

Stereoselectivity in Intramolecular Diene Cyclozirconation: A Combined Experimental and Theoretical Approach

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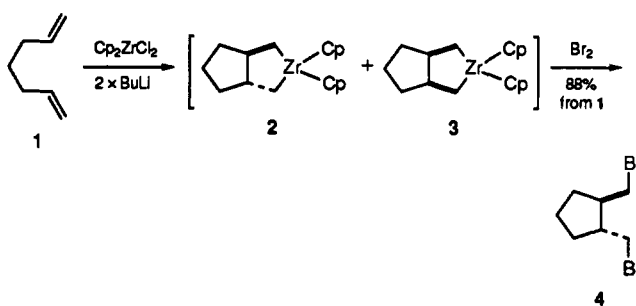
Received February 16, 1994[⊙]

Abstract: Intramolecular diene cyclozirconation ($1 \rightarrow 2 + 3 \rightarrow 4$) can be highly diastereoselective (97:3 trans/cis for **4**). It is suggested that the cis and trans diastereomers of the zirconacycle are equilibrating under the conditions of the reaction, and that the observed diastereomeric preference of **4** reflects the relative stability of the two diastereomeric zirconacycles. Results for the intramolecular cyclozirconation of two other dienes, **8** and **14**, as well as for the "heterodiene" N,N-diallylaniline are also reported. Computational results at the molecular mechanics, semiempirical molecular orbital ZINDO and nonlocal density functional theory levels are used to explain the observed stereochemistry in terms of thermodynamic and kinetic control.

Introduction

Organozirconium species play an important role in a variety of synthetic transformations and are of growing importance as polymerization catalysts.¹ There is currently a massive industrial effort aimed at developing zirconium-based "single site" olefin polymerization catalysts which provide unprecedented control of polymer tacticity.^{1c} The stoichiometric reactions of organozirconium reagents can also proceed with remarkable levels of stereoselectivity. For example, in 1989 we^{2a} and Negishi^{2b,3} independently reported that reduction⁴ of zirconocene dichloride in the presence of a 1,6- or 1,7-diene results in ring formation (e.g. **1** \rightarrow **4**), often with excellent stereochemical control.^{5,6} This reaction offers some obvious advantages: a new carbocyclic ring is constructed, in the course of which four sp²-hybridized carbons are converted into functionalized sp³-hybridized carbons. Because of the potential practical importance of Zr-based reagents and

catalysts, it is important to understand the stereochemistry of these transformations.



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[⊙] Abstract published in *Advance ACS Abstracts*, September 1, 1994.

(1) (a) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (b) Negishi, E.-i.; Takahashi, T. *Synthesis* **1988**, 1. (c) Wood, A.; Chynoweth, E. *Chemical Week* **1992**, May 13, 52. (d) Kaminsky, W.; Sinn, H., Eds. *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Springer-Verlag: New York, 1988. (e) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91. (f) Morken, J. P.; Didiuk, M. T.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1993**, *115*, 6997.

(2) (a) Nugent, W. A.; Taber, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 6435. (b) Rousset, C. J.; Swanson, D. R.; Lamaty, F.; Negishi, E.-i. *Tetrahedron Lett.* **1989**, *30*, 5105. (c) See also: Davis, J. M.; Whitby, R. J.; Albert, J.-C. *Tetrahedron Lett.* **1992**, *33*, 5655.

(3) There were, prior to this work, several isolated reports of cyclization of 1,7-octadiene by early transition metals: (a) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529. (b) Grubbs, R. H.; Miyashita, A. *J. Chem. Soc., Chem. Commun.* **1977**, 864. (c) McClain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558. (d) Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 244. (e) See also: Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1980**, *19*, 3106.

(4) For the first cyclization of enynes by reduction of zirconocene dichloride with BuLi, see: Negishi, E.-i.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.

(5) (a) For the first application of intramolecular diene cyclozirconation in natural product synthesis, see: Mori, M.; Uesaka, N.; Shibasaki, M. *J. Org. Chem.* **1992**, *57*, 3519. (b) Note that structure **8** in the preceding reference has been revised to the *exo*-methyl; Mori, M., personal communication.

(6) Intramolecular diene cyclozirconation can be effected with catalytic zirconocene dichloride, using excess alkyl magnesium bromide: (a) Knight, K. S.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6268. (b) Wischmeyer, U.; Knight, K. S.; Waymouth, R. M. *Tetrahedron Lett.* **1992**, *33*, 735. (c) Hourii, A. F.; Didiuk, M. T.; Xu, Z.; Horan, N. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1993**, *115*, 6614. (d) Lewis, D. P.; Muller, P. M.; Whitby, R. J.; Jones, R. V. H. *Tetrahedron Lett.* **1991**, *32*, 6797. (e) Knight, K. S.; Wang, D.; Waymouth, R. M.; Ziller, J. *J. Am. Chem. Soc.* **1994**, *116*, 1845.

An important result from the experimental work described below is that, depending on the structure of the diene and the zirconium reagent, there are clear differences in the product stereochemistry. For example, in some cases, cis-fused zirconacycles predominate whereas in other cases trans-fused zirconacycles are formed. The question that needs to be answered is whether these reactions are under thermodynamic or kinetic control. The answer to this question is not always readily accessible by experimentation. However one could use theoretical methods to predict the thermodynamic differences between the cis and trans isomers of the intermediate zirconacycles and use this with the experimental product distributions to determine whether the reaction is under thermodynamic or kinetic control. In order to do this, since the structures of the intermediates are not all available, one needs a computational method that can predict structures as well as energy differences.

There are a number of computational methods that can be used to predict the structures and thermodynamic properties of organometallic compounds that contain transition metals. The simplest means would be to use molecular mechanics (MM)⁷ if the appropriate parameters are available. For Zr-based compounds, only a minimal set of MM parameters is available, and in order to optimize a structure, it is necessary to freeze the geometry at the Zr and allow for relaxation of the organic fragment. Because we expect the energy differences to be small, this method may not prove to be accurate enough for this study.

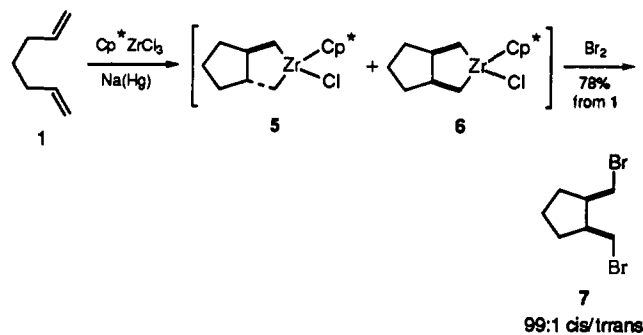
(7) Burkert, U.; Allinger, N. L. *Molecular Mechanics*, ACS Monograph 177, American Chemical Society: Washington, DC, 1982.

