C5H5(CO)2Fe-.eta.1-homoallylidene to C5H5(CO)2Fe-.eta.1-allylidene rearrangement, a new route to vinylmethylidenes via ligand rearrangement. Synthesis and 1,4-additions to {C5H5(CO)2Fe-.eta.1-[2-(bicyclo[3.2.1]oct-3-enylidene)]}+CF3SO3-

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$C_5H_5(CO)_2Fe$-η^1-homoallylidene to $C_5H_5(CO)_2Fe$-η^1-allylidene Rearrangement, a New Route to Vinylmethylidenes via Ligand Rearrangement. Synthesis and 1,4-Additions to $\{C_5H_5(CO)_2Fe$-η^1-[2-(bicyclo[3.2.1]oct-3-enylidene)]$\}^+CF_3SO_3^-$

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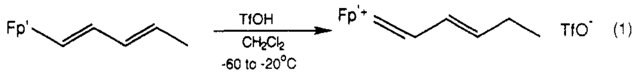
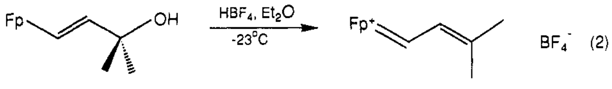
Received September 28, 1989

An epimeric mixture of [η^1-(1-bicyclo[2.2.1]hept-2-enyl)methoxymethyl]$C_5H_5(CO)_2Fe$, **4** and **5**, was prepared by sequential treatment of 1-bicyclo[2.2.1]hept-2-enecarbonyl chloride with sodium dicarbonyl(η^5-cyclopentadienyl)ferrate, methyl triflate, and sodium borohydride in basic methanol. Treatment of **4** and **5** in methylene chloride at −78 °C with fluoroboric acid/diethyl ether or with trimethylsilyl triflate yields $C_5H_5(CO)_2Fe$-η^1-(2-bicyclo[3.2.1]oct-3-enylidene) tetrafluoroborate or triflate, $\mathbf{9}^+BF_4^-$ or $\mathbf{9}^+TfO^-$, respectively. Attempts to detect the putative η^1-1-(bicyclo[2.2.1]hept-2-enyl)methylidene intermediate $\mathbf{6}^+$ by monitoring the conversion of **4** and **5** to $\mathbf{9}^+$ at −78 °C by ^1H and/or ^{13}C NMR were unsuccessful. This iron(II) homoallylidene to allylidene rearrangement constitutes a new route to β,γ-unsaturated iron(II) methylidenes. Molecular mechanics calculations (PCMODEL/MMX) employing ametallic carbocations as models for the iron(II) methylidenes are utilized to predict the course and relative facility of the rearrangement. A variety of nucleophiles (Nu), viz., lithium triethylborohydride, methyllithium, methyllithium in the presence of Cu(I) or Ce(III), lithium dimethylcuprate, dilithium dimethylcyanocuprate, methanol/$NaHCO_3$, *p*-methylthiophenoxide, dimethyl lithiomalonate, and vinyllithium react stereoselectively with $\mathbf{9}^+$ at the γ-position to yield a single complex, **10**–**15**, respectively, in each case. Addition is exo with methyllithium, lithium dimethylcuprate, and dilithium dimethylcyanocuprate and is presumed to be so with methanol/sodium bicarbonate, dimethyl sodiomalonate, and vinyllithium as well. When protonated with trifluoroacetic acid in methylene chloride at −78 °C, both **10** (Nu = H) and **11** (Nu = Me) yield $C_5H_5(CO)_2Fe$-*exo*-η^2-(*exo*-4-Nu-bicyclo[3.2.1]oct-2-ene) trifluoroacetates, $\mathbf{9}^+$ (Nu = H) and $\mathbf{19}^+CF_3CO_2^-$ (Nu = Me), respectively, which rearrange when warmed above −40 °C to $C_5H_5(CO)_2Fe$[*exo*-η^2-(4-Nu-bicyclo[3.2.1]oct-2-ene)], $\mathbf{21}^+CF_3CO_2^-$ (Nu = H), or *exo*-4-Nu-bicyclo[3.2.1]oct-2-ene, **22** (Nu = Me), respectively. Methyl triflate alkylates **10** (Nu = H) at the β-position to form a new alkylidene (η^1-2-(3-methylbicyclo[3.2.1]octylidenyl)dicarbonyl(η^5-cyclopentadieneyl)iron triflate?), which rearranges and dissociates—3-methylbicyclo[3.2.1]oct-2-ene (**23**) is the final product.

Two routes have been used for the synthesis of iron(II) allylidenes: protonation of $C_5H_5(CO)(L)Fe$-η^1-(dienyl) complexes, L = CO or $P(OCH_3)_3$,[1] eq 1, and protonation of a $C_5H_5(CO)_2Fe$-η^1-4-(2-methyl-3-buten-2-ol),[2] eq 2.

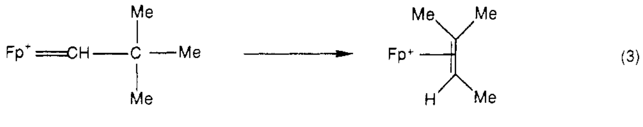


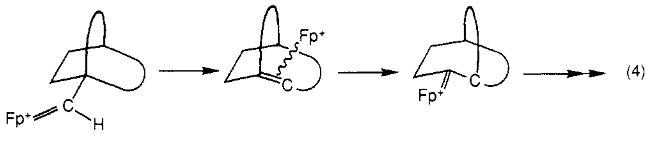
Fp'= Cp(CO)[P(OMe)3]Fe

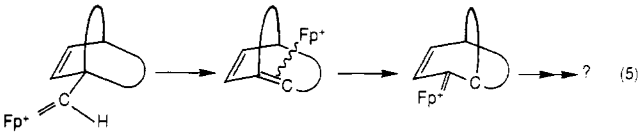


Fp= Cp(CO)2Fe

We have recently shown that protonation of $C_5H_5(CO)_2Fe$-α-alkoxyneopentyl-type complexes produces cationic $C_5H_5(CO)_2Fe$-neopentylidenes which rearrange to η^2-olefin complexes,[3] eq 3. If the complexed alkene is highly strained, as is an "unstable"[4] bridgehead olefin for example, further bond migrations can occur,[5] forming a new, rearranged alkylidene, eq 4. If the original $C_5H_5(CO)_2Fe$-neopentylidene were to contain a homoallylic double bond, its rearrangement could produce a $C_5H_5(CO)_2Fe$-allylidene, eq 5.







To test this possibility and hopefully to extend the original rearrangement to include functionally substituted derivatives, we have investigated the synthesis and rearrangement of the unsaturated methylidene [$C_5H_5(CO)_2Fe$-η^2-(1-bicyclo[2.2.1]hept-2-enyl)methylidene]$^+$ ($\mathbf{6}^+$). We now report the results of our study which include a new method for the formation of cationic, $C_5H_5(CO)_2Fe$-[η^1-(3-allylidenes)],[1,2] i.e., vinylmethylidenes, by rearrangement of cationic, $C_5H_5(CO)_2Fe$[η^1-(4-homoallylidenes)], i.e. 3-allylmethylidenes, as well as some nucleophilic and electrophilic additions to this relatively new but potentially useful functionality.

Results

After some initial difficulties[6] the requisite [η^1-(1-bicy-

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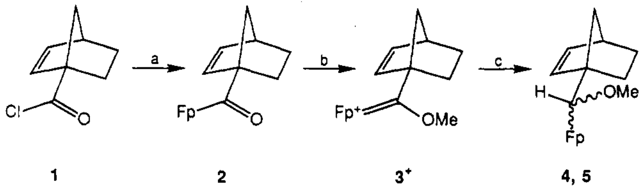
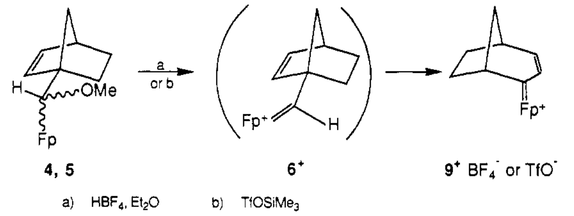
Scheme I



^{a}NaFp or KFp, THF, 25 °C. ^{b} MeOTf, CH_2Cl_2, 25 °C. ^{c} Na-$BHEt_3$, THF, CH_2Cl_2, -78 to +20 °C.

Scheme II



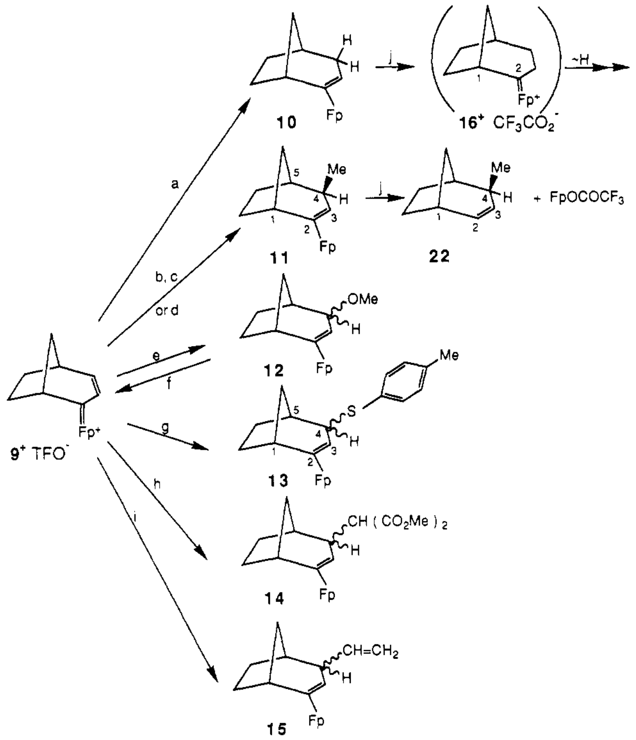
clo[2.2.1]hept-2-enyl)methoxymethyl]$C_5H_5(CO)_2Fe$ was prepared as a ~3:2 mixture of diastereomers **4** and **5** from the known 1-bicyclo[2.2.1]hept-2-enecarbonyl chloride[7] (**1**) as outlined in Scheme I.

Treatment of a mixture of **4** and **5** in methylene chloride at -78 °C with fluoroboric acid/diethyl ether[8,9] or with trimethylsilyl triflate[10] yields $C_5H_5(CO)_2Fe[\eta^1$-(2-bicyclo-[3.2.1]oct-3-enylidene)] tetrafluoroborate or triflate, $\mathbf{9}^+BF_4^-$ or $\mathbf{9}^+TfO^-$, respectively, Scheme II.

