Carbon–Carbon Bond Formation by Condensation of $CpFe(CO)_2(\eta^1$-allyl) Complexes with $CpFe(CO)_2(\eta^2$-olefin) Cations. Regio- and Stereospecificity, Sequential Reactions Leading to Cycloadducts

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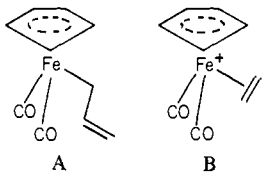
Abstract: The formation of carbon–carbon bonds by condensation of η^1-allyliron complexes with cationic iron–olefin complexes is described. $CpFe(CO)_2(\eta^1$-allyl) (**1**) reacts with $CpFe(CO)_2(\eta^2$-ethylene)$^+$ (**2a**) at room temperature to give dinuclear complex (**3a**), which may be selectively demetallated. Similarly **1** condenses with the corresponding cationic propene and styrene complexes **2b** and **2c** to give mixtures of regioisomeric adducts **3b–3e**. $CpFe(CO)_2(\eta^1$-cyclopentenyl) (**7**) condenses with **2a** to give adduct **8** but fails to react with **2b**. Complex **1** reacts smoothly with the $CpFe(CO)_2(\eta^2$-propenal) and $CpFe(CO)_2(\eta^2$-methyl *trans*-crotonate) cations (**2d** and **2e**) to give adducts **15** and **16**, respectively, resulting from conjugate addition. Both of these latter reactions exhibit a diastereoselectivity, which suggests that association of reacting components in a gauche configuration, in which olefin–olefin interactions are maximized, may be preferred over an anti configuration. The reaction of **1** with $CpFe(CO)_2(\eta^2$-butadiene)$^+$ (**23**) leads through two successive condensations to give a 1:1 mixture of cyclohexene and cyclopentane adducts (**26**, **27**). The latter may be alternatively prepared by monodeprotonation of the $[CpFe(CO)_2]_2(\eta^2$-1,6-heptadiene) dication (**31**) in a reaction which is highly stereospecific.

Introduction

Olefin-coupling reactions which are catalyzed by transition-metal complexes are numerous and varied.[2] However, fewer reagents are available for effecting this change employing well-defined complexed components in a stoichiometric reaction. The chemistry of dicarbonylcyclopentadienyliron complexes, which encompasses the reactions of neutral η^1-allyl derivatives (A) and cationic η^2-olefin complexes (B), provides a unique illustration



A B

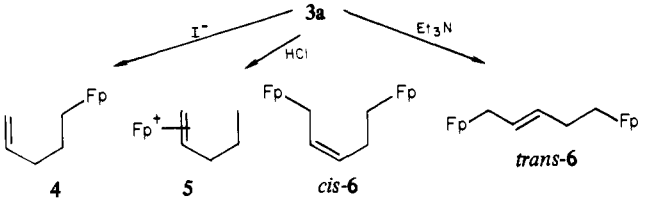
of this mode of reaction. In each of these classes of complex, the reactivity of the unsaturated center is profoundly affected Complexes of type A exhibit enhanced nucleophilic reactivity while those possessing structure B behave as moderate electrophiles.[3] (Hereafter, the η^5-$C_5H_5Fe(CO)_2$ radical is replaced by the symbol Fp.)

We had earlier described the reactions of a number of charged electrophiles with $Fp(\eta^1$-allyl) complexes[4] and of nucleophilic additions to cationic Fp(olefin) complexes.[5] The present report provides an account of the reactions of members of one class of reagents with those of a second. A preliminary account of this chemistry was given earlier.[6]

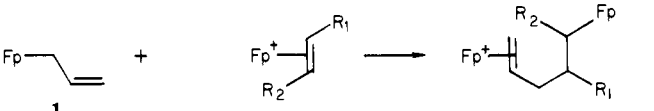
Results and Discussion

General Aspects. The parent complexes of each type (**1** and **2a**) were found to undergo condensation in nitromethane solution

Scheme I



at room temperature, affording the dinuclear condensation product **3a** in 60% yield after 4 h of reaction. In general, condensation



1

2a, R_1 = H, R_2 = H	**3a**, R_1 = H, R_2 = H
2b, R_1 = Me, R_2 = H	**3b**, R_1 = H, R_2 = Me
2c, R_1 = Ph, R_2 = H	**3c**, R_1 = Me, R_2 = H
2d, R_1 = CHO, R_2 = H	**3d**, R_1 = H, R_2 = Ph
2e, R_1 = COOEt, R_2 = Me	**3e**, R_1 = Ph, R_2 = H
2f, R_1 = COOMe, R_2 = Me	

products are readily isolated as crystalline solids by precipitation with ether. Their IR and proton NMR spectra exhibit those carbonyl absorption peaks and cyclopentadienyl proton resonances which characterize the separate cationic and neutral Fp centers. [Fp(olefin)$^+$: ν_{CO} 2040, 2090; δ 5.7. FpR: ν_{CO} 1940, 2012; δ 4.90.]

An indication of the measure of selectivity which may be exercised in the further transformations of such dinuclear species is provided in the simple conversions summarized in Scheme I. Fp(olefin) cations undergo facile displacement of the olefin ligand by halide ions, especially in aprotic solvents. Brief exposure of the dinuclear complex to NaI in acetone selectively removed the cationic Fp group, while treatment with HCl cleaved the Fe–C σ bond[7] leaving the π-bonded group intact. Finally the $Fp(\eta^1$-allyl) function may be regenerated as a mixture of cis and trans isomers (**6**) by treatment of the dinuclear complex with triethylamine. The presence of both geometrical isomers in approximately equal proportion is clearly evidenced by the presence of four distinct

(1) Taken in part from the Ph.D. theses of Patrick J. Lennon (1978), J. M. Tancrede (1973), and A. M. Rosan (1975).
(2) Tsuji, J. "Organic Synthesis by Means of Transition Metal Complexes"; Springer-Verlag: Berlin, 1975; Chapter VII.
(3) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122.
(4) Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93. Rosan, A.; Rosenblum, M. *J. Org. Chem.* **1975**, *40*, 3621.
(5) Lennon, P.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8426.
(6) Rosan, A.; Rosenblum, M.; Tancrede, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 3062.
(7) For a review of mechanisms of electrophilic cleavage of M–C bonds, see: Johnson, M. D. *Acc. Chem. Res.* **1974**, *7*, 122. Kochi, J. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; Chapter 16, 18.

