[Fp-η^1-(1-polycycloalkyl)methylidene]$^+$ to [Fp-η^2-(1-homopolycycloalkene)]$^+$ Rearrangement. Carbon Migration in Iron(II) Alkylidenes. A New Route to Stabilized Bridgehead Olefins

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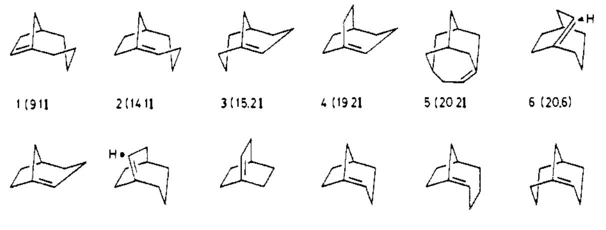
Abstract: Acyls $(CO)_2(\eta^5\text{-}C_5H_5)FeCOR$ (**18**: **a**, R = 1-bicyclo[3.2.1]octyl; **b**, R = 1-bicyclo[2.2.2]octyl; **c**, R = 1-adamantyl) are synthesized from the corresponding 1-polycycloalkanecarbonyl chlorides and $(CO)_2(\eta^5\text{-}C_5H_5)FeK$. The acyls, **18**, react with $(C_2H_5)_3O^+BF_4^-$ or with $CH_3OSO_2CF_3$ to form 1-alkoxy-1-polycycloalkylmethylidene salts, $[(CO)_2(\eta^5\text{-}C_5H_5)Fe{=}C(OC_2H_5)R]^+BF_4^-$ (**19**: **a**, R = 1-bicyclo[3.2.1]octyl) or $[(CO)_2(\eta^5\text{-}C_5H_5)Fe{=}C(OCH_3)R]^+CF_3SO_3^-$ (**22**: **a**, R = 1-bicyclo[3.2.1]octyl; **b**, R = 1-bicyclo[2.2.2]octyl; **c**, R = 1-adamantyl), which react with $LiHB(C_2H_5)_3/CH_2Cl_2$ or $NaBH_4/CH_3OH/CH_3ONa$ to form an ~50:50 mixture of the racemic, diastereomeric alkoxyalkyls, $(CO)_2(\eta^5\text{-}C_5H_5)FeCH(OR')R$ (**20a** and **21a**, R′ = C_2H_5, R = 1-bicyclo[3.2.1]octyl or **23a** and **24a**, R′ = CH_3, R = 1-bicyclo[3.2.1]octyl) or the racemic **23** (**b**, R′ = CH_3, R = 1-bicyclo[2.2.2]octyl; **c**, R′ = CH_3, R = 1-adamantyl). The alkoxyalkyls **20a** and **21a**, **23a** and **24a**, and **23b** and **23c** react with either $HBF_4/(C_2H_5)_2O/CH_2Cl_2$ or $(CH_3)_3SiOSO_2CF_3/CH_2Cl_2$ to form alkylmethylidene salts, $[(CO)_2(\eta^5\text{-}C_5H_5)Fe{=}CHR]^+$ (**25**$^+$: **a**, R = 1-bicyclo[3.2.1]octyl; **b**, R = 1-bicyclo[2.2.2]octyl; **c**, R = 1-adamantyl), of BF_4^- or $CF_3SO_3^-$, respectively, which are unstable and rearrange at −78 °C or below to the corresponding $[(CO)_2(\eta^5\text{-}C_5H_5)Fe(\eta^2\text{-}1\text{-homopolycycloalkene})]^+$, **26**$^+$ (η^2-1-bicyclo[3.3.1]nonene), **29**$^+$ and **30**$^+$ (*re*- and *si*-η^2-1-bicyclo[3.2.2]nonene, respectively), or **31**$^+$ (η^2-3-homoadamantene) BF_4^- or $CF_3SO_3^-$ salts. The products are identified by ^1H and $^{13}C\{^1H\}$ NMR and, in the cases of **26**$^+BF_4^-$, **29**$^+CF_3SO_3^-$, and **30**$^+CF_3SO_3^-$, by single-crystal X-ray diffraction. Complex **26**$^+BF_4^-$ reacts with $(CH_3)_3NO$ to form (*Z*)-1-bicyclo[3.3.1]nonene, **3**. Alkylidene **25a**$^+$ reacts with $LiBH(C_2H_5)_3/CH_2Cl_2$ at −78 °C to form $(CO)_2(\eta^5\text{-}C_5H_5)Fe(\eta^1\text{-bicyclo[3.2.1]octylcarbinyl})$, **28**, prepared independently by treatment of **18a** with BH_3/THF. These 1-polycyclomethylidene to 1-homopolycycloalkene rearrangements and the rearrangement of $[(CO)_2(\eta^5\text{-}C_5H_5)Fe{=}CHC(CH_3)_3]^+$ (**32**$^+$) have been followed and the first-order rate constants determined by variable-temperature ^1H and/or $^{13}C\{^1H\}$ NMR: **25a**$^+$, $k_1(-95\ °C) = 2.3 \times 10^{-6}\ s^{-1}$; **25b**$^+$, $k_1(-95\ °C) = 9.0 \times 10^{-6}\ s^{-1}$; **25c**$^+$, $k_1(-95\ °C) = 9.4 \times 10^{-10}\ s^{-1}$; **32**$^+$, $k_1(-95\ °C) = 4 \times 10^{-3}\ s^{-1}$. The $-\log k_1$'s, statistically corrected for the number of conformations that can rearrange to the observed product, correlate ($r^2 = 0.924$) with the differences in estimated strain energies of the 1-alkyl substituent and the rearranged (bridgehead) cation unstabilized by the adjacent iron(II) moiety. These rearrangements constitute the first reported examples of a β- to α-carbon shift in a transition-metal alkylidene.

A double bond at the bridgehead of a bicyclic hydrocarbon can be strained and highly reactive. Molecular mechanics has been used to estimate the difference in total strain energy of a bicyclic hydrocarbon and the related bridgehead olefin(s) in a number of cases, Chart I.[1-3] Maier and Schleyer have noted that when this calculated "olefin strain" (OS, kcal/mol) is less than ~17, the free olefin is "isolable" at room temperature and can be characterized both chemically and spectroscopically, when ~17 < OS < ~21, the olefin is "observable" spectroscopically at reduced temperature but cannot be isolated at room temperature, and when OS > ~21, the olefin is "unstable" and can be observed only in a matrix at greatly reduced temperature.[2] Thus **1**[4] **2**,[4] and **3**[5-7] have been isolated (**3** has a $t_{1/2}$ for [2 + 2] dimerization of ~3 days at room temperature[8]), **4**,[9] **5**,[1] and **6**[9] have been detected spectroscopically at −80 °C or less but dimerize rapidly when warmed (at 0 °C the $t_{1/2}$ of **4** is ~20 min and of **6** < 3 min[9]), **7** and **9** are known only through trapping[10,11] and/or retro-Diels–Alder products,[12] and **12** can only be inferred from stereochemical considerations.[13]

Chart I. Some Bridgehead Olefins and Olefin Strain (OS, kcal/mol)



Because of their kinetic instability, bridgehead olefins are frequently condensed or formed in the presence of the reagent with which they are intended to react.[10,11,14] In this manner several isolable bridgehead olefins have been trapped as neutral Pt(0)– or Pt(II)–(η^2-olefin) complexes[8,15,16] (eq 1–3). These π-complexes are considerably less reactive than the free bridgehead olefins themselves.