Attempts to detect the putative η^1-[1-(bicyclo[2.2.1]-hept-2-enyl)methylidene] intermediate $\mathbf{6}^+$ by monitoring the conversion of **4** and **5** to $\mathbf{9}^+$ at -78 °C by ^1H and by ^{13}C NMR were unsuccessful. Although the rearranged, β,γ-unsaturated alkylidene $\mathbf{9}^+TfO^-$ can be isolated as a yellow precipitate when the cold (-78 °C) reaction mixture is diluted with diethyl ether, it too is apparently unstable above about -20 °C.[2,3,5]

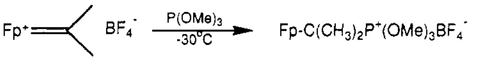
Allylidene $\mathbf{9}^+TfO^-$ adds a variety of nucleophiles at reduced temperature, a single product being formed in each case. The regiochemistry of the addition follows from the resonance at δ 157–146, which appears in the ^{13}C NMR spectrum of each product, corresponds to a "quaternary" carbon (INEPT[11]), and is attributable to $(C_5H_5(CO)_2FeC(-)=)^+$.[2b,12] Thus $\mathbf{9}^+$ is attacked by nucleophiles at the "γ-position", C(4), forming "1,4-addition" products, viz., **10**–**15**, exclusively, Scheme III. In no case was any "1,2-addition" product observed.

Scheme III



^{a}LiHBEt$_3$. ^{b} MeLi. ^{c} Li_2Me_2CuCN. ^{d} MeLi, Cu(I), or Ce(III). ^{e} $MeOH/NaHCO_3$. ^{f} HBF_4, Et_2O. ^{g} p-$MeC_6H_4S^-$. ^{h} $LiCH(CO_2Me)_2$. ^{i} $LiCH{=}CH_2$. ^{j} CF_3CO_2H, CH_2Cl_2, -78 °C.

Attempts to induce "1,2-addition" to $\mathbf{9}^+TfO^-$ were unsuccessful. With methyllithium in the presence of Ce(III)[13] at -78 °C **11** was the only addition product detected. Triphenylphosphine and trimethyl phosphite, which attack the α-position of simple Fe(II) alkylidenes and of the β,-γ-unsaturated alkylidene $[(CO)(\eta^5\text{-}C_5H_5)[P(OCH_3)_3]Fe{=}CH{-}CH{=}C(CH_3)_2]^+BF_4^-$ to form stable phosphonium salts,[1,5,14] eqs 6 and 7, *may* add to the methylene carbon, C(2) of $\mathbf{9}^+$ at reduced temperature, but the products are apparently unstable and revert to starting material, which decomposes when warmed to room temperature.



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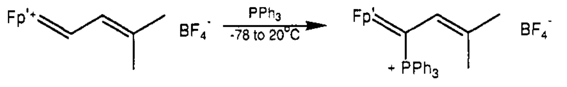
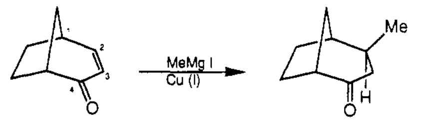


(7)

The stereochemistry of nucleophilic 1,4-addition to $\mathbf{9}^+$-TfO^- is expected to be exo for this is the kinetically preferred pathway of both electrophilic addition to bicyclo-[3.2.1]oct-2-enes[15] and 1,4-nucleophilic addition to bicyclo[3.2.1]oct-2-en-4-one,[16,17] eq 8. Both methyllithium and



(8)

dilithium dimethylcyanocuprate[18] react in this manner:

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[6] Our early attempts to prepare pure $\mathbf{3}^+TfO^-$ were frustrated by the quixotic formation of varying amounts of a saturated, polycyclic Fischer carbene of fairly high local symmetry which could not be separated from $\mathbf{3}^+TfO^-$ by fractional crystallization. We were able later to identify this material as dicarbonyl(η^5-cyclopentadienyl)[η^1-(1-nortricyclyl)methoxymethylidene]iron triflate. Its identification, separate preparation, and reactions will be reported subsequently.

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[11] These assignments are supported by refocused INEPT (cf.: Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760), a routine made available to us by our colleague Dr. Ron Garber.

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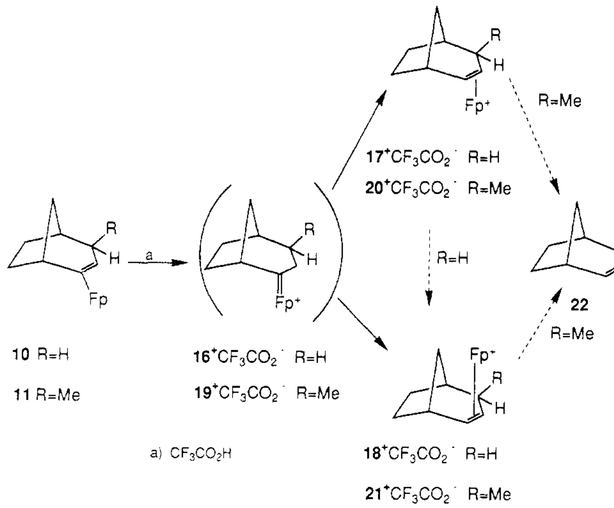
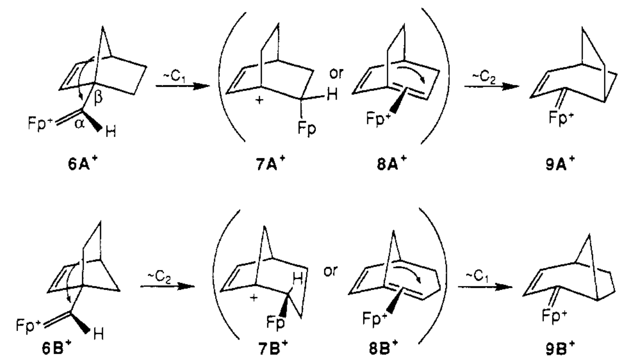
Scheme IV



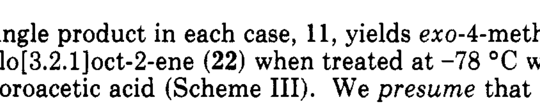
a) CF$_3$CO$_2$H

Scheme V



the single product in each case, **11**, yields *exo*-4-methylbicyclo[3.2.1]oct-2-ene (**22**) when treated at −78 °C with trifluoroacetic acid (Scheme III). We *presume* that the single diastereomers formed by 1,4-addition with methanol/sodium bicarbonate, dimethyl lithiomalonate, or vinyllithium, viz., **12**, **14**, and **15**, respectively, are also exo. The 1,4-addition product, **13**, which we observe with *p*-tolylthioxylate *may* be endo rather than exo. Cheminat and Mege, who have examined 1,4-nucleophilic additions of alkylthioxylates to bicyclo[3.2.1]oct-2-en-4-one[19] suggest that though the kinetic product in each case is exo, it rapidly epimerizes to the endo in strongly acidic or basic media.

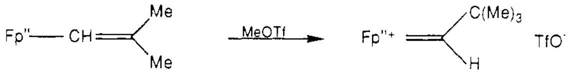
Neutral Fe(II) vinyls form Fe(II) alkylidenes when protonated,[1,2,5,14,20] eq 9. Thus at −90 to −78 °C, **10** and **11** react with trifluoroacetic acid to form **16**$^+$ and **19**$^+$, respectively. These alkylidenes, being thermally unstable,[4] rearrange to η^2-complexes as the temperature is raised. As in the case of **16**$^+$,[5] the rearrangement of **19**$^+$ at reduced temperature can be followed by ^{13}C NMR. It parallels that of **16**$^+$ except that the ultimate π-complex, [C$_5$H$_5$(CO)$_2$Fe-*exo*-η^2-(*exo*-4-methylbicyclo[3.2.1]oct-2-ene)]$^+$CF$_3$CO$_2^-$ (**21**$^+$CF$_3$CO$_2^-$), is unstable above ~0 °C and decomposes to the free olefin, *exo*-4-methylbicyclo[3.2.1]oct-2-ene (**22**), when allowed to warm to ambient temperature (Scheme IV).



(9)

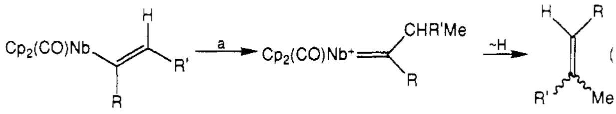
Not surprisingly,[2,8,9] **12** reacts with HBF$_4$·Et$_2$O at −78 °C to reform **9**$^+$BF$_4^-$, thus rendering the 1,4-addition of methoxide formally reversible (Scheme III).

Alkylating agents have been shown to react with Fe(II) and other neutral, late-transition-metal vinyl's at the "β-position",[14b,21,22] eqs 10 and 11. Thus methyl triflate reacts with **10** to form 3-methylbicyclo[3.2.1]oct-2-ene (**23**). The position of methylation, deduced by ^{1}H and ^{13}C NMR, was confirmed by catalytically hydrogenating **23** to *exo*-3-methylbicyclo[3.2.1]octane (**24**), whose ^{13}C{^{1}H}NMR spectrum is similar to that of the known material,[23] eq 12.



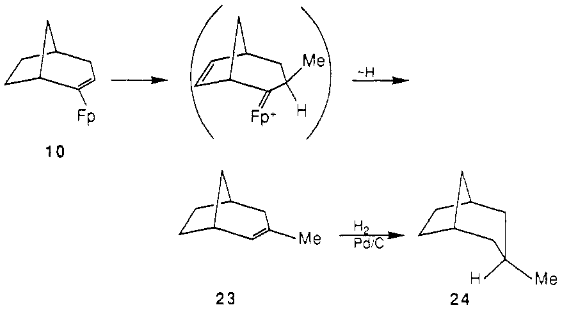
(10)

Fp'' = Cp(-PPh$_2$CH$_2$CH$_2$PPh$_2$-)Fe



(11)

a) MeOSO$_2$F



(12)

Discussion

The formation of **9**$^+$BF$_4^-$ or TfO$^-$ from the reaction of **4** and **5** with either HBF$_4$·Et$_2$O or Me$_3$SiOTf probably occurs as outlined in Scheme V. The putative initial alkylidene **6**$^+$, like the saturated analogue [C$_5$H$_5$(CO)$_2$Fe-η^1-1-norbonylmethylidene]$^+$ (**25**$^+$)[5] is unstable and shifts a β-carbon bridge to the α-methylidene carbon. The reactive, spectroscopically unobservable, C$_5$H$_5$(CO)$_2$Fe-substituted, bridgehead bicyclooctyl cation **7**$^+$ or bridgehead bicyclooctene π-complex **8**$^+$ thus produced rearranges to the observed β,γ-unsaturated C$_5$H$_5$(CO)$_2$Fe-alkylidene **9**$^+$. Of the six possible bisected, i.e., perpendicular, rotamers about the sp^2–sp^3 C(α)–C(β) bond available to the initial alkylidene, only two, **6A**$^+$ and **6B**$^+$, can lead directly—via methano (**7A**$^+$) or ethano (**7B**$^+$) bridge migration—to a C$_5$H$_5$(CO)$_2$Fe-substituted, bridgehead cation or bridgehead alkene π-complex capable of rearranging directly to **9**$^+$.