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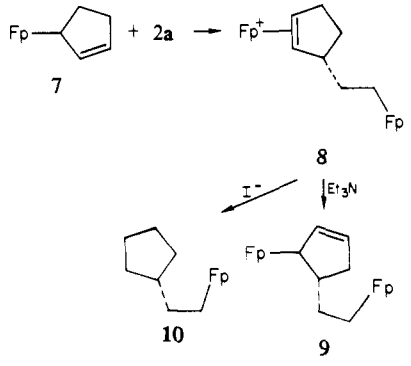
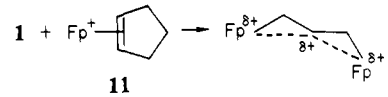
Scheme II



cyclopentadienyl resonances in the proton NMR spectrum of this product.

Condensation also takes place between **2a** and Fp(cyclopentyl) (**7**) acting as donor component. The dinuclear product (**8**), obtained in 80% yield, is assigned trans stereochemistry in accord with earlier findings for the reactions of carbon and heteroatomic nucleophiles with Fp(olefin) cations.[5] This assignment is further supported by conversion of **8** with triethylamine to the olefin (**9**), in a process shown earlier to proceed preferentially by removal of an allylic proton trans to the activating Fp(olefin) group.[8] This latter substance isolated as a yellow crystalline material (60%) clearly shows the presence of two one-proton resonances at δ 5.87 and 5.30 in addition to two Cp resonances at δ 4.65 and 4.63 in its NMR spectrum. As before, selective removal of the cationic Fp group from (**8**) is readily achieved by treatment with NaI in acetone. These transformations are summarized in Scheme II.

An attempt to effect the condensation of **7** with the Fp(propene) cation (**2b**) was unsuccessful. When equimolar amounts of these components were allowed to react for 2 h at 0 °C followed by 3 h at room temperature, the donor component could be recovered in 61% yield with no evidence for the presence of condensation material in the crude product. The inverse condensation of **1** and the Fp(cyclopentene) cation (**11**) likewise failed. Even under forcing conditions of heating the reactants in methylene chloride for several hours, the only product obtained was dinuclear complex **12** (see eq 1). This substance is evidently formed by Fp group



(1)

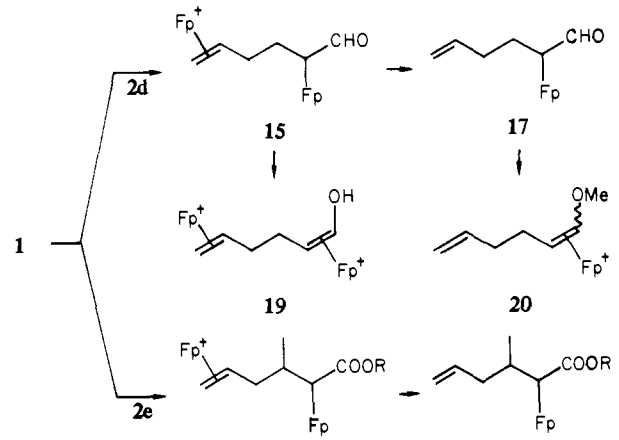
11 12

transfer from **11**, and its high chemical stability may be ascribed to stabilization of charge on the ligand by equal interaction with both Fp groups.[9,10] We have since observed that a number of acyclic and cyclic analogues of **12** may be conviently prepared from Fp(allyl) complexes employing Fp(isobutylene) salts as exchanging reagent.[11]

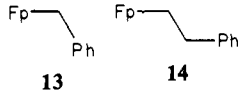
The failure of these reactions suggests a relatively high steric demand in condensations of these donor and acceptor complexes. A single alkyl substituent on either donor or acceptor component is tolerated, but substitution of both or symmetrical substitution of the acceptor component appears to foreclose reaction, in the absence of a functional group which may further activate the acceptor component (vide infra).

Monosubstituted olefin complexes do however function as acceptors with the parent allyl complex. The product of the reaction of Fp(propene) cation with **1b**, following release of the π-bond Fp group with iodide, is a 1:1 mixture of the two regioisomeric adducts **3b** and **3c**, reflecting the balance between steric factors,

Scheme III



which would be expected to favor reaction of the acceptor at the methylene center and electronic factors which should promote reaction at the substituted site. With the more highly polarized Fp(styrene) cation (**2c**) as reaction partner, the product, after removal of the cationic Fp group, is a 3:1 mixture of regioisomers **3e** and **3d**. Assignments are based on a comparison of product Ph and Cp proton chemical shifts with those in model compounds **13**[12] and **14**.[13] Since the overall energy change in these condensation reactions is likely to be favorable to the extent of about 20 kcal/mol, isomeric product ratios are assumed to be kinetically determined.



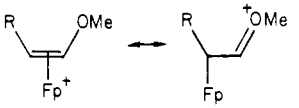
Solvent does not markedly affect the proportion of isomeric adducts **3e**:**3d**; this remains 3:1 in methylene chloride as in nitro methane and is 3:2 in acetone solution. However, an attempt to effect the above condensation reaction in dimethylformamide solution led to the recovery of 60% of unreacted Fp(allyl) even after heating these solutions at 50 °C for 5 h. No condensation product was detected, and it is possible that the more basic solvent impedes the reaction by solvation of the cationic complex.

Michael-Type Condensations. The moderate acceptor capacity of simple alkyl- or aryl-substituted Fp(olefin) cations, and in particular the low regiospecificity of their reactions with donor complex components, prompted us to examine the reactions of acceptor complexes which would be additionally activated by an electron-withdrawing function.

