 51% yield. The stoichiometric reaction of **27** with *n*-Bu_2ZrCp_2 gave the expected conjugated diene-zirconocene **30** in 75% yield. Its iodinolysis produced a 4:1 mixture of the *E,E* and *E,Z* isomers of the free diene (**31**). The D content at the C-2 position of either stereoisomer was ≥91%, whereas no more than a few % of D was found at either C-1 or C-3 position. These results once again support the 1,3-hydrogen shift mechanism.

Scheme 4



CONCLUSIONS

1. The reaction of nonconjugated dienes, *e.g.*, 1,7-octadiene, with Et_2ZrCp_2 initially gives **2** and **4**, the ratio of which depends on the reactant ratio. Both **2** and **4** are subsequently converted to **1** most probably via **3**. This mechanism summarized in Scheme 1 appears to be operating even in cases where **2** and/or **4** may not be detectable. Dissociative and other associative mechanisms are less likely.

2. Although the *trans* ring fusion has been the predominant mode in the $ZrCp_2$-promoted bicyclization of nonconjugated dienes containing two terminal vinyl groups, the stereochemistry of ring fusion in a more general sense depends on various factors including the overall steric hindrance and ring strains. The *cis* fusion observed in the conversion of **12** into **16** and the low stereoselectivity observed in the conversion of **13** into **18** are readily interpretable in these terms. Favorable effects of amino and *gem*-dialkyl groups in the tether of **12** and **13** are evident in the light of the alkene migration reaction observed with those dienes which lack these groups but have otherwise similar structures, *e.g.*, **5** and **14**.

3. Nonconjugated dienes having either a parent vinyl or 1,2-disubstituted alkene at one end and a 1,1-disubstituted or trisubstituted alkene at the other react with a "$ZrCp_2$" equivalent to undergo double bond migration to produce conjugated diene-zirconocene complexes. This process appears to share a considerable portion of the mechanism with the diene bicyclization. However, the greater steric requirements of the 1,1-di or trisubstituted alkene moieties not only block or slow down the final ring expansion step fo the bicyclization reaction but also permit double bond migration via 1,3-hydrogen shift. Deuterium labelling experiments indicate that the 1,2-hydrogen shift does not operate in this double bond migration process.

EXPERIMENTAL

General Procedures. All reactions were conducted under a dry N_2 or Ar atmosphere. All commercial reagents were used without further purification unless otherwise stated. THF was distilled from sodium benzophenone ketyl. Hexanes were distilled from CaH_2. Alkyllithiums were titrated with 2-butanol-1,10-phenanthroline. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini-200 and GE QE-300 spectrometers.

Reaction of 1,7-Octadiene with *n*-Bu_2ZrCp_2. To a solution of Cl_2ZrCp_2 (0.585 g, 2 mmol) in THF (6 mL) was added at -78 °C *n*-BuLi (2.5 M in hexanes, 1.64 mL, 4.1 mmol). After 1 h, 1,7-octadiene (295 µL, 2 mmol) was added, and the mixture was warmed to 23 °C. Analysis after 2 h of a protonolyzed aliquot by GLC (SE-30) using nonane as an internal standard indicated the presence of a 93% yield of 1,2-dimethylcyclohexane[2] (*cis/trans* = 4). Examination by NMR spectroscopy using mesitylene as an internal standard indicated the formation of *cis*- and *trans*-8,8-bis(η^5-cyclopentadienyl)-8-zircona-bicyclo[4.3.0]nonane (**1a**)[2] in 96% yield (*cis/trans* = 4): ^1H NMR (C_6D_6, THF, mesitylene, Me_4Si) δ Cp_{cis} 6.14, 6.18; δ Cp_{trans} 6.13; ^{13}C NMR (C_6D_6, THF, mesitylene, Me_4Si) δ Cp_{cis} 111.85, 111.97; δ Cp_{trans} 111.53.