We speculate that the reaction occurs by way of the [3.2.1], i.e., B, rather than the [2.2.2] intermediate A, cf. Scheme V. The rearrangement of an iron(II) alkyl-

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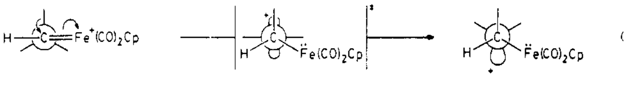
Table I. Estimated Relative Stabilities and Relative Stability Differences of Model Saturated and Unsaturated Bicyclic Bridgehead Cations and Bridgehead Carbinyl Cations

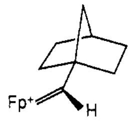
init cation	SE	PE	HF	rearranged cation	SE	PE	HF	δSE[a]	δPE[b]	δHF[c]
26$^+$	22.3	−62.4	439.7	**27**$^+$	32.9	−133.0	253.3	10.6	−70.6	−186.4
				28$^+$	33.1	−145.4	239.9	10.8	−83.0	−199.8
29$^+$	19.4		220.1	**30**$^+$	21.3		177.1	1.9		−42.9
				31$^+$	22.8		178.6	3.4		−41.4

[a] δSE = SE(rearranged bridgehead cation) − SE(initial cation). [b] δPE = PE(rearranged bridgehead cation) − PE(initial cation). [c] δHF = HF (rearranged bridgehead cation) − HF(initial cation).

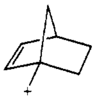
methylidene to an η^2-olefin π-complex involves a cation-like late, i.e., rearranged, transition state essentially unstabilized by the vicinal iron(II) moiety,[24] eq 13. Such transition states can be modeled as simple carbocations, and the relative migratory aptitude of differing β-substituents can be inferred from the relative stabilities of the alternate carbocation models.[3,4,25] In the present case such an approach entails comparison of the unsaturated, formally allyl, bridgehead cations **27**$^+$ and **28**$^+$.



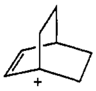
(13)



25$^+$

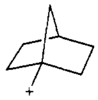


26$^+$

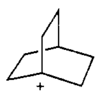


27$^+$

28$^+$



29$^+$



30$^+$

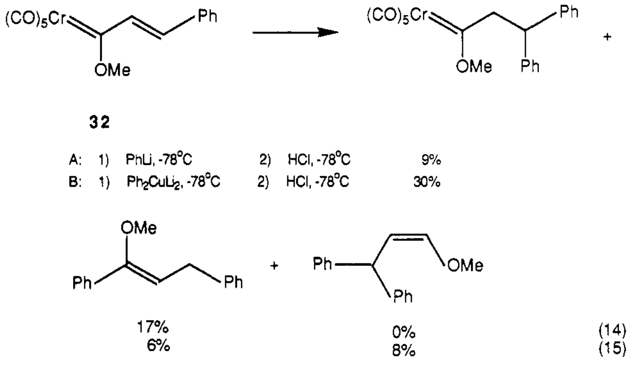
31$^+$

We and others have previously assessed the relative stabilities of saturated (bridgehead) cations by comparing their strain energies (SE) derived from molecular mechanics calculations.[3,4,26] Such a simple approach is inadequate in unsaturated bicyclic cations such as **27**$^+$ and **28**$^+$, whose stabilities clearly depend not only on their SE's but also upon the extent of charge delocalization by the "allyl" double bond.[27] We utilize PCMODEL/MMX[28] to calculate both the SE and the Pariser, Parr, "Pople π energy" (PE)[29] of each of these bridgehead cations (Table I).

From the results of these calculations it is apparent that, in accord with our earlier interpretation of the relative acetolytic rates of the relevant bridgehead brosylates,[27] the slightly greater SE of **28**$^+$ relative to **27**$^+$ is more than compensated for by the considerably greater π-electron stabilization. Path "B" via the [3.2.1] intermediate is clearly preferred![30]

The putative unsaturated methylidene **6**$^+$ is expected to be more reactive than the saturated analogue **25**$^+$. This can be inferred crudely from the differences in the calculated "heats" (enthalpies) of formation (HF) of the starting and rearranged methylidenes modeled as bridgehead carbinyl and homobridgehead cations, respectively, i.e., $\delta H \simeq$ HF(rearranged cation) − HF(starting cation), and estimated approximately by PCMODEL/MMX[28,31] (cf. Table I). Our inability to observe **6**$^+$ by low-temperature ^{13}C NMR as we had the saturated **25**$^{+\,5}$ is thus not surprising.

Michael additions[32] of carbanions to the electron-deficient carbon–carbon double bond of **9**$^+$ are highly regiospecific: only 1,4-addition is observed with methyllithium, methyllithium in the presence of Cu(I) or Ce(III) salts,[13] vinyllithium, lithium dimethylcuprate, dilithium dimethylcyanocuprate, and dimethyl sodiomalonate (Scheme III). Normally, alkyllithiums in the absence of Cu(I) add only 1,2 to α,β-unsaturated methyl ketones and ethyl esters.[33] Even additions of simple dialkylcuprates and of higher order cuprates are seldom completely 1,4 in the absence of a bulky substituent of the α-carbon.[34] Phenyllithium adds predominantly 1,2 to the neutral "Fischer" carbene $(CO)_5Cr{=}C(OCH_3){-}CH{=}CHC_6H_5$ (**32**),[35] eq 14.



(14)
(15)

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(24) (a) Cutler, A.; Fish, R. W.; Giering, W. P.; Rosenblum, M. *J. Am. Chem. Soc.* **1972**, *94*, 4354. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979; **1983**, *105*, 258.

(25) Cf.: Bly, R. S.; Wu, R.; Bly, R. K. *Organometallics*, in press.

(26) Cf.: (a) Schleyer, P. von R.; Isele, P. R.; Bingham, R. C. *J. Org. Chem.* **1968**, *33*, 1239. (b) Bingham, R. C.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1971**, *93*, 3189.

(27) (a) Bly, R. S.; Quinn, E. K. *Abstracts of Papers*, 153rd National Meeting of the American Chemical Society, Miami, FL, April 1967; American Chemical Society: Washington, DC, 1967; Abstract 91–0. (b) Quinn, E. K. Ph.D. Dissertation, Department of Chemistry, University of South Carolina, 1967. (c) Keller, T. M. Ph.D. Dissertation, Department of Chemistry, University of South Carolina, 1972.

(28) (a) PCMODEL (88.0) and MMX (88.5) are molecular mechanics software routines designed to run on an IBM-PC, cf.: Midland, M. M. *J. Am. Chem. Soc.* **1986**, *108*, 5042. They utilize the MMP2 (77) force field of N. Allinger (Georgia) (QCPE No. 395) supplemented by the generalized parameters of C. Still (Columbia) and extended to other nuclei including carbocations by J. J. Gajewski and K. E. Gilbert (Indiana). MMX (88.5) uses the same force field as PCMODEL but slightly different minimization algorithms and incorporates the PI routine of Allinger (QCPE No. 318) to permit inclusion of the Pople[29] semiempirical, SCF, π-orbital delocalization energies in the overall minimization and in the resulting, estimated heat of formation. (b) PCMODEL (88.0) utilizes the correlations of Haasnoot, DeLeeuw, and Altona (*Tetrahedron* **1981**, *36*, 2783) and of E. W. Garbisch, Jr. et al. (*J. Am. Chem. Soc.* **1964**, *86*, 5561) to calculate the three-bond (vicinal) coupling constants of C(sp^3)-C(sp^3)H's and C(sp^3)-C(sp^2)H's, respectively, from a (minimized) structure.

(29) (a) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 767. (b) Pople, J. A. *Trans. Faraday Soc.* **1953**, *49*, 1375.

(30) We cannot exclude the possibility of $C_5H_5(CO)_2Fe$ migration prior to the second carbon shift which produces the actual allylidene, **9**$^+$; cf. ref 3, through PCMODEL/MMX estimates such a shift to be endothermic in the present, unsaturated case.

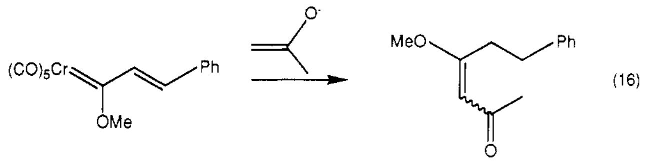
(31) Though many of the necessary enthalpy and particularly entropy contributions of the requisite carbocations **26**–**31**$^+$ are unknown and are counted by PCMODEL/MMX as zero; we presume that errors resulting from such omissions will be largely minimized or eliminated when energy differences are considered.

(32) Orchin, M.; Kaplan, F.; Macomber, R. S.; Wilson, R. M.; Zimmer, H. *The Vocabulary of Organic Chemistry*; Wiley: New York, 1980; p 388.

(33) Rozhkov, I. N.; Makin, S. M. *J. Gen. Chem. USSR* **1964**, *34*, 57.

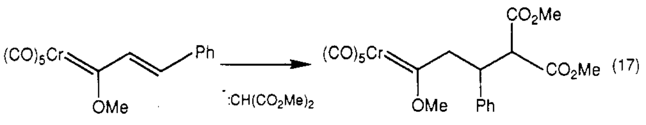
(34) Cf. Posner, G. H. *Org. React.* **1972**, *19*, 1.