Both acrolein and *trans*-crotonate complexes **2d**[8] and **2e**[8] react readily with Fp(allyl) at 0 °C, affording moderate yields of Michael-type adduct **15** and **16** (Scheme III). Each of the products show the long wavelength carbonyl absorption near 1640 cm^{-1} typical of the Fp–C–COR chromophore and interaction of the organometallic substituent with the adjacent carbonyl group.[14] These complexes are readily monodemetallated by brief exposure to sodium iodide at room temperature, while protonation of acrolein adduct **15** converts it to vinyl alcohol dication **19**. The NMR spectrum of the substance does not allow assignment of geometrical structure to the vinyl alcohol ligand, but treatment of **17** with trimethyloxonium tetrafluoroborate yields the vinyl ether complex (**20**) as a mixture of cis and trans (5:1) isomers. The predominance of the cis isomer in this reaction is probably a consequence of the generally greater thermodynamic stability of cis compared with trans metal–olefin complexes.[15] Moreover,

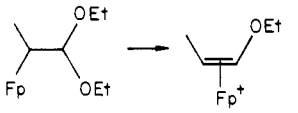
(8) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495.
(9) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *7*, 311. Kerber, R. C.; Giering, W. P.; Bauch, T. E.; Waterman, P.; Chou, E.-Hua *Ibid.* **1976**, 120.
(10) Laing, M.; Moss, J. R.; Johnson, J. *J. Chem. Soc., Chem. Commun.* **1977**, 656.
(11) Priester, W.; Rosenblum, M.; Samuels, S. B., unpublished results.
(12) Bibler, J. P.; Wojcicki, A. *J. Am. Chem. Soc.* **1966**, *88*, 4862.
(13) Ehntholt, D. J.; Emerson, G. F.; Kerber, R. C. *J. Am. Chem. Soc.* **1969**, *91*, 7547.
(14) Green, M. L. H.; Ariyaratne, J. K. P.; Bjerrum, A. M.; Ishaq, M.; Prout, C. K. *J. Chem. Soc., Chem. Commun.* **1967**, 430.
(15) Herberhold, M. "Metal π Complexes"; Elsevier: Amsterdam, 1974; Vol. II, Part 2, p 119.

the interconversion of cis and trans isomers through rotation about the putative double bond in **20** should be facile,[16] owing to contributions of forms in which charge is transferred to the oxygen atom (see eq 2).



(2)

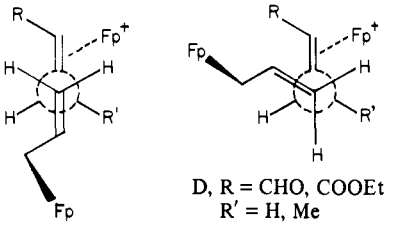
A closely related example of this thermodynamic control is to be found in the conversion of the acetal (**21**) exclusively to the *cis*-propenyl ether complex (**22**) on treatment with triethyloxonium hexafluorophosphate[17] (see eq 3).



21 22

(3)

The condensation of **1** with **2d** or **2e** results in the formation of chiral centers in the dinuclear products at the two iron-bound sites. The relative configurations of these two centers depends both on the relative orientation of Fp groups in the donor and acceptor complexes in the course of reaction and on the directional orientation of olefinic ligands in this state. Much evidence has already been accumulated to show that electrophilic addition to Fp(η^1-allyl) complexes and nucleophilic addition to Fp(olefin) cations take place trans to the activating metal–carbon bond.[5,8] Accordingly a trans relationship of both Fp centers in the activated reaction complex seems most probable. The stereochemistry of the product (**8**), formed in the condensation of **2a** with Fp(cyclopentyl) (**7**) lends further credence to these conclusions. With respect to the relative directional orientation of the reacting ligands, two idealized configurations are considered. The first of these (C), an anti arrangement of ligands, involving an end-on approach of reacting centers, minimizes steric interactions between the ligands. Configuration D is sterically more crowded, but the gauche relationship of olefinic centers allows for stabilizing electronic interactions between donor and acceptor ligands. Each of these configurations is shown in the Newman-type projection below in the form which further minimizes steric interactions between R′ and $FpCH_2$ groups.



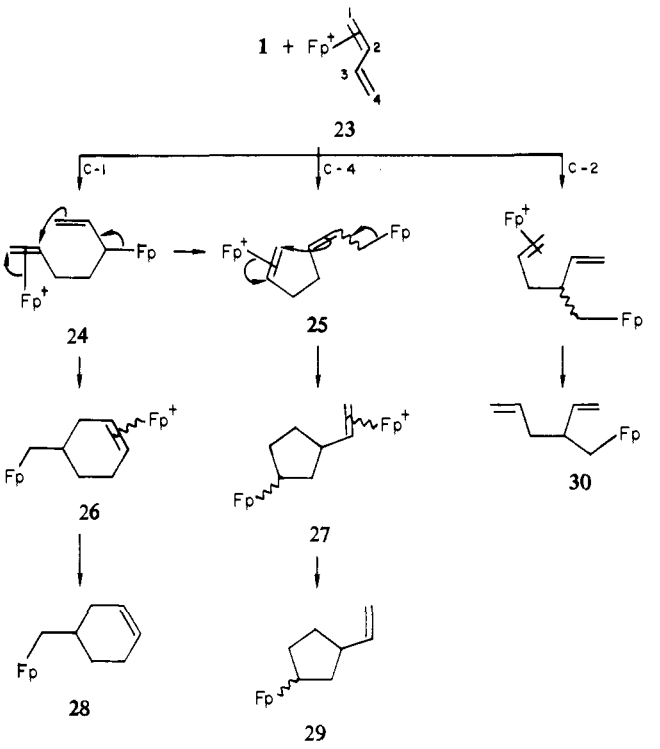
C, R = CHO, COOEt
R′ = H, Me

D, R = CHO, COOEt
R′ = H, Me

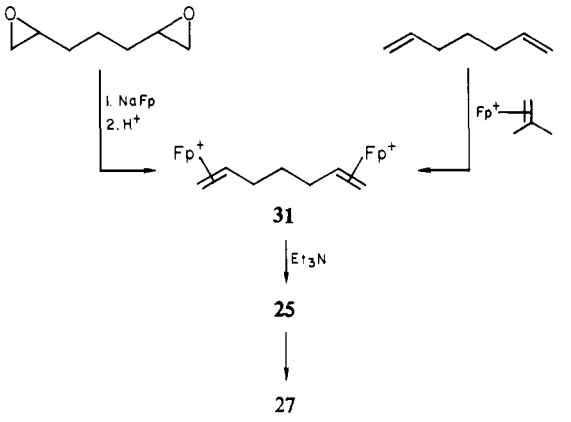
The available evidence does not allow a clear choice between these two configurations. However, the proton NMR spectrum of **15** suggests that it is a single diastereomer. Configuration C would appear to provide little ground for such diastereospecificity, while configuration D does through potential steric interaction between R and $FpCH_2$ groups. The condensation of **1** with **2e** leads to the formation of two diastereomeric products, in a ratio of approximately 2:1, but here the result is accountable in terms of either configuration C or D. Further work will be needed to clarify this point.