One then needs to resort to computational methods in which the electrons are actively treated. The most efficient computational method is semiempirical molecular orbital theory. The only such method which is parametrized reliably for Zr is the ZINDO method.⁸ One could also perform some type of *ab initio* calculation. However, traditional molecular orbital methods do not work well for transition metal species, especially those containing dative bonding to ligands such as cyclopentadienyl unless large basis sets and extensive levels of correlation are included. Furthermore, the computational times for the systems to be studied here would be prohibitive. Density functional theory,^{9,10} on the other hand, is a computationally efficient method that can be used to treat transition metal systems with reasonable accuracy. Below, we describe our calculations at the MM, ZINDO, and DFT levels in conjunction with the experimental measurements.

Results and Discussion

Cyclozirconation of 1,6-Heptadiene. Quite striking diastereoselectivity was observed in the cyclozirconation of 1,6-heptadiene (**1** → **4**, above). The *trans*-fused diastereomer **4** predominated, by a ratio of 97:3. The structure of the pure crystalline *trans* zirconacycle **2**, which is the major product, was confirmed by X-ray analysis (Figure 1). Waymouth^{6e} has recently reported the crystal structure of a related zirconacycle derived from a 9,9-diallylfluorene; it likewise exhibits the *trans*-fused metallacyclopentane structure.

In contrast, the cyclization of heptadiene **1** with Cp*ZrCl₃¹¹ (1 equiv) and 0.5% sodium amalgam (2 equiv), followed by bromination, gave the *cis* diastereomer **7** of the dibromide. Again, the structure of the dominant intermediate zirconacycle **6** was



confirmed by X-ray crystallography (Figure 2). The ORTEP diagram clearly shows that the metallacycle adopts the *cis exo* configuration (i.e., with the cyclopentane ring directed toward

(8) For leading references to ZINDO, a semiempirical program that has been parametrized for the first two rows of transition elements, see: (a) Zerner, M. C.; Loew, G. W.; Kirchner, R. F.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589. (b) Anderson, W. P.; Cundari, T. R.; Drago, R. S.; Zerner, M. C. *Inorg. Chem.* **1990**, *29*, 1.

(9) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (b) Salahub, D. R. In *Ab Initio Methods in Quantum Chemistry-II*; Lawley, K. P., Ed.; J. Wiley & Sons: New York, 1987, p 447. (c) Wimmer, E.; Freeman, A. J.; Fu, C.-L.; Cao, P.-L.; Chou, S.-H.; Delley, B. In *Supercomputer Research in Chemistry and Chemical Engineering*; Jensen, K. F., Truhlar, D. G., Eds.; ACS Symp. Ser., No. 353; American Chemical Society: Washington, DC, 1987, p 49. (d) Jones, R. O.; Gunnarsson, O. *Rev. Mod. Phys.* **1989**, *61*, 689. (e) Zeigler, T. *Chem. Rev.* **1991**, *91*, 651.

(10) (a) Sosa, C.; Andzelm, J.; Elkin, B. C.; Wimmer, E.; Dobbs, K. D.; Dixon, D. A. *J. Phys. Chem.* **1992**, *96*, 6630. (b) Dixon, D. A.; Andzelm, J.; Fitzgerald, G.; Wimmer, E.; Delley, B. In *Science and Engineering on Supercomputers*; Pitcher, E. J., Ed.; Computational Science Publications: Southampton, England, 1990; p 285. (c) Dixon, D. A.; Andzelm, J.; Fitzgerald, G.; Wimmer, E.; Jasien, P. In *Density Functional Methods in Chemistry*; Labanowski, J., Andzelm, J., Eds.; Springer-Verlag: New York, 1991, p 33. (d) Dixon, D. A.; Andzelm, J.; Fitzgerald, G.; Wimmer, E.; Jasien, P. *J. Phys. Chem.* **1991**, *95*, 9197.

(11) For the preparation of Cp*ZrCl₃ (Cp* is the pentamethylcyclopentadienyl ligand), see: Blenkins, J.; de Lief de Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383.

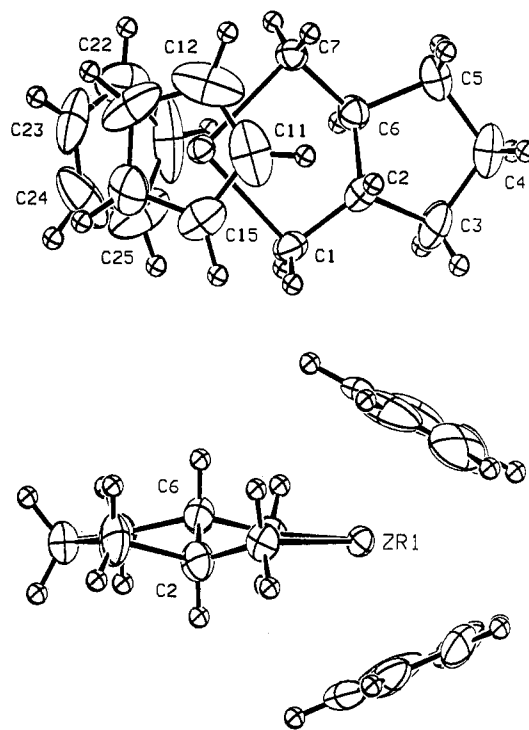


Figure 1. ORTEP drawing showing two views of one conformation of zirconacycle **2** which possesses *trans*-fused bicyclic structure. Bond distances for the metallacyclic ring (Å): Zr–C(1) 2.275(2), Zr–C(7) 2.286(2), C(1)–C(2) 1.510(7), C(2)–C(6) 1.507(8), C(6)–C(7) 1.574(6). Bond angles (°): C(1)–Zr–C(7) 89.2(1), Zr–C(1)–C(2) 97.9(2), Zr–C(7)–C(6) 96.0(2), C(1)–C(2)–C(6) 114.9(5), C(2)–C(6)–C(7) 116.6(5).