Even with diphenylcuprate, ~14% of the overall addition occurs in a 1,2 manner,[35] eq 15. The enolate anion of acetone adds 1,2 to **32**, eq 16, and to the related carbene $(CO)_5Cr{=}C(OCH_3){-}CH{=}C(CH_3)_2$ (**33**) although other, more bulky anions add 1,4 to both **32**, eq 17, and **33**.[36] This latter observation led Casey and Brunswold to suggest that "nucleophilic attack at the remote site of a vinylcarbene complex is...insensitive to steric effects...[while] nucleophilic attack at the carbene carbon atom is very sensitive to the size of the entering nuclophile."[36] In view of this observation, it would be tempting to ascribe the exclusive conjugate Michael additions that we observe to steric hindrance by $C_5H_5(CO)_2Fe$ in the vicinity of the methylidene carbon of $\mathbf{9}^+$ but for the fact that both triphenylphosphene and methylsulfide anion add only 1,2 to the more bulky phosphite-ligated alkylidene $[C_5H_5(CO)[P(OCH_3)_3]Fe{=}CHCH{=}C(CH_3)_2]^+$ ($\mathbf{34}^+$), eqs 18 and 19.[1] Perhaps these latter two additions are reversible, vide supra, and therefore not really comparable to the effectively irreversible Michael additions, or perhaps the differing steric environments of the acyclic allylidenes and a bicyclic Fe(II) allylidene such as $\mathbf{9}^+$ render the companion inappropriate.[37]



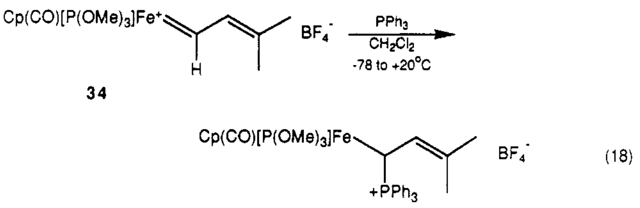
32

(16)



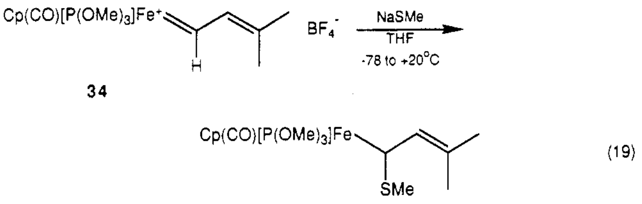
32

(17)



34

(18)



34

(19)

52%

In summary, we have developed a new method for the synthesis of a $C_5H_5(CO)_2Fe$-allylidene, viz., the $C_5H_5(CO)_2Fe$-homoallylidene to $C_5H_5(CO)_2Fe$-allylidene rearrangement, and applied it to the synthesis of a new bicyclic $C_5H_5(CO)_2Fe$-allylidene (vinylmethylidene). We have demonstrated for the first time that a cationic $C_5H_5(CO)_2Fe$-alkylidene can undergo highly regiospecific conjugative Michael additions and hydride reductions and that the resulting $C_5H_5(CO)_2Fe$-vinyls can be alkylated in good yield at the β-carbon. We continue to explore the synthetic capabilities of this relatively new functional group.

Experimental Section

General Procedures. All operations were carried out under dry, oxygen-free nitrogen or helium atmospheres using standard Schlenk-line or drybox techniques. Proton NMR spectra were recorded either on a Varian EM-390 spectrometer at 90 MHz or on an AM-300.13 at 300 MHz; the ^{13}C NMR spectra were recorded on an IBM NR-80 at 20.13 MHz, on the AM-300.13 at 75 MHz, or on an AM-500.13 at 125 MHz. Proton chemical shifts (δ) are reported in ppm downfield from TMS; ^{13}C resonances at all temperatures were recorded by using the δ 53.8 (CD_2Cl_2) or 77.0 resonance of the solvent as an internal reference and are reported in ppm down field from TMS. Some of the ^{13}C assignments were made by the refocused insensitive nucleus enhancement through polarization transfer (INEPT) technique,[11] modified and made available to us by Dr. Ron Garber. Infrared (IR) spectra were recorded on a Beckman IR-4210. The unit mass spectra were determined on a Finigan 4021 GC-MS spectrometer using a direct probe at ionization potentials of 70 eV and the accurate-mass and fast-atom bombardment (FAB) mass spectra were run on a VG Analytical, Ltd., 70SQ high-resolution, double-focusing mass spectrometer equipped with a VG 11/250 data system and analyzed by comparison with isotopic ion distributions calculated by the ISO program of VG Analytical, Ltd. Microanalyses were performed either by Atlantic Microlab, Inc., or by Robertson Laboratory, Inc.

Solvents and Reagents. Reagent grade benzene, diethyl ether, and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade dichloromethane was distilled under nitrogen from P_2O_5. Reagent grade pentane was stirred overnight with concentrated sulfuric acid, washed with water, distilled from P_2O_5, stored over sodium ribbon, and distilled from sodium under nitrogen immediately prior to use. Solvents used for spectrochemical determinations were degassed by the freeze-pump-thaw technique and stored under vacuum. Unless otherwise indicated, column chromatography was carried out either on neutral, 70–230 mesh Merck EM aluminum oxide 90, deactivated to activity stage III by the addition of 4.6 wt % water, or on Baker analyzed reagent 60–200 mesh silica gel.

Preparation of [η^1-(1-Bicyclo[2.2.1]hept-2-enyl)carbonyl]dicarbonyl(η^5-cyclopentadienyl)iron, 2.[38,39] A solution of $NaC_5H_5(CO)_2Fe$ in 200 mL of THF was prepared by reducing $C_5H_5(CO)_2Fe_2$ (2.75 g, 7.77 mmol) by using Na/Hg.[40] To this solution was added a solution of 1.902 g (12.17 mmol) of 1-bicyclo[2.2.1]hept-2-enecarbonyl chloride[7] (**1**) in 30 mL of THF, and the resulting mixture was stirred at ambient temperature for 4 h and then concentrated to dryness at reduced pressure. The resulting residue was extracted with a hexane/diethyl ether mixture (15:2, 3 × 170 mL) and filtered through a short column of alumina. The filtrate was concentrated under reduced pressure to about 200 mL and maintained at −20 °C overnight to yield 1.982 g of yellow crystals. Further concentration and cooling of the mother liquor produced an additional 0.355 g of yellow crystals. The combined yield of crystalline **2**, mp 80–83 °C, was 2.337 g (64%). The $C_5H_5(CO)_2Fe$-acyl has the following spectral properties: IR ($CHCl_3$)[38b] 2005, 1951 (—C≡O), 1648 cm^{-1} (>C=O); ^1H NMR ($CHCl_3$)[38b] δ 6.10 (m, 2 H, H(2) and H(3)), 4.79 (s, 5 H, Cp H's), 2.88 (br s, 1 H, H(4)), 1.41 (m, 6 H, >C(5,6,7)H_2's); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 260.55 (>C=O), 214.68, 214.45 (-C≡O's), 135.33, 135.27 (CH=CH), 86.21 (Cp), 81.47 (>C<), 51.58 (>CH), 41.43, 28.54, 26.68 (>CH_2's). Anal. Calcd. for $C_{15}H_{14}FeO_3$: C, 60.43;, H, 4.73; O, 16.10. Found:[38a] C, 60.29; H, 4.77; O, 16.28.

Preparation of [η^1-(1-Bicyclo[2.2.1]hept-2-enyl)methoxymethylidene]dicarbonyl(η^5-cyclopentadienyl)iron(II) Triflate, $\mathbf{3}^+$TfO$^-$. To a solution of 0.325 g (1.09 mmol) of **2** in 3 mL of CH_2Cl_2 was added 1.00 mL (1.45 g, 8.84 mmol) of methyl trifluoromethanesulfonate (MeOTf), and the resulting solution was stirred at room temperature for 13 h. The reaction mixture was diluted with 40 mL of freshly distilled Et_2O to precipitate

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[35] Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1974**, *77*, 345.

[36] Casey, C. P.; Brunsvold, W. R. *Inorg. Chem.* **1977**, *16*, 391.

[37] Cf.: Negishi, E.-I. *Organometallics in Organic Synthesis*: Wiley-Interscience: New York, 1980; Vol. I.

[38] We thank: (a) Easley Wallace, M.S. Thesis, University of South Carolina, 1978, and (b) Gary Silverman, Ph.D. Dissertation, University of South Carolina, 1984, for earlier preparations of this compound.

[39] Cf.: King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1918.

[40] Wilkinson, G.; Piper, T. S. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

the desired complex 3^+TfO^- as a yellow, apparently hydroscopic, microcrystalline solid, which was further purified by two sequential precipitations from CH_2Cl_2/Et_2O. The precipitate was dried at reduced pressure to yield 0.395 g (78%), mp 97–98 °C, of 3^+TfO^-, which has the following spectral properties: IR (CH_2Cl_2) 2050, 2005 cm^{-1} (–C≡O); ^{1}H NMR (CD_2Cl_2) δ 6.28 (m, 1 H, H(3)), 6.17 (d, J = 5.6 Hz, 1 H, H(2)), 5.45 (s, 5 H, Cp H's), 5.01 (s, 3 H, OCH_3), 3.09 (br s, 1 H, H(4)), 2.05–1.14 (m, 6 H, >C(5,6,7)H_2's); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 343.91 ((C_5H_5)(CO)$_2$Fe=*C*(R)O–), 208.57 (—C≡O's), 137.71 and 133.94 (CH=CH), 88.03 (Cp), 83.99 (>C<), 72.49 (OCH_3), 42.69 ($\geqslant$CH), 53.80, 31.90, 26.96 (>CH_2's). Anal. Calcd for $C_{17}H_{17}F_3FeO_6S$: C, 44.17; H, 3.71. Found:[43] C, 40.62 ± 3.55; H, 3.84 ± 0.13. FAB MS, *m/e* for $[M]^{\bullet +}$ ($C_{16}H_{17}FeO_3S$) calcd 313.0557, found 313.0527, $[M - CO]^{\bullet +}$ ($C_{15}H_{17}FeO_2$) calcd 285.0605, found 285.0578.

Preparation of [η^1-(1-Bicyclo[2.2.1]hept-2-enyl)methoxymethyl]dicarbonyl(η^5-cyclopentadienyl)iron(II) as a Mixture of Epimers, 4 and 5. To a solution of 0.175 g (0.379 mmol) of 3^+TfO^- in 5 mL of CH_2Cl_2 was added slowly 0.5 mL of a 1 M solution of $LiBHEt_3$ in THF. The reaction mixture was stirred at −78 °C for 10 min and then allowed to warm to ambient temperature as the volatiles were removed at reduced pressure. The resulting residue was extracted with 3 × 10 mL of 10:1 pentane/diethyl ether and filtered through a short column of alumina to provide a clear yellow filtrate, which upon concentration at reduced pressure yielded a yellow solid. This residue was dissolved in a minimum volume of hexane and chromatographed on alumina at −10 °C using hexane as eluant. Both diastereomers, i.e., **4** and **5**, were eluted as a single yellow band by using 19:1 hexane/diethyl ether. The isolated yield after purification was 0.105 g (88%). The composition of the diastereomeric mixture was determined to be ~62:38 by $^{13}C\{^1H\}$ NMR, vide infra, but no attempt was made either to determine the stereochemistry of or to separate the individual components.