Formation of Carbocyclic Rings. The successful condensation of simple Fp(olefin) cations prompted us to extend these reactions to 1,3-diene complexes. The reaction of Fp(η^1-allyl) with the simplest of such cations Fp(1,3-butadiene)$^+$ (**23**) can in principle proceed through initial attack at C-1 or C-2 or by conjugate addition at C-4 of the activated diene. Attack at either C-1 or C-4 leads to the formation of dinuclear complexes (**24**, **25**), which by subsequent intramolecular condensation could give either the cyclohexenyl or cyclopentyl complexes (**26**, **27**), while initial attack of Fp(η^1-allyl) at C-2 would yield a dinuclear complex incapable of intramolecular reaction (Scheme IV).

Scheme IV



Scheme V



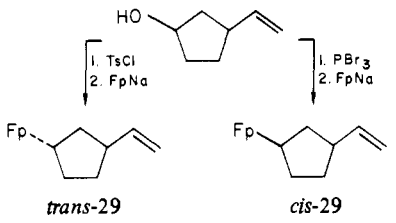
In the event, condensation of **1** and **23** for 3 h at room temperature, followed by treatment of the crude reaction mixture with NaI to remove the olefin-bound Fp group, led to the isolation of a product which was shown to be a 1:1 mixture of **28** and **29** (vide infra). The presence of appreciable amounts of diene **30** in the product could at the outset be excluded, since the product NMR spectrum exhibited only two cyclopentadienyl ring proton signals, and the ratio of olefinic to aliphatic protons was very nearly 3:8.

Intermediate **25**, the precursor of **27** and thence **29**, could be formed either by a 1,3-migration of the Fp group in **24** or directly in the condensation step. Similar 1,3-shifts of an Fp group have been shown to be rapid and to proceed in the direction shown, from a secondary to a primary carbon center.[8] Formation of **25** directly by addition of **1** to Fp(η^2-butadiene)$^+$ would be expected to yield a trans diene complex[5] while its formation via **24** should give a mixture of both cis and trans diene complexes.[8]

The synthesis of **27** through **25** alone may, however, be achieved by employing the dinuclear complex (**31**). This latter substance is readily formed either through the ligand-exchange reaction

(16) Unpublished work with W. Priester.
(17) Cutler, A.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* **1974**, *77*, 381.

Scheme VI



involving Fp(isobutylene)$^+$ and 1,6-heptadiene or by treatment of the corresponding diepoxide with 2 equiv of NaFp, followed by HBF_4, as shown in Scheme V. Treatment of the dication with 1 molar equiv of triethylamine at room temperature results in rapid deprotonation, yielding **25** most likely as a mixture of cis and trans isomers[18] and thence **27**. Complex **28** was prepared by metallation of 4-(hydroxymethyl)cyclohexene benzenesulfonate with NaFp.

A comparison of the NMR and IR spectra of the product obtained in the condensation of Fp(allyl) with Fp(η^2-butadiene)BF_4 with a 1:1 mixture of **28** and **29** shows them to be essentially superimposable.

The stereochemistry of complex **29** remained to be determined. The spectral evidence at hand was insufficient to determine whether **29** consisted of a mixture of stereoisomers or was a single species. Accordingly these stereoisomeric complexes were prepared independently by metallation of *trans*-3-vinylcyclopentyl bromide and *cis*-3-vinylcyclopentanol tosylate, synthesized in turn from *cis*-3-vinylcyclopentanol via degradation of norbornanone[19] (Scheme VI).

The stereochemical course of the metallation step shown for the tosylate in Scheme VI is well precedented,[20] and although reactions of alkyl iodides with Fp anion are complicated by one-electron-transfer processes which compete with nucleophilic displacement, such reactions do not appear to intervene with saturated primary, secondary, and tertiary alkyl bromides.[21] The more limited experience, involving metallation of optically active 2-bromobutane with NaFp, has shown that this reaction too proceeds with greater than 75% inversion of configuration.[22] Accordingly the product obtained by metallation of the bromide is assigned cis stereochemistry.

The 60-MHz ^{1}H NMR spectra of *trans*-**29** and *cis*-**29** were very nearly identical, but the ^{13}C NMR spectra allow a clear identification of each and show that the vinylcyclopentyl complex obtained from the dication **31** by monodeprotonation is exclusively trans isomer **29**. In fact, the organometallic cyclization sequence proved to be more highly stereospecific than did the synthetic sequences outlined in part in Scheme VI. The ^{13}C NMR spectra of the isomers obtained in these syntheses show each to be contaminated by 20–30% of the other isomer.

Two features of the reaction, which proceeds by deprotonation of the dication **31** and yields *trans*-**27**, deserve further comment. The regiospecificity of the reaction is perhaps unremarkable since the cyclization of intermediate **25** may be a reversible process, but in any event cyclopentane ring formation would be expected to occur in preference to cyclobutane ring formation even were this not so.[23] That cyclobutane ring formation is not a favorable process in these metal-assisted cyclization reactions is seen in the behavior of the dinuclear complex derived from 1,5-hexadiene (**32**). Monodeprotonation of this complex under conditions similar to those applied to **31**, followed by iodide treatment of the crude product gave only small amounts of ferrocene, Fp(η^1-cyclopentadiene) and 6-Fp(η^1-1,4-hexadiene) (**33**) (see eq 4).

