How can one have a relatively strong "bond" without much bonding character? This question is being explored by calculating the energy changes on stretching the central bond in the propellane by using the GVB formalism,[27] which allows correct dissociation, as well as by both a theoretical and experimental study of the molecular vibrations of the [1.1.1]propellane. The results of these investigations will be reported at a later time.

Calculations

The calculations were carried out with the program GAMESS[28] along with standard basis sets.[14] The geometry optimization criterion for the smaller compounds was 0.0005 H/Bohr, whereas for the larger compounds it was 0.001 H/Bohr. In the tables, the basis set for the calculation is given above the line, and that used for the optimization is given below the line.

Acknowledgment. This investigation was supported by NSF Grant CHE-81-21421. The computer was obtained with the aid of grants from the NSF (CHE-80-23366) and the Dreyfus and Heyl Foundations.

Registry No. [1.1.1]Propellane, 35634-10-7; [2.1.1]propellane, 36120-91-9; [2.2.1]propellane, 36120-90-8; [2.2.2]propellane, 36120-88-4; ethane, 74-84-0; butane, 106-97-8; cyclopropane, 75-19-4; cyclobutane, 287-23-0; bicyclo[1.1.0]butane, 157-33-5; bicyclo[2.1.0]pentane, 185-94-4; bicyclo[2.2.0]hexane, 186-04-9; hydrogen, 1333-74-0; methane, 74-82-8; propane, 74-98-6; cyclopentane, 287-92-3; cyclohexane, 110-82-7; bicyclo[1.1.1]pentane, 311-75-1; bicyclo[2.1.1]hexane, 285-86-9; bicyclo[2.2.1]heptane, 279-23-2; bicyclo[2.2.2]octane, 280-33-1.

(27) Bobrowicz, F. W.; Goddard, W. A. *Mod. Theor. Chem.* **1978**, *3*.
(28) Dupuis, M.; Spangler, D.; Wendoloski, J. J. National Resource for Computation in Chemistry Program QG01, 1980. The program is based on HONDO: Dupuis, M.; Rys, J.; King, H. *QCPE* **1977**, *11*, 338.

Carbon–Carbon Bond Formation by Condensation of Metal-Activated Olefins. Regio- and Stereoselectivity of Cycloaddition Reactions

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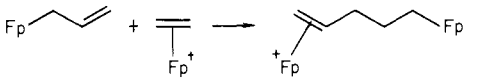
Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254. *Received April 27, 1982*

Abstract: Monodeprotonation of $Fp_2(\eta^2,\eta^2$-1,7-octadiene$)(BF_4)_2$ [**4**, Fp = $C_5H_5Fe(CO)_2$] at 0 °C with *n*-Bu_3N leads to the formation of the trans-1,2-disubstituted cyclopentane complex **6**-t as the major product. Evidence is provided that this is the kinetic product. The structure of **6**-t is established by degradation to *trans*-1-methyl-2-vinylcyclopentane and by comparison of this with synthetic material. By contrast, the homologous 1,8-nonadiene complex **11** is converted to a 1:1 mixture of cis- and trans-1,2-disubstituted cyclohexane complexes **13**-c and **13**-t on treatment with *n*-Bu_3N. The structures of these complexes were also established by degradation and synthesis. The relationship between geometrical isomerism in the intermediate dinuclear complexes **5** and **12**, generated by deprotonation of **4** and **11**, and the stereochemistry of the product complexes **6** and **13** have been examined. The synthesis of cis and trans isomers of **5** and **12** has been accomplished through monoprotonation of the related *cis,cis*- and *trans,trans*-octadiene and -nonadiene complexes **17** and **18**. Protonation of **17**-t gave almost entirely **6**-t, while similar treatment of **17**-c led to the formation of a mixture of **6**-c and **6**-t in low yield. The behavior of the homologous diene complexes **18**-c and **18**-t was substantially different. Monoprotonation of **18**-c gave a 3:1 mixture of **13**-c and **13**-t, while protonation of **18**-t gave a 2:1 mixture of **13**-t and **13**-c. These are minimum measures of the stereoselectivities for these reactions since recovered starting material is partially isomerized. The results may be accommodated if the cyclization reaction is initiated by preferential interaction of the proton with *both* activated olefin centers in an extended form of complexes **17** and **18**. This results in the generation of transition state III from **18**-c and of II′ from **18**-t, which in turn leads to the formation of cyclization products **13**-c and **13**-t, respectively.

Polyene cyclization is now well established as an important step in the biogenesis of terpenes, and an extensive literature concerned with the mechanism and synthetic applications of polyene cyclization and of the closely related ene reaction exists.[1] Within this class of reaction may be included the large number of transition-metal-catalyzed polyene cyclizations,[2] although a detailed mechanism for some of these reactions is as yet undefined. For those cyclization reactions which proceed through well-defined ionic intermediates the methodologies by which initiating electrophile centers are generated and by which ultimate cationic centers are quenched have been classical ones. However, we have shown that olefins may be activated as nucleophilic centers or transformed to electrophilic centers through allylic substitution by the $C_5H_5Fe(CO)_2$ group or by π complexation with the $C_5H_5Fe(CO)_2$ cation.[3] The olefin components so activated undergo a rapid condensation at room temperature, in a reaction which may be regarded as an analogue of a classical ionic condensation (eq 1, Fp = $C_5H_5Fe(CO)_2$).

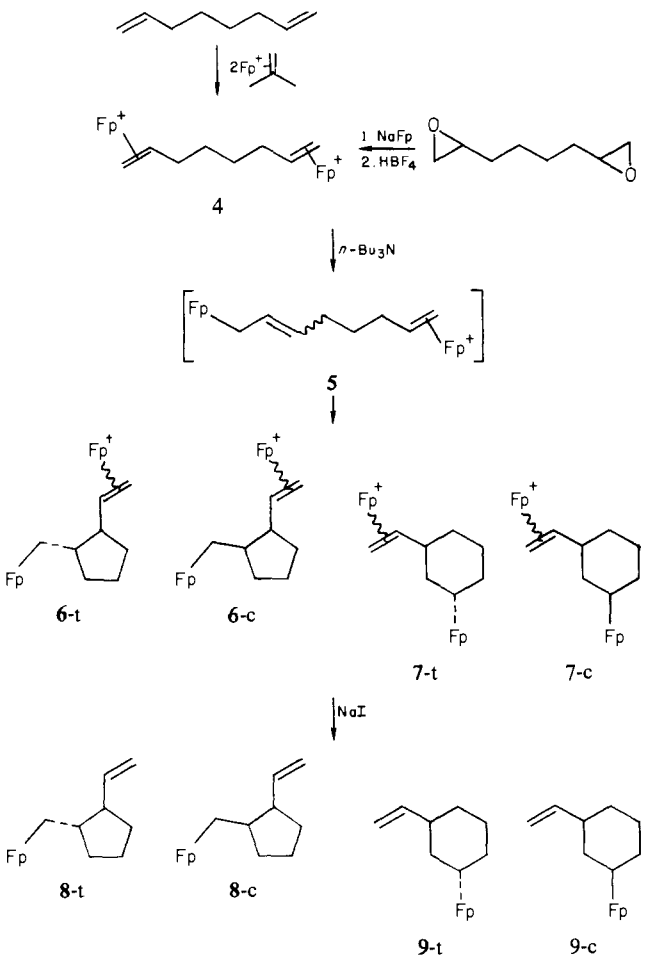


(1)

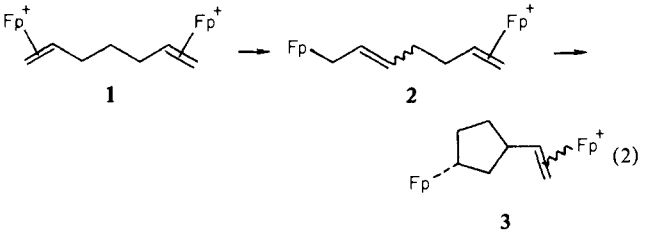
(1) For a recent review, with leading references, see: Sutherland, J. K. *Chem. Soc. Rev.* **1980**, *13*, 426.
(2) Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1975; Vol. II, Chapter III. Tsuji, J. "Organic Synthesis by Means of Transition Metal Complexes"; Springer-Verlag: Berlin, 1975; Chapter VII. Baker, R.; Cookson, R. C.; Vinson, J. R. *J. Chem. Soc., Chem. Commun.* **1974**, 575. Davis, R. E.; Dodds, T. A.; Hseu, T.-H.; Wagnon, J. C.; Devon, T.; Tancrede, J.; McKennis, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1974**, *96*, 7562. Davis, R.; Green, M.; Hughes, R. P. *J. Chem. Soc., Chem. Commun.* **1975**, 405. Paquette, L. A.; Ley, S. V.; Maiorana, S.; Schneider, D. F.; Broadhurst, M. J.; Boggs, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 4658.
(3) Lennon, P. J.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Waterman, P. *J. Am. Chem. Soc.* **1980**, *102*, 7033.

0002-7863/83/1505-1233$01.50/0

Scheme I



The related intramolecular process has been examined with the diene complex **2**, derived by deprotonation of the heptadiene complex **1**, and was shown to give **3** in moderate yield as the exclusive product (eq 2).



In order to examine the generality of the reaction and its regio- and stereoselectivity as a function of both chain length and the stereochemistry at the (η^1-allyl)Fp donor center, we have now extended these studies to several homologous dienes.