The mixture of **4** and **5** has the following spectral properties: IR (CH_2Cl_2) 1992, 1932 cm^{-1} (—C≡O); ^{1}H NMR (CD_2Cl_2) δ 6.07 (m, 2 H, CH=), 4.89 (s, 5 H, Cp H's), 3.30 (s, 3 H, OCH_3), 2.79 (br s, 1 H, $\geqslant$CH), 1.86–1.02 (m, 6 H, >CH_2's); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) the major epimer, δ 218.50, 216.52 (—C≡O's), 137.08 (CH=), 133.56 (CH=), 85.69 (Cp), 86.40 (FeCH(O)–), 67.38 (>C<), 58.24 (OCH_3), 53.80 (>CH_2), 41.63 ($\geqslant$CH), 33.25 and 27.79 (>CH_2's), the minor epimer, δ 218.50, 216.52 (—C≡O's), 137.66 (CH=), 134.05 (CH=), 85.84 (Cp), 84.18 (FeCH(O)–), 67.57 (>C<), 57.96 (OCH_3), 52.62 (>CH_2), 41.63 ($\geqslant$CH), 29.23 and 27.18 (>CH_2's); mass spectrum, *m/e* 314 $[M]^{\bullet +}$, 286 $[M - CO]^{\bullet +}$, 258 $[M - 2CO]^{\bullet +}$. Anal. Calcd for $C_{16}H_{18}FeO_3$: C, 61.15; H, 5.78. Found:[38a] C, 60.98; H, 5.65.

Formation and Spectral Characterization of [η^1-2-Bicyclo[3.2.1]oct-3-enylidene]dicarbonyl(η^5-cyclopentadienyl)iron(II) Tetrafluoroborate, $9^+BF_4^-$. To a cold (−78 °C), nitrogen-blanketed solution of 0.045 g (0.143 mmol) of **4** and **5** (~62:38) in 0.6 mL of CD_2Cl_2 in a 5-mm NMR tube was added 0.05 mL of cold (−78 °C) $HBF_4{\cdot}Et_2O$. After the contents had been mixed at −78 °C, the cold tube was placed in the precooled (−78 °C) probe of an NR-80 spectrometer, and the $^{13}C\{^1H\}$ NMR spectrum was recorded: δ 352.48 (C_5H_5(CO)$_2Fe^+$=C<), 208.66, 208.30 (C≡O's), 156.46 (C(3)H=), 148.28 (C(4)H=), 91.75 (Cp), 49.71 ($\geqslant$CH), 41.49 (>CH_2), 40.39 ($\geqslant$CH), 25.66 and 25.54 (>CH_2's).

Attempts to isolate $9^+BF_4^-$ as a crystalline material were unsuccessful. The addition of diethyl ether to the cold (−78 °C) methylene chloride solution, vide supra, produced an oily material that could not be crystallized at this temperature and that decomposed when allowed to warm above that −20 °C.

Formation, Isolation, and Spectral Characterization of [η^1-2-Bicyclo[3.2.1]oct-3-enylidene]dicarbonyl(η^5-cyclopentadienyl)iron(II) Triflate, 9^+TfO^-. A nitrogen-blanketed solution of 0.035 g (0.111 mmol) of **4** and **5** was prepared in a standard 5-mm NMR tube at −78 °C. To this cooled solution was added 0.035 mL of (0.04 g, 0.181 mmol) of $Me_3SiOSO_2CF_3$. The resulting solution was well mixed at −78 °C and placed in the precooled probe of an NR-80, and the $^{13}C\{^1H\}$ NMR spectrum determined. It is, insofar as the cation is concerned, identical with that of $9^+BF_4^-$, vide supra.

When prepared on a somewhat larger scale, 9^+TfO^- can be precipitated from cold (−78 °C) methylene chloride by the addition of cold diethyl ether and isolated as a bright orange solid at that temperature by careful decantation or cannulation of the supernatant solvent. Solutions of the triflate salt of 9^+ appear to decompose above about −20 °C.

Reaction of [η^1-2-Bicyclo[3.2.1]oct-3-enylidene]dicarbonyl(η^5-cyclopentadienyl)iron(II) Triflate, 9^+TfO^-, and Lithium Tri-*sec*-butylborohydride. Preparation of [η^1-2-Bicyclo[3.2.1]oct-2-enyl]dicarbonyl(η^5-cyclopentadienyl)iron(II), 10. Precipitated 9^+TfO^-, prepared as described above from 0.095 g (0.303 mmol) of **4** and **5** and 0.2 mL (1.0 mmol) of trimethylsilyl triflate, was washed at −78 °C with 20 mL of precooled (−78 °C) diethyl ether and then suspended in 10 mL of the same. To this suspension was added 1 mL of an ~1.0 M solution of lithium tri-*sec*-butylborohydride (L-Selectride) in THF. The resulting clear solution was stirred at −78 °C for 45 min, and then 3 mL of degassed methanol was added to decompose the excess borohydride. At this point, the reaction mixture was allowed to warm to room temperature, stirred for 30 min, and then concentrated to dryness at reduced pressure. The resulting residue was dissolved in 10 mL of pentane and placed on an alumina column at −10 °C. Elution with 9:1 pentane/ether provided 0.062 g (72%) of the C_5H_5(CO)$_2$Fe-vinyl complex **10** as a fast-moving yellow band.

This material is identical with that produced when [η^1-(2-bicyclo-[3.2.1]octylidene)]dicarbonyl(η^5-cyclopentadienyl)iron(II) tetrafluoroborate, $16^+BF_4^-$, reacts with excess triethylamine in methylene chloride at ~−82 °C.[3] It has the following spectral properties: IR (CH_2Cl_2) 1995, 1945 cm^{-1} (—C≡O); ^{1}H NMR (CD_2Cl_2) δ 5.15 (m, 1 H, CH=), 4.83 (s, 5 H, Cp H's), 2.49–1.04 (m, 10 H, 2 $\geqslant$CH's + 4 >CH_2's); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 217.44, 217.27 (—C≡O's), 147.25 (-C(C_5H_5(CO)$_2$Fe)=), 132.33 (CH=), 85.80 (Cp), 53.59, 34.09 ($\geqslant$CH's), 42.73, 38.08, 33.78 and 31.21 (>CH_2's); mass spectrum, *m/e* 284 $[M]^{\bullet +}$, 256 $[M - CO]^{\bullet +}$, 228 $[M - 2CO]^{\bullet +}$. Anal. Calcd for $C_{15}H_{16}FeO_2$: C, 63.41; H, 5.68. Found: C, 63.47; H, 5.64.

Reaction of [η^1-2-Bicyclo[3.2.1]oct-3-enylidene]dicarbonyl(η^5-cyclopentadienyl)iron(II) Triflate, 9^+TfO^-, and Methyllithium. Preparation of [η^1-2-(*exo*-4-Methylbicyclo[3.2.1]oct-2-enyl)]dicarbonyl(η^5-cyclopentadienyl)iron(II), 11. Cold, precipitated 9^+TfO^-, prepared as before from 0.092 g (0.293 mmol) of **4** and **5** and 0.15 mL (0.173 g, 0.776 mmol) of trimethylsilyl triflate, was suspended in 15 mL of cold diethyl ether, stirred at −78 °C for 1 h, and then treated with 0.2 mL of ~1.5 M methyllithium in diethyl ether. The suspension dissolved immediately to give a clear, yellow-orange solution, which was stirred at −78 °C for an additional 30 min. The cooling bath was removed and the solution was concentrated to dryness under vacuum as it warmed to room temperature. The resulting residue was extracted with 20:1 pentane/diethyl ether and filtered through a short column of alumina. Concentration of the filtrate at reduced pressure gave 0.054 g (62%) of the C_5H_5(CO)$_2$Fe-vinyl complex **11** as a yellow oil: IR (CH_2Cl_2) 2000, 1947 cm^{-1} (—C≡O); ^{1}H NMR ($CDCl_3$) δ 5.07 (d, J = 4.7 Hz, 1 H, =C*H*CH(CH_3)), 4.81 (s, 5 H, Cp H's), 2.38 (m, 1 H, >CHMe), 2.12–0.83 (m, 8 H, 3 >CH_2's + 2 $\geqslant$CH's including a multiplet at 1.85 ppm due to =CHC*H*(CH_3) which, when the doublet at 5.07 ppm is irradiated, is converted into quintet (doublet of a triplet?) and when the doublet at 0.91 ppm is irradiated, is converted into a quarter (doublet of a doublet), 0.91 (d, J = 6.9 Hz, 3 H, CH_3); $^{13}C\{^1H\}$ NMR δ 217.33, 216.99 (—C≡O's), 146.74 (–C(C_5H_5(CO)$_2$Fe)=), 138.47 (CH=), 85.71 (Cp), 53.60, 45.98, 39.52 ($\geqslant$CH's), 33.31, 32.03, 31.00 (>CH_2's), 21.46 (CH_3); MS, $[M]^{\bullet +}$ cald for $C_{16}H_{18}FeO_2$ 298.0656, found 298.0642. Anal. Calcd for $C_{16}H_{18}FeO_2$: C, 64.43; H, 6.09. Found: C, 62.57 ± 0.26; H, 5.97 ± 0.03.

Reaction of [η^1-2-Bicyclo[3.2.1]oct-3-enylidene]dicarbonyl(η^5-cyclopentadienyl)iron(II) Triflate, 9^+TfO^-, and Methyllithium in the Presence of Cerous Chloride. An Attempt To Induce 1,2-Addition. Cold, precipitated 9^+TfO^-, prepared as before from 0.115 g (0.366 mmol) of **4** and **5** and 0.2 mL (1.034 mmol) of trimethylsilyl triflate, was suspended in 20 mL of cold diethyl ether at −78 °C. A clear, greenish yellow solution formed as a cold (−78 °C) solution of methyllithium/Ce(III) in THF, prepared as outlined[13b] from 0.34 g (1.40 mmol) of anhydrous[13b] $CeCl_3$ and 1.4 mL of ~1 M CH_3Li (~1.40 mmol) in 20 mL of THF at −20 °C, was added by cannula. The cooling bath was removed after 10 min, and the solution was allowed to warm slowly to room temperature, filtered through a short column of alumina, and concentrated under vacuum to produce a residue, which was dissolved in pentane and chromatographed on alumina using 10:1 pentane/Et_2O. The eluted yellow band was concentrated to yield 0.075 g (0.25 mmol, 69%) of a yellow oil whose ^{13}C NMR is identical with that of [η^1-2-(4-methylbicyclo[3.2.1]oct-2-enyl)]dicarbonyl(η^5-cyclopentadienyl)iron(II), **11**.