In view of the tendency of strained bridgehead olefins to dimerize, it could be advantageous to form the π-complex in a unimolecular fashion, for lower concentrations might then be employed. 3-Homoadamantene (**5**),[1,17] and probably adamantene

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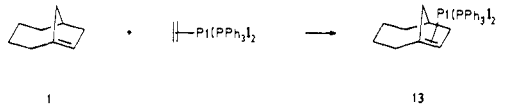
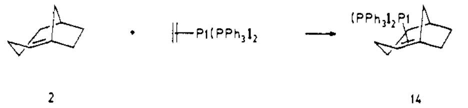


(1)



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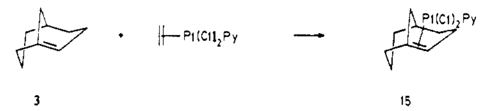
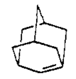


(3)

(**16**, OS = 39.5)[18] and **9** as well,[12] have been prepared in this manner by the intramolecular, gas-phase rearrangement of 1-polycycloalkylcarbenes (eq 4). If this approach could be extended to metal-complexed carbenes (alkylidenes) in solution, π-complexed bridgehead olefins could result (eq 5).



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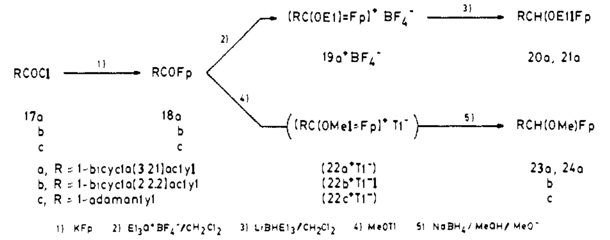
(4)

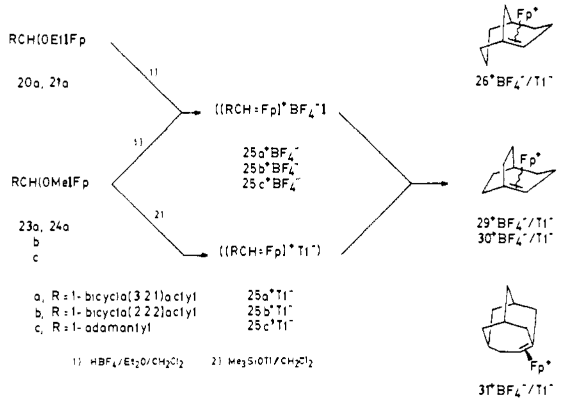
(5)

When we initially considered this project we could find no reports of β- to α-carbon shifts in transition-metal alkylidenes[19] though comparable hydrogen shifts are relatively common.[25-32] Not surprisingly perhaps, none of the many nucleophilic alkylidenes of Nb or Ta or the 16-electron imido- or oxoalkylidenes of W shift either β-hydrogen or β-alkyl.[33-35] Nor, apparently, do the more electrophilic $[\mathrm{Cp(Ph_2PCH_2CH_2PPh_2)Fe{=}CHC(CH_3)_3}]^+$[36] and $[\mathrm{Cp(NO)(Ph_3P)Re{=}CHC(CH_3)_3}]^+$[37] shift β-methyl. Phosphorus ligands such as diphos, phosphines, and phosphites are known to stabilize alkylidenes and to slow β- to α-hydrogen shifts,[27,28,38,39] so perhaps the absence of β-methyl migration in these particular cases is understandable.

Scheme I



Scheme II



Even though β- to α-carbon shifts had not been previously observed, we felt that two factors could favor them in Cp(CO)$_2$Fe neopentylidenes (eq 5): the carbenoid carbon is especially electrophilic,[38] and there are no β-hydrogens to shift in preference to carbon.[25,30] Here, we report the preparation and rearrangement of three 1-polycycloalkyl-substituted dicarbonyl(η^5-cyclopentadienyl)iron(II), i.e. Fp, methylidenes: [Fp(1-bicyclo[3.2.1]octyl)methylidene]$^+$ (**25a**$^+$), [Fp(1-bicyclo[2.2.2]octyl)methylidene]$^+$ (**25b**$^+$), and [Fp(1-adamantyl)methylidene]$^+$ (**25c**$^+$).

Results

The required Fp-η^1-(1-polycycloalkyl)alkoxymethyl starting materials were prepared from 1-polycycloalkanecarbonyl chlorides **17** as outlined in Scheme I. The acyl complexes **18** can be alkylated with either triethyloxonium tetrafluoroborate[40,41] or methyl triflate.[28] In view of the high diastereoselectivities that are obtained when certain racemic, chiral metal alkylidenes react with nucleophiles,[30,37,42-45] it is notable that at −78 °C the reduction of neither **19a**$^+$BF$_4^-$ with lithium triethylborohydride in dichloromethane[27] nor **22a**$^+$Tf$^-$ with sodium borohydride in basic methanol[28] exhibits any such selectivity: an approximately 50:50 mixture of diastereomers, **20a** and **21a** or **23a** and **24a**, respectively, is formed in each case. Evidently, the influence of the larger, adjacent chiral metal center is sterically significant whereas that

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(19) Some rearrangements that occur during metal-catalyzed valence isomerizations of certain strained polycyclic hydrocarbons may be of this type,[20-22] but alternate paths are sometimes possible, there is some uncertainty about the nature of the actual intermediate,[23,24] and a stable π-complex is not the final product.

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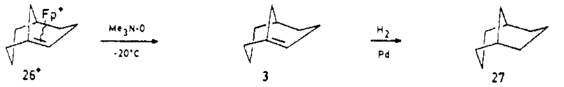
of the smaller, adjacent chiral carbon is not.[46]

The reactive, cationic [Fp-η^1-(1-polycycloalkylmethylidenes)]$^+$ **25** were generated from the (1-polycycloalkyl)alkoxymethyls by the well-precedented routes outlined in Scheme II. Protonation of the 50:50 mixture of ethoxyalkyls **20a** and **21a** in dichloromethane at 25 °C with excess HBF_4/Et_2O[47,48] provides a single air-stable, yellow crystalline salt, **26**$^+BF_4^-$, in 92% yield. The terminal C≡O stretches of this salt at 2080 and 2040 cm^{-1} in the infrared region together with the single Cp carbon resonance at δ 89.7,[49,50] the >C= and =CH– vinyl carbon resonances at δ 106.4 and 71.5, respectively, the single ⋗CH resonance at δ 37.8, and the six distinct >CH$_2$ resonances in the ^{13}C NMR characterize it as an [Fe(η^2-bicyclonon-1-ene)]$^+BF_4^-$. It is worthy of emphasis, vide infra, that a single π-complex is formed from the diastereomeric mixture of ethoxyalkyls **20a** and **21a**. The somewhat less soluble, analogous cationic triflate, **26**$^+$Tf$^-$, is formed in comparable yield when the mixture of methoxyalkyls **23a** and **24a** reacts in dichloromethane with trimethylsilyl triflate.[28]

Decomplexation of **26**$^+BF_4^-$ reveals that the olefinic ligand is a bicyclo[3.3.1]non-1-ene rather than a bicyclo[4.2.1]non-1-ene or a bicyclo[3.2.2]non-1(7)-ene. In sharp contrast to most cationic Fp(η^2-olefin) complexes, **26**$^+$ is unreactive toward sodium iodide in acetone even at reflux.[51] However, at −20 °C in dichloromethane **26**$^+BF_4^-$ reacts with excess anhydrous trimethylamine oxide[52] to produce a single olefin (GC yield 75%) whose $^{13}C\{^1H\}$ NMR matches that reported for (*Z*)-bicyclo[3.3.1]non-1-ene (**3**)[8] and whose catalytic hydrogenation product exhibits a mass spectrum identical with that of bicyclo[3.3.1]nonane (**27**)[53] (eq 6).[54]



(6)

The structure of **26**$^+BF_4^-$ was confirmed, and the stereochemistry of π-complexation was revealed by single-crystal X-ray diffraction.[60]