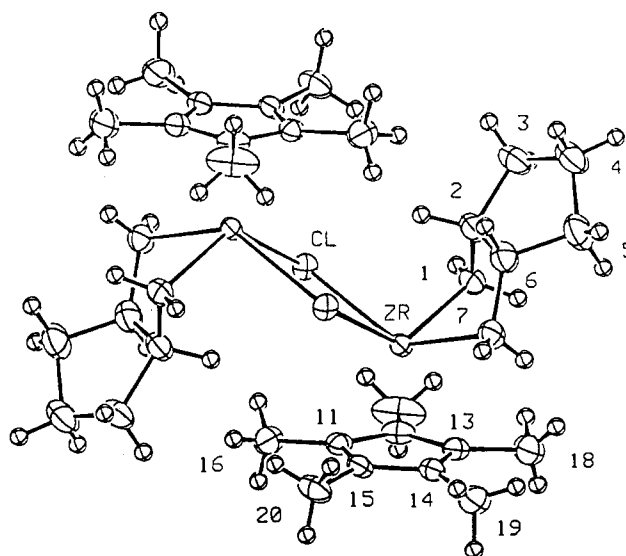
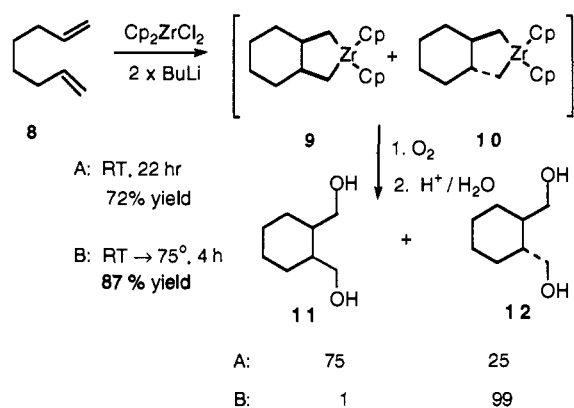


Figure 2. ORTEP drawing of the chloride-bridged dimer of zirconacycle **6** showing the *cis*-fused bicyclic structure. Bond distances for the metallacyclic ring (Å): Zr–C(1) 2.226(2), Zr–C(7) 2.258, C(1)–C(2) 1.538(4), C(2)–C(6) 1.560(3), C(6)–C(7) 1.525(3). Bond angles (°): C(1)–Zr–C(7) 77.6(1), Zr–C(1)–C(2) 89.1(1), Zr–C(7)–C(6) 99.1(1), C(1)–C(2)–C(6) 111.7(2), C(2)–C(6)–C(7) 112.3(2).

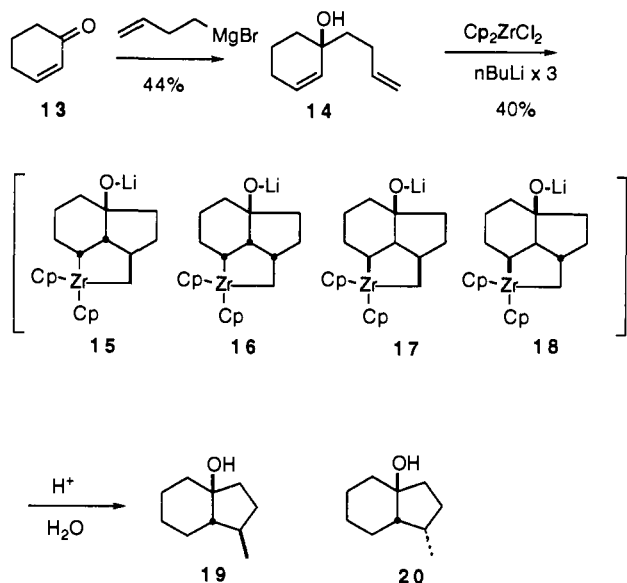
the pentamethylcyclopentadienyl ligand). A remarkably similar structure was observed by Churchill^{3e} in a related tantalum metallacycle derived from 1,6-heptadiene and Cp*TaCl₄ and 2 equiv of sodium amalgam. The metallacyclic ring in Cp*Ta(C₇H₁₂)Cl₂ also adopts the *cis exo* configuration.

Cyclozirconation of 1,7-Octadiene. 1,7-Octadiene (**8**, Scheme 1) could also be cyclized to either the *cis* or the *trans* product. In this case, even with Cp₂ZrCl₂/2BuLi the *cis* product dominated when the cyclization was carried out at room temperature. When

Scheme 1



Scheme 2



the cyclozirconation was repeated at elevated temperature, the trans diastereomer was the dominant product from the reaction.^{6b,12}

It is important to monitor this cyclozirconation by oxidation of the intermediate cis and trans zirconacycles **9** and **10** to the corresponding diols. Initially, we followed the reaction by protonolysis, analyzing the product *cis*- and *trans*-1,2-dimethylcyclohexanes by capillary column gas chromatography. The resulting kinetics were peculiar. This discrepancy was reconciled by the observation that the zirconacycles **9** and **10** can thermally degrade to a monoalkene¹³ which then disproportionates directly to a mixture of xylene and the diastereomeric 1, 2-dimethylcyclohexanes. The high (87%) material balance achieved in these studies is significant; a low material balance would raise the possibility that the apparent equilibrium is skewed by selective destruction of one isomer.

Cyclozirconation of Diene 14. To test whether or not a cyclic alkene could participate in intramolecular diene cyclozirconation, we prepared (Scheme 2) the (unstable) allylic alcohol **14**. Assuming that cyclozirconation is concerted, so that the alkene geometry is maintained, **14** could cyclize to four possible tricyclic zirconacycles, **15**, **16**, **17**, and **18**. The stereochemistry of **19** implies that cyclozirconation proceeds via the metallacycle **15**. Protonolysis of the reaction mixture after 24 hours at room

(12) While our work was in progress, the equilibration at elevated temperature of zirconacycles **9** and **10**, prepared by an alternative procedure, was independently observed: Akita, M.; Yasuda, H.; Yamamoto, H.; Nakamura, A. *Polyhedron* **1991**, *10*, 1.

(13) We observed (gas chromatography–mass spectrometry) substantial quantities of 2-methylmethylenecyclohexane (structure confirmed by independent synthesis) in the reaction mixtures.

Table 1. Relative Energies (kcal/mol) of Diastereomeric Zirconacycles

| zirconacycle | relative energies | | DFT ^c |
|---------------|-------------------|--------------------|------------------|
| | MM ^a | ZINDO ^b | |
| 2 | 0.0 | 0.0 | 0.0 |
| 3 | 3.6 | 2.5 | 2.5 |
| 5 | 0.0 | 0.3 | 0.0 |
| 6-exo | 1.0 | 0.7 | 2.8 |
| 6-endo | 1.3 | 0.0 | 4.1 |
| 9 | 0.9 | 2.8 | 0.5 |
| 10 | 0.0 | 0.0 | 0.0 |
| 15 | 0.0 | 0.0 | 0.0 |
| 16 | 5.9 | 1.1 | 9.8 |
| 17 | 5.1 | 6.2 | 8.8 |
| 18 | 7.0 | 9.0 | 7.6 |
| 21 | 0.0 | 0.7 | 1.0 |
| 22 | 0.0 | 0.0 | 0.0 |