Reaction of [η^1-2-Bicyclo[3.2.1]oct-3-enylidene]dicarbonyl(η^5-cyclopentadienyl)iron(II) Triflate, 9^+TfO^-, and Dilithium Dimethylcyanocuprate. An Alternate Preparation of [η^1-2-(*exo*-4-Methylbicyclo[3.2.1]oct-2-enyl)]dicarbonyl(η^5-cyclopentadienyl)iron(II), 11. Cold, precipitated 9^+TfO^-, prepared as before from 0.152 g (0.484 mmol) of **4** and **5** and 0.30 mL (0.345 g, 1.55 mmol) of trimethylsilyl triflate, was suspended in 10 mL of cold diethyl ether and treated with 25 mL of a cold (-78 °C) solution containing 0.581 mmol of "$Li_2Cu(CH_3)_2CN$", which had been prepared at ~0 °C by adding 2 mol equiv of methyllithium in diethyl ether to a slurry of 0.052 g (0.581 mmol) of cuprous cyanide in diethyl ether.[18] The reaction mixture was stirred at -78 °C for 10 min, and the cooling bath was then removed to allow the temperature of the mixture to rise gradually to room temperature. After 30 min the reaction mixture was filtered through a short column of alumina, and the resulting filtrate was concentrated to dryness at reduced pressure. Further purification of the resulting yellow oil was achieved by placing it on a short column of alumina with a minimum volume of pentane and eluting with a pentane/diethyl ether mixture. Concentration of the resulting clear yellow solution at reduced pressure yielded 0.132 g (92%) of the methyl adduct, **11**, whose spectral properties are identical with those of the product of the reaction of 9^+TfO^- and methyllithium, vide supra.

Reaction of [η^1-2-Bicyclo[3.2.1]oct-3-enylidene]dicarbonyl(η^5-cyclopentadienyl)iron(II) Triflate, 9^+TfO^-, and Methanol. Preparation of [η^1-2-(4-Methoxybicyclo[3.2.1]oct-2-enyl)]dicarbonyl(η^5-cyclopentadienyl)iron(II), 12. Cold 9^+TfO^-, prepared from 0.107 g (0.341 mmol) of **4** and **5** and 0.2 mL (0.23 g, 1.04 mmol) of trimethylsilyl triflate as described above was suspended in 10 mL of cold (-78 °C) diethyl ether and treated with 0.150 g of sodium bicarbonate. A cold (-78 °C), 1:10 methanol/diethyl ether mixture was added to the suspended 9^+ salts, and the resulting slurry was stirred at -78 °C for 30 min. The cooling bath was removed, and the reaction mixture was allowed to warm slowly to room temperature. Filtration through a short column of alumina and concentration to dryness under vacuum provided a residue, which was taken up in a minimum volume of pentane and eluted as a pale yellow band from a column of alumina with 1:1 ether/pentane. The yield was 0.087 g (81%) of methoxy $C_5H_5(CO)_2Fe$-vinyl **12**: IR (CH_2Cl_2) 2004, 1952 cm^{-1} ($-C\equiv O$); ^1H NMR (CD_2Cl_2) δ 5.41 (dd, 1 H, $J_{H(3)-H(4)} = 3.99$ Hz, $J_{H(3)-H(5)} = 1.39$ Hz, =CH, which, when the doublet of doublets at 3.10 ppm is irradiated, is converted into a doublet, $J = 1.39$ Hz), 4.85 (s, 5 H, Cp H's), 3.29 (s, 3 H, OCH_3), 3.10 (dd, 1 H, $J_{H(3)-H(4)} = 3.99$ Hz, $J_{H(4)-H(5)} = 2.37$ Hz, >CHOMe, which when the doublet of doublets at 5.41 ppm is irradiated is converted into a doublet, $J = 2.37$ Hz), 2.55–0.88 (m, 8 H, 2 ⩾CH's + 3 >CH_2's) [PCMODEL[28b] predicts $J_{H(4)-H(5)} = 0.15$ Hz, $J_{H(3)-H(4)} = 4.16$ Hz for the exo isomer, $J_{H(4)-H(5)} = 1.87$ Hz, $J_{H(3)-H(4)} = 3.09$ Hz for the endo isomer]; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 216.85, 216.60 ($-C\equiv O$'s), 157.14 ($-C(C_5H_5(CO)_2Fe)=$), 132.24 (CH=), 85.76 (Cp), 83.42 (>CHOMe), 55.55 (OCH_3), 53.99 and 35.21 (⩾CH's), 33.64, 29.74 and 25.28 (>CH_2's); mass spectrum, *m/e* 314 $[M]^{\bullet+}$, 286 $[M - CO]^{\bullet+}$, 258 $[M - 2CO]^{\bullet+}$. Anal. Calcd for $C_{16}H_{18}FeO_3$: C, 61.15; H, 5.78. Found: C, 60.98; H, 5.73.

Reaction of [η^1-2-Bicyclo[3.2.1]oct-3-enylidene]dicarbonyl(η^5-cyclopentadienyl)iron(II) Triflate, 9^+TfO^-, and Sodium *p*-Methylthiophenoxide. Preparation of {η^1-2-[4-(*p*-Tolylthio)bicyclo[3.2.1]oct-2-enyl]}dicarbonyl(η^5-cyclopentadienyl)iron(II), 13. Cold 9^+TfO^-, prepared from 0.104 g (0.331 mmol) of **4** and **5** and 0.2 mL (1.00 mmol) of trimethylsilyl triflate as described above, was dissolved in 5 mL of cold (-78 °C) methylene chloride and treated with 0.07 g (0.479 mmol) of sodium *p*-methylthiophenoxide. The resulting mixture was stirred briefly at -78 °C and then allowed to warm slowly to room temperature. Volatiles from the reaction mixture were removed at reduced pressure, and the resulting residue was extracted with 9:1 pentane/diethyl ether. The extract was filtered through a short column of alumina to give a filtrate, which when concentrated at reduced pressure provided a residue that when dissolved in 5 mL of pentane and held overnight at -78 °C yielded 0.118 g (87%) of yellow, crystalline **13**, mp 68–69 °C: IR (CH_2Cl_2) 2005, 1955 cm^{-1} ($-C\equiv O$); ^1H NMR (CD_2Cl_2) δ 7.19 (m, 4 H, Ar H's), 5.28 (d, $J = 2.6$ Hz, 1 H, C*H*=CH(SAr), which when the triplet at 3.60 ppm is irradiated is converted into a singlet), 4.83 (s, 5 H, Cp H's), 3.60 (br t, $J \simeq 2.7$ Hz, 1 H, CH=C*H*(SAr), which when the doublet at 5.28 ppm is irradiated is converted into a doublet, $J = 1.7$ Hz), 2.53–0.88 (m, 8 H, 2 ⩾CH's + 3 >CH_2's), 2.31 (s, 3 H, CH_3) [PCMODEL[28b] predicts $J_{H(4)-H(5)} = 0.76$ Hz, $J_{H(3)-H(4)} = 3.54$ Hz for the exo isomer, $J_{H(4)-H(5)} = 3.32$ Hz, $J_{H(3)-H(4)} = 2.97$ Hz for the endo isomer]; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 216.74 ($-C\equiv O$'s), 157.01 ($-C(C_5H_5(CO)_2Fe)=$), 136.42, 133.31 (>C='s), 131.45, 129.63 (Ar CH='s), 130.50 (CH=), 86.03 (Cp), 58.14, 54.27 and 39.04 (⩾CH's), 34.99, 32.46 and 29.58 (>CH_2's), 20.99 (CH_3); mass spectrum, *m/e* 406 $[M]^{\bullet+}$, 378 $[M - CO]^{\bullet+}$, 350 $[M - 2CO]^{\bullet+}$. Anal. Calcd for $C_{22}H_{22}FeO_2S$: C, 65.03; H, 5.46. Found: C, 65.12; H, 5.46.

Reaction of [η^1-2-Bicyclo[3.2.1]oct-3-enylidene]dicarbonyl(η^5-cyclopentadienyl)iron(II) Triflate, 9^+TfO^-, and Dimethyl Lithiomalonate. Preparation of {η^1-2-[4-(Dicarbomethoxymethyl)bicyclo[3.2.1]oct-2-enyl]}dicarbonyl(η^5-cyclopentadienyl)iron(II), 14. Cold 9^+TfO^-, prepared from 0.135 g (0.430 mmol) of **4** and **5** and 0.27 mL (0.311 g, 1.40 mmol) of trimethylsilyl triflate as described above, was suspended in 20 mL of cold (-78 °C) diethyl ether. To this slurry was added 5 mL of a cold ethereal solution containing ~1.5 equiv of $LiCH(CO_2Me)_2$ (previously prepared at ~0 °C by taking 1 equiv of *n*-BuLi in Et_2O to an ethereal solution of $CH_2(CO_2Me)_2$). The resulting slurry was stirred at -78 °C for 10 min, the cooling bath was removed, and the reaction mixture was allowed to warm to ambient temperature. Filtration through a short alumina column, concentration to dryness under vacuum, dissolution in pentane, and chromatography on alumina using 3:1 pentane/diethyl ether to elute the slow-moving yellow band provided 0.095 g (53%) of **14**: IR (CH_2Cl_2) 2004, 1952 ($-C\equiv O$), 1732, 1750 cm^{-1} (C(=O)-OMe); ^1H NMR (CD_2Cl_2) δ 4.94 (d, 1 H, CH=), 4.80 (s, 5 H, Cp H's), 3.70 (d, 6 H, OCH_3's), 3.32 (d, 1 H, $CH(CO_2Me)_2$), 2.62–0.90 (m, 9 H, ⩾CH's + >CH_2's); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 216.40 ($-C\equiv O$'s), 169.21, 169.12 (the diastereotropic >CO=O's), 153.59 (-*C*($C_5H_5(CO)_2Fe$)=), 130.33 (CH=), 85.43 (Cp), 53.45, 49.33 and 36.01 (⩾CH's), 52.77, 52.68 (the enantiotopic OCH_3's), 33.61, 31.94, 29.97 (>CH_2's); mass spectrum, *m/e* 386 $[M - CO]^{\bullet+}$, 358 $[M - 2CO]^{\bullet+}$. Anal. Calcd for $C_{20}H_{22}FeO_6$: C, 57.97; H, 5.35. Found: C, 57.70; H, 5.12.