Reaction of 1,7-Octadiene with Et_2ZrCp_2. (a) In a 1:1 ratio. A solution of Cl_2ZrCp_2 (0.585 g, 2 mmol) and naphthalene (0.128 g, 1 mmol) in THF (6 mL) was treated with EtMgBr (1.05 M in THF, 4 mL, 4.2 mmol) at -78 °C. After 1 h, 1,7-octadiene (295 µL, 2 mmol) was added, and the mixture was stirred at 0 °C for 1 h. Examination of the reaction mixture by ^1H NMR spectroscopy as well as by GLC analysis of a protonolyzed aliquot indicated the formation of 3-(5-hexenyl)-1,1-bis(η^5-cyclopentadienyl)-1-zirconacyclopentane (**2a**) and 1,4-bis(3,3-bis(η^5-cyclopentadienyl)-3-zirconacyclopentyl)butane (**4a**) (δ Cp 6.18 ppm) in 48 and 10% yield, respectively, along with a 38% of unreacted 1,7-octadiene. The reaction mixture was then warmed to 23 °C and monitored by GLC and NMR spectroscopy. After 10 h, **1a** was formed in 53% yield (*cis/trans* = 4) as judged by GLC and NMR analyses, together with a 24% NMR yield of tetramethylenezirconocene. Also present were 8% of **2a** and 31% of 1,7-octadiene. No more than 1-2% of **4a** was detected. These experimental results are summarized in Table I. This mixture was treated at 0 °C with I_2 (2.03 g, 8 mmol) in THF (10 mL) and stirred at 23 °C for 20 h. After quenching with 3 N HCl, extracting with Et_2O, washing with $NaHCO_3$, $Na_2S_2O_3$, and H_2O, drying over $MgSO_4$, filtering, and evaporating the solvents, the crude product was passed through a silica gel column using pentane as an eluent. After concentration, analysis by ^1H and ^{13}C NMR spectroscopy of the product (0.551 g) indicated that it consisted of 0.7 mmol of naphthalene, 0.11 mmol (6%) of 9-iodo-7-iodomethyl-1-nonene, 0.26 mmol (13%) of 1,4-diiodobutane, and 0.93 mmol (47%) of 1,2-bis(iodomethyl)cyclohexane[2] (*cis/trans* = 4): ^{13}C NMR ($CDCl_3$, Me_4Si) *cis* δ 8.47, 22.64, 28.89, 41.81; *trans* δ 15.74, 25.35, 32.12, 40.94.

(b) In a 1:2 ratio. This case was performed similarly to the previous one by preforming Et_2ZrCp_2

from Cl_2ZrCp_2 (0.585 g, 2 mmol) and EtMgBr (1.05 M in THF, 4 mL, 4.2 mmol), and reacting it with 1,7-octadiene (148 μL, 1 mmol) for 1 h at 0 °C. GLC analysis indicated that **2a** and **4a** were formed in 42 and 39% yields, respectively, with only 5% of 1,7-octadiene remaining. Stirring the reaction mixture at 23 °C for 12 h resulted in the transformation of **2a** and **4a** into **1a** (75% GLC yield; *cis/trans* = 4) and **9** (41% NMR yield). No more than 2% each of **2a**, **4a**, and 1,7-octadiene were present. Iodinolysis followed by column chromatography (silica gel, pentane) gave 0.483 g of a material consisting of 0.71 mmol of naphthalene, 0.76 mmol (76%) of 1,2-bis(iodomethyl)cyclohexane (*cis/trans* = 3.5), 0.03 mmol (3%) of 9-iodomethyl-7-iodo-1-nonene, and 0.32 mmol (32%) of 1,4-diiodobutane.

(c) In a 1:3 ratio. The reaction of Et_2ZrCp_2 generated from Cl_2ZrCp_2 (0.877 g, 3 mmol) and EtMgBr (1.05 M in THF, 6 mL, 6.3 mmol) with 1,7-octadiene (148 μL, 1 mmol) at 0 °C produces **2a** and **4a** in 6 and 73% GLC yields, respectively, with no more than traces, if any, of 1,7-octadiene remaining. After 11 h at 23 °C, **1a** was formed in 60% GLC yield with no more than 4% of **4a** remaining. Iodinolysis followed by column chromatography gave 0.47 mmol (47%) of 1,2-bis(iodomethyl)cyclohexane (*cis/trans* = 4) and 0.21 mmol (21%) of 1,4-diiodobutane.

3-(5-Hexenyl)cyclopentanone. The 1:1 reaction mixture (2 mmol scale) containing **2a** (49%) was treated with CO (1.1 atm) at 0 °C and then with I_2 (0.76 g, 3 mmol) in THF (4 mL). The reaction mixture was stirred for 12 h at 23 °C, quenched with 3N HCl, extracted with ether, washed with $NaHCO_3$, $Na_2S_2O_3$, and NaCl, dried over $MgSO_4$, filtered , and concentrated. Purification by column chromatography (silica gel/pentane:Et_2O = 9:1) provided 103 mg (31%) of the title compound: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.2-1.6 (m, 7 H), 1.79 (dd, *J* = 18 and 10 Hz, 1 H), 1.95-2.45 (m, 7 H), 4.9-5.1 (m, 2 H), 5.7-5.9 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 27.14, 28.75, 29.38, 33.51, 35.36, 37.00, 38.35, 45.12, 114.27, 138.62, 219.62. IR (neat) 1742 (s), 994 (m), 910 (s) cm^{-1}; High resolution MS calcd for $C_{11}H_{18}O$, 166.1358; found, 166.1358.

9-Iodo-7-iodomethyl-1-nonene. Treatment of the 1:1 reaction mixture (2 mmol scale) after 1 h at 0 °C with I_2 (2.13 g, 8.4 mmol) in THF (10 mL) at 23 °C for 24 h followed by the usual workup and column chromatography (silica gel/pentane) afforded 0.86 mmol (43% yield) of the title compound: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.2-1.5 (m, 7 H), 1.7-1.95 (m, 2 H), 2.07 (dt, *J* = 7 and 7 Hz, 2 H), 3.1-3.35 (m, 4 H), 4.9-5.1 (m, 2 H), 5.7-5.9 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 4.00, 14.70, 25.59, 28.66, 33.37, 33.47, 37.96, 38.51, 114.51, 138.51.