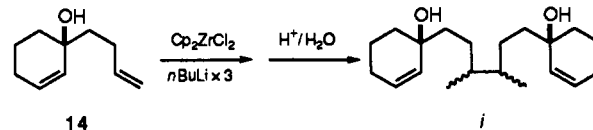
^a MM strain energies (kcal/mol) of the most stable isomer: $E(\mathbf{2}) = 18.73$; $E(\mathbf{5}) = 11.04$; $E(\mathbf{10}) = 25.73$; $E(\mathbf{15}) = 38.15$. ^b ZINDO energies (au) of the most stable isomer: $E(\mathbf{2}) = -128.488\ 28$; $E(\mathbf{6}) = -47.409\ 13$; $E(\mathbf{10}) = -136.400\ 86$; $E(\mathbf{15}) = -167.642\ 28$. ^c NLDFT energies (au) of the most stable isomer: $E(\mathbf{2}) = -4\ 202.243\ 603$; $E(\mathbf{5}) = -4\ 665.552\ 210$; $E(\mathbf{10}) = -4\ 241.567\ 314$; $E(\mathbf{15}) = -4\ 394.244\ 348$.

temperature^{14,15} provided the volatile alcohol **19**, as a single diastereomer (¹H, ¹³C NMR). The relative configuration of **19** was established by comparison with known material.¹⁶ Diastereomer **20**, which co-elutes (TLC)¹⁶ with **19**, was not observed. Thus, cyclic alkenes¹⁷ can participate in intramolecular cyclozirconation, and the reaction can proceed with high diastereoselectivity.¹⁸

Computational Studies

Molecular Mechanics. It is important to know whether the intramolecular diene cyclozirconations described above are under thermodynamic or kinetic control. The cyclization is readily reversible,¹⁵ even though the equilibrium lies toward the cyclized product. To understand (and, perhaps, predict) diastereoselectivity, it was then important to evaluate the thermodynamic stability of the diastereomeric zirconacycles. This can be done in the most straightforward manner by using computational approaches. Molecular mechanics^{7,19} has been parametrized for zirconium, with the constraint that the bonds to zirconium and bond angles involving Zr are fixed at a pre-specified "optimal" level. These constraints may lead to less accuracy in the relative energetics. For example, the value of the Zr–C bond is fixed at 2.24 Å, yet the X-ray structure of the trans zirconacycle **2** (Figure

(14) As expected,¹⁵ on cyclozirconation of **14** at room temperature starting material was rapidly consumed. The formation of a new product was complete (TLC) after 2 h. Workup of the reaction at this point provided the intermolecular dimer **i**.



(15) For the ready reversibility of *intermolecular* alkene cyclozirconation, see: (a) Taber, D. F.; Louey, J. P.; Lim, J. A. *Tetrahedron Lett.* **1993**, *34*, 1993. (b) Takahashi, T.; Fujimori, T.; Takashi, S.; Saburi, M.; Uchida, Y.; Rousset, C. J.; Negishi, E.-i. *J. Chem. Soc., Chem. Commun.* **1990**, 182.

(16) (a) Rawal, V. H.; Newton, R. C.; Krishnamurthy, V. J. *Org. Chem.* **1990**, *55*, 5181. (b) Rawal, V. H., personal communication.

(17) For highly diastereoselective cyclozirconations of cyclic allylic amines, see ref 5.

(18) Ease of cyclozirconation clearly depends on the substitution pattern of the diene. Attempted cyclozirconation of related substrates having trisubstituted cyclic alkenes led only to alkene migration: Maye, J. P.; Negishi, E.-i. *Tetrahedron Lett.* **1993**, *34*, 3359.

(19) Molecular mechanics calculations were carried out using the program Mechanics, implemented on a Tektronix CAChe workstation. This code is based on Allinger's MM-2 molecular mechanics code with extensions provided by the CAChe group.

Table 2. Structural Parameters of Zirconacycles^a

| | Zr-sub1 ^b | Zr-sub2 ^c | Zr-C1 | Zr-C2 | $\theta(\text{Zr-C1-C})$ | $\theta(\text{Zr-C2-C})$ | $\theta(\text{C1-Zr-C2})$ | R_{av}^d | | method |
|---------------------|----------------------|----------------------|-------|-------|--------------------------|--------------------------|---------------------------|-------------------|--------|--------|
| 2 | 2.547–2.600 | 2.554–2.595 | 2.325 | 2.323 | 99.3 | 99.0 | 86.6 | 2.576* | 2.579* | DFT |
| 2 | 2.589–2.623 | 2.573–2.617 | 2.393 | 2.391 | 99.9 | 99.6 | 82.7 | 2.600* | 2.600* | ZINDO |
| 2 | 2.505–2.543 | 2.470–2.518 | 2.275 | 2.286 | 97.0 | 96.8 | 89.2 | 2.523* | 2.496* | X-ray |
| 3 | 2.578–2.600 | 2.568–2.630 | 2.288 | 2.286 | 108.4 | 109.4 | 77.4 | 2.591* | 2.599* | DFT |
| 3 | 2.597–2.608 | 2.577–2.632 | 2.378 | 2.380 | 107.8 | 108.5 | 75.2 | 2.598* | 2.600* | ZINDO |
| 5 | 2.524–2.567 | 2.446 | 2.260 | 2.253 | 90.7 | 96.6 | 92.3 | 2.545* | | DFT |
| 5 | 2.530–2.578 | 2.884 | 2.301 | 2.295 | 88.7 | 89.6 | 94.7 | 2.565* | | ZINDO |
| 6-exo ^e | 2.483–2.643 | 2.447 | 2.230 | 2.238 | 98.7 | 100.0 | 80.7 | 2.576* | | DFT |
| 6-exo ^e | 2.486–2.513 | 2.610–2.683 | 2.26 | 2.258 | 89.1 | 99.1 | 77.6 | 2.498* | | X-ray |
| 6-endo ^e | 2.503–2.601 | 2.448 | 2.252 | 2.261 | 102.9 | 99.3 | 89.3 | 2.546* | | DFT |
| 6-endo ^e | 2.543–2.578 | 2.889 | 2.284 | 2.278 | 90.9 | 90.0 | 96.4 | 2.568* | | ZINDO |
| 9 | 2.559–2.597 | 2.546–2.613 | 2.310 | 2.324 | 104.1 | 107.7 | 81.7 | 2.581* | 2.582* | DFT |
| 9 | 2.572–2.616 | 2.572–2.624 | 2.385 | 2.395 | 104.5 | 108.0 | 77.9 | 2.599* | 2.599* | ZINDO |
| 10 | 2.557–2.609 | 2.550–2.618 | 2.316 | 2.320 | 105.2 | 105.9 | 81.7 | 2.585* | 2.584* | DFT |
| 10 | 2.571–2.608 | 2.570–2.626 | 2.388 | 2.392 | 104.4 | 105.1 | 78.9 | 2.598* | 2.598* | ZINDO |
| 21 | 2.555–2.641 | 2.574–2.613 | 2.290 | 2.285 | 108.0 | 109.0 | 75.6 | 2.596* | 2.595* | DFT |
| 22 | 2.556–2.637 | 2.543–2.628 | 2.312 | 2.297 | 95.9 | 96.4 | 89.4 | 2.596* | 2.588* | DFT |

^a Bond distances in Å. Bond angles in deg. ^b Range of Zr–Cp Zr–C bond distances. ^c Range of Zr–Cp Zr–C bond distances except for 5 and 6 where the Zr–Cl distances are given. ^d Average of the 5 Zr–C distances in a Cp or Cp* ring. ^e There are two diastereomers of 6. See text.