Results and Discussion

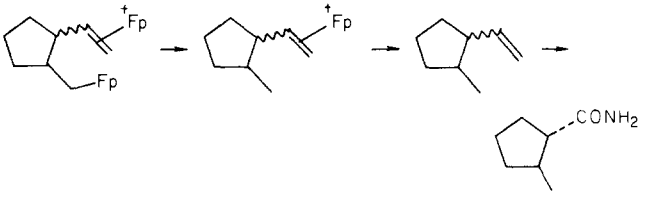
The 1,7-octadiene complex **4** is readily available, either from the diene by exchange complexation with Fp(η^2-isobutylene)BF_4[4] or through the diepoxide[5] (Scheme I). Both routes gave good yields of **4**, but the latter is better suited to large scale (20 g) preparations. Deprotonation of **4** with tri-*n*-butylamine at 0 °C in nitromethane solution yields the reactive intermediate **5**, which spontaneously cyclizes. Selective demetallation of the complex by brief exposure to sodium iodide in acetone solution gave a product that appeared to be very largely a single species, as indicated by the presence of a single cyclopentadienyl proton signal in its NMR spectrum. The presence of a vinyl group, consistent with structures **8** and **9** is also clearly evidenced by one- and two-proton multiplet signals at δ 5.72 and 5.03. ^{13}C spectra provided grounds for a more definitive structural assignment. The presence of a high-field signal at δ 8.01, which appears as a triplet in the off-resonance decoupled spectrum, is particularly significant. Such a highly shielded methylene carbon atom is characteristic of one bonded directly to an Fp group. The methyl carbon atom in $FpCH_3$ is similarly shielded (δ −23.5)[6] compared to that in methane (δ 2.1).[7] By contrast, methine carbon atoms bonded

Table I. ^{13}C NMR Chemical Shifts of Carbons α and β to the Fp Group

compound		chemical shift,[a] δ α	β	ref
CH_3CH_3		5.9		*d*
Fp—		−2.41	22.63	*c*
$CH_3CH_2CH_3$		15.6	16.1	*d*
Fp—		7.08	32.17	*c*
Fp—	$n = 1$	11.00	20.13	*c*
	$n = 4$	11.10	44.0	*c*
Fp—		5.11		*c*
Fp— R O	R = H	1.43	42.46	9
	R = Me	7.51[b]	47.40	9
		9.92	50.94	
	R = Ph	5.22[b]		9
		9.88	52.80	
Fp— CN COOEt		4.03[b]	41.81	9
		7.09	41.22	
Fp— CHO		4.42	43.82	9
Fp—		15.80	33.03	*c*
Fp— Ph		22.04	28.41	9
			52.86	
		26.5		*e*
Fp— R R	R = H	23.69	41.36	*c*
	R = $CH(COOMe)_2$	26.53		9
Fp—		23.37	40.59	3
			49.91	
Fp—		22.01	42.66	3
			47.38	

[a] In ppm downfield from internal Me_4Si; solvent CD_3NO_2. [b] Pair of diastereomers. [c] This work. [d] Reference 7, p 56. [e] Reference 7, p 60.

Scheme II

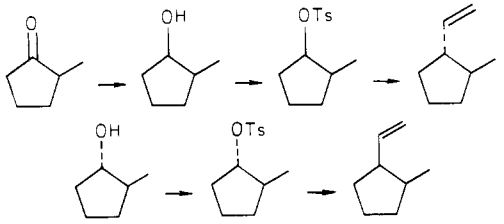


(4) Giering, W. P.; Rosenblum, M. *J. Chem. Soc., Chem. Commun.* **1971**, 441. Cutler, A.; Ehntholt, D.; Lennon, P.; Nicholas, K.; Marten, D. F.; Madhavarao, M.; Raghu, S.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1975**, *97*, 3149.

(5) Giering, W. P.; Rosenblum, M.; Tancrede, J. *J. Am. Chem. Soc.* **1972**, *94*, 7170.

(6) Farnell, L. F.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc. D* **1971**, 1078.

Scheme III



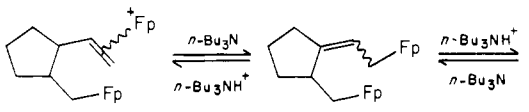
to an Fp group are comparatively unaffected, while methylene carbon atoms β to the Fp group appear to be deshielded. Data relevant to these observations are collected in Table I.[8]

The major product from the cyclization reaction may consequently be formulated as a vinylcyclopentane complex (**6**-c or **6**-t). The presence of two minor products is also evident from inspection of the ^{13}C spectrum of the partially demetallated reaction mixture. One of these shows high-field resonance at δ 5.33 and is therefore stereoisomeric with the major product, while the second, lacking high-field absorption, is tentatively assigned structure **9**-c or **9**-t. These latter substances comprise 5–10% and 10–15%, respectively, of the total product.

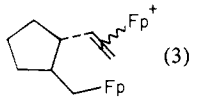
The stereochemistry of the principal cyclization product was determined by degradation as shown in Scheme II. Successive treatment of the reaction product with gaseous HCl in methylene chloride followed by tetra-*n*-butylammonium iodide gave the parent hydrocarbon. We had earlier shown that similar dinuclear complexes incorporating σ- and π-bound Fp groups could be selectively demetallated,[3,10] and the sequence of these steps was chosen to take advantage of the protection provided the olefin center by π complexation during protonolysis of the σ-bound Fp group. Ozonolysis of the product olefin and conversion of the resulting acid to the amide gave a product whose melting point was in accord with that reported for *trans*-2-methylcyclopentanecarboxamide.[11] Final confirmation of the stereochemistry of the cyclization product was obtained by synthesis of both *cis*- and *trans*-2-vinyl-1-methylcyclopentane as shown in Scheme III.

Reduction of 2-methylcyclopentanone with L-Selectride (Aldrich) gave *cis*-2-methylcyclopentanol.[12] Tosylation, followed by treatment with lithium divinylcuprate gave *trans*-1-methyl-2-vinylcyclopentane. Similar treatment of *trans*-2-methylcyclopentanol gave the cis isomer. A comparison of the ^1H NMR spectra of the synthetic materials with the demetallated cyclization product showed unequivocally that it was *trans*-1-methyl-2-vinylcyclopentane.

At this point, we considered the possibility that the preponderance of the trans product **6**-t in the cyclization reaction might be the consequence of thermodynamic control operating through the equilibrium



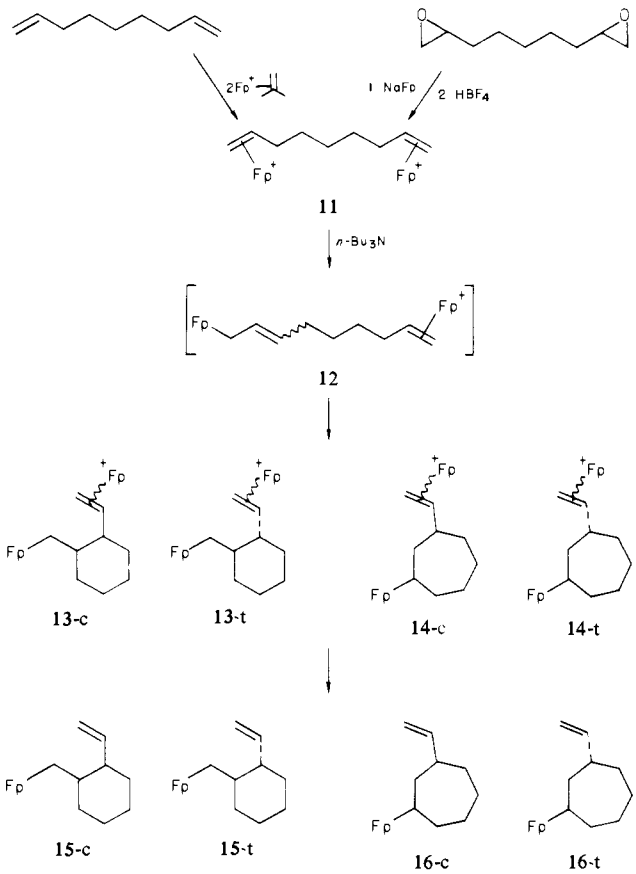
6-c 10



(3)

6-t

Scheme IV



11 12 13-c 13-t 14-c 14-t 15-c 15-t 16-c 16-t

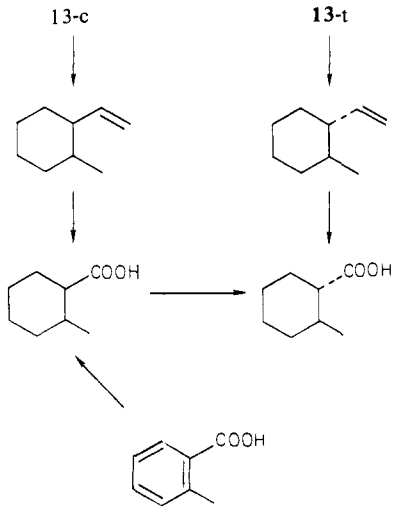
In an attempt to generate complex **10**, the uncharged member of this equilibrium, we treated product **6**-t with tri-*n*-butylamine. However, the product was instead the partially demetallated complex **8**-t. The failure of **6**-t to undergo allylic deprotonation, a process that is generally facile and complete for Fp(olefin) cations in the presence of tertiary amines, is most likely due to the relatively hindered nature of the allylic proton in this complex. The corresponding cis product **6**-c would not be expected to be resistant to allylic deprotonation, and its conversion through deprotonation and reprotonation might therefore provide a pathway for isomerization to the more stable trans isomer **6**-t. This can be ruled out. When cyclization of **4** is carried out with tri-*n*-butylamine in the presence of a large excess of tri-*n*-butyl-*N*-deuterioammonium tetrafluoroborate, the product **6**-t showed no incorporation of deuterium. Thus **6**-t is formed directly from the intermediate dinuclear complex **5**, in a kinetically controlled process.

We next extended these studies to cyclization of the homologous nonadiene complex **11**. As shown in Scheme IV, such cyclization can in principle yield two stereoisomeric cyclohexane or cycloheptane products. As before, the requisite dinuclear complex **11** is available either by an exchange reaction of 1,8-nonadiene with Fp (isobutylene)BF_4, or more conveniently, for large scale work, through NaFp opening of the diene diepoxide. Treatment of **11** with tri-*n*-butylamine in nitromethane at 0 °C for 1 h, followed by partial demetallation of the product with sodium iodide in acetone solution, gave a mixture of neutral, mononuclear complexes in 45% yield. This was shown to be comprised of principally two products in approximately equal amounts plus a minor component. The presence of two high-field resonances at δ 6.18 and 9.10 in the ^{13}C NMR spectrum of the product, both of which appear as triplets in the off-resonance decoupled spectrum, suggests that these substances are **15**-c and **15**-t. This was confirmed by degradative experiments.