The intermediate [Fp(alkylidene)]$^+$, **25a**$^+$, can be detected by ^1H and ^{13}C NMR. Protonation of an equimolar, dichloromethane solution of **20a** and **21a** in an NMR tube at −78 °C with excess HBF_4/Et_2O produces inter alia transient resonances at δ 397 and 94.0 in the $^{13}C\{^1H\}$ NMR spectrum of the mixture and at δ 17.9 in the ^1H NMR. We attribute these resonances to the methylidene and Cp carbons, respectively, and to the methylidenic hydrogen of the intermediate alkylidene **25a**$^+$. There is precedent for these assignments[61] and for this method of generating a cationic Fp(alkylidene).[47,48]

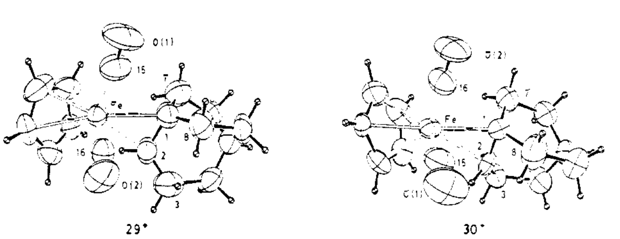
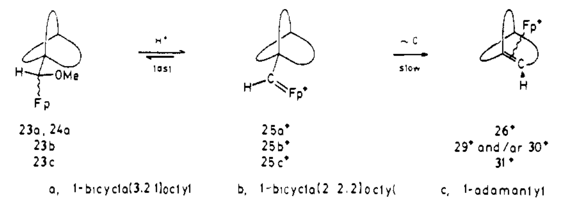


Figure 1. ORTEP plots of single enantiomers of the diasteriomeric *re*- and *si*-(η^2-bicyclo[3.2.2]non-1-ene)(η^5-C_5H_5)(CO)$_2$Fe cations **29**$^+$ and **30**$^+$, which make up half the unit cell, showing thermal ellipsoids at the 50% probability level; unlabeled large atoms are carbon. Hydrogen atoms (small) are not refined. Bond distances [**29**$^+$ (*re*), **30**$^+$ (*si*)] (Å): Fe–C(1), 2.239 (9), 2.175 (7); Fe–C(2), 2.241 (7), 2.157 (7); C(1)–C(2), 1.38 (1), 1.353 (9); C(1)–C(7), 1.49 (1), 1.54 (1); C(1)–C(8), 1.68 (1), 1.54 (1); C(2)–C(3), 1.43 (1), 1.48 (1). Angles [**29**$^+$, **30**$^+$] (deg): C(1)C(2)C(3), 115.6 (7), 121.9 (6); C(2)C(3)C(4), 104.3 (7), 103.9 (7); C(2)C(1)C(7), 112.5 (7), 118.8 (6); C(2)C(1)C(8), 103.4 (7), 91.5 (6); FeC(1)C(8), 106.7 (5), 119.7 (6); FeC(2)C(3), 129.4 (6), 130.6 (5).

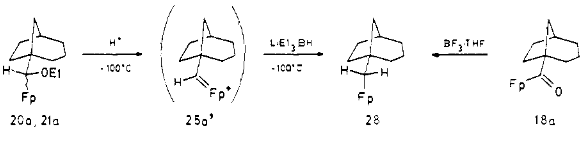
Table I. Rate and Activation Parameters of β- to α-Alkyl Migration in [Fp(η^1-alkylmethylidenes)]$^+$ **25**$^+$ and **32**$^+$

compd	k_1(−95 °C), s^{-1}	δ(H*), kcal/mol	δ(S*), eu	δ(G*), kcal/mol	k_1 (rel)
32$^+$	~4 × 10^{-3}			~12	10^0
25b$^+$	9.0 × 10^{-6}	13	−10	14	10$^{-2.6}$
25a$^+$	2.3 × 10^{-6}	21	33	15	10$^{-3.2}$
25c$^+$	9.4 × 10^{-10}	19	6	18	10$^{-6.6}$

Scheme III



Alkylidene **25a**$^+$ can also be detected chemically. Protonation of a solution of **20a** and **21a** in dichloromethane at −100 °C followed immediately by addition of an equally cold solution of excess lithium triethylborohydride in THF[27] provides a neutral σ-complex, **28**, identical in all respects to Fp[η^1-(1-bicyclo[3.2.1]octyl)methyl] formed by reduction of acyl **18a** with BH_3/THF (eq 7).[66] This neopentyl-type σ-complex is stable at ambient temperature since it has no β-hydrogen.[67]



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(54) Attempts to convert **26**$^+$ to **3** using either methyllithium[55,56] or KFp[57,58] at 25 °C produced mixtures of **3** and 2-bicyclo[3.3.1]nonene, identified by comparison of its ^{13}C NMR spectrum with that of an authentic sample graciously provided by Dr. Andreas Heumann, Laboratoire de Stéréochimie, CNRS, Université d'Aix-Marseille III, Faculté de Saint-Jérôme. Decomplexation of **26**$^+$ with methyllithium at −25 to −20 °C produces a single bicyclononene which reacts with 1,3-diphenylisobenzofuran under these conditions to yield a mixture of Diels–Alder adducts,[6] the infrared spectrum of which is identical with that of a comparable product mixture prepared earlier from authentic **3**.[59] We thank Prof. J. A. Marshall for providing a spectrum of this original product mixture.[6]

(55) Aris, K. R.; Brown, J. M.; Taylor, K. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2222.

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(57) Sanders, A.; Giering, W. P. *J. Am. Chem. Soc.* **1975**, *97*, 919; *J. Organomet. Chem.* **1976**, *104*, 49.

(58) Bauch, T. E.; Giering, W. P. *J. Organomet. Chem.* **1976**, *114*, 165.

(59) Hossain, M. M., Ph.D. Dissertation, Department of Chemistry, University of South Carolina, 1985.

(60) Bly, R. S.; Hossain, M. M.; Lebioda, L. *J. Am. Chem. Soc.* **1985**, *107*, 5549.

(61) (a) [Fp═CMe$_2$]$^+$: δ 419 (═C<).[29] (b) [(CO)Cp(PPh$_3$)Fe═CMe$_2$]$^+$: δ 406.5 (═C<).[29] (c) [(CO)Cp(PPh$_3$)Fe═CHEt]$^+$: δ 383.2 (═C<).[28] (d) [(CO)Cp(PPh$_3$)Fe═CHMe]$^+$: δ 380.0 (═C<),[28] 17.85 (q, J = 8 Hz, ═CHMe).[27] (e) [Fp═CH(*c*-C_3H_5)]$^+$: δ 365 (═CH–) and 16.73 (d, $^1J_{CH}$ = 13 Hz, ═CH–).[62] (f) [Cp(diphos)Fe═CHCMe$_3$]$^+$: δ 359.5 (t, $^2J_{PC}$ = 26.4 Hz, ═CH–) and 13.68 (t, $^3J_{PH}$ = 14.0 Hz, ═CH–).[36] (g) [Fp(η^1-1-benzocyclobutenylidene]$^+$: δ 352 (═C<).[63] (h) [Fp═CHPh]$^+$: δ 342.4 (d, $^1J_{CH}$ = 146 Hz, ═CH–) and 16.86 ppm (s, ═CH–); [(CO)Cp(PPh$_3$)Fe═CHPh]$^+$: δ 341.2 (dd, $^1J_{CH}$ = 136 Hz, J_{CP} = 21 Hz, ═CH–) and 17.43 ppm (d, J_{PH} = 1.12 Hz, ═CH–).[64] (i) [Cp(diphos)Fe═CH$_2$]$^+$: δ 317.5 (J_{PC} = 32 Hz, J_{CH} = 140 Hz, ═CH$_2$), 13.89 (t, J_{PH} = 14 Hz, ═CHH) and 17.29 (brs, ═CHH).[65]

(62) Brookhart, M.; Studabaker, W. B.; Husk, G. R. *Organometallics* **1985**, *4*, 943.