1) has an average Zr–C distance of 2.28 Å. The relative stabilities for the diastereomeric zirconacycles (Table 1) 2 and 3, 9 and 10, and 15–18 as calculated with molecular mechanics give the following orderings in order of stability: 2 > 3, 10 > 9, and 15 > 17 > 16 > 18.

ZINDO. In order to improve the computational level, we next used the semiempirical method ZINDO^{8,20} to calculate the energies and structures of the zirconacycles. Although this method was originally parametrized to give good spectroscopic results, it has been employed previously in studies of the energetics and structures of transition metal-based catalytic systems.²¹ The geometry results are summarized in Table 2 and the energetic results are given in Table 1. The ZINDO calculations give the following stability order 2 > 3, 6 > 5, 10 > 9, and 15 > 17 > 16 > 18.

Density Functional Theory. The highest level of theory used in this study is ab initio gradient corrected (non-local) density functional theory (DFT).^{10,22,23} The optimized geometry parameters of the diastereomeric zirconacycles reported above are given in Table 2. The stability ordering (Table 1) for each set is 2 > 3, 5 > 6, 10 > 9, and 15 > 18 > 17 > 16.

Comparing the results of the three calculations, we find that the ordering and relative energies for the 5,5-zirconacycles 2 and 3 are the same at all of the computational levels and the relative energies are similar. For mono-Cp* zirconacycles 5 and 6 the ZINDO results cannot really distinguish between the two, but the DFT results show a clear favoring of trans isomer 5. For the 5,6-zirconacycles 9 and 10, all of the methods predict trans isomer 10 to be the most stable with ZINDO giving the largest energy difference. All of the methods predict tricyclic zirconacycle 15 to be the most stable, but the ordering of the energies for the remaining isomers differs depending on the method. It is noteworthy that DFT predicts a much larger energy difference between 15 and 16 than does ZINDO, and this is the largest difference noted for all of the methods.

The predicted geometries can be directly compared to experiment for 2 and approximately for 6 which is actually a dimer in the crystal. For bis-Cp zirconacycle 2, the DFT Zr–C bond distances are all long by about 0.05 Å, with the Zr–Cp distances being slightly longer. The angles are in reasonable agreement

considering the differences in the bond distances. The ZINDO values for the Zr–Cp distances are slightly longer than the DFT distances, but the Zr–C distances are 0.07 Å longer than the DFT values, which makes them 0.11–0.15 Å longer than experiment. For the mono-Cp* derivative 6, the Zr–C distances are in good agreement and the Zr–C distances are again too long at the DFT level. The Zr–Cl distances cannot be compared exactly, because the experimental structure is a dimer. Thus the X-ray distances are about 0.20 Å longer than the DFT value. The Zr–Cl value can be compared to the Zr–Cl bond distance in ZrCl₄ ($r(\text{Zr-Cl}) = 2.32 \text{ \AA}$)²⁴ and, as would be expected, is longer than this value. ZINDO predicts the Zr–Cl bond to be too long by >0.4 Å as compared to the DFT results. Thus, the ZINDO Zr–C bond distances for 6 are closer in agreement with the DFT and experimental values. The very long Zr–Cl bond distance at the ZINDO level suggests that the Cl is only weakly interacting with the Zr. This could be the reason that the energies of the two isomers 5 and 6 are so similar at the ZINDO level.

From these calculations, one would expect that the trans-fused 5,5-diastereomer 2 should predominate over the cis-fused diastereomer 3 if the reaction is under thermodynamic control. Tricyclic zirconacycle 15, also, should be the predominant diastereomer from cyclozirconation of dienol 14, again if the reaction is under thermodynamic control. Thus the calculations are consistent with the proposal that the reactions producing 2 and 15 are under thermodynamic control.

The energy difference between the 6,5-cis- and 6,5-trans-fused diastereomers 9 and 10 is predicted to be much smaller, though trans isomer 10 is still predicted to be the more stable of the two. The results from cyclozirconation of 1,7-octadiene (Scheme 1) are particularly striking. These can be understood if the activation energy for the equilibration of zirconacycles 9 and 10 is significantly higher than the activation energy for the equilibration of zirconacycles 2 and 3. Thus, the dominant kinetic product from the cyclozirconation of 1,7-octadiene is the cis-fused zirconacycle 9, and this diastereomer is sufficiently stable to survive for some time at room temperature. At elevated temperature, the less stable cis-diastereomer 9 equilibrates to the more stable trans-diastereomer 10 (10 is calculated to be more stable than 9 by about 0.5 kcal/mol by DFT or 2.8 kcal/mol by ZINDO).

This analysis is consistent with a mechanism proposed by Waymouth^{6c} to explain the contrasting diastereoselectivity observed when the cyclozirconation of 1,7-heptadiene is effected

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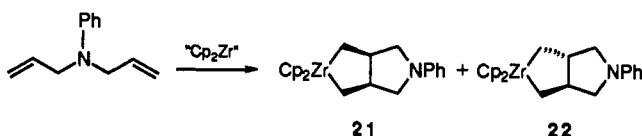
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with a catalytic amount of zirconocene dichloride. In this model the alkyl magnesium halide (or dialkyl magnesium) intercepts the kinetically-formed cis-fused zirconacycle before it can fully equilibrate to the thermodynamically-preferred trans-fused zirconacycle. This would explain the increased fraction of cis-fused products observed under such catalytic conditions.

The DFT calculations show that the trans-Cp*-zirconacycle **5** is significantly more stable than the cis isomer **6**. Because the dimer of **6** is the observed species, we suggest that these Cp* zirconacycles are not equilibrating, but rather that the Cp*ZrCl₂-mediated cyclization is under kinetic control. This explanation seems reasonable also from the standpoint of organometallic chemistry. The presence of an electronegative chloride ligand in **6** should disfavor the reductive process required for isomerization when compared with the bis(cyclopentadienyl)zirconacycles. Of course, there is always the possibility that the dimerization is driving the reaction.