Sequential treatment of the cyclization product with gaseous HCl in methylene chloride and then with tetra-*n*-butylammonium iodide in the same solvent, followed by preparative gas chroma-

(7) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 56.
(8) These α and β effects find a close parallel in the related alkyl iodides: α-methylene carbon atoms in primary alkyl iodides are shielded, β-carbon centers are deshielded, and α-methine centers are deshielded, ref 7, p 133, and Marker et al. (Marker, A.; Doddrell, D.; Riggs, N. V. *J. Chem. Soc., Chem. Commun.* **1972**, 724).
(9) Lennon, P.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8426.
(10) Rosan, A.; Rosenblum, M.; Tancrede, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 3062.
(11) Brook, P. R.; Duke, A. J. *J. Chem. Soc. C* **1971**, 1764.
(12) Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1972**, *94*, 7159.

Scheme V



tographic separation of the components, gave two products in a ratio of 1:1.35. Both of these exhibited an ABX set of vinyl protons in addition to a methyl doublet signal in their NMR spectra, consistent with their assignment as stereoisomeric 1-methyl-2-vinylcyclohexanes. Their ^{13}C NMR spectra confirm these assignments and allow the assignment of trans stereochemistry to the more abundant product, since its methylene carbon atoms are all deshielded relative to those in the isomeric component.[13]

Finally, each of these products was ozonized and converted to isomeric 2-methylcyclohexanecarboxylic acids. These were in turn unequivocally identified by comparison with authentic synthetic samples. The cis acid was prepared by hydrogenation of *o*-toluic acid and the trans acid by base-catalyzed isomerization of this (Scheme V).

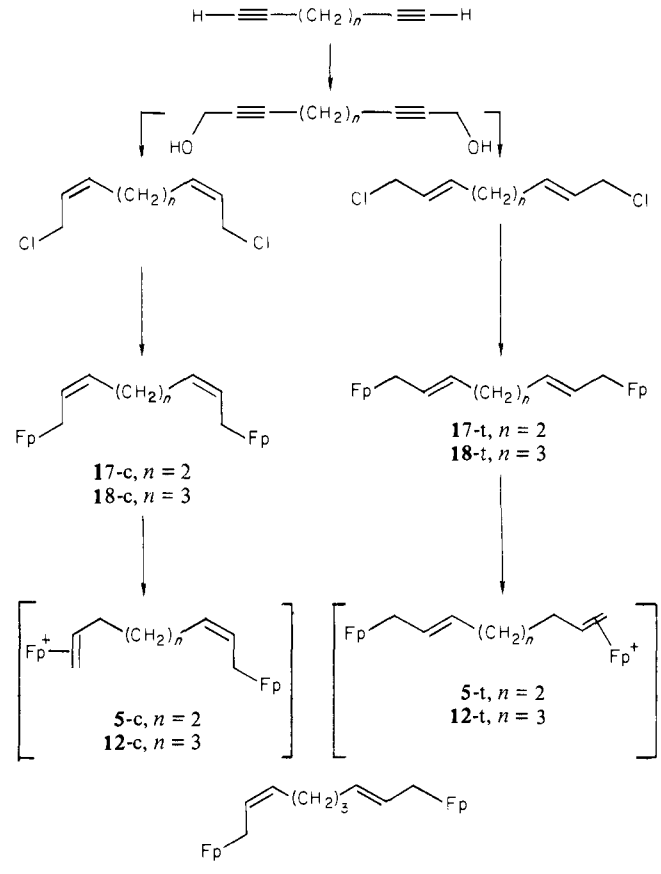
Thus, cyclization of the nonadiene complex **11**, like that of the octadiene complex **4**, is regioselective, but in contrast to **4**, which gave largely a trans-1,2-disubstituted ring, complex **11** shows little stereoselectivity. These results led us to consider what relationship if any existed between the geometrically isomeric intermediate complexes **5** and **12**, generated by deprotonation of **4** and **11**, and the stereochemistry of the product complexes **6** and **13**. We had earlier shown that deprotonation of the Fp(1-butene) cation gave a mixture of *cis*- and *trans*-1-Fp-2-butene,[15] and it seemed plausible therefore to anticipate that deprotonation of **4** or **11** would lead to similar mixtures of geometrical isomers. We therefore sought to examine this point through the synthesis of stereochemically well-defined intermediate complexes **5** and **12**.

Scheme VI sumarizes the synthetic routes used for the preparation of cis and trans isomers of **5** and **12**. In each sequence the diyne starting material was homologated by conversion to the diacetylide with butyllithium and condensation with paraformaldehyde. The diyne–diol was then reduced stereospecifically either with Lindlar catalyst or sodium in liquid ammonia, and the resulting isomeric diene–diols were then converted to the corresponding dichlorides with *N*-chlorosuccinimide and dimethyl sulfide.[14] Metallation of these with NaFp gave the corresponding *cis,cis*- and *trans,trans*-octadiene and -nonadiene complexes **17**-c,t and **18**-c,t.

Cyclization of the trans,trans-diene complex **17**-t was effected by treatment with 1 mol equiv of tetrafluoroboric acid etherate in methylene chloride at 0 °C for 17 min. The crude product (68%) was precipitated by addition of ether and then partially demetallated by brief exposure to sodium iodide in acetone solution. Final purification by chromatography on alumina gave a product shown to be almost entirely the *trans*-vinylcyclopentane complex **8**-t by examination of its ^{13}C NMR spectrum. A small

(13) Wehrli, R. W.; Wirthlin, T. "Interpretation of Carbon-13 Spectra"; Heyden: London, 1978; p 37.
(14) Corey, E. J.; Kim, C. U.; Takeda, M. *Tetrahedron Lett.* **1972**, 4339.

Scheme VI



19

amount (ca. 5%) of a cyclohexane complex, **9**-c or **9**-t, is present in the product, but none of the *cis*-vinylcyclopentane complex was evident.

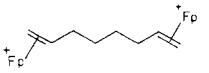
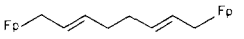
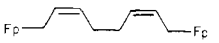
By contrast, similar protonation of the cis,cis complex **17**-c gave a mixture of **8**-c, **8**-t, and either **9**-c or **9**-t in relatively low yield (29%). The ratio of these, on the basis of integrated olefinic carbon resonances, is estimated to be 6.5:2.5:1.

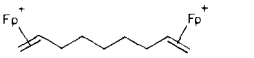
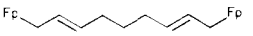
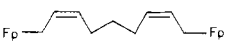
The factors responsible for the relatively poor yield of cyclization product from the reaction are not clear but may reflect unfavorable steric interactions in the intermediate monocationic complex **5**-c. The lower stereoselectivity of this reaction compared with that involving **5**-t could be due to partial isomerization of starting material competitive with cyclization. However, when incomplete protonation of **17**-c was carried out, no isomerization of recovered starting material was observed. This result does not however exclude isomerization of intermediate **5**-c through intramolecular proton exchange followed by cyclization.

The behavior of the homologous isomeric diene complexes **18**-c and **18**-t was substantially different. Monoprotonation of **18**-t, followed by demetallation with sodium iodide gave a mixture of cyclized products in 48% yield, in addition to 23% of recovered 1,9-Fp_2-2,7-nonadiene complexes. A ^{13}C NMR spectrum of the product showed it to be composed of **15**-t and **15**-c in a ratio of 2:1, in addition to a smaller amount of a complex, possibly **16**-c or **16**-t, identical with that obtained from deprotonation of complex **11**. If one corrects for the amount of neutral dinuclear complex recovered in this reaction and the fact that an equivalent amount of dicationic complex must consequently also be generated, the yield of **15**-t and **15**-c is estimated to be 70%.

Similar protonation of the *cis,cis*-nonadiene complex **18**-c, followed by demetallation, gave a mixture of **15**-c and **15**-t (3:1) in 41% yield. None of the complex of unknown structure was evident in this product, but as before, 20% of the product consisted of 1,9-Fp_2-2,7-nonadiene complexes. These results, together with those derived from the related cyclizations of the dicationic complexes are summarized in Table II.

Table II. Cyclization Products[a]

reactant	initiator	products		
	n-Bu_3N	52	4	6
	HBF_4	55		5
	HBF_4	19	7	3

reactant	initiator	products	
	Bu_3N	22	22
	HBF_4	24	12
	HBF_4	10	31

[a] After treatment of the initial product with sodium iodide.

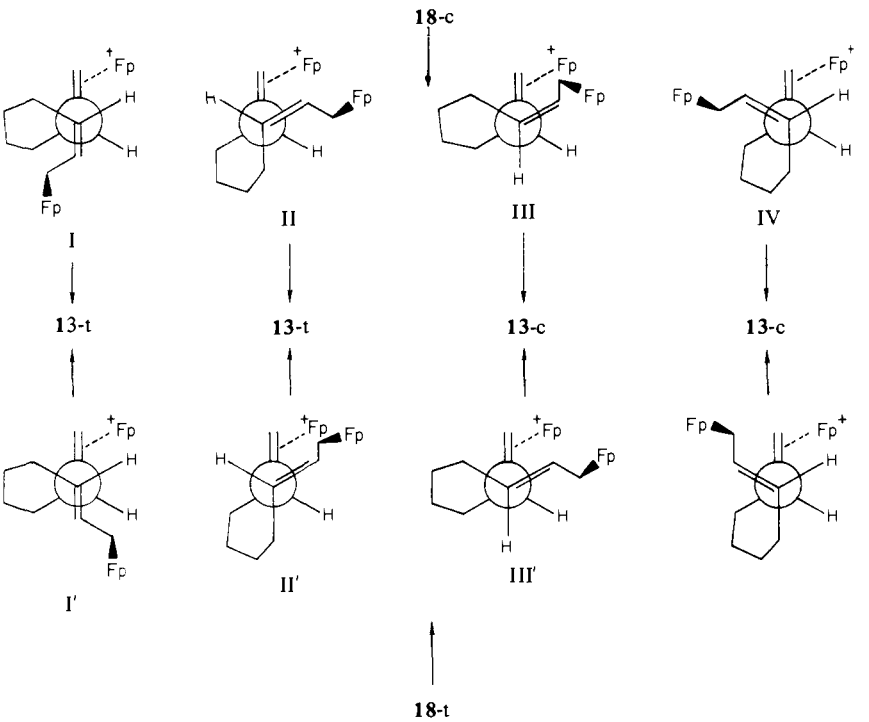


Figure 1.