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(64) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099.

(65) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203.

(66) van Doorn, J. A.; Mastis, C.; Vogler, H. C. *Organomet. Chem.* **1976**, *105*, 245.

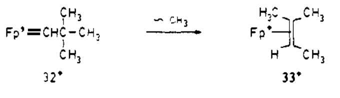
Table II. Estimated Relative Strain Energy Differences of $[Fp(\eta^1\text{-alkylmethylidenes})]^+$ and Rearranged 2-Fp-1-Homoalkyl (Bridgehead) Cations

$[Fp{=}CHR]^+$	R	SE of R[a]	rearranged cation (bridgehead)	intermed cation (polycyclic ring)	SE^{+}[b]	δSE[c]
32$^+$	*tert*-butyl	−0.9	**37**$^+$	2-methyl-2-butyl	3.7	4.5
25a$^+$	1-[3.2.1]octyl	10.3	**34**$^+$	[3.3.1]	17.3	7.0
			35$^+$	[3.2.2]	21.5	11.2
			38$^+$	[4.2.1]	26.3[d]	16.0
25b$^+$	1-[2.2.2]octyl	10.2	**35**$^+$	[3.2.2]	21.5	11.3
25c$^+$	1-adamantyl	3.5	**36**$^+$	3-homoadamantyl	21.6	18.1

[a] Reference 2. Engler, E. M.; Androse, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. [b] Calculated from the $\delta(H)_{calcd}$ values of Bingham and Schleyer,[80] and the SE(hydrocarbon) values of ref 2; cf. ref 81. [c] δSE = the strain energy of the rearranged (bridgehead) cation (SE$^+$) minus the strain energy of RH (SE). [d] δ(H) calculated from the solvolysis rate of 1-bicyclo[4.2.1]nonyl bromide in 80% EtOH at 70 °C (Becker, K. B. *Helv. Chim. Acta* **1977**, *60*, 94) and the linear free energy relationship $-\log k_{Br}$ (80% EtOH, 70 °C) = $0.41\delta_{calcd} - 0.12$; cf. footnote *b*.

Cationic Fp π-complexes of 1-bicyclo[3.2.2]nonene (**4**) and 3-homoadamantene (**5**) can be prepared in a similar manner. Treatment of **23b** in dichloromethane at −78 °C with trimethylsilyl triflate provides a yellow, crystalline salt in 89% yield. In contrast to that of $\mathbf{26}^+BF_4^-$, a single-crystal X-ray analysis of $[Fp(\eta^2\text{-bicyclo[3.2.2]non-1-ene})]^+Tf^-$ reveals a unit cell that contains enantiomeric pairs of *re*- and *si*-complexed cations,[68] **29**$^+$ and **30**$^+$, respectively (cf. Figure 1).[69] When crystals from the same batch used for this structure determination were dissolved in CD_2Cl_2 at −80 °C and a 75.4-MHz ^{13}C NMR of the resulting solution was determined at −78 °C without allowing it to warm above this temperature, a single isomer is apparent. By analogy with **26**$^+$, we assume it to be the *re* isomer **29**$^+$. When **23b** is protonated at −89 °C, the transient resonances of a cationic, monosubstituted Fp(methylidene), $[Fp{=}CHR]^+$, which we presume to be **25b**$^+$, can be observed; cf. the Experimental Section. No attempt has yet been made to trap this intermediate alkylidene chemically. In a similar manner **23c** can be converted to the somewhat less thermally stable, crystalline $\mathbf{31}^+Tf^-$ in 72% yield. The infrared spectrum of this material exhibits the characteristic C≡O stretches of a cationic Fp–(η^2-olefin) complex;[49] the $^{13}C\{^1H\}$ NMR resonances of two nonequivalent –C≡O's, the five equivalent Cp carbons of an $[Fp(\eta^2\text{-olefin})]^+$,[50] a "quaternary" vinyl (>C=), a monoprotonated vinyl (=CH–), three tertiary carbons (>CH), and six discrete methylenic carbons (>CH_2's). Here too, the intermediate alkylidene, **25c**$^+$, can be observed at reduced temperature by both ^{13}C and ^1H NMR; cf. the Experimental Section.

The rate of rearrangement of a 1-polycycloalkylmethylidene to a 1-homopolycycloalkene π-complex (eq 5) can be measured at reduced temperature by following the decrease with time of the methylidenic–hydrogen resonance at ~17 ppm.[61] The alkylidenes, **25a**$^+$, **25b**$^+$, and **25c**$^+$, were generated for this purpose by protonation of the corresponding methoxyalkyls **23** and **24** with excess HBF_4/Et_2O. The first-order rate constants corrected to −95 °C and the approximate activation parameters of the rearrangements are summarized in Table I. Also included are comparable values for the rearrangement of [Fp(*tert*-butylmethylidene)]$^+$ (**32**$^+$) to $[Fp(\eta^2\text{-2-methyl-2-butene})]^+$ (**33**$^+$) (eq 8).[70]



$$Fp^+{=}CH\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3 \xrightarrow{\sim CH_3} 33^+ \qquad (8)$$

Discussion

We formulate the reaction of these alkoxyalkyls with fluoroboric acid as outlined in Scheme III. The fact that a mixture of **23a** and **24a** (or of **20a** and **21a**) produces a single π-complex, **26**$^+$, implies that the ring enlargement is not concerted with the loss of alcohol from the protonated diastereomers but rather that a single racemic intermediate is involved in the rate-limiting step of the reaction. This intermediate is alkylidene **25a**$^+$. Rearrangement of alkylidene **25**$^+$ is also the rate-limiting step in the reaction of both **23b** and **23c** with either fluoroboric acid or trimethylsilyl triflate.

Scheme IV

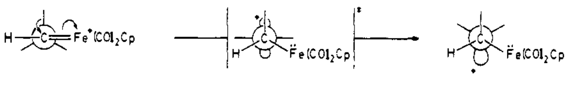
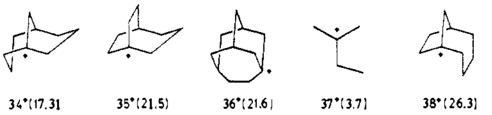


Chart II. Rearranged (Bridgehead) Cations and Strain Energy (SE$^+$)



Analogy has been drawn between "metal-stabilized carbocations", i.e. transition-metal alkylidenes, and ametallic carbocations.[71] In this light the rearrangement rates of the cationic alkylmethylidenes reported here might be expected a priori to parallel the solvolysis rates of the corresponding alkylcarbinyl tosylates. They do not. In CD_2Cl_2 at −95 °C neopentylidene **32**$^+$ rearranges $\sim 10^6$ times more rapidly than 1-adamantylmethylidene **25c**$^+$ (Table I) whereas at 50 to 100 °C in ethanol or in formic or acetic acids the neopentyl, 1-adamantylcarbinyl and, in fact, 1-norbornylcarbinyl and 1-bicyclo[2.2.2]octylcarbinyl derivatives all solvolyze at about the same rate.[72] Only 1-bicyclo[2.1.1]hexylcarbinyl tosylate, which is ~200 times as reactive as neopentyl tosylate,[73] appears to reflect in an appreciable way the strain of the bicyclic ring (SE ≈ 41).[2] Nordlander et al. have suggested that the similar solvolytic reactivities of neopentyl and 1-adamantylcarbinyl derivatives indicate that the rate-limiting step in each case is ionization to a unrearranged ion pair; the carbon shift that follows is more rapid.[72]

There is no indication in the three cases considered here that the rearrangement is reversible. If the cationic Fp(*tert*-alkylmethylidene) salts can be regarded as preformed ion pairs, their rearrangement rates should reflect the difference in potential energies of the alkylidene and the highest energy transition state on route to the product π-complex. We approximate this difference in the following manner.