Extension to a Heterocyclic System. In addition to the carbocyclic systems described above, we have now extended our studies to the cyclization of *N,N*-diallylaniline which proceeds according to the reaction



Whitby and co-workers^{2c} have converted the resultant mixture of cis and trans metallacycles **21** and **22** to bicyclic amines via treatment with phenyl isocyanide. Their results were consistent with predominant formation of the cis azirronacycle (**21/22** = 1.8:1).

In order to determine whether the cis isomer **21** predominates due to kinetic or thermodynamic factors, we have examined the equilibration of azirronacycles **21** and **22** in refluxing THF. Protonolysis and gas chromatographic analysis of the resultant *cis*- and *trans*-1-phenyl-3,4-dimethylpyrrolidines indicated that **21** and **22** were initially present in the proportions *cis/trans* = 2.63:1, and this ratio changed little on standing at room temperature for 1 h. However, upon heating the mixture at reflux (65 °C) the ratio changed so that the trans isomer **22** was the predominant species; after 2 h of heating the *trans/cis* ratio was 2.46:1. Continued heating did not further alter this ratio.

The small energy difference between the isomers in this case provides a challenge for our computation studies. Nevertheless, all three techniques correctly predict the trans isomer to be more stable by a small margin. ZINDO indicated that a zirconacycle **22** should be favored by 0.69 kcal/mol while by molecular mechanics the difference was just 0.04 kcal/mol. Finally with use of DFT, **22** was calculated to be more stable than **21** by 1.04 kcal/mol. Again DFT gave reasonable geometric parameters for both azirronacycles **21** and **22**; these bond distances and angles are included in Table 2.

Conclusion

Intramolecular diene cyclozirconation can be an effective tool for target-directed synthesis. Indeed, the first applications^{5,6c} have already appeared. To be most useful, it would be desirable to be able to assess before the fact the likely stereochemical outcome of a projected cyclozirconation. This research represents a first step in this direction. It is noteworthy that in the two cases where the relative stabilities of two isomeric zirconacycles is known with certainty, namely those derived from 1,7-octadiene and *N,N*-diallylaniline, all three computational levels correctly predict the trans isomer to be more stable. The highest level of theory, DFT, proved especially effective for predicting the geometry parameters for the zirconacycles. Nevertheless, our molecular mechanics calculations and semiempirical MO theory with the

ZINDO parametrization could provide useful insight into the stereochemical course of these reactions in some cases. This result is of interest because these latter two methods are computationally much cheaper than the more rigorous DFT approach.

Each of these methods provides an estimate of differences in the enthalpy of formation of the isomers, at absolute zero in the gas phase. These can only provide a guide to the differences in the free energy of the diastereomers in solution at the temperatures of the equilibrations. Nevertheless, our results show that the types of computations employed in this study provide a useful complement to experiment in understanding the stereochemical course of a transition metal mediated transformation.

Experimental Section

General. ¹H and ¹³C NMR spectra were obtained on a Bruker AM-250 spectrometer as solutions in CDCl₃. Carbon signals were assigned by an INEPT pulse sequence, u = methylene or quaternary carbon, d = methyl or methine. The infrared (IR) spectra were obtained as solutions in CCl₄ and are reported in cm⁻¹. Substances for which C, H analysis is not reported were purified as specified and gave spectroscopic data consistent with being >95% of the assigned structure. Organic chemicals were purchased from Aldrich Chemical Co. THF and Et₂O were distilled from sodium/benzophenone. The solvent mixtures used for chromatography are volume/volume mixtures. R_f values indicated refer to thin layer chromatography on Analtech 2.5 × 10 cm 250 μm analytical plates coated with silica gel GF. Column chromatography was carried out with TLC-mesh silica gel, using the procedure we have described.²⁵ Unless otherwise specified, all reactions were carried out in flame-dried glassware under an atmosphere of N₂.

X-ray Crystallographic Study of Zirconacycles 2 and 6. The crystallographic investigations of both compounds were carried out on a Syntex P3 diffractometer (graphite monochromator; Mo Kα radiation; λ = 0.710 69 Å) which was equipped with a low-temperature apparatus operating at -100 °C. The crystal system, space group, and approximate unit cell dimensions of each crystal were determined during preliminary investigations. The quality of both crystals was found to be adequate on the basis of ω scans which showed the peak width at half-height to be ca. 0.25°. The unit cell parameters were refined from the Bragg angles of at least 48 computer-centered reflections. Intensity data were collected using the ω-scan technique: 1.10° ω; variable scan speeds of 2.0 to 9.8° min⁻¹; 4° < 2θ < 55°. The intensities of standard reflections were monitored periodically but only statistical variations were noted over the course of each data collection. Azimuthal scans showed little variation in intensity with ψ. No correction for absorption was made for **6**; an empirical absorption correction (transmission factors ranged from 0.80 to 0.81) was applied in the case of **2**. Both structures were solved by direct methods. The refinement and analysis of the two structures were carried out using a package of local programs.²⁶ The atomic scattering factors were taken from the tabulations of Cromer and Waber; anomalous dispersion corrections for Zr and Cl were taken from Cromer.²⁷ In the full-matrix least-squares refinement, the function minimized was Σw(|F_o - |F_c||²) with the weights, w, assigned as [σ²(I) + 0.0009I²]^{-1/2}.

Zirconacycle 2. Suitable crystals of **2** were obtained by slow evaporation of a hexane solution. Crystal data for C₁₇H₂₂Zr, FW = 317.58: monoclinic, space group P2₁/c (No. 14); at -100 °C, a = 8.039(2) Å, b = 14.942(3) Å, c = 12.266(2) Å, β = 102.69(2)°, V = 1437.4 Å³, Z = 4, d_{calc} = 1.467 g cm⁻³, μ(Mo) = 7.33 cm⁻¹. All non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included as fixed contributions with an idealized C-H distance of 0.95 Å and assigned thermal parameters 1.0 greater than B_{iso}(carbon). Unfortunately, C2 and C6 were each found to be disordered over two sites. In one case, C2 is below the plane of the other atoms and C6 is above; in the other, C2' is above and C6' is below. Only one case is shown in Figure 1. The disorder was taken into account when the hydrogen positions were calculated. The refinement of 181 parameters using 2691 reflections with I > 3σ(I) converged at R = 0.027 and R_w = 0.034. The largest peak in the residual density was 0.39 eÅ⁻³, located near C21. Several other peaks, 0.30–0.37 eÅ⁻³ were also located near the Cp carbon atoms. These peaks plus the large thermal motions of the carbon atoms

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in the Cp rings are undoubtedly a reflection of the disorder of C2 and C6; through steric interactions, the Cp rings rotate to accommodate whichever carbon is closest to them. Because of the disorder, the bond distances and angles should be viewed with caution.