It is important to note at this point that the observed stereoselectivities for the cyclization of **18**-c and **18**-t must be minimum measures of their actual values since the neutral 1,9-Fp_2-2,7-nonadiene complexes recovered from these reactions are substantially isomerized starting materials. Thus the ^{13}C NMR spectrum of the nonadiene complex recovered from cyclization of **18**-c shows it to be a mixture of **18**-c and **18**-t, and in addition, three methylene carbon resonances not present in either of these dienes are observed. These may be assigned to the cis,trans isomer **19**. The remaining resonances for this complex are apparently very close to those found in the isomeric complexes of related geometry. Similarly, unreacted nonadiene complex recovered from the cyclization of **18**-t was found to be mixed with about 30% of the cis,trans isomer **19**.

The factors responsible for the stereoselection observed in the cyclization of **17**-t, **18**-t, and **18**-c are not easily identified. There is considerable evidence that nucleophilic additions to Fp(η^2-olefin) cations[9] and electrophilic attack on Fp(η^1-allyl) complexes[15] takes place preferentially trans to the activating metal–carbon bond for each complex. Condensation of these complexes with one another may be expected to follow a similar stereochemical course, and the transition state associated with each dinuclear reactant is capable of existing in any of four possible diastereomeric forms. These are depicted in Figure 1 for intermediates **12**-c and **12**-t,

(15) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosemblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495.

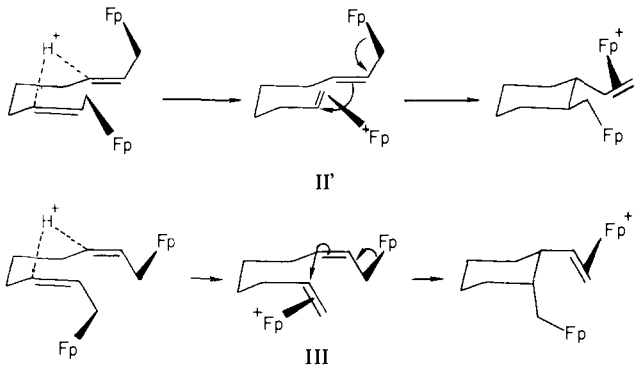


Figure 2.

derived from **18**-c and **18**-t. Steric factors that might contribute to the preference of one of these over the others are not evident. However, if proton transfer to an extended form of the bis(allyl) complex takes place stereoselectively through preferential interaction of the electrophile with *both* activated olefin centers, then transition state III is generated from **12**-c and transition state II' from **12**-t. This is depicted in Figure 2.

This hypothesis suggests that by using an electrophile other than a proton, it should be possible to establish a third chiral carbon center stereospecifically with respect to the other two on the ring. This point remains to be examined.

The application of Baldwin's rules for ring closure[16] to these organometallic reactions is at best problematic. If one regards the cationic site in the reactants as approximating that of a trigonal acceptor center, then the formation of **3** from **2** is at variance with the rules, which generally disfavor 5-endo trigonal reactions. But it should be noted that the corresponding 5-exo process for **2**, which would yield a cyclobutane, has not been observed for the related 1,4-hexadiene complex[3] where this is the only possible mode of cyclization. The cyclization of octadiene and nonadiene complexes conforms to the rules, but for these reactions the rules are not restrictive and allow for either 5- or 6-endo cyclization for **5** and 6- or 7-endo cyclization for **12**. Hence these ring closure reactions do not provide a test of Baldwin's rules.

In conclusion, the cyclization of 1,7-octadiene or 1,8-nonadiene, through either deprotonation of the dicationic $Fp_2(\eta^2,\eta^2$-diolefin) complex or protonation of the derived $Fp_2(\eta^1,\eta^1$-diolefin) complex, yields 1,2-disubstituted cyclopentane and cyclohexane complexes, respectively. The reactions appear to be kinetically controlled, and reaction stereoselectivity is shown to depend on the stereochemistry of the metal η^1-allyl ligand and possibly as well on the relative chirality of the metal π-complexed olefin center in the monocationic intermediate.

Further investigations related to the detailed mechanism of these organometallic cyclizations and their application in synthesis are being pursued.

Experimental Section

Solvents were routinely dried by standard procedures and stored under nitrogen.

All organometallic reactions and subsequent manipulations including reagent additions, filtrations, extractions, recrystallizations, and chromatographies as well as the preparation of NMR samples and solution IR samples were conducted under a nitrogen atmosphere.

Infrared spectra were recorded on Perkin-Elmer spectrophotometers Models 137 and 457. ^{1}H NMR spectra were recorded on the following spectrometers: Varian A-60 (NIH GM-13183), Perkin-Elmer R-32 (NSF GU 3852), Bruker WH-90 (NSF GU 3852, GP 37156). ^{13}C NMR spectra were determined at 22.62 MHz on the latter instrument. Both ^{1}H and ^{13}C chemical shifts are reported relative to internal tetramethylsilane (Me_4Si) at $\delta = 0$ with increasingly positive numbering to increasingly lower field of Me_4Si. ^{13}C NMR spectra were collected with broad-band proton decoupling for determination of chemical shifts and with single-frequency off-resonance proton decoupling for the determination of multiplicity.

Melting points were determined under a nitrogen atmosphere on a Kofler hot stage equipped with a polarizing microscope and are uncorrected.

Elemental analyses were determined by Galbraith Labs, Inc., Knoxville, TN.

Preparation of $Fp_2(\eta^2,\eta^2$-1,7-octadiene)$(BF_4)_2$ (4). A. From 1,7-Octadiene. 1,7-Octadiene (0.44 g, 4.0 mmol) and $Fp[\eta^2$-isobutylene$]BF_4$ (2.60 g, 8.15 mmol) were dissolved in 80 mL of 1,2-dichloroethane. While the solution was stirred, the temperature was brought to 60 °C and maintained between 60 and 63 °C for 21 min. During this period a precipitate formed. After cooling, excess ether was added to complete precipitation. The solid was filtered and washed with methylene chloride until the filtrate was colorless. Reprecipitation from a concentrated nitromethane solution by the careful addition of small volumes of ether until no additional precipitation occurred, gave, after washing the yellow solid with methylene chloride, 1.78 g, 69.5% of product.

B. From 1,2,7,8-Diepoxyoctane. A solution of 1,2,7,8-diepoxyoctane (6.122 g, 43.0 mmol) in 60 mL of THF was added to a 0.5 M solution of NaFp[17] in THF at 0 °C over a 1.5-h period. After an additional 30 min at 0 °C, the reaction was stirred for 3.5 h out of the ice bath. Water (5 mL) was added and the stirring continued for 10 min. The solution was filtered under nitrogen through activity III neutral alumina into a 1-L flask containing a vigorously stirred solution of 16.15 g (88 mmol) of 48% HBF_4 in 0.5 L of ether. The product immediately precipitated. Filtration of the solid followed by three reprecipitations—one from nitromethane/methylene chloride, two from acetonitrile/ether—yielded 20.44 g (74.7%) of **4** as a yellow solid: IR (KBr) 2078, 2037 cm^{-1}; ^{1}H NMR (CD_3NO_2) δ 5.67 (s, 10 H, η^5-C_5H_5), 5.12 (m, 2 H, =CH), 3.96 (d, 2 H, J = 8 Hz, cis =CH_2), 3.50 (d, 2 H, J = 15 Hz, trans =CH_2), 2.52 (m, 2 H, allylic H), 1.67 (m, 6 H, CH_2, allylic CH).

Anal. Calcd for $C_{22}H_{24}B_2F_8Fe_2O_4$: C, 41.59; H, 3.79. Found: C, 42.07; H, 4.23.

Deprotonation of $Fp_2(\eta^2,\eta^2$-1,7-octadiene)$(BF_4)_2$. Preparation of 8-t. Complex 4 (1.912 g, 3.0 mmol) was partially dissolved in a mixture of 135 mL of methylene chloride and 25 mL of nitromethane and cooled to 0 °C. Tri-*n*-butylamine (0.555 g, 3.0 mmol) was added dropwise with stirring over a 20-min period. After 2 h at 0 °C, the reaction flask was removed from the ice bath and reaction was continued for an additional 70 min. Solvents were then removed on the rotary evaporator and replaced by 100 mL of acetone, and sodium iodide (0.76 g, 5.07 mmol) was added. After stirring for 1.25 h, acetone was removed on the rotary evaporator and the residue taken up in ether and filtered through ether-washed activity III neutral alumina. Removal of the ether and chromatography on ether-washed activity III neutral alumina (Skelly B elution) gave a yellow band, which on rechromatography gave 0.414 g of product as an amber oil (48.2%): IR (hexanes) 2008, 1953 cm^{-1}; ^{1}H NMR (CD_3NO_2) δ 5.72 (m, 1 H, =CH), 5.03 (m, 2 H, =CH_2), 4.84 (s, 5 H, η^5-C_5H_5), 2.7–0.83 (several m, 10 H, CH, CH_2); ^{13}C NMR (CD_3NO_2) (major product) δ 8.01 (t), 24.03 (t), 33.86 (t), 36.35 (t), 54.81 (d), 56.66 (d), 86.95 (d), 113.80 (t), 144.41 (d), 218.53 (s), 219.11 (s), (minor isomer A) 5.33 (t), 23.67, 30.68 or 32.40, 34.33, 51.62, 52.28, 87.06 (d), 142.07, (minor isomer B) 26.79 (d), 31.32, 33.61, 43.95, 47.53 (d), 50.78, 87.19 (d), 111.83 (t), 145.97 (d).