3,8-Dimethyldecane. The 1:3 reaction mixture (1 mmol scale) containing **4a** (73%) was quenched with 3N HCl at 0 °C and worked up in the usual manner to give the title compound:[21] ^1H NMR ($CDCl_3$, Me_4Si) δ 0.8-0.9 (m, 12 H), 1.05-1.4 (m, 14 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 11.42, 19.24, 27.47, 29.51, 34.43, 36.70.

1,10-Dideuterio-3,8-dideuteriomethyldecane. Quenching the same mixture with DCl (20 wt % in D_2O) gave the title compound (42%): ^1H NMR ($CDCl_3$, Me_4Si) δ 0.75-0.9 (m, 9 H); 1.05-1.4 (m, 14 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 11.14 (t, *J* = 19 Hz), 18.95 (t, *J* = 19 Hz), 27.55, 29.47, 34.39, 36.76; Deuterium incorporation ≥97% at all four Me groups (^{13}C NMR).

Preparation of Nonconjugated Dienes. (a) 2-Methyl-1,6-heptadiene (5a). The reaction of 1-hepten-6-yne[1b] (4.7 g, 50 mmol) with Cp_2ZrCl_2 (2.2 g, 7.5 mmol) and Me_3Al (4.80 mL, 50 mmol) in 50 mL of CH_2Cl_2 at 20 °C for 5 h[22] produced, after workup, a 46% yield of **5a**: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.4-1.6 (m, 2 H), 1.80 (s, 3 H), 1.9-2.2 (m, 4 H), 4.6-4.8 (m, 1 H), 4.9-5.1 (m, 2 H), 5.8-6.0 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 22.45, 26.98, 33.51, 37.36, 110.26, 114.86, 139.23, 146.23.

(b) (*E*)-6-Methyl-1,6-octadiene (5b). (*E*)-1-Iodo-2-methyl-1,6-heptadiene was prepared in 67% yield by treatment of 1-hepten-6-yne[1b] with Me_3Al (1 equiv) and Cp_2ZrCl_2 (5 mol %), followed by iodinolysis with

1.2 equiv of I_2.[23] The iodide was successively treated with *t*-BuLi (2 equiv, -78 °C) and MeI (1.05 equiv, -79 to 20 °C) to give a 40% yield of **5b**: bp 75-77 °C (80 mm Hg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.4-1.17 (m, 8 H), 1.9-2.1 (m, 4 H), 4.9-5.1 (m, 2 H), 5.1-5.3 (m, 1 H), 5.7-6.0 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.34, 15.54, 27.25, 33.43, 39.14, 114.30, 118.44, 135.68, 139.05; IR (neat) 994 (m), 910 (s) cm^{-1}.

(c) (*E*)-3-Methyl-4-ethyl-3,8-nonadiene (5c). (*E*)-3-Iodo-4-methyl-3-hexene was prepared in 64% yield by the reaction of 3-hexyne with Me_3Al (1.1 equiv) and Cp_2ZrCl_2 (5 mol %).[22] It was then successively treated with *t*-BuLi (2 equiv) and 5-bromo-1-pentene (1 equiv) to give **5c**: bp 80-82 °C (10 mm Hg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.94 (5, *J* = 7.5 Hz, 3 H), 0.95 (t, *J* = 7.5 Hz, 3 H), 1.3-1.5 (m, 2 H), 1.62 (s, 3 H), 1.9-2.1 (m, 8 H), 4.9-5.1 (m, 2 H), 5.7-6.0 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.41, 139.95, 17.52, 24.82, 27.11, 28.14, 31.57, 34.12, 114.60, 130.39, 134.13, 139.53; IR (neat) 990 (m), 910 (s) cm^{-1}.

(d) 2,4,4-Trimethyl-1,6-heptadiene (12). It was prepared in 83% yield by treatment of 4,4-dimethyl-6-hepten-2-one[24] with an ylide derived from $MePPh_3Br$ and *n*-BuLi at -78 and 25 °C: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.88 (s, 6 H), 1.76 (s, 3 H), 1.94 (s, 2 H), 1.98 (d, *J* = 7.4 Hz, 2 H), 4.64 (s, 1 H), 4.85 (s, 1 H), 4.9-5.1 (m, 2 H), 5.7-6.0 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.53, 27.36, 34.17, 47.46, 49.88, 114.56, 117.23, 136.18, 144.00.28.