Zirconacycle 6. Crystals of **6** were obtained by cooling a toluene solution to -25°C . Crystal data for $\text{C}_{34}\text{H}_{34}\text{Cl}_2\text{Zr}$, FW = 716.15; monoclinic, space group $P2_1/n$ (No. 14); at -100°C , $a = 14.281(3)\text{ \AA}$, $b = 14.090(3)\text{ \AA}$, $c = 8.317(2)\text{ \AA}$, $\beta = 94.82(2)^{\circ}$, $V = 1667.6\text{ \AA}^3$, $Z = 2$, $d_{\text{calc}} = 1.426\text{ g cm}^{-3}$, $\mu(\text{Mo}) = 7.97\text{ cm}^{-1}$. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were refined with isotropic thermal parameters. The refinement of 280 parameters using 3044 reflections with $I > 3\sigma(I)$ converged at $R = 0.026$ and $R_w = 0.028$. The largest peak residual density of 0.67 e\AA^{-3} was located near C6. Several peaks, $0.4\text{--}0.6\text{ e\AA}^{-3}$, suggested that the C_7H_{12} moiety may be slightly disordered or that a trace of the trans isomer may have co-crystallized with **6**.

Preparation of trans-1,2-Bis(bromomethyl)cyclopentane (4). To a solution of 1,6-heptadiene (385 mg, 4.0 mmol) and zirconocene dichloride (1.17 g, 4.0 mmol) in THF (50 mL) at -78°C was added via syringe 1.6 M butyllithium in hexane (5.0 mL, 8.0 mmol). After 10 min the mixture was allowed to warm to room temperature and stirring was continued for 2 h. The mixture was cooled to -78°C and a solution of bromine (1.50 g, 9.4 mmol) in carbon tetrachloride (10 mL) was added. The reaction was quenched (room temperature) with 10% H_2SO_4 (50 mL), extracted into ether ($3 \times 50\text{ mL}$), washed with aqueous sodium bicarbonate and water, and dried (MgSO_4). Removal of solvent followed by flash chromatography afforded *trans*-1,2-bis(bromomethyl)cyclopentane as a colorless liquid (0.90 g, 88%). Anal. Calcd for $\text{C}_7\text{H}_{12}\text{Br}_2$: C, 32.85; H, 4.73; Br, 62.43. Found: C, 32.74; H, 4.67; Br, 62.13. ^{13}C NMR (CDCl_3): δ 23.93, 32.05, 38.05, 45.84.

Preparation of cis-1,2-Bis(bromomethyl)cyclopentane (7). To a solution of 1,6-heptadiene (385 mg, 4.0 mmol) and (pentamethylcyclopentadienyl)zirconium trichloride (1.33 g, 4.0 mmol) in THF (50 mL) at -30°C was added dropwise 0.5% sodium amalgam (40 g, 8.7 mmol). The mixture was stirred for 2 h at -20°C and 2 h at 0°C . Bromination and workup as in the preceding example afforded *cis*-1,2-bis(bromomethyl)cyclopentane as a pale yellow liquid (0.80 g, 78%). Anal. Calcd for $\text{C}_7\text{H}_{12}\text{Br}_2$: C, 32.85; H, 4.73; Br, 62.43. Found: C, 32.89; H, 4.50; Br, 62.24. ^{13}C NMR (CDCl_3): δ 22.63, 30.30, 33.97, 44.92.

Preparation of (R*,S*)-1,2-Cyclohexanedimethanol (11). *n*-Butyllithium (2.0 mL of a 2.2 M solution in hexane) was added to zirconocene dichloride (0.668 g, 2.28 mmol) and 1,7-octadiene (0.28 mL, 1.90 mmol) in toluene (5.9 mL) at -78°C . The reaction turned a pale yellow color. After 10 min the cooling bath was removed and the reaction was permitted to warm to room temperature. Stirring was continued for 22 h. During this time the reaction turned an orange tea color. The mixture was chilled to 0°C and a stream of O_2 was bubbled through the stirred reaction mixture for 5 min. The reaction turned a white, opaque color. The reaction was quenched with a 1:1 solution of 5% aqueous H_2SO_4 /saturated aqueous Na_2SO_4 (20 mL), extracted with ether ($6 \times 10\text{ mL}$), and dried (Na_2SO_4). The organic extract was concentrated and chromatographed to yield a 75:25 *cis*:*trans* mixture of diols **11** and **12** (0.197 g, 72% yield) as a colorless oil, TLC $R_f = 0.16$ (40% EtOAc/petroleum ether). The data for **11** were consistent with commercially available material. ^1H NMR δ 3.85 (bs, 2H), 3.78–3.69 (m, 2H), 3.58–3.51 (m, 2H), 1.96–1.88 (m, 2H), 1.56–1.37 (m, 8H). ^{13}C NMR: for **u** δ 63.7, 27.0, 23.8; for **d** δ 39.8. IR (cm^{-1}): 3324, 2925, 2888, 1476, 1451, 1336, 1288, 1098, 1045, 1021. MS (m/z , %): 126 (8), 96 (100), 95 (66).

Preparation of (R*,R*)-1,2-Cyclohexanedimethanol (12). *n*-Butyllithium (4.09 mL of a 2.16 M solution in hexane) was added dropwise over 5 min to zirconocene dichloride (1.29 g, 4.42 mmol) and 1,7-octadiene (414 mg, 3.68 mmol) in toluene (14 mL) at -78°C . After 15 min the cooling bath was removed and the reaction was heated in an oil bath at 75°C for 2 h. Subsequently, the reaction was chilled to 0°C and a gentle stream of O_2 was bubbled through the stirred reaction mixture for 90 min. During this time the reaction lightened to a yellow color, with some solids precipitating. The solids were broken up by the addition of sodium borohydride (418 mg, 11 mmol) in 95% ethanol (1 mL) at 0°C , and the mixture was stirred at room temperature overnight. The reaction was quenched with a 1:1 solution of 5% aqueous H_2SO_4 /saturated aqueous Na_2SO_4 (40 mL) and extracted with EtOAc ($5 \times 30\text{ mL}$). The organic layers were dried (Na_2SO_4), concentrated, and chromatographed to give the *trans* diol **12** (454 mg, 87% yield) as a white solid, mp = $51\text{--}53^{\circ}\text{C}$

(lit.²⁸ mp = $51\text{--}52^{\circ}\text{C}$), TLC $R_f = 0.16$ (40% EtOAc/petroleum ether). ^1H NMR: δ 4.61 (bs, 2H), 3.60 (dd, $J = 2.4, 11.1\text{ Hz}$, 2H), 3.48 (dd, $J = 6.2, 11.1\text{ Hz}$, 2H), 1.74–1.59 (m, 4H), 1.33–1.15 (m, 4H), 1.07–0.99 (m, 2H). ^{13}C NMR: for **u** δ 67.4, 29.7, 26.0; for **d** δ 44.5. IR (cm^{-1}): 3296, 2924, 2853, 1447, 1089, 1060, 1018, 969. MS (m/z , %): 126 (8), 96 (94), 95(73); HRMS for $\text{M} + 1\text{ C}_8\text{H}_{17}\text{O}_2$: calcd 145.1234, obsd 145.1226. Anal. Calcd for $\text{C}_8\text{H}_{16}\text{O}_2$: C, 66.63; H, 11.18. Found: C, 66.96; H, 11.29.