Reaction of [η^1-2-Bicyclo[3.2.1]oct-3-enylidene]dicarbonyl(η^5-cyclopentadienyl)iron(II) Triflate, 9^+TfO^-, and Vinyllithium. Preparation of [η^1-2-(4-Vinylbicyclo[3.2.1]oct-2-enyl)]dicarbonyl(η^5-cyclopentadienyl)iron(II), 15. Cold, precipitated $13^+CF_3CO_2^-$, prepared as detailed previously from 0.150 g (0.477 mmol) of **4** and **5** and 0.3 mL (0.345 g, 1.55 mmol) of trimethylsilyl triflate, was suspended in 25 mL of cold diethyl ether and treated with 0.95 mL of a 1.95 M solution of vinyllithium in THF. The resulting mixture was stirred at -78 °C for 10 min, and then the cold bath was removed slowly to allow the temperature of the reaction mixture to rise gradually to room temperature. After about 30 min the reaction mixture was filtered through a short column of alumina, and the resulting filtrate was concentrated to dryness at reduced pressure. The resulting residue was dissolved in a minimum volume of pentane and chromatographed on a column of activity II alumina maintained at -10 °C. The desired complex, 0.117 g (79%), eluted as a yellow band with a pentane/ether mixture: IR (CH_2Cl_2) 2005, 1950 cm^{-1} ($-C\equiv O$); ^1H NMR ($CDCl_3$) δ 5.82 (m, 1 H, C*H*=CH_2), 5.05 (d, 1 H, C*H*=C<), 4.90 (m, 2 H, H_2C=C<), 4.79 (s, 5 H, η^5-CpH's), 2.53–1.15 (m, 9 H, ⩾CH's and >CH_2's); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 216.75 and 216.65 ($-C\equiv O$'s), 148.18 ($-C(C_5H_5(CO)_2Fe)=$), 143.41, 133.95 (CH='s), 112.62 (CH=CH_2), 85.47 (Cp C's), 54.67, 53.78, 38.14 (⩾CH's), 33.54, 32.80, 30.58 (>CH_2's); mass spectrum, *m/e* $[M]^{\bullet+}$, calcd for $C_{17}H_{18}FeO_2$ 310.0656, found, 310.0631.

Reaction of [η^1-2-Bicyclo[3.2.1]oct-2-enyl]dicarbonyl(η^5-cyclopentadienyl)iron(II), 10, and Trifluoroacetic Acid. Formation of [η^1-2-Bicyclo[3.2.1]octylidene]dicarbonyl(η^5-cyclopentadienyl)iron(II), $16^+CF_3CO_2^-$. A solution of 10 mg (0.035 mmol) of the starting material in ~0.3 mL of methylene chloride was placed in a 5-mm NMR tube under an inert atmosphere, and the solvent was slowly removed under reduced pressure so as to coat the lower 1-in. portion of the tube with a thin layer of the viscous yellow solute, **10**. The tube was cooled in liquid nitrogen, and 0.5 mL of CD_2Cl_2 containing 25 mg (0.22 mmol) of trifluoroacetic acid was added. The cold tube containing the frozen reaction mixture was sealed under vacuum, inserted in the precooled (−89 °C) probe of the AM-300.13, and allowed to thaw and mix in the probe. The $^{13}C\{^1H\}$ NMR spectrum, determined after ~2 h, is essentially identical with that reported earlier[3] for $16^+BF_4^-$. The temperature of the probe was raised to −59 °C, and a second ^{13}C spectrum was recorded. It revealed the reaction mixture now to contain equal amounts of the *exo*- and *endo*-(η^2-3-bicyclo[3.2.1]octene)dicarbonyl(η^5-cyclopentadienyl)iron(II) cations, **17⁺** and **18⁺**, respectively. The sample tube was then removed from the cold probe, allowed to warm to room temperature, and reinserted in the −59 °C probe, and the contents were again analyzed by $^{13}C\{^1H\}$ NMR. The only material present in solution was the exo-π-complex,[5] $\mathbf{18}^+CF_3CO_2^-$, which was isolated by removing the solvent under vacuum and washing the residue with cold ether.

Reaction of [η^1-2-Bicyclo[3.2.1]oct-2-enyl]dicarbonyl(η^5-cyclopentadienyl)iron(II), 10, and Methyl Triflate. Formation of 3-Methylbicyclo[3.2.1]oct-2-ene, 23. A 0.4-mL (0.580 g, 3.53 mmol) aliquot of freshly distilled methyl triflate was added to 3 mL of nitrogen-blanketed solution containing 0.190 g (0.669 mmol) of **10** in CH_2Cl_2. The resulting mixture was stirred at room temperature for 20 h, and the volatiles were removed at reduced pressure (0.5 mmHg, 60 °C), washed with 2 mL of water, and dried over Na_2SO_4. About 2 mL of freshly distilled hexanes was added, and the volume of the solution was reduced by slowly distilling the low-boiling volatiles (mostly CH_2Cl_2) through a wire-spiral-packed column at atmospheric pressure. Gas chromatographic analysis of the residue on a 3 ft × 1/4 in. column packed with 20% Carbowax 20M on 100 mesh Chromosorb P at 120 °C indicated the presence of two olefins in the ratio of 1:10. The minor hydrocarbon was identified as bicyclo[3.2.1]oct-2-ene by admixture with a known pure (98%) sample.[41] The major component was identified as 3-methylbicyclo[3.2.1]oct-2-ene (**23**) from the ^{13}C NMR [$(CDCl_3)$[11] δ 131.24 (C(Me)=), 128.62 (CH=), 42.18, 35.73, 35.41 (>CH_2's), 35.02, 33.23 (>CH's), 30.39 (>CH_2), 22.93 (CH_3)] and from the molecular ion in the mass spectrum (*m/e* $[M]^{\bullet+}$ calcd for C_9H_{14} 122.20, found 122) as well as by comparison of the ^1H NMR [$(CDCl_3)$ δ 5.54 (*d*, *J* = 7 Hz, 1 H, CH=), 2.89 (m, 3 H, >*C*HCH=C(Me)C*H*$_2$), 1.81–1.39 (m, 10 H, >CH, >CH_2's, CH_3)] with that of known material.[42] The GLPC yield of **23**, determined by the addition of a known quantity of norbornene to the reaction mixture, was 94%.

When the above reaction was carried out for 6 h at −78 °C then allowed to warm slowly to room temperature, the ratio of bicyclo[3.2.1]oct-2-ene to **23** in the reaction mixture was ~2:1.

To confirm the identity of **23**, 3 mL of a solution of bicyclo[3.2.1]oct-2-ene and **23** in hexane, prepared at room temperature as described above, was hydrogenated at atmospheric pressure in the presence of a small amount of Pd/C. The mixture was filtered, dried over Na_2SO_4, and concentrated to about 1 mL by slow distillation through a wire-spiral-packed column at atmospheric pressure. The resulting 3-methylbicyclo[3.2.1]octane (**24**) was separated and collected by preparative GLPC on the Carbowax 20M column (vide supra) and characterized spectroscopically: ^1H NMR ($CDCl_3$) δ 2.11 (br s, 2 H), 1.68–1.01 (m, 9 H), 0.95 (m, 2 H), 0.80 (d, *J* = 7.5 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 41.99, 39.36 (>CH_2's), 35.21 (>CH's), 29.19 (>CH_2), 25.49 (>CH), 22.56 (CH_3). Although these ^{13}C chemical shifts are 0.3–0.5 ppm larger than those reported for *exo*-3-methylbicyclo[3.2.1]octane,[23] we take this as conformation that **23** is, in fact, 3-methylbicyclo[3.2.1]oct-2-ene.

Reaction of [η^1-2-(4-Methylbicyclo[3.2.1]oct-2-enyl)]dicarbonyl(η^5-cyclopentadienyl)iron(II), 11, with Trifluoroacetic Acid. Formation of *exo*-4-Methylbicyclo[3.2.1]oct-2-ene, 22. To a cold (−78 °C) solution of 0.072 g (0.242 mmol) of **11** in 10 mL of Et_2O was added 50 μL (0.565 mmol) of CF_3SO_3H. The mixture was stirred at −78 °C for 10 min, and the cold bath was removed. A yellow precipitate formed as the reaction mixture warmed to room temperature over a 30-min period. The supernatant solvent was removed by cannulation, and the precipitate was washed with 2 × 10 mL of ether and dried under vacuum to yield 0.082 g (76%) of a mixture whose $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2) indicated the presence of uncomplexed 4-methylbicyclo[3.2.1]oct-2-ene, **22**: δ 133.32 and 129.42 (−CH=CH−), 40.91, 38.74, 35.06, 33.69, 30.25 and 30.06 (3 >CH's and 3 >CH_2's), 20.15 (CH_3), and an unidentified $C_5H_5(CO)_2Fe$ derivative (δ 209.74 (−C≡O's), 84.59 (Cp)).

In a second experiment, 0.2 mL (0.296 g, 2.60 mmol) of freshly distilled CF_3SO_3H was added to a cold (−78 °C) solution of 0.095 g (0.319) mmol of **11** in 3 mL of CH_2Cl_2, and the mixture was stirred at −78 °C for 30 min and then allowed to warm to room temperature over a 30-min period. The volatiles were removed under vacuum (0.5 mmHg, 25 °C), washed successively with 2-mL portions of saturated, aqueous $NaHCO_3$ and water, and then dried over anhydrous Na_2SO_4. The dried solution was diluted by the addition of ~2 mL of freshly distilled hexanes, 0.018 g (0.167 mmol) of pure bicyclo[3.2.1]oct-2-ene was added as an internal reference, and the low-boiling components (mostly CH_2Cl_2) were removed by slow distillation through a wire-spiral-packed column at atmospheric pressure. The resulting olefins were separated and collected by the preparative GLPC at 120 °C on a 3 ft × 1/4 in. column packed with 20% Carbowax 20M on 100 mesh Chromosorb P. The yield of 4-methylbicyclo[3.2.1]oct-2-ene was 73% as calculated from the relative areas of the reference bicyclo[3.2.1]oct-2-ene and 4-methylbicyclo[3.2.1]oct-2-ene (**22**) peaks. It has the following spectra: ^1H NMR ($CDCl_3$) δ 5.81 (dddd, 1 H, *J* = 9.52, 6.60, 1.48, 1.49 Hz, >CHCH=C*H*CH(CH_3)), 5.25 (ddd, 1 H, *J* = 9.48, 3.76, 1.67 Hz, >CHC*H*=CHCH(CH_3)), 2.31 (m, 1 H, >C*H*CH=CHCH(CH_3)), 2.14–1.54 (m, 6 H, >CH_2's), 1.43–1.34 (m, 1 H, >CHCH=CHC*H*(CH_3)), 1.25–1.18 (m, 1 H, >CH), 0.97 (d, *J* = 7.1 Hz, >CH(C*H*$_3$); mass spectrum, *m/e* (rel intensity) $[M]^{\bullet+}$ 122 (32), 107 (25), 94 (22), 93 (100), 91 (19) 79 (95). PCMODEL[28b] predicts: $J_{H(1)-H(2)}$, 5.93 Hz, $J_{H(3)-H(4)}$ = 3.88 Hz, and $J_{H(4)-H(5)}$ = 1.04 Hz for the exo isomer; $J_{H(1)-H(2)}$ = 5.88 Hz, $J_{H(3)-H(4)}$ = 3.01 Hz, and $J_{H(4)-H(5)}$ = 3.82 Hz for the endo isomer.