(e) *N*-Allyl-*N*-benzyl-1-(cyclopentenyl)methylamine (13). *N*-Allylbenzylamine was prepared in 51% yield by the reaction of benzaldehyde with allylamine (1 equiv) at 20 °C for 1 h, followed by reduction with 1.1 molar equiv of $NaBH_4$ in EtOH (3 h at 20 °C), bp 69-71 °C (2 mm Hg). Treatment of this amine first with *n*-BuLi (1 equiv) and with 1-bromomethylcyclopentene[25] (1 equiv),followed by the usual workup provided a 96% yield of the title compound: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.7-2.0 (m, 2 H), 2.2-2.4 (m, 4 H), 2.9-3.1 (m, 4 H), 3.52 (s, 2 H), 5.0-5.3 (m, 2 H), 5.56 (s, 1 H), 5.7-6.0 (m, 1 H), 7.1-7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 23.38, 32.33, 33.96, 54.34, 56.58, 57.76, 116.90, 126.61, 127.02, 128.09, 128.62, 136.24, 139.98, 142.96.

(f) 1-(4-Pentenyl)cyclopentene (14). It was prepared in 56% yield by successive treatment of 1-iodocyclopentene[26] with *t*-BuLi (2 equiv) and 5-bromo-1-pentene (1 equiv, 16 h at 20 °C): bp 95 °C (60 mm Hg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.4-1.6 (m, 2 H), 1.7-1.95 (m, 2 H), 1.95-2.4 (m, 8 H), 4.85-5.1 (m, 2 H), 5.25-5.4 (m, 1 H), 5.7-6.0 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 23.53, 27.16, 30.72, 32.53, 33.72, 35.16, 114.73, 123.70, 139.33, 145.05.

(g) 1-(7-Octenyl)-cyclopentene (20a). The use of 8-iodo-1-octene in place of 5-bromo-1-pentene in the preparation of **14** gave a 65% yield of **20a**: bp 65-67 °C (1 mm Hg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.2-1.6 (m, 8 H), 1.7-1.95 (m, 2 H), 1.95-2.15 (m, 4 H), 2.15-2.4 (m, 4 H), 4.85-5.1 (m, 2 H), 5.25-5.4 (m, 1 H), 5.7-6.0 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 23.48, 27.80, 28.94, 29.06, 29.40, 31.21, 32.44, 33.84, 35.09, 114.13, 123.01, 139.19, 145.05. IR (neat) 910 (s), 992 (m) cm^{-1}.

(h) 1-(10-Undecenyl)cyclopentene (20b). The use of 11-iodo-1-undecene, prepared from 10-undecen-1-ol, in place of 5-bromo-1-pentene in the preparation of **14** provided a 58% yield of **20b**: bp 133-135 °C (2 mm Hg); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.2-1.5 (m 14 H), 1.75-1.95 (m, 2 H), 1.95-2.1 (m, 4 H), 2.1-2.4 (m, 4 H), 4.8-5.1 (m, 2 H), 5.25-5.35 (m, 1 H), 5.65-5.95 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 23.49, 27.89, 29.02, 29.21, 29.60, 31.26, 32.45, 33.88, 35.11, 114.11, 122.96, 139.20, 145.07; IR (neat) 992 (m), 910 (s) cm^{-1}.

Reaction of *N*-Allyl-*N*-benzyl-cyclopentenylmethylamine with *n*-Bu_2ZrCp_2. To Cp_2ZrCl_2 (0.91 g, 3.1 mmol) in THF (7 mL) was added at -78 °C *n*-BuLi (2.1 mL, 6.23 mmol, 2.9 M in hexane). After 30 min at -78 °C *N*-allyl-*N*-benzyl-1-cyclopentenylmethylamine (**12**) (0.68 g, 3.0 mmol) was added, and the mixture

was stirred for 2.5 h. The ^{1}H NMR spectrum of the reaction mixture, using *p*-xylene as an internal standard, showed two Cp signals at δ 6.11 and 6.14 ppm corresponding to the formation of **16** in 70% NMR yield. The mixture was cooled to 0 °C, quenched with 3N HCl, and washed with ether. The aqueous layer was treated with 15% NaOH, extracted with ether, washed with water and dried over $MgSO_4$. After evaporation of the volatiles under reduced pressure, flash chromatography (silica gel, ether) provided *N*-benzyl-4-methylpyrrolidine-3-spirocyclopentane: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.98 (d, *J* = 6.7 Hz, 3 H), 1.2-1.7 (m, 8 H), 1.9-2.2 (m, 2 H), 2.27 (d, *J* = 6.7 Hz, 3 H), 1.2-1.7 (m, 8 H), 1.9-2.2 (m, 2 H), 2.27 (d, *J* = 8.9 Hz, 1 H), 2.58 (d, *J* = 8.9 Hz, 1 H), 2.9-3.0 (m, 1 H), 3.5-3.7 (m, 2 H), 7.1-7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.73, 23.68, 24.51, 32.58, 39.05, 40.43, 51.90, 60.91, 62.21, 67.07, 126.60, 128.07, 128.53, 139.80. The assignment of ^{13}C NMR signals as shown in Scheme 2 was based in part on ^{13}C-^{13}C 2D INADEQUATE NMR measurements.

Deuterolysis of 16 to Give 15. Treatment of **16** with 3N DCl in D_2O gave **15** in 70% yield based on **12**. The integrations of ^{1}H NMR signals at δ 0.89 and 1.2-1.7 ppm indicated monodeuteration (≥95%) of each of the groups corresponding to these signals. The ^{13}C NMR signals at δ 14.43 and 32.23 ppm are both triplets with the same coupling constant of 19 Hz.