Preparation of 1-(3-Buten-1-yl)-2-cyclohexen-1-ol (14). The Grignard reagent prepared from 4-bromo-1-butene (5.0 mL, 49.2 mmol) and magnesium (1.2 g, 49.4 mmol) in THF (90 mL) was chilled to 0°C and 2-cyclohexen-1-one (3.87 mL, 40.0 mmol) was added as a solution in THF (10 mL) over 15 min. The mixture was warmed to reflux for 30 min and then poured into saturated aqueous NH_4Cl (50 mL) and extracted with ether ($3 \times 80\text{ mL}$). The combined organic layers were dried (K_2CO_3), concentrated, and chromatographed to give the unstable tertiary alcohol **14** (0.997 g, 16% yield) as a colorless oil, TLC $R_f = 0.27$ (10% EtOAc/petroleum ether), that decomposed in CDCl_3 overnight. ^1H NMR (benzene- d_6): δ 5.91–5.75 (m, 1H), 5.50–5.48 (m, 2H), 5.10–4.94 (m, 2H), 2.23–2.12 (m, 2H), 1.75–1.33 (m, 9H). ^{13}C NMR (benzene- d_6): for **u** δ 114.7, 69.6, 42.4, 36.4, 28.8, 26.0, 19.8; for **d** δ 140.0, 134.0, 129.6. IR (cm^{-1}): 3395, 3079, 3023, 2938, 2868, 2833, 1638, 1455, 1441, 1166, 1089, 998, 963, 913. MS (m/z , %): 152 (0.5), 134 (21), 111 (6), 109 (5), 106 (9), 105 (10), 98 (32), 97 (100). HRMS for $\text{C}_{10}\text{H}_{16}\text{O}$: calcd 152.1201, obsd 152.1222.

Preparation of Alcohol 19. *n*-Butyllithium (2.5 mL of a 2.2 M solution in hexane) was added to zirconocene dichloride (0.569 g, 1.95 mmol) and diene **14** (0.246 g, 1.62 mmol) in toluene (2.5 mL) at 0°C . The reaction turned an orange color immediately. After 10 min the cooling bath was removed, and stirring was continued for 24 h at room temperature. Prior to exposing the reaction mixture to air on workup, the reaction was quenched with a 1:1 solution of 5% aqueous H_2SO_4 /saturated aqueous Na_2SO_4 (20 mL). The quenched reaction mixture was extracted with ether ($8 \times 10\text{ mL}$) and dried (Na_2SO_4). The organic extract was concentrated and chromatographed to give the bicyclic alcohol **19** (0.100 g, 40% yield) as a colorless oil, TLC $R_f = 0.30$ (10% EtOAc/petroleum ether). ^1H NMR: δ 1.90–1.77 (m, 2H), 1.69–1.25 (m, 13H), 1.00 (d, $J = 6.3\text{ Hz}$, 3H). ^{13}C NMR: for **u** δ 79.2, 38.9, 35.0, 29.5, 24.0, 22.1, 21.2; for **d** δ 52.8, 34.3, 20.9. IR (cm^{-1}): 3423, 2931, 2868, 1448, 1377, 1356, 998. MS (m/z , %): 154 (6), 139 (35), 125 (89), 111 (32), 98 (100). HRMS for $\text{C}_{10}\text{H}_{16}\text{O}$: calcd 154.1358, obsd 154.1351.

Cyclization of *N,N*-Diallylaniline. A mixture of zirconocene dichloride (1.17 g, 4.0 mmol), *N,N*-diallylaniline (0.69 g, 4.0 mmol), tetradecane internal standard (0.25 g), and THF (50 mL) was cooled to -78°C . Then 1.6 M butyllithium (5.0 mL, 8 mmol) was added via syringe and the mixture was allowed to warm to room temperature. Samples (5.0 mL) were withdrawn after 1 and 2 h and quenched with 10% sulfuric acid (2.5 mL) under nitrogen. After 2 h the reaction mixture was heated at reflux (65°C) and additional samples were withdrawn at 3, 4, and 5 h. The samples were made basic with 10% potassium hydroxide (10 mL) and extracted into ether (20 mL) whereupon the ether phase was analyzed by gas chromatography. The observed *cis*/*trans* ratios (times, h) were 2.63 (1), 2.65 (2), 0.58 (3), 0.41 (4), 0.41 (5). Monitoring the total integration of the product peaks versus the internal standard indicated less than 20% decomposition of metallacycles **21** and **22** after 5 h.

Density Functional Theory Calculations. The density functional theory calculations were done with the program DGauss²⁹ which employs Gaussian orbitals on a Cray YMP computer. Calculations were done with all electron basis sets³⁰ of the following form: (41) for H, (621/41/1) for C, (6321/411/1) for Cl, and (633321/53211/531) for Zr. This corresponds to a polarized double- ζ valence basis set for all of the heavy atoms and a double- ζ basis set for H. The fitting basis sets for the electron density and the exchange-correlation potential have the following form: [4] for H, [7/3/3] for C, [9/4/4] for Cl, and [10/5/5] for Zr. The calculations were done at the self-consistent gradient corrected (non-

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local) level with the non-local exchange potential of Becke²² together with the non-local correlation functional of Perdew.²³ The local potential fit of Vosko, Wilk, and Nusair³¹ was used. The geometries were optimized by analytic gradient methods.^{29,32}

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society,

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for partial support of this work. We thank M. D. Bruch, G. Erker, H.-H. Brintzinger, and E.-i. Negishi for helpful discussions.

Supplementary Material Available: ¹H and ¹³C NMR spectra for compounds **12** and **19**; tables of atomic coordinates, anisotropic thermal parameters, and complete interatomic distances and angles for **2** and **6** (11 pages); tables of structure factor amplitudes for **2** and **6** (15 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the Journal and can be ordered from the ACS; see any current masthead page for ordering information.