Degradation of Complex 6-t. The crude product derived from reaction of 8.0 g (13.13 mmol) of **4** and 2.5 g (13.48 mmol) of tri-*n*-butylamine was dissolved in methylene chloride (175 mL) and filtered through Celite. Dry HCl was bubbled into this solution for 4 h. Solvent was removed, and the residue was washed repeatedly with ether and then dissolved in 15 mL of methylene chloride and stirred overnight at room temperature with 3.55 g (9.6 mmol) of tetra-*n*-butylammonium iodide. The crude product was purified by short-path distillation in vacuo. Further purification of a portion of this product by gas chromatography using a 3 m × 0.64 cm 10% SE-30 on Chromosorb W column gave *trans*-2-vinyl-1-methylcyclopentane: ^{1}H NMR ($CDCl_3$) δ 5.73 (m, 1 H, =CH), 4.95 (m, 2 H, =CH_2), 2.16–1.03 (m, 8 H, CH, CH_2), 0.95 (d, 3 H, J = 6 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 142.34 (d), 113.02 (t), 52.82 (d), 40.65 (d), 34.37 (t), 32.69 (t), 23.27 (t), 18.32 (q). The remaining product was taken up in methylene chloride and subjected to ozonolysis at −78 °C. Oxidative workup with 3 mL of 30% H_2O_2 in 10 mL of 2 N HCl led to the isolation of 0.22 g of acidic material as a brownish oil. This was sublimed (55 °C, 0.007 mm) to give *trans*-2-methylcyclopentanecarboxylic acid[18] as a clear oil; ^{1}H NMR (CCl_4) δ 12.00 (br s, 1 H, OH),

(16) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734. Baldwin, J. E.; Cutting, J.; Dupont, W.; Kruse, L.; Silberman, L.; Thomas, R. C. *Ibid.* **1976**, 736. Baldwin, J. E. *Ibid.* **1976**, 738. Baldwin, J. E.; Kruse, L. I. *Ibid.* **1977**, 233.

(17) Fischer, E. O.; Fichtel, K. *Chem. Ber.* **1961**, *94*, 1200; *Ibid.* **1962**, *95*, 2063.

(18) (a) Myers, A. I.; Mihelich, E. D.; Kamata, K. *J. Chem. Soc., Chem. Commun.* **1974**, 768. (b) Jorgenson, M. J.; Brattesani, A. J.; Thatcher, A. F. *J. Org. Chem.* **1969**, *34*, 1103.

2.86–1.18 (m, 8 H, CH, CH_2), 1.11 (d, 3 H, J = 5 Hz, CH_3) (lit.[18] 1.12 (d, CH_3)). The purified acid was dissolved in petroleum ether and treated with an excess of oxalyl chloride. After brief heating, excess oxalyl chloride was removed under reduced pressure, and 3 mL of concentrated ammonium hydroxide was added slowly to the cooled (0 °C) acid chloride. After the solution stood overnight, the mixture was extracted with ether, dried, and evaporated to give 0.062 g of a white solid. This was recrystallized several times (ether–petroleum ether) and finally sublimed to give the *trans*-2-methylcyclopentanecarboxamide; mp 154–155 °C (sealed capillary) (lit.[11] 152–155 °C); IR (KBr) 1660, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.37 (br, NH_2), 2.31–1.13 (2 m, CH, CH_2), 1.06 (d, J = 6 Hz, CH_3).

***trans*-1-Methyl-2-vinylcyclopentane.** Vinyllithium in benzene–ether solution was prepared from 20.4 mmol of phenyllithium and 5.04 mmol of tetravinyltin following the procedure of Seyferth and Weiner.[19] This was converted to the divinylcuprate salt by treatment of the filtered vinyllithium solution with a suspension of cuprous iodide (1.92 g, 10.1 mmol) and dimethyl sulfide (3 mL, 40.8 mmol) following the procedure of Chavdarian and Heathcock.[20] The black reaction mixture was stirred at −45 °C while 1.35 g, 5.3 mmol) of *cis*-2-methylcyclopentane tosylate[21,22] in 25 mL of ether was added slowly. After stirring for 8 h at −25 °C and 3 h at 0 °C, the reaction was quenched with saturated ammonium chloride solution and worked up. A sample of the product was purified by preparative gas chromatography using a 2 m × 0.64 cm 20% SE-30 on Chromosorb W column (99 °C, flow 50 mL/min, retention time 14.0 min). The yield of *trans*-1-methyl-2-vinylcyclopentane was (ethylbenzene internal standard) 8.4%: ^1H NMR ($CDCl_3$) δ 5.71 (ddd, 1 H, J = 17.5, 9.6, 7.2 Hz, =CH), 4.96 (m, 2 H, $=CH_2$), 2.1–1.1 (m, 8 H, CH, CH_2), 0.99 (d, 3 H, J = 5.9 Hz, CH_3).

***cis*-1-Methyl-2-vinylcyclopentane.** This compound was prepared by using the same procedure as for the *trans*-1-methyl-2-vinylcyclopentane, starting with *trans*-2-methylcyclopentyl tosylate.[21] After the addition of the tosylate to the lithium divinylcuprate solution, the reaction was stirred at −45 °C for 9 h, at 25 °C for 3 h, and then at 0 °C for 0.75 h, with the quenching and workup as before. The yield of *cis*-1-methyl-2-vinylcyclopentane (GC internal standard, ethylbenzene) was 4.9%: ^1H NMR ($CDCl_3$) δ 5.78 (ddd, 1 H, J = 17.3, 9.5, 8.1 Hz, =CH), 4.95 (m, 2 H, $=CH_2$), 2.6–1.1 (m, 8 H, CH, CH_2), 0.86 (d, 3 H, J = 7.2 Hz, CH_3). About 1% yield of the trans isomer was also isolated.

Tri-*n*-butyl-*N*-deuterioammonium Tetrafluoroborate. Deuterium oxide (99.8%, 23 mL) was added to tri-*n*-butylammonium tetrafluoroborate (8.2 g, 30 mmol) under nitrogen, forming two phases. After 6 h of stirring, the mixture was heated under vacuum to remove as much D_2O as possible, and then 15 mL of fresh D_2O was added. This mixture was stirred for 6 h, then dry CH_2Cl_2 (25 mL) was added, and the resulting mixture was transferred via cannula to a flask containing anhydrous $NaBF_4$. The CH_2Cl_2 phase was removed, and two more CH_2Cl_2 extractions were done under N_2. The combined methylene chloride extracts were dried with $MgSO_4$, which had been vigorously flame dried under a stream of nitrogen. Filtration under nitrogen followed by evaporation of the solvent yielded a white powder, which was subjected to another exchange with 15 mL of D_2O followed by methylene chloride extraction and isolation as above. The product (7.1 g, 25.9 mmol, 86.3%) had at least a 92% deuterium content: ^1H NMR ($CDCl_3$) δ 6.9 (br s, 0.08 H, NH), 3.18 (m, 6 H, NCH_2), 1.95–1.17 (2 m, 12 H, CH_2CH_2), 0.9 (t, 9 H, J = 6 Hz, CH_3).

Cyclization of $Fp_2(\eta^2,\eta^2\text{-}1,7\text{-octadiene})(BF_4)_2$ in the Presence of $[DN(n\text{-}Bu)_3](BF_4)$. $Fp_2(1,7\text{-octadiene})(BF_4)_2$ (1.917 g, 3.01 mmol) was dissolved in 150 mL of dry acetonitrile, and an excess of the deuterated tri-*n*-butylammonium tetrafluoroborate (7.097 g, 25.9 mmol, 92% DBu_3NBF_4, prepared by exchange of Bu_3NHBF_4) was added. After cooling to 0 °C, tri-*n*-butylamine (0.557 g, 3.0 mmol) was added over a 1.5-min period. The reaction was stirred for 8.5 h at 0 °C and then 1.5 h without the ice bath. Solvent was removed, and the residue was taken up in 50 mL of acetone and treated with 0.75 g (5.0 mmol) of sodium iodide. Acetone was removed, and the residue was extracted with Skelly B and then chromatographed on activity III alumina. The product (0.535 g, 62.3%) was obtained as an amber oil, whose ^{13}C NMR spectrum was identical with that of the product obtained in the absence of deuterated ammonium salt. Specifically no reduction in the intensity of either of the tertiary ring carbon resonances was observed compared with the spectrum of an undeuterated sample.

2,6-Octadiyne-1,8-diol. Hexadiyne (4.729 g, 60.5 mmol) was dissolved in 160 mL of dry ether under N_2 and cooled to −13 °C. *n*-Butyllithium (52.5 mL of a 2.4 M solution in hexane, 126 mmol) was added dropwise over a 20-min period. Paraformaldehyde (4.3 g, 143.2 mmol) was added to the suspension of dilithio salt, along with 240 mL of dry THF, and the reaction was refluxed for 2.25 h. After cooling, water (50 mL) was added, the aqueous layer was saturated with salt, and the organic layer was removed. The aqueous layer was extracted three times with ether, the combined organic layers were dried over $MgSO_4$, and solvent was removed under reduced pressure. The residue was recrystallized three times from boiling benzene to give 3.994 of (28.9 mmol, 47.8%) of a white solid: mp 86–87 °C (lit.[23] 88.5–89.5 °C); ^1H NMR ($CDCl_3$) δ 4.28 (br s, 4 H, CH_2OH), 2.46 (br s, 4 H, CH_2CH_2), 1.78 (br s, 2 H, OH).