The actual stabilities, i.e. heats of formation, of the $[Fp(\eta^1\text{-monoalkylmethylidenes})]^+$ **25a**$^+$, **25b**$^+$, and **25c**$^+$ are not known but, as the stereoelectronic environment in the vicinity of the methylidene carbon is similar in each, each must be comparably stabilized by the metal.[74] Thus, the relative stabilities of these

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(67) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; p 95.

(68) Hanson, K. R. *J. Am. Chem. Soc.* **1966**, *88*, 2731.

(69) The details of this fully refined (except of hydrogen atoms) structure, $R = 0.044$ and $R_w = 0.052$, will be reported separately.

(70) Bly, R. S.; Bly, R. K. *J. Chem. Soc., Chem. Commun.* **1986**, 1046.

(71) Cf.: Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, The Netherlands, 1985; Chapter 9.

(72) Nordlander, J. E.; Jindal, S. P.; Schleyer, P. v. R.; Fort, R. C., Jr.; Harper, J. J.; Nicholas, R. D. *J. Am. Chem. Soc.* **1966**, *88*, 4475, and references cited therein.

(73) Wiberg, K. B.; Lowery, B. R. *J. Am. Chem. Soc.* **1963**, *85*, 3188.

(74) Support for this assumption can be found in the virtually identical ^{13}C chemical shifts of the methylidene carbons of **25a**$^+$ (δ 397), **25b**$^+$ (δ 397), **25c**$^+$ (δ 397), and $[Fp{=}CH(1\text{-norbornyl})]^+$ (δ 394).[75,76]

(75) Olah, G. A.; White, A. M.; O'Brian, D. H. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1973; Vol. IV, p 1697 ff.

(76) Vogel, P. *Carbocation Chemistry*; Elsevier, Amsterdam, The Netherlands, 1985; p 130 ff, and references cited therein.

(77) Bly, R. S.; Silverman, G. S.; Bly, R. K. *J. Am. Chem. Soc.*, companion paper in this issue.

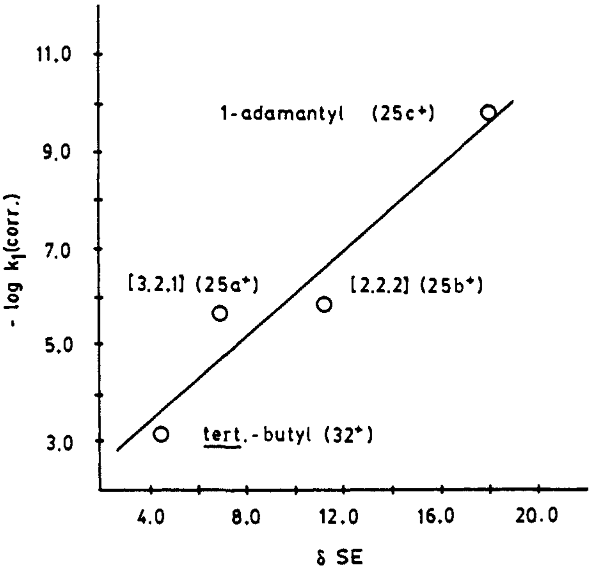
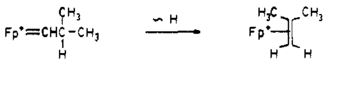


Figure 2. Plot of δSE, the difference in strain energy between the 1-alkyl substituent and the rearranged cation vs the negative logarithm of the statistically corrected first-order rate constant, k_1(corr.), for the rearrangement of Fp[η^1-(1-alkyl)methylidene]$^+$ at −95 °C.

alkylmethylidenes are expected to parallel the SE's of the 1-polycycloalkyl substituents (cf. Table II).

The overall conversion of alkylidene to π-complex is clearly exothermic, but the highest energy transition state does not resemble the initial alkylidene energetically.[78] Were it to do so, the more highly strained polycycloalkylmethylidenes would rearrange more rapidly than the less strained *tert*-butylmethylidene, but they do not (cf. Table I). As Rosenblum[25,79] and Brookhart[28] have emphasized, when a transition-metal alkylidene rearranges to a π-complex by shifting an adjacent hydrogen, e.g., eq 9, the developing empty p orbital at the β-carbon initially overlaps poorly with the metal–carbon σ-bond and the transition state is only weakly stabilized by d_π–p_π back-bonding (cf. Scheme IV). Migrating carbon is comparable in this sense to migrating hydrogen, hence the rearranged (bridgehead) cations **34–37⁺** should be better models energetically for the transition states of these rearrangements than the more stable (bridgehead) olefin π-complexes **26⁺** and **29–31⁺**. Schleyer has used molecular mechanics to estimate the strain energies (SE⁺) of several such rearranged (polycyclic bridgehead) cations[80,81] (cf. Chart II).

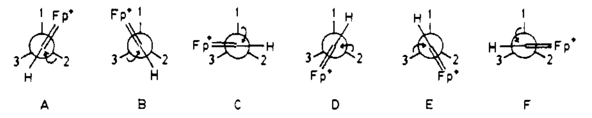


(9)

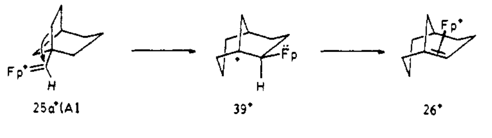
If our analysis is correct, the rates of these presumably kinetically controlled, cationic Fp(η^1-alkylidene) ring enlargements (Table I)—statistically corrected for the number of conformations that could produce the observed product[82]—should reflect the difference in strain energies (δSE) of the methylidene substituent (SE) and the rearranged (bridgehead) cation (SE⁺), i.e. δSE = SE⁺ − SE (Table II). A plot of δSE vs −log k_1(corr.)[82] is shown in Figure 2.

Considering the assumptions and approximations inherent in this analysis the correlation, −log k_1(corr.) = +0.44(δSE) + 1.58, is good (r^2, the coefficient of determination, =0.924). It emphasizes that the rates of these ring enlargements reflect in a modest way the approximate difference in strain energy of the initial polycyclic ligand and the rearranged (bridgehead) cation essentially unstabilized by the adjacent Fp.[83] Brookhart has used a similar argument in a qualitative way to rationalize the observed reactivities of a series of related Fe(II) alkylidenes toward a C_β- to C_α-hydrogen shift.[28]

Chart III. Possible Conformations of [Fp(1-bicyclo[3.2.1]octyl)methylidene]$^+$ (**25⁺**)



The ring enlargement of the 1-bicyclo[3.2.1]octylmethylidene (**25a⁺**) is of particular interest for it is the only one of the three 1-polycycloalkylmethylidenes potentially capable of forming (after decomplexation) more than one isomeric bridgehead alkene. Discounting enantiomers, six η^2-olefin complexes are possible, yet only one, **26⁺**, is formed. We cannot determine whether the observed stereoselectivity results from conformational control in the alkylidene[84] or from the lower δ(H*) for formation of the [3.3.1] bridgehead cation: ring enlargement from what is probably the most stable conformation of **25a⁺**, viz. A[44] (Chart III), should produce the most stable bridgehead cation, the [3.3.1], in its most stable conformation (bulky Fp equatorial), **39⁺**, and ultimately form the observed product, **26⁺**BF_4^-/Tf⁻ (eq 10). The ^{13}C and ^{1}H NMR spectra of **25a⁺** between −86 and −76 °C show no evidence of line broadening, but we are prevented by the reactivity of this alkylidene ($t_{1/2}$ ∼15 min at −76 °C) and the freezing point of the solution (∼−100 °C) from measuring and/or detecting the rotational barrier about the C_α–C_β bond. We presume it to be considerably lower than either the estimated rotational barrier of ∼10 kcal/mol about the Fe–C_α bond[44,64,65,84b,85] or the estimated δ(H*) of the rearrangement (cf. Table II).