Carbonylation of 16. The reaction of **16** with CO in a balloon was carried out at 0 °C for 18 h. After the mixture was cooled to -55 °C, it was treated with I_2 in THF. The usual workup provided a 50% yield of 3-N-benzylamino-7-oxotricyclo[6.3.0.0^{1,5}]-undecane: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.1-1.4 (m, 1 H), 1.5-2.0 (m, 5 H), 2.2-2.7 (m, 7 H), 2.83 (d, *J* = 9.1 Hz, 1 H), 3.57 (s, 2 H), 7.1-7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 26.47, 30.94, 40.11, 44.50, 46.38, 57.43, 59.47, 59.58, 61.78, 66.98, 126.83, 128.18, 128.40, 139.13, 222.63; IR (neat) 1736 (s) cm^{-1}. High resolution MS for $C_{17}H_{21}NO$: calcd, 255.1624; found, 255.1653.

Reaction of 2,4,4-Trimethyl-1,6-heptadiene with *n*-Bu_2ZrCp_2. This reaction was run similarly in a 1:1 molar ratio to give a 2:1 mixture of two isomers (^{1}H NMR Cp signals at δ 6.00 and 6.06 as well as 6.09 and 6.12 ppm) in 88% combined yield (NMR). Treatment of the products with 3N HCl, followed by the usual workup provide 1,1,2,4,4-pentamethylcyclopentane[27] (**17**) as the single predominant product in 85% yield, which established that the two zirconabicycles were stereoisomeric to each other. The spectral data for **17** were as follows: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.78 (s, 3 H), 0.81 (d, *J* = 7 Hz, 3 H), 0.94 (s, 3 H), 0.98 (s, 3 H), 1.03 (s, 3 H), 1.2-1.6 (m, 1 H), 1.37 (s, 2 H), 1.50 (dd, *J* = 12.5 and 7 Hz, 1 H), 1.73 (dq, *J* = 12.5 and 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.48, 23.17, 29.37, 32.15, 32.62, 35.50, 41.64, 43.73, 49.48, 57.45; IR (neat) 2960 (s), 2860 (s), 1460 (m), 1360 (m) cm^{-1}.

Reaction of Nonconjugated Dienes with *n*-Bu_2ZrCp_2 to Form Conjugated Diene-Zirconocenes. (a) *s-cis*-(*E*)-1-(1-Pentyl)cyclopentenezirconocene (21a). Representative Procedure: To 1-(4-pentenyl)cyclopentene (0.163 g, 1.28 mmol) and Cp_2ZrCl_2 (0.402 g, 1.37 mmol), in THF (2 mL) was added at -78 °C *n*-BuLi (1.05 mL, 2.75 mmol, 2.62 M in hexane). After 1 h at -78 °C and 18 h at 20 °C, the ^{1}H NMR spectrum of the mixture showed two Cp signals at δ 5.00 and 5.51 ppm, whose quantitative analysis using *p*-xylene as an internal standard indicated the formation of the title compound in 73% NMR yield: ^{1}H NMR (C_6D_6, Me_4Si) δ 1.09 (t, *J* = 7.3 Hz, 3 H), 4.37 (d, *J* = 11 Hz, 1 H), 4.91 (s, 5 H), 5.42 (s, 5 H); ^{13}C NMR (C_6D_6, Me_4Si) δ 14.57, 24.85, 28.38, 36.12, 40.40, 40.99, 69.53, 71.58, 101.00, 103.81, 104.53. **(*E*)-1-Pentenyl-1-cyclopentene.** Treatment of **21a** with 1.2 equiv of I_2 in THF at 0 °C followed by dilution with ether, washing with aqueous $Na_2S_2O_3$ and water, drying over $MgSO_4$, evaporation, and column chromatography provided a 65% yield of the title compound: ≥95% *E*; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, *J* = 7.2 Hz, 3 H), 1.3-1.6 (m, 2 H), 1.8-2.0 (m, 2 H), 2.0-2.22 (m, 2 H), 2.3-2.5 (m, 4 H), 5.3-5.7 (m, 2 H), 6.26 (d, *J* = 15.6 Hz, 1 H); ^{13}C

NMR ($CDCl_3$, Me_4Si) δ 13.91, 22.89, 23.33, 31.61, 32.91, 35.23, 127.62, 128.58, 131.53, 143.25; IR (neat) 962 (s) cm^{-1}. High resolution MS for $C_{10}H_{16}$: calcd, 136.1253; found, 136.1247.