***trans,trans*-2,6-Octadiene-1,8-diol.** Liquid ammonia (200 mL) was twice distilled from sodium into a 500-mL three-necked flask equipped with a dry ice condenser, overhead stirrer, and nitrogen inlet. Sodium (4.85 g, 211 mmol) was added as small chunks with vigorous stirring while the reaction flask was cooled to −78 °C. The dry ice bath was removed, and 2,6-octadiyne-1,8-diol (2.76 g, 20 mmol) was added quickly in small portions. After 2.5 h of reflux, the reaction was carefully quenched by the addition of solid NH_4NO_3 and then 70 mL of ammonium hydroxide solution. Ammonia was allowed to evaporate, and the aqueous solution was saturated with sodium chloride and extracted with ether. Removal of solvent left 2.1 g (74%) of product as a pale yellow oil: ^1H NMR ($CDCl_3$) δ 5.65 (m, 4 H, olefinic H), 4.07 (br s, 4 H, CH_2OH), 3.53 (br s, 2 H, OH), 2.15 (br s, 4 H, CH_2CH_2). An NMR spectrum of this product (0.017 g in 0.4 mL $CDCl_3$) taken in the presence of Eu(fod)$_3$ (0.087 g) showed olefinic resonances as a doublet of triplets (J = 5.5, 16 Hz) and a broad doublet (J = 16 Hz).

***trans,trans*-1,8-Dichloro-2,6-octadiene.** *N*-Chlorosuccinimide (4.22 g, 31.6 mmol) was dissolved in 20 mL of dry methylene chloride and stirred at 0 °C while dimethyl sulfide (2.54 mL, 34.6 mmol) was added dropwise[14] via syringe. The solution was cooled to −20 °C and *trans,trans*-2,6-octadiene-1,8-diol (2.04 g, 14.35 mmol) was added dropwise over 12 min. The reaction was warmed to 0 °C, stirred for 1.25 h, and then poured into saturated NaCl solution at 0 °C. Workup by extraction of the product into low-boiling petroleum ether and chromatography on silica gel, using CCl_4 as eluent, gave 1.20 g (46.5%) as a clear liquid: ^1H NMR ($CDCl_3$) δ 5.8 (m, 4 H, olefinic H), 4.03 (d, 4 H, J = 6 Hz, CH_2Cl), 2.18 (m, 4 H, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 134.59 (d), 126.72 (d), 45.19 (t), 31.27 (t).

***trans,trans*-1,8-Fp_2-2,6-octadiene.** Sodium η^5-cyclopentadienyldicarbonylferrate (NaFp) was prepared from 2.127 g (6.0 mmol) of the dimer, $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]_2$, and an excess of sodium amalgam in 100 mL of dry THF.[17] After this solution was cooled to 0 °C, *trans,trans*-1,8-dichloro-2,6-octadiene (1.007 g, 5.62 mmol) dissolved in 5 mL of THF was added dropwise over 3 min. The ice bath was removed, and after stirring for 1 h, solvent was removed in vacuo and the residue was extracted with Skelly-B. This solution was filtered twice, through activity III neutral and then basic alumina, with 4% ether in Skelly B. On concentration, the product crystallized as an orange-yellow solid (1.51 g, 58%): mp 79–80 °C (moderately stable in air); IR (CH_2Cl_2) 2009, 1940 cm^{-1}; ^1H NMR (CS_2) δ 5.8–4.95 (2 m, 4 H, olefinic H), 4.58 (s, 10 H, $\eta^5\text{-}C_5H_5$), 2.0 (d, 4 H, J = 8 Hz, Fp-CH_2), 1.89 (t, 4 H, J = 1.5 Hz, CH_2CH_2) [irradiation of the resonance at δ 2.0 produces a sharp doublet at δ 5.58 (J = 15 Hz), irradiation of the resonance at δ 1.89 produces a sharp doublet resonance at δ 5.19 (J = 15 Hz)].

Anal. Calcd for $C_{22}H_{22}Fe_2O_4$: C, 57.18; H, 4.80. Found: C, 57.43; H, 4.76.

***cis,cis*-2,6-Octadiene-1,8-diol.** A solution of 2,6-octadiyne-1,8-diol (2.63 g, 19.03 mmol) and 0.3 mL of quinoline in 120 mL of absolute ethanol was vigorously stirred with 0.088 g of Lindlar's catalyst[24] under a hydrogen atmosphere until H_2 uptake stopped (less than 2 h). Workup gave 2.34 g of product (86%) as a viscous liquid: ^1H NMR ($CDCl_3$) δ 5.57 (m, 4 H, olefinic H), 4.13 (d, 4 H, J = 5 Hz, CH_2OH), 3.59 (s, 2 H, OH), 2.12 (t, 4 H, J = 3 Hz, CH_2CH_2). Using Eu(fod)$_3$ in $CDCl_3$ (a 1.04:1 molar ratio of Eu(fod)$_3$ to diene–diol), one finds that the olefinic resonances separated into (from lower to higher field) a multiplet that is a doublet of triplets (J = 10.5, 7 Hz) and a broadened doublet (J = 10.5 Hz), which appears to be a doublet of triplets.

***cis,cis*-1,8-Dichloro-2,6-octadiene.** This compound was prepared from *cis,cis*-2,6-octadiene-1,8-diol by the same procedure as for the trans,trans isomer in 63.4% yield as a colorless liquid: ^1H NMR ($CDCl_3$) δ 5.66 (m, 4 H, olefinic H), 4.07 (d, 4 H, J = 7 Hz, CH_2Cl), 2.21 (t, 4 H, J = 3 Hz, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 133.74 (d), 126.40 (d), 39.21 (t), 27.79 (t).

***cis,cis*-1,8-Fp_2-2,6-octadiene (17-c).** Preparation of this complex was

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(20) Chavdarian, C.; Heathcock, C. *J. Am. Chem. Soc.* **1975**, *97*, 3822.
(21) Umland, J. B.; Jeffraim, M. I. *J. Am. Chem. Soc.* **1956**, *78*, 2788.
(22) Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1972**, *94*, 7159.
(23) Lespieau, R. *C. R. Hebd. Seances Acad. Sci.* **1914**, 707.
(24) Fieser, M.; Fieser, L. F. "Reagents for Organic Synthesis"; Wiley-Interscience: New York, 1967; Vol. 1, p 556.
(25) Everett, J. L.; Kon, G. A. R. *J. Chem. Soc.* **1950**, 3131.

carried out by following the procedure for the trans,trans isomer employing *cis,cis*-1,8-dichloro-2,6-octadiene and sodium η^5-cyclopentadienyldicarbonylferrate. Complex **17**-c was obtained as a yellow solid in 47% yield: mp 73–74 °C; IR (CH_2Cl_2) 2005, 1944 cm^{-1}; ^1H NMR (CS_2) δ 5.54 (q, 2 H, J = 10, 10 Hz, $FpCH_2CH$=), 4.96 (m, 2 H, =$CHCH_2CH_2$), 4.64 (s, 10 H, η^5-C_5H_5), 2.08 (d, 4 H, J = 9 Hz, Fp-CH_2), 1.99 (m, 4 H, CH_2CH_2) [irradiation of the resonance at δ 2.08 produced a sharp doublet at 5.54 (J = 10 Hz), irradiation of the resonance at δ 1.99 produces a sharp doublet at 4.97 (J = 10.5 Hz)]; ^{13}C NMR (CD_3NO_2) δ 219.2 (s, CO), 141.16 (d, Fp-CH_2CH=), 123.47 (d, Fp-CH_2CH=CH—), 87.13 (d, η^5-C_5H_5), 28.61 (CH_2CH_2), –0.98 (Fp-CH_2).

Anal. Calcd for $C_{22}H_{22}Fe_2O_4$: C, 57.18; H, 4.80. Found: C, 57.56; H, 4.91.

Protonation of *trans,trans*-1,8-Fp_2-2,6-octadiene (17-t). Complex **17**-t (1.321 g, 2.86 mmol) was dissolved in 100 mL of methylene chloride, and the solution was cooled to 0 °C. Fluoroboric acid etherate (0.4 mL, 2.87 mmol) was added dropwise over a few minutes to the rapidly stirred solution, followed by ether. The yellow precipitate was collected and washed with ether and then with methylene chloride, and the latter filtrate was treated with excess ether to precipitate the cyclic monocation as a slightly gummy solid (1.072 g, 68%): IR (acetone) 2077, 2039, 2006, 1938 cm^{-1}. Also recovered, undissolved by methylene chloride, was 0.223 g (12.2%) of diprotonated product, $Fp_2(\eta^2,\eta^2$-1,7-octadiene$)(BF_4)_2$. The cyclized product was dissolved in 25 mL of acetone and stirred for 2 h with 0.793 g (5.1 mmol) of sodium iodide. After removal of the solvent in vacuo, the residue was extracted with ether and filtered through activity IV neutral alumina with Skelly B as eluant. Chromatography on activity IV neutral alumina with Skelly B as eluant yielded 0.452 g (1.58 mmol, 55.2%) of **8**-t as an amber liquid. The ^{13}C NMR spectrum showed the presence of about 5% of the isomeric cyclohexyl complex **9**-t or **9**-c.

Protonation of *cis,cis*-1,8-Fp_2-2,6-octadiene. Complex **17**-c (1.218 g, 2.64 mmol) was dissolved in 125 mL of dry methylene chloride and stirred at 0 °C while fluoroboric acid etherate (0.38 mL, 2.72 mmol) was added dropwise over a 12-min period. After an additional 5 min at this temperature, the solvent was concentrated and dry ether was slowly added. The collected precipitate was washed with ether and then with methylene chloride. Slow addition of ether to the latter filtrate resulted in the formation of an oil. Solvent was removed, and 20 mL of acetone and then 0.415 g (2.77 mmol) of sodium iodide were added. After 3 h at room temperature, the acetone was evaporated and the residue extracted with ether. The ethereal solution was filtered through activity III neutral alumina with Skelly B as eluant. The concentrated filtrate was chromatographed on activity III neutral alumina (which had been deactivated with ether) with Skelly B as eluant. A yellow liquid, 0.218 g, was recovered, which was shown by ^{13}C NMR to contain three isomeric cyclized complexes, **8**-t, **8**-c, and **9**-t or **9**-c in a ratio of 6.5:2.5:1.0.