(10)

Electrophilic transition-metal alkylidenes, which have a β-hydrogen, frequently rearrange to η^2-olefin complexes[25–32] (eq 9). Such β-hydrogen shifts do not change the electron count and therefore do not require the prior dissociation of a ligand.[35,86] They are especially facile in cationic 18-electron alkylidenes, which have highly electrophilic methylidene or monoalkylmethylidene ligands.[25–29,37,38,85]

Electrophilic, primary- or secondary-alkyl-substituted methylidenes, which could in principle shift either a β-hydrogen or a β-alkyl, shift only hydrogen.[25–32] In the case of cationic alkylidenes such as [Fp=CHR]$^+$ (R = primary or secondary alkyl), this

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(78) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(79) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122.

(80) Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3189.

(81) Gleicher, G. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 582.

(82) The ring enlargement of 1-bicyclo[2.2.2]octylmethylidene (**25b⁺**) produces a mixture of *re*- and *si*-complexed η^2-1-bicyclo[3.2.2]nonenes (**29⁺** and **30⁺**); apparently β-carbon migration can occur from any of the six possible noneclipsed methylidene conformations. Presumably the same is true of **25c⁺** and **32⁺**, which also have a local C_{3v} axis coincident with the C_α–C_β bond. To put the rearrangement rates of these three methylidenes of the same statistical basis with that of **25a⁺**, which utilizes a single conformation to produce a single bridgehead olefin complex, **26⁺**, their measured rate constants, Table II, are divided by 6.

(83) We note that the slope of our correlation line, 0.44, is similar to that, e.g. 0.41, of the linear free energy relation derived by plotting −log *k* solvolysis of 1-polycycloalkyl bromides in 80% ethanol at 70 °C vs the estimated strain energy differences of the polycycloalkane and the corresponding 1-polycycloalkyl cation,[80] indication perhaps of a similarity in the rate-limiting transition states of these two reactions.

(84) For examples of determinative conformational effects in transition–metal alkyl, alkylidene, and η^2-olefin complexes, see ref 27, 36, and 43–46 and: (a) 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. (b) Georgiou, S.; Gladysz, J. A. *Tetrahedron* **1986**, *42*, 1109, and references cited therein.

(85) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(86) We sidestep the question of whether a metal hydride is intermediate in the reaction: in some cases it definitely is, and in other cases, it probably is not.

presumably occurs in order that the positive charge, which is developing in the transition state, be located on a more highly substituted β-carbon.[28] A similar though less pronounced effect may be responsible for the exclusive hydrogen migration, which is also observed in formally neutral electrophilic alkylidenes.[31,32]

To our knowledge the examples reported here constitute the first cases of β- to α-carbon shift in which both the starting transition-metal alkylidene and the product π-complex have been observed and/or isolated.[19] Because the incipient positive charge at the β-carbon should be similar in the two cases, it is unlikely that an alkyl shift would be observed in a *tert*-alkylmethylidene unless a hydrogen shift occurs in the analogous *sec*-alkylmethylidene.

Given the facility of β-hydrogen shifts in electrophilic W(0),[31] Re(I),[30] Fe(II),[25,27-29] and some Mn(I)[32] alkylidenes, comparable β-alkyl shifts might be anticipated in analogous neopentylidene-type complexes. Few such alkylidenes are known; none shift β-carbon. The $\mathrm{(CO)_5W}[\eta^1$-(α-methylbenzylidene)], though neutral, is electrophilic and shifts β-hydrogen.[31] The analogous neopentylidene is unknown; attempts to prepare it have thus far been unsuccessful.[87] $\mathrm{(CO)_2}(\eta^5$-Cp)-Mn(η^1-neopentylidene) is also unknown. Although the analogous ethylidene and propylidene shift β-hydrogen,[32] the isopropylidene apparently does not.[88,89]

Summary

In the couse of this study we have developed a new method for the synthesis of bridgehead olefins stabilized as Fe(II) π-complexes and, through decomplexation, of the bridgehead olefins themselves. Using this methodology a bridgehead carboxylic acid can be converted to a homobridgehead olefin π-complex in about 40% overall yield. The bridgehead olefin can be recovered from the π-complex in 50–75% yield. The method is presently best suited for the preparation of isolable bridgehead olefins but, if better techniques for decomplexation can be developed, it may prove useful for the synthesis of some observable ones as well.

More importantly, we have demonstrated a hitherto unobserved reaction of cationic transition-metal alkylidenes, viz. β- to α-carbon shifts in tertiary-alkyl-substituted methylidenes, an analogue of the well-known β- to α-hydrogen shifts that occur in primary and secondary alkylmethylidenes. By noting that the rates of such carbon shifts parallel the difference in stability of the alkylidene and that of the rearranged cation essentially unstabilized by the adjacent metal moiety, we have extended the previously recognized analogy between carbocations and transition-metal alkylidenes.[71]

Experimental Section

General Procedures. All operations were carried out under a dry, oxygen-free nitrogen or helium atmosphere by standard Schlenk-line or drybox techniques. ^{1}H NMR spectra were recorded either on a Varian EM-390 spectrometer at 90 MHz or on a Bruker ASPECT 3000 at 300 MHz; the ^{13}C NMR spectra were recorded on an IBM NR-80 at 20.13 MHz. Proton chemical shifts (δ) are reported (ppm) downfield from TMS; ^{13}C resonances were recorded with the resonance of the solvent, δ 53.8 for $\mathrm{CD_2Cl_2}$ or δ 77.0 for $\mathrm{CDCl_3}$, as the internal reference at all temperatures. Infrared (IR) spectra were recorded on a Beckman IR-4210. The unit-mass mass spectra were determined on a Finnigan 4021 GC–MS spectrometer with a direct probe at ionization potentials of 70 eV unless otherwise specified. The unit-mass, fast atom bombardment (FAB) mass spectra and the accurate-mass mass spectra were run on a VG Analytical, Ltd., 70SQ high-resolution, double-focusing mass spectrometer equipped with a VG 11/250 data system. A *m*-nitrobenzyl alcohol matrix was employed for the FAB spectra; ions were generated from impact on the target matrix of a neutral argon atom derived from an $\mathrm{Ar^+}$ ion beam at an accelerating potential of 8 kV. The accurate-mass spectra were analyzed by comparison to isotopic ion distributions calculated by the ISO program of VG Analytical, Ltd. Microanalyses were performed by Atlantic Microlab, Inc., Alfred Bernhardt Mikroanalytisches Laboratorium, or 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 $\mathrm{P_2O_5}$. Reagent-grade pentane was stirred overnight with concentrated sulfuric acid, washed with water, distilled from $\mathrm{P_2O_5}$, 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. 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.