(b) *s-cis*-(*E*)-2-Methyl-1,3-heptadienezirconocene (6a). It was prepared in 59% yield by the reaction of 2-methyl-1,6-heptadiene with *n*-Bu_2ZrCp_2 for 70 h at 20 °C: ^1H NMR (C_6D_6, Me_4Si) δ -9.90 (dd, *J* = 1.3 Hz, *J* = 7.8 Hz, 2 H), -0.4 to -0.2 (m, 1 H), 1.07 (t, *J* = 7.3 Hz, 3 H), 1.81 (s, 3 H), 4.45 (d, *J* = 10.9 Hz, 1 H), 4.97 (s, 5 H), 5.45 (s, 5 H); ^{13}C NMR (C_6D_6, Me_4Si) δ 14.48, 28.11, 29.19, 39.89, 53.83, 70.04, 100.60, 103.85.

(c) *s-cis*-(*E, E*)-3-Methyl-2,4-octadienezirconocene (6b). This compound was prepared in 78% yield by the reaction of (*E*)-6-methyl-1,6-octadiene with *n*-Bu_2ZrCp_2 for 18 h at 20 °C: ^1H NMR (C_6D_6, Me_3Si) δ -0.95 (q, *J* = 5.9 Hz, 1 H), -0.4 to -0.6 (m, 1 H), 1.07 (t, *J* = 7.3 Hz, 3 H), 1.5-1.75 (m, 2 H), 1.80 (s, 3 H), 1.99 (d, *J* = 5.9 Hz, 3 H), 2.0-2.3 (m, 2 H), 4.33 (d, *J* = 11.2 Hz, 1 H), 4.88 (s, 5 H), 5.42 (s, 5 H); ^{13}C NMR (C_6D_6, Me_4Si) δ 14.54, 17.93, 24.14, 28.19, 40.12, 69.46, 69.99, 100.50, 103.63, 112.14, 122.66. **(*E, E*)-3-Methyl-2,4-octadiene**: 79% yield; ≥95% *E,E*; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, *J* = 7.3 Hz, 3 H), 1.3-1.5 (m, 2 H), 1.70 (d, *J* = 7.0, 3 H), 1.72 (s, 3 H), 1.9-2.2 (q, *J* = 7.3 Hz, 2 H), 5.3-5.7 (m, 2 H), 6.05 (d, *J* = 15.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.08, 13.68, 13.77, 22.94, 35.02, 124.32, 127.12, 134.52, 134.86; IR (neat) 962 (s) cm^{-1}. High resolution MS for C_9H_{16}: calcd, 124.1253; found, 124.1251.

(d) Reaction of a Mixture of 20a and 22 with *n*-Bu_2ZrCp_2. To 1-(7-octenyl)cyclopentene (0.36 g, 2.0 mmol) and Cp_2TiCl_2 (0.03 g, 0.12 mmol) in 0.4 mL of ether was added *n*-BuLi (95 μL, 0.25 mmol, 2.63 M in hexane). After 18 h at 20 °C, the mixture was quenched with 3 N HCl, extracted with ether, washed with aqueous $NaHCO_3$ and NaCl, dried over $MgSO_4$, and evaporated to give 0.35 g of an oil consisting of 40% of **20a** and 60% of **22** (*E*/*Z* = 2): ^{13}C NMR ($CDCl_3$, Me_4Si) δ 17.94, 124.60, 131.65; *Z*: δ 12.76, 123.65, 130.84. The reaction of the above mixture of **20a** and **22** with *n*-Bu_2ZrCp_2 was performed as in the representative case. After 18 h at 20 °C, the ^1H and ^{13}C NMR spectra of the crude product were indistinguishable from those of **21b** prepared by the reaction of **20a** with *n*-Bu_2ZrCp_2. Iodinolysis of the complex obtained above cleanly produced (*E*)-1-(1-octenyl)cyclopentene.

(e) *s-cis*-(*E*)-1-Octenyl-1-cyclopentenezirconocene (21b). This compound was prepared from 1-(7-octenyl)cyclopentene in 66% yield: ^1H NMR (C_6D_6, Me_4Si) δ 4.40 (d, *J* = 10.1 Hz, 1 H), 4.935 (s, 5 H), 5.44 (s, 5 H); ^{13}C NMR (C_6D_6, Me_4Si) δ 14.45, 23.25, 24.82, 29.90, 32.52, 35.42, 36.07, 38.10, 40.95, 69.79, 71.50, 100.92, 103.72, 104.48. **(*E*)-1-(1-Octenyl)cyclopentene**: ≥95% *E*; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.88 (t, *J* = 6.3 Hz, 3 H), 1.1-1.5 (m, 8 H), 1.8-2.2 (m, 4 H), 2.2-2.5 (m, 4 H), 5.4-5.7 (m, 2 H), 6.25 (d, *J* = 15.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.12, 22.67, 23.16, 28.99, 29.57, 31.42, 31.82, 32.71, 32.95, 126.94, 128.02, 131.31, 142.72. High resolution MS for $C_{13}H_{22}$: calcd, 178.1723; found, 178.1697.