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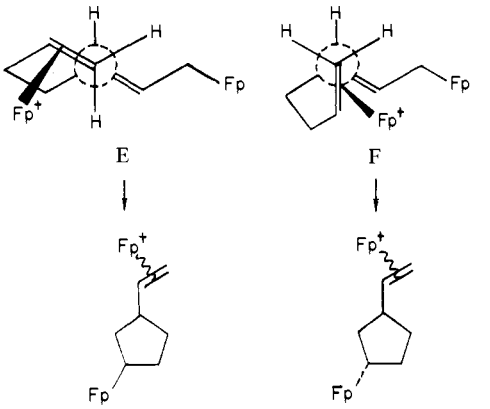
(4)

33

Scheme VII



What is perhaps more remarkable about the cyclization reaction is the exclusive formation of 1,3-trans product. The relatively little data available bearing on the comparative stabilities of 1,3-disubstituted cyclopentanes[24] provide little ground for supposing that *trans*-**27** should be thermodynamically significantly more stable than *cis*-**27**. It seems more likely then that cyclization is kinetically controlled and that a combination of structural and electronic effects determined the stereochemistry. As with the intermolecular analogue of these reactions, two idealized directional orientations of donor and acceptor ligands in the transition state, each with trans-activating organometallic Fp groups, may be depicted (E and F). In contrast to the corresponding configurations associated with intermolecular reactions, here there is a more clearly identifiable product relationship with each configuration; the anti approach E leads to a 1,3-cis product while the gauche approach F leads to a 1,3-trans product. Although E would probably be preferred on steric grounds, models show that the methylene chain is of insufficient length to accommodate this orientation of reacting centers without appreciable valence angle distortion in the chain. The gauche conformation F is relatively free of such strain (Scheme VII).

In summary, the condensation of activated ligands in Fp(η^1-allyl) complexes with those in Fp(olefin) cations has been demonstrated. In the absence of a strong polarizing group on the acceptor component, the components exhibit only moderate reactivity toward one another and low regiospecificity of addition. However, when the acceptor component is additionally activated by an electron-withdrawing group, condensations are more facile and regiospecificity is complete. A further examination of these reactions and of their application in synthesis is in progress.

Experimental Section

Solvents were routinely dried by standard procedures, maintained under nitrogen over molecular sieves, and degassed by passing through a stream of nitrogen prior to use.

All reactions and subsequent manipulations as well as the preparation of NMR samples and of 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

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

(19) Schafer, J. P.; Higgins, J. *J. Org. Chem.* **1967**, *32*, 533.

(20) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814. Nicholas, K. M.; Rosenblum, M. *Ibid.* **1973**, *95*, 4449.

(21) Krusic, P. J.; Fagan, P. J.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 250.

(22) Johnson, R. W.; Pearson, R. G. *J. Chem. Soc., Chem. Commun.* **1970**, 986.

(23) Capon, B.; McManus, S. P. "Neighboring Group Participation"; Plenum Press: New York, 1976; Vol. 1.

(24) Fuchs, B. *Top. Stereochem.* **1978**, *10*, 1.

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. Melting points were determined either in sealed capillaries or under a nitrogen atmosphere on a Kofler hot stage and are uncorrected.

Elemental Analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

Condensation of 1 and Fp(ethylene)BF_4 (2a). A solution of **1** (1.09 g, 5.0 mmol) and of **2a** (1.46 g, 5.0 mmol) in 50 mL of nitromethane was stirred 4 h at room temperature. The reaction solution was then poured into 500 mL of anhydrous ether and the product was collected by filtration. Recrystallization from methylene chloride–ether gave 1.52 g (60%) of **3a** as a yellow crystalline solid: IR (KBr) 1938, 2008, 2045, 2088 cm^{-1}; ^1H NMR (CD_3NO_2) δ 5.67 (s, 5, Cp^+), 5.22 (m, 1, CH=), 4.92 (s, 5, Cp), 3.92 (d, 1, J = 8 Hz, *cis*-CH_2=), 3.47 (d, 1, J = 15 Hz, *trans*-CH_2=), 2.83–1.17 (m, 6, CH_2).

Anal. Calcd for $C_{19}H_{19}BF_4Fe_2O_4$: C, 44.75; H, 3.72. Found: C, 44.90; H, 3.87.

Conversion of 3a to 4. Dinuclear complex **3a** (0.51 g, 1.0 mmol) was added to a solution of sodium iodide (0.20 g, 1.3 mmol) in 20 mL of acetone. Reaction was allowed to proceed at room temperature for 15 min. Solvent was removed under reduced pressure, and the residue was extracted with methylene chloride and filtered. The filtrate was concentrated and then chromatographed on an ether washed Camag alumina column (neutral, activity 2). Skellysolve B eluted 100 mg (69%) of product **4** as a yellow oil: IR (neat) 1639, 1946, 2004 cm^{-1}; ^1H NMR (CS_2) δ 5.70 (m, 1, CH=), 4.87 (m, 2, CH_2=), 4.65 (s, 5, Cp), 2.02 (m, 2, CH_2Fp), 1.47 (m, 4, CH_2CH_2).

Anal. Calcd for $C_{12}H_{14}FeO_2$: C, 58.57; H, 5.69. Found: C, 58.40; H, 5.86.

Conversion of 3a to 5. HCl gas was bubbled through a solution of **3a** (0.42 g, 0.8 mmol) in 20 mL of methylene chloride at room temperature for 20 min, during which time the color of the solution turned from orange to red. The solution was filtered, and anhydrous ether was added slowly to the filtrate until precipitation was complete. Filtration gave 0.2 g (56%) of **5** as a yellow crystalline solid: IR (KBr) 2033, 2070 cm^{-1}; ^1H NMR (CD_3NO_2) δ 5.67 (s, 5, Cp), 5.07 (m, 1, CH=), 3.95 (d, 1, J = 8 Hz, *cis*-CH_2=), 3.50 (d, 1, J = 15 Hz, *trans*-CH_2=), 2.67–0.83 (m, 7, CH_2—CH_2, CH_3).

Anal. Calcd for $C_{12}H_{15}BF_4FeO_2$: C, 43.16; H, 4.49. Found: C, 42.97; H, 4.44.

Conversion of 3a to 6. Triethylamine (0.20 g, 2.0 mmol) was added dropwise to a solution of **3a** (0.51 g, 1.0 mmol) in 10 mL of methylene chloride at room temperature. Reaction was continued for 45 min, solvent was removed under reduced pressure, and the residue was extracted with ether. After filtration and concentration, the residue was chromatographed on 30 g of an ether washed Camag alumina column (neutral, activity 3). Elution with 10% ether–Skellysolve B yielded 100 mg (31%) of **6** as an amber oil: IR (CS_2) 1953, 2000 cm^{-1}; ^1H NMR (CS_2) δ 5.32 (m, 2, CH=CH), 4.68, 4.67, 4.65, 4.62 (4s, 10, Cp), 2.20–1.17 (m, 6, CH_2).

Anal. Calcd for $C_{19}H_{18}Fe_2O_4$: C, 54.03; H, 4.36. Found: C, 54.11; H, 4.49.