(η^1-1-Bicyclo[3.2.1]octanecarbonyl)dicarbonyl(η^5-cyclopentadienyl)iron (18a). A 1.35-g (7.8 mmol) sample of 1-bicyclo[3.2.1]octanecarbonyl chloride[90] (**17a**) was dissolved in 30 mL of dry, freshly distilled THF and degassed. A 2.1-g (9.8 mmol) sample of potassium dicarbonyl (η^5-cyclopentadienyl)ferrate[91] was weighed in a drybox into a solid addition tube and added to the acid chloride at ambient temperature, and the mixture was stirred for 12 h. The solvent was removed under reduced pressure; the residue was digested in 10% ether/pentane and filtered through Celite and sand. The Celite was washed several times with 10% ether/pentane and the filtrate was concentrated to ca. 10 mL at reduced pressure and eluted from an alumina column with 2% ether/pentane. Two fractions were collected: the first contained 1.43 g of pure acyl **18a**; the second constituted a mixture and was rechromatographed of alumina using benzene as eluent. The initial benzene fraction contained a mixture of dicarbonyl(η^5-cyclopentadienyl)iron dimer ($\mathrm{Fp_2}$) and acyl **18a**; the second benzene fraction provided an additional 0.3 g of pure **18a**.[60] The combined yield of **18a**, mp 91–92 °C, was 1.73 g (70%): IR ($\mathrm{CH_2Cl_2}$) 2020, 1955, ($\mathrm{C{\equiv}O}$), 1650 cm^{-1} ($\mathrm{>C{=}O}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ 4.84 (s, 5 H, Cp), 2.26 (br s, 1 H, $\geqslant$CH), 2.0–1.30 (m, 12 H, $\mathrm{>CH_2}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$) δ 262.1 ($\mathrm{>C{=}O}$), 215.4, 215.2 ($-\mathrm{C{\equiv}O}$'s), 86.4 (Cp), 71.6 (>C<), 35.3 ($\geqslant$CH), 42.6, 34.8, 32.1, 31.2, 28.5, 19.7 ($\mathrm{>CH_2}$); MS *m/e* 314 $[\mathrm{M}]^{\bullet+}$, 286 $[\mathrm{M-CO}]^{\bullet+}$, 258 $[\mathrm{M-2CO}]^{\bullet+}$, 230 $[\mathrm{M-3CO}]^{\bullet+}$. Anal. Calcd for $\mathrm{C_{16}H_{18}FeO_3}$: C, 61.17; H, 5.78. Found: C, 61.08; H, 5.70.[60]

(η^1-1-Bicyclo[2.2,2]octanecarbonyl)dicarbonyl(η^5-cyclopentadienyl)iron (18b) was prepared from the known carboxylic acid[92] in the same manner as **18a** and purified by chromatography on alumina with benzene as the eluent. The yield of yellow solid, mp 118–120 °C, was 63%: IR ($\mathrm{CH_2Cl_2}$) 2007, 1950 ($\mathrm{C{\equiv}O}$), 1620 cm^{-1} ($\mathrm{>C{=}O}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ 4.79 (s, 5 H, Cp), 1.61–1.58 (m, 13 H, $\mathrm{>CH_2}$ and $\geqslant$CH); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$) δ 264.9 ($\mathrm{>C{=}O}$), 215.8 ($-\mathrm{C{\equiv}O}$'s), 86.2 (Cp), 58.5 ($\geqslant$CCO–), 28.1, 25.7 (3 $-\mathrm{CH_2CH_2}-$'s), 24.7 ($\geqslant$CH). Anal. Calcd for $\mathrm{C_{16}H_{18}FeO_3}$: C, 61.17; H, 5.78. Found: C, 61.24; H, 5.74.

(η^1-1-Adamantanecarbonyl)dicarbonyl(η^5-cyclopentadienyl)iron (18c) was prepared similarly in 90% yield; mp 144–145 °C. The infrared spectrum matches that reported previously[93] showing $\mathrm{C{\equiv}O}$ and $\mathrm{>C{=}O}$ stretches at 2000, 1950, and 1640 cm^{-1}, respectively: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 4.82 (s, 5 H, Cp), 2.03 (br s, 3 H, $\geqslant$CH), 1.76 (d, $J = 2.6$ Hz, 6 H, $\mathrm{>CH_2}$), and 1.66 (br s, 6 H, $\mathrm{>CH_2}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$) δ 265.9 ($\mathrm{>C{=}O}$), 215.6 ($\mathrm{C{\equiv}O}$), 86.0 (Cp), 60.0 (>C<), 38.8, 36.4 ($\mathrm{>CH_2}$), and 28.5 ($\geqslant$CH). Anal. Calcd for $\mathrm{C_{18}H_{20}O_3Fe}$: C, 63.55; H, 5.93. Found: C, 63.46; H, 5.84.

[η^1-(1-Bicyclo[3.2.1]octyl)ethoxymethylidene]dicarbonyl(η^5-cyclopentadienyl)iron(II) Tetrafluoroborate ($\mathbf{19a^+BF_4^-}$). A 2.0-g (6.37 mmol) sample of **18a** was dried under vacuum for 2 h. A 1.8-g (9.47 mmol) sample of triethyloxonium tetrafluoroborate was dissolved in 12 mL of dichloromethane, degassed, and added to the acyl complex. The reaction mixture was stirred for 48 h at ambient temperature. The excess reagent was decomposed by adding 2 mL of degassed water and stirring the mixture for 1 h. The aqueous layer was separated, and the dichloromethane was evaporated under vacuum. Unreacted acyl was washed from the residue with diethyl ether. Recrystallization of the ether-insoluble product from dichloromethane/pentane gave a light yellow solid, 2.6 g (94%), with the following spectral characteristics: IR ($\mathrm{CH_2Cl_2}$) 2070, 2020 cm^{-1} ($\mathrm{C{\equiv}O}$); ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 5.4 (s, 5 H, Cp), 5.2 (q, 2 H, $J = 7.5$ Hz, $-\mathrm{OC}H_2\mathrm{CH_3}$), 2.33 (br s, 1 H, $\geqslant$CH), 2.0–1.2 (m, 12 H, $\mathrm{>CH_2}$), overlapping with 1.70 (t, $J = 7$ Hz, $-\mathrm{CH_2C}H_3$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$

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NMR (CD_2Cl_2, −10 °C) δ 344.3 (Fp^+=C(OEt)–), 209.5, 209.3 (–C≡O), 88.3 (Cp), 84.3 ($-OCH_2-$), 75.3 (Fp^+=C(OEt)C<), 43.7, 36.8 (>CH_2), 35.2 (≥CH), 33.9, 31.5, 28.7, 19.8 (>CH_2), 14.6 ($-CH_3$).[94] Anal. Calcd for $C_{18}H_{23}BF_4FeO_3$: C, 50.28; H, 5.39. Found: C, 50.09; H, 5.28.

[η^1-(1-Bicyclo[3.2.1]octyl)ethoxymethyl]dicarbonyl(η^5-cyclopentadienyl)iron (20a and 21a). A 2.6-g (6.05 mmol) sample of carbene **19a**$^+BF_4^-$ was dissolved in 20 mL of dichloromethane and degassed. The solution was cooled to −78 °C, 8 mL of 1 M $LiEt_3BH$ in THF was added slowly by syringe over a 10-min period, and the mixture was stirred for an additional 1 h at −78 °C. A 0.4-mL sample of dry, degassed methanol was added to decompose excess hydride. The solvent was evaporated under vacuum, and the residue was dissolved in pentane and chromatographed on alumina with pentane as the eluent. Vacuum evaporation of the solvent gave 1.28 g (62%) of a thick yellow oil, the spectral properties of which have been previously reported:[60] IR (CH_2Cl_2) 1995, 1935 cm^{-1} (C≡O); ^{1}H NMR ($CDCl_3$) δ 4.90, 4.80 (s, s, 1 H FpCH(OEt)'s), 4.75 (s, 5 H, Cp's), 3.6, 3.2 (m, 2 H, $COCH_2CH_3$'s), 2.1 (br s, 1 H, ≥CH's), 1.9–0.9 (m, 12 H, >CH_2's) superimposed on a 3 H, t, at 1.05 ($COCH_2CH_3$'s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, −10 °C) δ 216.7, 201.1 (–C≡O's), 91.1, 89.6 (FpCH(OEt)'s), 86.1, 85.9 (Cp's), 65.9, 56.3, 56.1, 45.6, 45.0, 36.5, 36.3, 36.1, 35.4, 34.2, 32.7, 32.2, 29.8, 29.0, 20.3, 15.3, 15.2 (>C<'s, ≥CH's, and >CH_2's). Comparison of the relative areas of comparable resonances in these NMR spectra indicates the presence of an approximately 50:50 mixture of diastereomers. Anal. Calcd for $C_{18}H_{24}FeO_3$: C, 62.81; H, 7.03. Found: C, 62.81; H, 6.80.