Reaction of (*E*)-3-Methyl-4-ethyl-3,8-nonadiene (5c) with *n*-Bu_2ZrCp_2. To (*E*)-3-methyl-4-ethyl-3,8-nonadiene (0.17 g, 10.04 mmol) and Cp_2ZrCl_2 (0.32 g, 1.09 mmol) in THF (2.0 mL) was added dropwise *n*-BuLi (0.83 mL, 2.19 mmol, of 2.63 M in hexane). After 1 h at -78 °C and 18 h at 20 °C, the mixture was diluted with ether, washed with 3N HCl, aqueous $NaHCO_3$ and NaCl, dried over $MgSO_4$ and evaporated under reduced pressure to give, after column chromatography, (*E, E*)-3-methyl-4-ethyl-3,5-nonadiene (**19**) in 73% yield: ≥95% *E,E*; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.7-1.1 (m, 9 H), 1.3-1.5 (m, 2 H), 1.77 (s, 3 H), 1.9-2.3 (m, 6 H), 5.65 (dt, *J* = 6.9 Hz, 15.6 Hz, 1 H), 6.33 (d, *J* = 15.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.01, 13.80, 14.27, 17.59, 21.22, 23.10, 27.99, 35.70, 128.05, 128.14, 132.17, 133.66. High resolution MS for $C_{12}H_{22}$: calcd, 166.1723; found, 166.1745.

(2-Deuterio-2-propenyl)benzene. To Cl_2ZrCp_2 (10.7 g, 36.6 mmol) in THF (80 mL) was added at

23 °C $LiAlD_4$ (0.405 g, 9.65 mmol, 98% D) in THF (20 mL). The reaction mixture was stirred for 1.5 h at 23 °C, and 3-phenyl-1-propyne (3.1 mL, 25 mmol) was added. After 2 h at 23 °C, the mixture was cooled to 0 °C, quenched with 3 N HCl, and worked up in the usual manner. Filtration through a silica gel pad (pentane) followed by evaporation of the solvents provided 2.17 g (73%) of the title compound: ≥94% D by ^1H NMR; ^1H NMR ($CDCl_3$, Me_4Si) δ 3.36 (bs, 2 H), 5.05 (bs, 2 H), 7.15-7.3 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 40.08, 115.54, 125.99, 128.34, 128.52, 137.05 (t, J = 24 Hz), 139.93; IR (neat) 2234 (w) cm^{-1}.

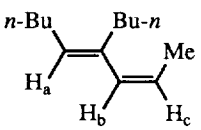
Reaction of (2-Deuterio-2-propenyl)benzene with a Catalytic Amount of *n*-Bu_2ZrCp_2. To Cl_2ZrCp_2 (0.146 g, 0.5 mmol) in THF (1.5 mL) cooled at -78 °C, was added *n*-BuLi (2.5 M in hexanes, 0.41 mL, 1.03 mmol). After stirring for 1 h, a solution of (2-deuterio-2-propenyl)benzene (0.596 g, 5 mmol) in THF (1.5 mL) was added, and the reaction mixture was warmed to 23 °C and heated at 60 °C for 2 h. GLC analysis of a protonolyzed aliquot using nonane as an internal standard indicated that an 82% of (*E*)-(2-deuterio-1-propenyl)benzene was formed along with 3% of the (*Z*)-isomer. Analysis by NMR spectroscopy of the crude product after workup confirmed the formation of (*E*)-(2-deuterio-1-propenyl)benzene: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.81 (s, 3 H), 6.33 (bs, 1 H), 7.0-7.3 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 18.24, 125.09 (t, J = 23 Hz), 125.78, 126.64, 128.38, 131.00, 137.87; IR (neat) 2236 (w) cm^{-1}; Deuterium incorporation, ≥91% (^1H NMR). Examination of the ^{13}C NMR spectrum indicated that no more than 3-4% each, if any, of (1-deuterio-1-propenyl)benzene and (3-deuterio-1-propenyl)benzene were present.

Reaction of Allylbenzene with the Stoichiometric Amount of *n*-Bu_2ZrCp_2. To a reaction mixture containing *n*-Bu_2ZrCp_2 (2 mmol), generated at -78 °C from Cl_2ZrCp_2 (0.585 g, 2 mmol) and *n*-BuLi (2.5 M in hexanes, 1.64 mL, 4.1 mmol) in THF (6 mL), was added allylbenzene (0.27 mL, 2 mmol). After stirring the mixture for 2.5 h at 23 °C, examination by ^1H NMR spectroscopy using mesitylene as an internal standard as well as GLC analysis of a protonolyzed aliquot using nonane as an internal standard indicated the formation of 4-ethyl-3-methyl-2-phenyl-1,1,-bis(η^5-cyclopentadienyl)-1-zirconacyclopentane (**29**) (δ Cp 5.67 and 6.25 ppm) in 51% yield along with the formation of (*E*)-β-methylstyrene (**28b**) in 22% yield. Hydrolysis of this reaction mixture with 3N HCl followed by the usual extractive workup with Et_2O gave (*E*)-β-methylstyrene (22% by NMR) and 2,3-dimethyl-1-phenylpentane: 47% by NMR; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.15, 16.02 (2 C), 25.56, 39.07, 39.42, 39.80, 125.42, 128.02, 129.03, 142.10.