Condensation of Fp(3-cyclopentenyl) (7) and Fp(ethylene)BF_4 (2a). Following the procedure used in the condensation of **1** with **2a**, reaction of 0.73 g of **7** and 0.88 g of **2a** gave 1.3 g (80%) of recrystallized product (**8**) as a yellow solid: IR (KBr) 1957, 1996, 2020, 2062 cm^{-1}; ^1H NMR (CD_3NO_2) δ 5.65 (s, 5, Cp), 5.53 (s, 2, CH=CH), 4.93 (s, 5, Cp), 3.7–1.3 (m, 8, CH, CH_2).

Anal. Calcd for $C_{21}H_{21}BF_4Fe_2O_4$: C, 47.01; H, 3.92. Found: C, 46.86; H, 3.56.

Conversion of 8 to 9. Treatment of 0.27 g of **8** with 0.10 g of triethylamine, as in the conversion of **3a** to **6**, gave an oily product which was then taken up in 2 mL of ether. Skellysolve B (10 mL) was then added, and slow evaporation of this solution in a stream of dry nitrogen gave 136 mg (60%) of product (**9**) as a yellow crystalline solid: IR (KBr) 1960, 1988 cm^{-1}; ^1H NMR (CS_2) δ 5.87 (m, 1, CH=), 5.30 (m, 1, CH=), 4.65, 4.63 (2s, 10 Cp), 3.32 (m, 1, FpC*H*), 2.5–1.2 (m, 7, CH, CH_2).

Anal. Calcd for $C_{21}H_{20}Fe_2O_4$: C, 56.23; H, 4.46. Found: C, 56.40; H, 4.55.

Conversion of 8 to 10. As for **3a**, treatment of 0.54 g of **8** with 0.2 g of NaI for 2 h at room temperature gave 167 g (62%) of **10** as a yellow oil: IR (neat) 1942, 2000 cm^{-1}; ^1H NMR (CS_2) δ 5.65 (s, 2, CH=CH), 4.65 (s, 5, Cp), 3.7–1.1 (m, 9, CH, CH_2).

Anal. Calcd for $C_{14}H_{16}FeO_2$: C, 61.79; H, 5.88. Found: C, 61.54; H, 5.97.

Condensation of 1 and Fp(propene)BF_4 (2b). Reaction was effected as with **1** and **2a**, but instead of precipitating the product, solvent was removed in vacuo and the residue was treated with 1.5 equiv of NaI in acetone. In this manner. 0.61 g (2.0 mmol) of **2b** and 0.20 g (2.0 mmol) of **1** yielded 0.20 mg (38%) of a 50:50 mixture of **3b** and **3c** after chromatography: IR (neat) 2000, 1942, 1639 cm^{-1}; ^1H NMR (CS_2) δ 5.58 (m, 1, CH=), 4.92 (m, 2, CH_2=), 4.67, 4.63 (2s, 5, Cp), 2.67–0.75 (m, 8, CH, CH_2, CH_3), 1.30 (d, 1.5, J = 7 Hz, $FpCCCH_3$).

Anal. Calcd for $C_{13}H_{16}FeO_2$: C, 60.00; H, 6.15. Found: C, 60.12; H, 6.07.

Attempted Condensation of Fp(3-cyclopentenyl) (7) with Fp(propene)BF (2b). Treatment of 0.23 g of **7** with 0.29 g of **2b** for 5 h at 0 °C, in nitromethane, followed by reaction with 0.2 g of NaI and chromatographic workup gave only recovered **7** (61%).

Attempted Condensation of Fp(allyl) (1) with Fp(cyclopentene)BF_4 (11). A solution of **1** (0.44 g, 2.0 mmol) and **11** (0.66 g, 2.0 mmol) in 20 mL of methylene chloride was stirred 4 h at room temperature and then 7.5 h at reflux. The solution was cooled to room temperature, and 200 mL of ether was added to precipitate cationic complexes, which were removed by filtration. The filtrate was concentrated, yielding 140 mg (35%) of unreacted **1**. The precipitate was washed with methylene chloride until the filtrate was colorless. The residue proved to be the dinuclear complex **12** (80 mg, 11%) by comparison with an authentic sample prepared from Fp(allyl) and Fp(isobutene)BF_4.[11] The filtrate from the above extraction was treated with ether, precipitating 0.5 g (83%) of unreacted **11**.

Condensation of 1 and Fp(styrene)BF_4 (2c). A solution of **1** (0.44 g, 20 mmol) and of Fp(styrene)BF_4 (**2c**) (0.74 g, 2.0 mmol) in 20 mL of nitromethane was stirred 5 h at room temperature. Workup of the product as in the reaction of **1** with **2b** gave 360 mg (75%) of a mixture of 4-Ph-5-Fp-1-pentene (**3e**) and 5-Ph-5-Fp-1-pentene (**3d**): IR (neat) 1639, 1949, 2000 cm^{-1}; ^1H NMR (CS_2) δ 7.13, 7.03 (2s, 5, Ph), 5.60 (m, 1, CH=), 4.83, (m, 2, CH_2=), 4.50, 4.40 (2s, 5, Cp), 2.7–1.6 (m, 5, CH, CH_2). Analysis of the NMR spectral data was made by comparing phenyl and cyclopentadienyl proton chemical shifts with those observed in the model compounds benzyl Fp[13] and 2-phenethyl Fp.[12] These were prepared by metallation of benzyl chloride and phenethyl bromide with NaFp.

Anal. Calcd for $C_{18}H_{18}FeO_2$: C, 67.08; H, 5.59. Found: C, 67.22; H, 5.74.

Condensation of 1 with Fp(acrolein)PF_6 (2d). A solution of Fp(allyl) (0.55 g, 2.5 mmol) and Fp(acrolein)PF_6 (0.84 g, 2.5 mmol) in 20 mL of nitromethane was stirred for 3 h at 0 °C. The solution was poured into 250 mL of anhydrous ether, and the precipitate was collected by filtration. Purification by reprecipitation from methylene chloride–ether gave 1.39 g (72%) of **15** as a yellow solid: IR (CH_2Cl_2) 2072, 2037, 2020, 1972, 1640 cm^{-1}; ^1H NMR (CD_3NO_2) δ 9.25 (m, 1, CHO), 5.67 (s, 5, Cp), 5.20 (m, 1, CH=), 4.93 (s, 5, Cp), 3.90 (d, 1, J = 8 Hz, *cis*-CH_2=), 3.48 (d, 1, J = 14 Hz, *trans*-CH_2=), 2.67–1.17 (m, 5, CH_2, CH).