Incomplete Protonation of *cis,cis*-1,8-Fp_2-2,6-octadiene. A solution of 0.556 g (1.2 mmol) of *cis,cis*-1,8-Fp_2-2,6-octadiene in 50 mL of methylene chloride was stirred at 0 °C while fluoroboric acid etherate (0.08 mL, 0.573 mmol) was added dropwise over a 3-min period. After concentration of this solution to 10–20 mL, approximately 150 mL of ether was slowly added, and the resulting mixture was filtered. The filtrate was concentrated and then chromatographed on activity III neutral alumina with 10% ether in Skelly B as eluant. A yellow solid was obtained, which was shown to be unchanged starting material (**17**-c) by ^{13}C NMR, 0.347 g (62.6% recovery).

1,2,8,9-Diepoxynonane. This substance was prepared from 1,8-nonadiene by treatment with *m*-chloroperbenzoic acid in methylene chloride at 0 °C for 1.5 h and then at room temperature for 17 h. Workup gave the product in 99% yield as a colorless oil that solidified below room temperature: ^1H NMR ($CDCl_3$) δ 2.9 (m, 2 H, CH), 2.70 (t, 2 H, J = 4.5 Hz, terminal CH_2), 2.43 (dd, 2 H, J = 3, 5 Hz, terminal CH_2), 1.48 (s, 10 H, $(CH_2)_5$).

Preparation of $Fp_2(\eta^2,\eta^2$-1,8-nonadiene$)(BF_4)_2$ (11). A. From 1,8-Nonadiene. 1,8-Nonadiene (0.504 g, 4.05 mmol) and Fp(η^2-isobutylene)BF_4 (2.561 g, 8.02 mmol) were dissolved in 70 mL of 1,2-dichloroethane and heated to 60 °C for 10 min with swirling. After cooling to room temperature, excess ether was added. The resulting precipitate was filtered, washed with methylene chloride, and reprecipitated from nitromethane by the addition of methylene chloride and then excess ether to yield 1.073 g (40.8%) of **11** as a yellow solid.

B. From 1,2,8,9-Diepoxynonane. A solution of 274 mL of 0.357 M NaFp[17] in THF was cooled to 0 °C and stirred while a solution of 7.68 g (49.1 mmol) of 1,2,8,9-diepoxynonane in 25 mL of THF was added over a 15-min period. After 1 h, the ice bath was removed, and the reaction was stirred for 2 h. Water (9 mL) was added, and stirring was continued for 5 min. The reaction mixture was filtered through activity III neutral alumina into a rapidly stirred solution of 18.3 g (100 mmol) of 48% HBF_4 in 0.5 L of ether. The resulting yellow precipitate was collected and reprecipitated from nitromethane with methylene chloride. Excess ether was added to complete the precipitation and yielded 23.92 g of product (74.8%): IR (KBr) 2068, 2024 cm^{-1}; ^1H NMR (CD_3NO_2) δ 5.66 (s, 10 H, η^5-C_5H_5), 5.14 (m, 2 H, =CH), 3.94 (d, 2 H, J = 8 Hz, cis =CH_2), 3.49 (d, 2 H, J = 15 Hz, trans =CH_2), 2.45 (m, 2 H, allylic CH), 1.51 (m, 8 H, $(CH_2)_3$, allylic CH).

Anal. Calcd for $C_{23}H_{26}B_2F_8Fe_2O_4$: C, 42.39; H, 4.02. Found: C, 41.76; H, 3.94.

Deprotonation of $Fp_2(\eta^2,\eta^2$-1,8-nonadiene$)(BF_4)_2$. The dication **11** (1.31 g, 2.01 mmol) was dissolved in 100 mL of methylene chloride and 25 mL of nitromethane and was cooled to 0 °C. Rapid addition of tri-*n*-butylamine (0.385 g, 2.08 mmol) was followed by continued stirring at this temperature. After 35 min, the ice bath was removed, and stirring was continued for 1 h. The solvents were removed on the rotary evaporator, and 40 mL of acetone and 0.593 g (3.96 mmol) of sodium iodide were added. After 17 h of stirring, the acetone was evaporated, and the residue was extracted with ether and then filtered through (ether washed) activity III neutral alumina. The concentrated residue was twice chromatographed on ether-washed activity III neutral alumina, with Skelly B as eluant. In each chromatography the first yellow band was collected. Removal of solvent yielded 0.27 g (44.8%) of an amber oil: IR (hexanes) 2004, 1951 cm^{-1}; ^1H NMR (CD_3NO_2) δ 6.2–4.83 (several m, 3 H, olefinic H), 4.79, 4.78 (2 s, 5 H, η^5-C_5H_5), 2.45–0.67 (several m, 12 H, CH, CH_2); ^{13}C NMR (CD_3NO_2) (**15**-c) 6.18 (t) 23.60 (t), 25.94 (t), 31.79 (t), 47.01 (d), 47.46 (d), 87.00 (d), 114.95 (t), 142.26 (d) (**15**-t) 9.10 (t), 27.11, 27.83, 35.11, 35.70, 48.63, 53.58 (d), 87.00 (d), 113.91 (t), 146.42 (d).

Degradation of Complexes 13-c and 13-t. A. *cis*- and *trans*-1-Methyl-2-vinylcyclohexanes. A mixture of cyclized complexes **13**-c and **13**-t derived from the reaction of 15 mmol of dication **11** was taken up in 300 mL of methylene chloride, and HCl was slowly bubbled in over a period of 8 h. Solvent was then removed, and the residue was washed repeatedly with ether and then taken up in 15 mL of methylene chloride. Tetra-*n*-butylammonium iodide (4.41 g, 11.9 mmol) was then added, and the solution was stirred overnight and then trap-to-trap distilled at 10^{-5} mm. The product was separated by gas chromatography (2.5 m × 0.635 cm, 33% $AgNO_3$–ethylene glycol on Chromsorb P). Two fractions were collected (column temperature 40 °C, He flow 85 mL/min). Fraction 1 (trans isomer) retention time 22.8 min: ^1H NMR ($CDCl_3$) δ 5.63 (ddd, 1 H, J = 17.3, 9.9, 7.2 Hz, =CH), 4.94 (m, 2 H, =CH_2), 2.14–1.09 (m, 10 H, CH, CH_2), 1.005 (d, 3 H, J = 5.1 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 143.95 (d), 113.41 (t), 50.30 (d), 36.85 (d or t), 35.35 (d or t), 33.53 (t), 26.65 (t), 26.26 (t), 20.80 (q). Fraction 2 (cis isomer) retention time 39.3 min: ^1H NMR ($CDCl_3$) δ 5.85 (m, 1 H, =CH), 4.95 (m, 2 H, =CH_2), 2.39–1.32 (m, 10 H, CH, CH_2), 0.853 (d, 3 H, J = 6.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 140.83 (d), 114.12 (t), 44.84 (d), 34.12 (d), 31.72 (t), 29.31 (t), 23.92 (t), 23.66 (t), 16.83 (q).

B. *cis*- and *trans*-2-Methylcyclohexanecarboxylic Acids. Each of the olefins isolated above was ozonized at –78 °C in methylene chloride solution and was worked up by allowing the solution to warm to room temperature and removing solvent in vacuo. A 30% H_2O_2 solution (3 mL) and 10 mL of 2 N HCl were then added, and the mixture was refluxed for 3 h. Workup gave *trans*-2-methylcyclohexanecarboxylic acid from fraction 1 [^1H NMR ($CDCl_3$) δ 10.77 (br s, OH) 2.51–1.33 (m, CH, CH_2), 0.936 (d, J = 5.6 Hz, CH_3)] and *cis*-2-methylcyclohexanecarboxylic acid from fraction 2 [^1H NMR ($CDCl_3$)] δ 9.13 (br s, OH), 2.69–1.17 (m, CH, CH_2), 0.971 (d, J = 7.0 Hz, CH_3).

***cis*-2-Methylcyclohexanecarboxylic Acid.** This acid was prepared by catalytic hydrogenation of *o*-toluic acid under 50 psi of H_2 according to the procedure of House and Richey:[26] ^1H NMR ($CDCl_3$) δ 10.3 (br s, 1, OH), 2.7–1.1 (m, 10, CH, CH_2), 0.968 (d, 3, J = 7 Hz, CH_3).

***trans*-2-Methylcyclohexanecarboxylic Acid.** Epimerization of the cis acid with base by the method of House and Richey[26] produced a mixture of cis and trans acids, the trans isomer largely predominating: ^1H NMR ($CDCl_3$) δ 10.6 (br s, OH), 2.2–1.0 (m, CH, CH_2), 0.929 (d, J = 5.6 Hz, CH_3).

2,7-Nonadiyne-1,9-diol. This compound was prepared from 1,6-heptadiyne by following the procedure used for 2,6-octadiyne-1,8-diol. After workup, the ether extractions were concentrated to a yellow-orange liquid, which was Kugelrohr distilled (100 °C, 0.02 mm) to give the product as a white waxy solid (63%) that melted at room temperature: ^1H NMR ($CDCl_3$) δ 4.28 (t, 4 H, J = 2 Hz, CH_2OH), 3.68 (br s, 2 H, OH), 2.40 (tt, 4 H, J = 6.5, 2 Hz, $CH_2CH_2CH_2$), 1.73 (quintet, 2 H, J = 6.5 Hz, $CH_2CH_2CH_2$).

***trans,trans*-2,7-Nonadiene-1,9-diol.** The preparation of this compound by sodium in liquid ammonia reduction of 2,7-nonadiyne-1,9-diol was

(26) House, H. O.; Richey, F. A. *J. Org. Chem.* **1967**, *32*, 2151.

accomplished by following the procedure used for the preparation of *trans,trans*-2,6-octadiene-1,8-diol. After workup, the product was obtained in 62% yield as a liquid: ^{1}H NMR ($CDCl_3$) δ 5.65 (m, 4 H, olefinic H), 4.08 (d, 4 H, J = 3 Hz, CH_2OH), 3.28 (br s, 2 H, OH), 2.1 (br m, 4 H, $CH_2CH_2CH_2$), 1.48 (quintet, 2 H, J = 7 Hz, $CH_2CH_2CH_2$).