(*E*)-2-Deuterio-4-butyl-1,4-nonadiene. This compound was prepared by a modification of a literature procedure.[20] To Cl_2ZrCp_2 (2.05 g, 7 mmol) in THF (21 mL) at -78 °C was added *n*-BuLi (2.5 M, 5.75 mL, 14.4 mmol). After 1 h, PMe_3 (0.87 mL, 0.64 g, 8.4 mmol) was added, and the mixture was warmed to 23 °C. The resulting mixture was treated with 5-decyne (1.25 mL, 0.96 g, 7 mmol) for 3 h followed by 2-deuterioallyl phenyl ether (0.66 g, 4.9 mmol), prepared in 68% yield via deuteriozirconation with $DZrCp_2Cl$ of phenyl propargyl ether, for 15 h. Hydrolysis of the reaction mixture with 3N HCl followed by the usual extractive workup with Et_2O provided after filtration through silica gel (pentane) and Kugelrohr distillation 0.55 g (62%) of the title compound:[28] 92% D; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.8-1.0 (m, 6 H), 1.2-1.4 (m, 8 H), 1.9-2.1 (m, 4 H), 2.71 (s, 2 H), 4.95-5.05 (m, 2 H), 5.14 (t, J = 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.03 (2 C), 22.47, 22.82, 27.56, 29.83, 30.59, 32.34, 41.49, 115.17, 126.12, 137.20 (t, J = 23 Hz), 137.66.

Reaction of (*E*)-2-Deuterio-4-butyl-1,4-nonadiene with the Stoichiometric Amount of *n*-Bu_2ZrCp_2. The reaction of (*E*)-2-deuterio-4-butyl-1,4-nonadiene (1 mmol) with *n*-Bu_2ZrCp_2 (1 mmol) for 4 h at 23 °C provided the corresponding diene-zirconocene complex **30** in 75% NMR yield. After treatment with I_2 (0.76 g, 3 mmol) in THF (4 mL) and the usual workup, analysis by NMR spectroscopy of the product indicated the formation of 2-deuterio-4-butyl-2,4-nonadiene in 85% yield as a 4:1 mixture of the *E,E* and *E,Z*

isomers: ^{1}H NMR ($CDCl_3$, Me_4Si) for the *E,E* isomer δ 0.8-1.0 (m, 6 H), 1.2-1.5 (m, 8 H), 1.74 (s, 3 H), 2.05-2.25 (m, 4 H), 5.30 (t, *J* = 7 Hz, 1 H), 5.94 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) for the *E,E* isomer δ 13.98 (2C), 18.09, 22.48, 23.07, 26.71, 27.73, 31.37, 32.09, 120.96 (t, *J* = 23 Hz), 130.17, 134.88, 138.18. The extent of D incorporation at the C-2 atom was >91%, and those at the C-1 and C-3 atoms were <3-4% each. ^{1}H NMR signals for the *E,Z* isomer that are distinct from those of the *E,E* isomer were as follows: δ 1.78 (s, 3 H), 5.21 (t, *J* = 7 Hz, 1 H), 6.32 (s, 1 H). **Determination of the Stereochemistry of the Conjugated Dienes.** To unequivocally establish the stereochemistry of the conjugated dienes, the same reaction was performed using (*E*)-4-butyl-1,4-nonadiene prepared in 51% yield by the Pd-catalyzed cross coupling[29] of (*cis*-5-decenyl)diisobutylalane with allyl chloride. Inspection of ^{1}H and ^{13}C NMR spectra indicated that the two compounds obtained in a 4/1 ratio were stereoisomers of 4-butyl-2,4-nonadiene. The above conclusion that the two isomers obtained are *2E,4E* and *2E,4Z* is based on the following. An authentic sample of the *2Z,4E* isomer (**32**) was prepared by (i) the reaction of 5-decyne with DIBAH followed by iodinolysis[30] to give (*E*)-5-iodo-5-decene,[31] (ii) Pd/Cu-catalyzed cross coupling[32] of the iodoalkene with propyne to produce (*E*)-4-butyl-4-nonen-2-yne, and (iii) hydroboration of the triple bond with $(Sia)_2BH$[33] followed by protonolysis to give (*Z,E*)-4-butyl-2,4-nonadiene. Comparison of the NMR spectra of the two stereoisomers **33** and **34** produced by the above reaction, and **32** indicated that neither **33** nor **34** was **32**. The coupling constant for H_b in **33** and **34** is 16 Hz, whereas that for **32** is 12 Hz. Any stereoisomer in which the disubstituted double bond is *Z* may therefore be ruled out. ^{1}H-^{13}C 2D HETCOR NMR spectroscopic experiment showed that the chemical shift of the carbon bearing H_b in the major and minor stereoisomers obtained are 134.94 and 127.61 ppm, respectively, permitting the assignment of **33** and **34** to the major and minor isomers, respectively.



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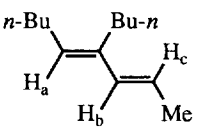

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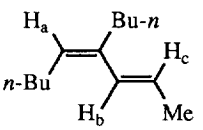

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