Anal. Calcd for $C_{20}H_{19}F_6Fe_2O_5P$: C, 40.26; H, 3.26. Found: C, 40.48; H, 3.39.

Conversion of Dinuclear Complex 15 to 17. The dinuclear complex (0.59 g, 1.0 mmol) was treated with 0.20 g (1.3 mmol) of sodium iodide in 10 mL of acetone for 2 h at room temperature. Solvent was removed, and the residue was extracted with methylene chloride and filtered. Chromatography on 30 g of an ether washed Camag alumina column (neutral, activity III), eluting with 1% methanol–methylene chloride, gave 200 mg of **17** (73%) as a yellow oil: IR (CS_2) 2008, 1970, 1650 cm^{-1}; ^1H NMR (CD_3NO_2) δ 9.27 (d, 1, J = 2.5 Hz, CHO), 5.80 (m, 1, CH=), 4.90 (s, m, 7, Cp and CH_2=), 2.78–1.17 (m, 5, CH, CH_2).

Anal. Calcd for $C_{13}H_{14}FeO_2$: C, 56.96; H, 5.31. Found: C, 56.71; H, 5.76.

Protonation of Dinuclear Complex 15 Conversion to 19. Excess hexafluorophosphoric acid etherate (ca. 0.5 mmol) was added to the PF_6 salt of **15** (150 mg, 0.25 mmol) dissolved in 10 mL of methylene chloride. The resulting precipitate was filtered and washed several times with anhydrous ether, yielding 170 mg (92%) of **19** as a yellow solid: IR (Nujol) 3472, 3333, 2083, 2041 cm^{-1}. The salt is highly insoluble in liquid SO_2 and in nitromethane, and good NMR spectra could not be obtained, except that in SO_2 two Cp resonances were observed at δ 5.63 and 5.46.

Conversion of 15 to the Vinyl Ether Complex (20). Trimethyloxonium hexafluorophosphate (55 mg, 0.026 mmol) was added to a solution of **15** (70 mg, 0.026 mmol) in 30 mL of methylene chloride at 0 °C. The solution was then allowed to warm to room temperature, and after the solution was stirred for 20 min, diethyl ether was added to precipitate an oily solid. Solvent was decanted, and the solid was dissolved in methylene chloride and filtered through Celite. Removal of solvent left 83 mg of product (75%) as a mixture of cis and trans isomers. The ratio of products was determined from the integration of methoxyl proton resonances: IR (CH_2Cl_2) 2080, 2040 cm^{-1}; ^1H NMR (CD_3NO_2) δ 7.60 (d, J = 4 Hz, MeOCH=, major isomer), 7.45 (d, J = 12 Hz,

MeOCH=, minor isomer), 5.80 (m, uncomplexed CH=), 5.60 (s, Cp, minor isomer), 5.55 (s, Cp, major isomer), 5.20–5.00 (m, 2, CH_2=), 4.15 (s, OCH_3, major isomer), 4.05 (s, OCH_3, minor isomer), 3.50 (m, 1, complexed CH=), 2.5–1.8 (m, 4, CH_2).

Condensation of 1 with Fp(ethyl *trans*-crotonate)BF_4 (2e) and Demetallation. A solution of Fp(allyl) (0.44 g, 2.0 mmol) and Fp(ethyl crotonate)BF_4 in 20 mL of nitromethane was stirred at 0 °C for 3 h. After treatment of the product with NaI, followed by chromatographic workup, four bands were collected. The first yielded 140 mg (32%) of starting material, the second was identified as FpI, and the fourth was identified as ethyl *trans*-crotonate, while the third yielded 180 mg (40%) of **18**: IR (neat) 2020, 1972, 1684, 1942; ^{1}H NMR (CS_2) δ 5.33 (m, 1, CH=), 4.72 (s, m, 7, Cp and CH_2=), 3.94 (q, 2, J = 7 Hz, OCH_2), 2.3–1.3 (m, 4, CH, CH_2), 1.2 (t, 3, J = 7 Hz, OCH_2CH_3), 0.95 (d, 3, J = 6 Hz, CH_3).

Anal. Calcd for $C_{16}H_{20}FeO_4$: C, 57.83; H, 6.02. Found: C, 57.39; H, 6.52.

Condensation of 1 with Fp(methyl *trans*-crotonate) (2f). Isolation of 16 (R = Me). Fp(*trans*-methylacrylate) hexafluorophosphate (0.533 g, 1.26 mmol) was added to 25 mL of a 6:1 methylene chloride–nitromethane solution containing **3** (0.275 g, 1.26 mmol) and cooled to 0°. The solution was stirred at 0 °C for 2 h and then at room temperature for 30 min. Addition of ether precipitated a yellow solid, which was recrystallized from methylene chloride–ether to give 0.53 g (64%) of **16** (R = Me) as a yellow solid: IR (CH_2Cl_2) 2090, 2055, 2030, 1963, 1679 cm^{-1}); ^{1}H NMR (CD_3NO_2) δ 5.65 (s, 5, Cp), 5.65–5.10 (m, 1, CH=), 4.95, 4.94 (2s, 5, Cp), 4.00 (d, 1, J = 8 Hz, *cis*-CH_2=), 3.65, 3.64 (2s, 3, OMe), 3.45 (m, 1, *trans*-CH_2=), 2.9–2.6 (m, 1, CHCMe), 2.2–1.9 (m, 3, CHFp, CH_2), 1.15 (2d, 3, CH_3).

Condensation of 1 with Fp(η^2-butadiene)BF_4 (23). A solution of Fp(allyl) (0.44 g, 2.0 mmol) and **23** (0.26 g, 2.0 mmol) in 20 mL of nitromethane was stirred for 3 h at room temperature and was then treated with 0.45 g (3.0 mmol) of sodium iodide dissolved in 20 mL of acetone for 2 h. Chromatographic workup gave 210 mg (40%) of a mixture subsequently determined to be a 1:1 mixture of **28** and **29**: IR (neat) 2000, 1942, 1637 cm^{-1}; ^{1}H NMR (C_6D_6) δ 6.0–4.8 (m, *ca.* 3, CH=, CH_2=), 4.13, 4.10 (2s, 5, Cp), 2.8–0.8 (m, ca. 9, CH, CH_2).