The stereochemistry of the 4-methyl group of **22** was confirmed as exo by comparison of these spectra with those of authentic *exo*-4-methylbicyclo[3.2.1]oct-2-ene,[19] viz: "^1H NMR ($CDCl_3$) δ 5.83 (dddd, 1 H, *J* = 10, 7.1, 1.5, 1.5 Hz), 5.27 (ddd, 1 H, *J* = 10, 4, 2 Hz), 2.3–2.4 (7, 1 H), 1.6–2.1 (m, 6 H), 1.4–1.5 (m, 1 H), 1.2–1.3 (m, 1 H), 1.00 (d, 3 H, *J* = 7 Hz); mass spectrum, *m/e* (rel intensity) $[M]^{\bullet+}$ 122 (12), 107 (11), 94 (24), 93 (61), 91 (18), 81 (18), 80 (20), 79 (100), 78 (12), 77 (27)" and *endo*-4-methylbicyclo[3.2.1]oct-2-ene: "^1H NMR ($CDCl_3$) δ 5.77 (dddd, 1 H, *J* = 10, 6, 2, 1 Hz), 5.16 (ddd, 1 H, *J* = 10, 2, 2 Hz), 2.5 (m, 1 H), 2.3 (m, 1 H), 2.1 (m, 1 H), 1.5–1.8 (m, 6 H), 0.92 (d, 3 H, *J* = 7.5 Hz); mass spectrum, *m/e* (rel intensity) $[M]^{\bullet+}$ 122 (40), 107 (27), 94 (32), 93 (100), 91 (21), 81 (38), 80 (33), 79 (98), 78 (20), 77 (29)".

Reaction of [η^1-2-(*exo*-4-Methylbicyclo[3.2.1]oct-2-enyl)]dicarbonyl(η^5-cyclopentadienyl)iron(II), 11, and Trifluoroacetic Acid Followed by Variable-Temperature $^{13}C\{^1H\}$ NMR. A cold solution of 20 μL of CF_3CO_2H in 0.6 mL of CD_2Cl_2 under N_2 was syringed into a 5-mm NMR tube at −78 °C containing 0.027 g of **11**. After the resulting mixture had been quickly mixed at −78 °C, the tube was inserted into the precooled (−78 °C) probe of the NR-80 and the $^{13}C\{^1H\}$ NMR spectrum of alkylidene **19⁺** was recorded: δ 422.82 (>Fe^+=C<), 206.83 and 206.52 (−C≡O's), 92.63 (η^5-Cp C's), 78.85, 71.85, 49.29, 39.34, 35.75, 30.45, 29.17 (>CH's + >CH_2's), 20.19 (CH_3).

The probe temperature was slowly increased to −70 °C, and a second ^{13}C spectrum was recorded. Judging from the absence of resonances attributable to **19⁺** and the presence of two distinct Cp resonances in the ratio of ~2.4:1 characteristic of an $C_5H_5(CO)_2Fe(\eta^2\text{-olefin})$,[44] we presume the reaction mixture now primarily to contain an ~2.4:1 mixture of *endo*- and *exo*-η^2-(*exo*-4-methylbicyclo[3.2.1]oct-2-ene)dicarbonyl(η^5hcyclopentadienyl)iron(II), **20⁺** and **21⁺** respectively. $^{13}C\{^1H\}$ NMR δ 211.46 and 207.58 (−C≡O's), 88.37 and 88.14 (η^5-Cp C's), and

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[41] Organic Technology, Inc., Coshocton, OH.

[42] Brun, P.; Waegell, B. *Tetrahedron* **1976**, *32*, 1125.

[43] Average of three separate determinations; the sample is apparently hygroscopic.

[44] Laycock, D. E.; Baird, M. C. *Inorg. Chim. Acta* **1980**, *42*, 263.

severely overlapping resonances at 89.34 and 80.34, 42.93, 39.25, 38.64, 34.87, 33.67, 29.56, 23.11 (>CH's, >CH_2's and CH_3's).

The probe temperature was slowly raised to −50 °C, and a third ^{13}C spectrum was recorded of the reaction mixture, viz., δ 210.57 and 208.30 (—C≡O's), 88.58 (η^5-Cp C's), 90.16 and 86.86 (η^2-(CH=CH's)), 39.16 (2, >CH's), 38.25 (>CH), 34.15, 32.11 and 28.52 (>CH_2's), 23.45 (CH_3). We attribute these resonances to [*exo*(?)-η^2-(*exo*-4-methylbicyclo[3.2.1]oct-2-ene)dicarbonyl(η^5-cyclopentadienyl)iron(II)]$^+$, **21**$^+$.

The NMR tube containing the reaction mixture was removed from the probe and maintained at 0 °C overnight, and a fourth ^{13}C spectrum identical with that of *exo*-4-methylbicyclo[3.2.1]oct-2-ene, **22**, was recorded.

Reaction of [η^1-2-(4-Methoxybicyclo[3.2.1]oct-2-enyl)]dicarbonyl(η^5-cyclopentadienyl)iron(II), 12, and Tetrafluoroboric Acid. Formation of [η^1-2-Bicyclo[3.2.1]oct-3-enylidene]dicarbonyl(η^5-cyclopentadienyl)iron(II) Tetrafluoroborate, 9$^+$BF$_4^-$. A nitrogen-blanketed solution of 12 (0.035 g, 0.111 mmol) in 0.6 mL of CD_2Cl_2 was cooled to −78 °C in a 5-mm NMR tube. To this cold solution was added 0.1 mL of $HBF_4{\cdot}Et_2O$, the contents were mixed at −78 °C, the tube was placed in the precooled (−78 °C) probe of the NR-80, and the $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture was determined. It is identical in all respects to that of **9**$^+BF_4^-$ formed when an ~3:2 mixture of **4** and **5** is protonated under similar conditions.

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Organolanthanide-Catalyzed Cyclodimerizations of Disubstituted Alkynes

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The lanthanide alkyls $Cp_2{}^*LnCH(SiMe_3)_2$ (Ln = La, Ce) are efficient catalysts for the cyclodimerization of 2-alkynes MeC≡CR (R = Me, Et, *n*-Pr) to 1,2-disubstituted 3-alkylidenecyclobutenes. The first step in the reaction is a propargylic metalation of the α-methyl group, giving $Cp^*{}_2LnCH_2C{\equiv}CR$ compounds and free $CH_2(SiMe_3)_2$.

Various lanthanide alkyls and hydrides are active alkene polymerization catalysts.[1,2] In fact, $Cp^*{}_2LnH$ (Ln = La, Nd, Sm, Lu)[2c] compounds appear to be the most active ethylene polymerization catalysts known to date. The bis(pentamethylcyclopentadienyl)lanthanides are excellent models for the study of alkene polymerization. Mechanistic studies with this class of compounds have led to a better understanding of polymerization pathways and related reactions such as termination and chain transfer.[2a] In contrast, relatively little is known about organolanthanide-catalyzed alkyne oligomerization and polymerization. The reported literature deals mainly with acetylene polymerization by Ziegler–Natta type systems.[3] Our interest in this area stems from the observation that $Cp^*{}_2Y$– and $Cp^*{}_2Sc$–alkyl species are active catalysts for the selective dimerization of α-alkynes to 2,4-disubstituted enynes.[4] In this communication we report the reactivity of some well-defined lanthanide alkyls with various disubstituted alkynes.

Reaction of $Cp^*{}_2LnCH(SiMe_3)_2$ (Ln = La, Ce) with an excess of 2-butyne (benzene-d_6, 2-butyne/$Cp^*{}_2LnCH(SiMe_3)_2$ ratio 20:1) results in the catalytic formation of a cyclic dimer: 1,2-dimethyl-3-ethylidenecyclobutene (**1**; eq 1, characterized by MS and ^1H and ^{13}C NMR methods).[5] The reaction proceeds to completion in ca. 10 h at

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(1) The following abbreviations are used in this article: Cp* = η^5-C_5Me_5 ring, Ln = lanthanide or group 3 element, lw = line widths of NMR resonances at half-maximum.

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(5) Cyclic dimer 1 was separated from the catalysts by vacuum transfer (25 °C, 0.01 mmHg) and obtained as a benzene-d_6 (or benzene) solution. Attempts to purify 1 by vacuum distillation (bp 38–40 °C, 24 mmHg) resulted in partial decomposition. Spectroscopic data for 1: ^1H NMR (benzene-d_6) δ 4.96 (q, $^3J_{HH}$ = 6.6 Hz, 1 H, =C(*H*)Me), 2.72 (s, 2 H, CH_2), 1.66 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, =C(H)*Me*), 1.61 (s, 3 H, Me), 1.51 (s, 3 H, Me); ^{13}C NMR (benzene-d_6) δ 141.3 (s), 140.4 (s), 139.2 (s), 102.5 (d, $^1J_{CH}$ = 153 Hz, =*C*(H)Me), 36.4 (t, $^1J_{CH}$ = 137 Hz, *C*H_2), 13.5 (q, $^1J_{CH}$ = 126 Hz, Me), 13.1 (q, $^1J_{CH}$ = 126 Hz, Me), 9.1 (q, $^1J_{CH}$ = 126 Hz, Me); MS $M^{\bullet +}$ = m/e 108. 1 slowly decomposes in air and must be stored under nitrogen. NMR and GC methods and a successful computer simulation of ^1H NMR spectra including all long-range proton–proton coupling constants suggest the formation of a single isomer. Attempts to determine the exact geometry of the ethylidene moiety by ^1H NOE difference measurements were not successful. However, 2D NOESY spectra display a clear NOESY cross-peak between the ring CH_2 and the ethylidene methyl group and imply that the latter is pointing toward the ring CH_2 protons.

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