***trans,trans*-1,9-Dichloro-2,7-nonadiene.** The substance was prepared in 69% yield as a colorless liquid from *trans,trans*-2,7-nonadiene-1,9-diol by following the procedure used for the preparation of *trans,trans*-1,8-dichloro-2,6-octadiene: ^{1}H NMR ($CDCl_3$) δ 5.69 (m, 4 H, olefinic H), 4.02 (d, 4 H, J = 6 Hz, CH_2Cl), 2.07 (q, 4 H, J = 6 Hz, $CH_2CH_2CH_2$), 1.48 (quintet, 2 H, J = 7 Hz, $CH_2CH_2CH_2$).

***trans,trans*-1,9-Fp$_2$-2,7-nonadiene.** This substance was prepared from *trans,trans*-1,9-dichloro-2,7-nonadiene by following the procedure used for the preparation of *cis,cis*-1,9-Fp$_2$-2,7-nonadiene and was obtained in 90% yield as an amber liquid: IR (CH_2Cl_2) 2003, 1940 cm^{-1}; ^{1}H NMR (CS_2) δ 5.8-5.0 (m, 4 H, olefinic H), 4.60 (s, 10 H, η^5-C_5H_5), 2.07 (d, 4 H, J = 8 Hz; Fp-CH_2), 1.88 (q, 4 H, J = 7 Hz, $CH_2CH_2CH_2$), 1.31 (m, 2 H, $CH_2CH_2CH_2$); ^{13}C NMR (CD_3NO_2) δ 218.46 (s, CO), 141.09 (d, C_2, C_8), 123.73 (d, C_3, C_7), 86.80 (d, η^5-C_5H_5), 32.83 (t, C_4, C_6), 31.47 (t, C_5), 4.49 (t, C_1, C_9).

***cis,cis*-2,7-Nonadiene-1,9-diol.** Preparation of this compound was carried out according to the procedure used for *cis,cis*-2,6-octadiene-1,8-diol from 2,7-nonadiyne-1,9-diol. The product obtained in 99% yield as a clear orange-tinted liquid was not further purified: ^{1}H NMR ($CDCl_3$) δ 5.54 (m, 4 H, olefinic H), 4.17 (d, 4 H, J = 6 Hz, CH_2OH), 3.6 (br s, 2 H, OH), 2.09 (q, 4 H, J = 7 Hz, $CH_2CH_2CH_2$), 1.48 (quintet, 2 H, J = 7 Hz, $CH_2CH_2CH_2$).

***cis,cis*-1,9-Dichloro-2,7-nonadiene.** The preparation of this compound from *cis,cis*-2,7-nonadiyne-1,9-diol followed the procedure used in the preparation of *trans,trans*-1,8-dichloro-2,6-octadiene and yielded the dichloride as a colorless liquid (62%): ^{1}H NMR ($CDCl_3$) δ 5.64 (m, 4 H, olefinic H), 4.08 (d, 4 H, J = 7 Hz, CH_2Cl), 2.16 (q, 4 H, J = 6.5, 7 Hz, $CH_2CH_2CH_2$), 1.50 (quintet, 2 H, J = 7 Hz, $CH_2CH_2CH_2$).

***cis,cis*-1,9-Fp$_2$-2,7-nonadiene.** This complex was prepared from *cis,cis*-1,9-dichloro-2,7-nonadiene by reaction with a 25% excess of NaFp according to the procedure for *trans,trans*-1,8-Fp$_2$-2,6-octadiene. After direct filtration of the reaction solution through activity III neutral alumina with ether as eluant, the concentrated filtrate was refiltered by eluting with 7–10% ether in Skelly B. Chromatography of the filtrate on activity III neutral alumina with 5–7% ether in Skelly B as eluant yielded a major yellow band preceded by a thin yellow band and followed by a dark reddish brown band (Fp$_2$). Collection and concentration of the major yellow band yielded 4.3 g (80.3%) of product as an amber liquid: IR (CH_2Cl_2) 2006, 1944 cm^{-1}; ^{1}H NMR (CS_2) δ 5.55 (br q, 2 H, J = 10 Hz, Fp-CH_2CH=), 4.93 (m, 2 H, Fp-CH_2CH=CH), 4.64 (s, 10 H, η^5-C_5H_5), 2.25–1.8 (d plus m, 8 H, J = 8 Hz, Fp-CH_2, $CH_2CH_2CH_2$), 1.32 (quintet, 2 H, J = 8 Hz, $CH_2CH_2CH_2$) [irradiation at the high-field doublet plus multiplet collapsed both olefinic resonances into sharp doublets (J = 10 and 10.5 Hz)]; ^{13}C NMR (CD_3NO_2) δ 218.27 (s, CO), 140.25 (d, C_2, C_8), 123.08 (d, C_3, C_7), 86.28 (d, η^5-C_5H_5), 30.82 (t, C_5), 27.57 (t, C_4, C_6), −1.30 (t, C_1, C_9).

Protonation of *trans,trans*-1,9-Fp$_2$-2,7-nonadiene. A solution of 2.06 g (4.33 mmol) of *trans,trans*-1,9-Fp$_2$-2,7-nonadiene in 100 mL of dry methylene chloride was stirred at 0 °C while 0.61 mL (4.37 mmol) of fluoroboric acid etherate in 50 mL of CH_2Cl_2 was added dropwise over a 90-min period. The reaction was stirred for 0.75 h after the end of the addition without the ice bath. The solvent was removed under reduced pressure and replaced by 10 mL of acetone. Sodium iodide (1.44 g, 9.6 mmol) was added, and the reaction was stirred for 3 h. The acetone was removed on the rotary evaporator, and the residue was filtered through activity IV basic alumina with 10% ether in Skelly B as eluant. Chromatography on activity IV basic alumina gave 0.625 g of an amber liquid on elution with Skelly B followed by 0.420 g of an amber liquid on elution with 5–7% ether in Skelly B. The first fraction contained cyclized products while the second contained mostly starting material. The ^{13}C NMR spectrum showed the presence of **15**-t and **15**-c in an approximate 2:1 ratio.

Protonation of *cis,cis*-1,9-Fp$_2$-2,7-nonadiene. The protonation of *cis,cis*-1,9-Fp$_2$-2,7-nonadiene (1.734 g, 3.64 mmol) was carried out according to the procedure for the trans,trans isomer. Chromatography yielded 0.445 g of cyclized products on elution with Skelly B followed by 0.338 g of starting material isomers on elution with 6% ether in Skelly B. The ^{13}C NMR spectrum showed the presence of **15**-c and **15**-t in an approximate ratio of 3:1.

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Registry No. 4, 84172-80-5; ***cis*-5**, 84117-63-5; ***trans*-5**, 84171-26-6; **6**-c, 84117-64-6; **6**-t, 84171-27-7; **8**-c, 84117-65-7; **8**-t, 84171-28-8; **9**-c, 84117-66-8; **9**-t, 84234-84-4; **11**, 84117-68-0; ***cis*-12**, 84117-69-1; ***trans*-12**, 84234-85-5; **13**-c, 84117-70-4; **13**-t, 84171-29-9; **15**-c, 84117-71-5; **15**-t, 84171-30-2; **17**-c, 84117-72-6; **17**-t, 84171-31-3; **18**-c, 84130-21-2; **18**-t, 84172-81-6; Fp[η^2-isobutylene]BF_4, 41707-16-8; NaFp, 12152-20-4; 1,7-octadiene, 3710-30-3; 1,2,7,8-diepoxyoctane, 2426-07-5; tri-*n*-butylamine, 102-82-9; *trans*-2-vinyl-1-methylcyclopentane, 56827-08-8; *trans*-2-methylcyclopentanecarboxylic acid, 4541-43-9; *trans*-2-methylcyclopentanecarboxamide, 4541-44-0; vinyllithium, 917-57-7; phenyllithium, 591-51-5; tetravinyltin, 1112-56-7; cuprous iodide, 7681-65-4; *cis*-2-methylcyclopentyl tosylate, 53596-65-9; *cis*-1-methyl-2-vinylcyclopentane, 56827-05-5; *trans*-2-methylcyclopentyl tosylate, 5857-77-2; tri-*n*-butyl-*N*-deuterioammonium tetrafluoroborate, 84117-73-7; deuterium oxide, 7789-20-0; tri-*n*-butylammonium tetrafluoroborate, 41584-11-6; 2,6-octadiyne-1,8-diol, 58471-75-3; hexadiyne, 76187-88-7; *n*-butyllithium, 109-72-8; paraformaldehyde, 30525-89-4; *trans,trans*-2,6-octadiene-1,8-diol, 70475-68-2; *trans,trans*-1,8-dichloro-2,6-octadiene, 84117-74-8; 1,2,8,9-diepoxynonane, 24829-11-6; *cis,cis*-2,6-octadiene-1,8-diol, 84117-75-9; *cis,cis*-1,8-dichloro-2,6-octadiene, 84117-76-0; 1,8-nonadiene, 4900-30-5; *cis*-2-methylcyclohexanecarboxylic acid, 7076-91-7; *trans*-2-methylcyclohexanecarboxylic acid, 15177-62-5; *o*-toluic acid, 118-90-1; 2,7-nonadiyne-1,9-diol, 81077-35-2; 1,6-heptadiyne, 2396-63-6; *trans,trans*-2,7-nonadiene-1,9-diol, 84117-77-1; *trans,trans*-1,9-dichloro-2,7-nonadiene, 84117-78-2; *cis,cis*-2,7-nonadiene-1,9-diol, 81077-36-3; *cis,cis*-1,9-dichloro-2,7-nonadiene, 84117-79-3.