Anal. Calcd for $C_{14}H_{16}FeO_2$: C, 61.76; H, 5.88. Found: C, 61.79; H, 5.96.

Preparation of (3-cyclohexenylmethyl)Fp (28). A solution of NaFp was prepared from Fp_2 and Na(Hg) in THF.[25] The solution was cooled to 0 °C and to this was added dropwise an equimolar solution of 4-(hydroxymethyl)cyclohexene benzenesulfonate. After 1 h, the cooling bath was removed and the reaction was allowed to continue for an additional hour at room temperature. Normal workup and chromatography on Camag alumina gave **28** in 20% yield as an orange oil: IR (neat) 2000, 1942, 1653 cm^{-1}; ^{1}H NMR (C_6D_6) δ 5.80 (m, 2, CH=), 4.10 (s, 5, Cp), 2.7–1.2 (m, 9, CH, CH_2).

Anal. Calcd for $C_{14}H_{16}FeO_2$: C, 61.76; H, 5.88. Found: C, 61.76; H, 5.88.

Preparation of (*trans*-3-vinylcyclopentyl)Fp (*trans*-29). *cis*-3-vinylcyclopentanol *p*-toluenesulfonate[19] (1.14 g, 4.3 mmol) was added to a 5 mM solution of NaFp in THF at room temperature. After 8 h, solvent was removed and the residue was extracted with Skelly-B and then filtered through a small amount of neutral alumina (activity 3). The filtrate was concentrated and placed on a 30 g column of neutral alumina (activity 3). Elution with Skelly-B gave 0.54 g (46%) of *trans*-**29**: IR (neat) 2000, 1950, 1637 cm^{-1}; ^{1}H NMR (C_6D_6) δ 5.85 (m, 1, CH=), 5.00 (m, 2, CH_2=), 4.12 (s, 5, Cp), 2.7–1.3 (m, 8, CH, CH_2); ^{13}C NMR (CD_3NO_2) δ 22.07 (C-1), 42.66, 47.38 (C-2, C-5), 44.86 (C-3), 35.08 (C-4), 86.55 (Cp), 111.59 (CH_2=), 145.71 (CH=), 218.79 (CO).

Preparation of (*cis*-3-vinylcyclopentyl)Fp (*cis*-29). *trans*-3-vinylcyclopentyl bromide (1.03 g, 5.89 mmol) was dissolved in 5 mL of THF and the solution cooled to 0 °C. To this was added dropwise 20 mL of a 0.4 M solution of NaFp in THF. After addition was complete, the reaction was allowed to continue at room temperature for 5 h. Solvent was then removed, the residue was extracted with Skelly-B, and the extracts were filtered through a small volume of Camag alumina (neutral, activity III). The filtrate was concentrated and then placed on 30 g of alumina. Elution with Skelly-B yielded 0.38 g of product (24%): IR (neat) 2000, 1942, 1639 cm^{-1}; ^{1}H NMR (C_6D_6) δ 5.83 (m, 1, CH=), 5.01 (m, 2, CH_2=), 4.10 (s, 5, Cp), 2.5–1.3 (m, 8, CH, CH_2); ^{13}C NMR (CD_3NO_2) δ 23.37 (C-1), 40.59, 49.91 (C-2, C-5), 33.47, 46.28 (C-3, C-4), 86.61 (Cp), 112.05 (CH_2=), 145.06 (CH=), 218.85 (CO).

Synthesis of Fp_2(η^2-1,6-heptadiene)$(BF_4)_2$ (31). To 0.48 g (5.0 mmol) of 1,6-heptadiene, dissolved in 80 mL of 1,2-dichloroethane, was added 3.5 g (11.0 mmol) of Fp(isobutylene)BF_4. The resulting solution was heated to 60 °C for 20 min by which time evolution of gas had ceased and the product had begun to precipitate from solution. Precipitation was completed by cooling the solution to room temperature and addition of ether. The crude product was collected, washed with methylene chloride, and reprecipitated from nitromethane ether to give 2.0 g of **31** (64%) as a yellow solid: IR (KBr) 2060, 2020 cm^{-1}; ^{1}H NMR (CD_3NO_2) δ 5.70 (s, 10, Cp), 5.08 (m, 1, CH=), 4.00 (d, 2, J = 8 Hz, *cis*-CH_2=), 3.57 (d, 2, J = 14 Hz, *trans*-CH_2=), 2.8–1.2 (m, 6, CH_2).

Anal. Calcd for $C_{21}H_{22}B_2F_8Fe_2O_4$: C, 40.38; H, 3.52. Found: C, 40.33; H, 3.39.

Conversion of 31 to *trans*-29. Dication **31** (2.44 g, 3.91 mmol) was dissolved in 25 mL of nitromethane, and 0.50 g (4.9 mmol) of triethylamine in 1 mL of nitromethane was added dropwise over a period of 25 min. After 4 h, solvent was removed in vacuo and replaced with 15 mL of acetone containing 0.87 g (5.78 mmol) of sodium iodide. The solution was stirred for 2 h at room temperature, solvent was removed, and the residue was chromatographed on alumina (neutral, activity 3), to give 0.29 g of *trans*-**29** (28%), identical by IR and ^{1}H and ^{13}C NMR with the product obtained from *cis*-3-vinylcyclopentyl bromide.

Anal. Calcd for $C_{14}H_{16}FeO_2$: C, 61.76; H, 5.88. Found: C, 61.90; H, 6.00.

Attempted Cyclization of Fp_2(η^2-1,5-hexadiene)$(BF_4)_2$ (32). The dication (0.82 g) was treated with tri-*n*-butylamine (0.25 g), and the product was treated with sodium iodide, following the procedure used with **31**. Chromatographic workup gave 6 mg of ferrocene, followed by 9 mg of an unstable amber oil: NMR ($CDCl_3$) δ 6–4.8 (several m), 4.70 (s, Cp), 2.68 (t, J = 6 Hz, CH_2), 2.10 (d, J = 8 Hz, $FpCH_2$) assigned structure (**33**). Further elution with ether–Skelly-B gave 9 mg of Fp(η^1-Cp).

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