[η^1-(1-Bicyclo[3.2.1]octyl)methoxymethyl]dicarbonyl(η^5-cyclopentadienyl)iron (23a and 24a). To a solution of 0.325 g (1.035 mmol) of **18a** in 2 mL of dichloromethane was added 1.45 g (8.7 mmol) of methyl trifluoromethanesulfonate.[27] The mixture was stirred at room temperature for 3 days, diluted with dichloromethane to 25 mL, and transferred to a separatory funnel. A slurry of 1.25 g (33 mmol) of sodium borohydride and 1.9 g (35 mmol) of sodium methoxide in 25 mL of methanol was stirred at room temperature for 1 h and cooled to −78 °C in dry ice/isopropyl alcohol. The dichloromethane solution of the carbene was added to the cold reducing agent with rapid stirring. When the addition was complete, the cold bath was removed and 10 mL of degassed water was added. The methylene chloride layer was withdrawn, and the aqueous layer was washed with 25 mL of dichloromethane. The combined dichloromethane extracts were dried over sodium sulfate, and the solvent was removed under vacuum. The resulting residue was chromatographed on alumina at 10 °C with pentane. Vacuum evaporation of the solvent gave 0.225 g (66%) of amber-colored oil shown by $^{13}C\{^1H\}$ NMR to consist of an approximately 50:50 mixture of **23a** and **24a**; $^{13}C\{^1H\}$ NMR ($CDCl_3$, −10 °C) δ 219.1, 216.6 (C≡O's), 93.7, 92.4 (FpCH(OMe)'s), 85.9, 85.8 (Cp's), 58.8 (OCH_3's), 56.4, 56.3, 45.3, 44.8, 36.4 (both isomers), 36.1, 35.4, 34.3 (both isomers), 32.6, 32.2, 29.9, 29.0, and 20.3 (both isomers). Anal. Calcd for $C_{17}H_{22}FeO_3$: C, 61.84; H, 6.72. Found: C, 62.09; H, 6.92. No attempt was made to separate these diastereomers; the mixture was used for the preparation of alkylidene **25a**$^+$.

[η^1-(1-Bicyclo[2.2.2]octyl)methoxymethyl]dicarbonyl(η^5-cyclopentadienyl)iron (23b) and [η^1-(1-adamantyl)methoxymethyl]dicarbonyl(η^5-cyclopentadienyl)iron (23c) were prepared from **22b**$^+$ and **22c**$^+$, respectively, in 60–80% yield in a manner similar to that used for the preparation of **23a** and **24a**. These yellow crystalline solids have the following properties. **23b**: mp 90–92 °C; IR (CH_2Cl_2) 1995, 1935 cm^{-1} (C≡O); ^{1}H NMR (CD_2Cl_2) δ 4.86 (s, 5 H, Cp), 4.73 (s, 1 H, >$CHOCH_3$), 3.21 (s, 3 H, $-OCH_3$), 1.52 (br, 13 H, 6 >CH_2's and 1 ≥CH); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 219.6 and 216.9 (–C≡O's), 93.4 (>-CH(OCH_3), 86.0 (Cp), 58.4 ($-OCH_3$), 42.2 (>C<), 29.7, 26.2 (3 $-CH_2CH_2-$'s), and 24.6 (≥CH). Anal. Calcd for $C_{17}H_{22}O_3Fe$: C, 61.81; H, 6.72. Found: C, 61.66; H, 6.83. **23c**: mp 102–104 °C; IR (CH_2Cl_2) 1995, 1935 cm^{-1} (C≡O); ^{1}H NMR (CD_2Cl_2) δ 4.89 (s, 5 H, Cp), 4.67 (s, 1 H >CH(OCH_3)), 3.24 (s, 3 H, $-OCH_3$), 1.97–1.67 (br, 15 H, 6 >CH_2's and 3 ≥CH's); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 219.5, 217.0 (–C≡O's), 95.1 (>CH(OCH_3), 85.8 (Cp), 58.6 ($-OCH_3$), 44.0 (>C<), 41.2, 36.8, (3 >CH_2's and 3 >CH_2's), 28.8 (3 ≥CH's). Anal. Calcd for $C_{19}H_{24}FeO_3$: C, 64.06; H, 6.79. Found: C, 64.13; H, 6.73.

Conversion of 23a and 24a into (η^2-1-Bicyclo[3.3.1]nonene)dicarbonyl(η^5-cyclopentadienyl)iron(II) Tetrafluoroborate (26$^+BF_4^-$) Using Tetrafluoroboric Acid. To a stirred solution of 1.28 g (3.72 mmol) of **23a** and **24a** in 10 mL of dichloromethane was added dropwise at ambient temperature 0.8 mL of HBF_4/Et_2O. The mixture was stirred for 10 min, concentrated under reduced pressure to ~4 mL, and combined with 8 mL of diethyl ether. Filtration followed by two recrystallizations from dichloromethane/ether gave 1.32 g (92%) of yellow crystalline **26**$^+BF_4^-$:[60] IR (CH_2Cl_2) 2080, 2040 cm^{-1} (C≡O's); ^{1}H NMR (CD_2Cl_2) δ 5.55 (s, 5 H, Cp), 5.04 (t, 1 H, J = 7.2 Hz, >C=$CHCH_2$–), 3.0–0.8 (m, 13 H, 1 ≥CH + 6 >CH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −5.0 °C) 211.8, 207.3 (–C≡O's), 106.4 (>C=), 89.7 (Cp), 71.5 (=CH–), 37.8 (≥CH), 43.3, 41.0, 32.3, 31.3, 31.0, 29.1 (>CH_2). Anal. Calcd for $C_{16}H_{19}BF_4FeO_2$: C, 49.79; H, 4.96. Found: C, 49.56; H, 5.01.

Conversion of 23b into *re*- and *si*-[η^2-(1-Bicyclo[3.2.2]nonene)]dicarbonyl(η^5-cyclopentadienyl)iron(II) Triflate (29$^+$ and 30$^+$Tf$^-$) Using Trimethylsilyl Triflate. To a solution of **23b** (0.110 g, 0.33 mmol) in 5 mL of dichloromethane at −78 °C was added by syringe 0.2 mL of trimethylsilyl triflate[27] (0.230 g, 1.02 mmol). The reaction mixture was stirred at −78 °C for 10 min and then at ambient temperature for ~15 min. After the volume had been reduced under vacuum, ~15 mL of diethyl ether was added. The resulting pale yellow precipitate was washed well with ether and dried under vacuum to yield 0.132 g (89%): mp 158–159 °C dec; IR (CH_2Cl_2) 2030, 2010 cm^{-1} (C≡O); ^{1}H NMR (CD_2Cl_2) δ 5.55 (s, 5 H, Cp), 4.59 (d, 1 H, –CH=), 2.74–1.34 (m, 13 H, >CH_2's and ≥CH's); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 208.8, 208.6 (–C≡O's), 97.4 (>C=), 90.4 (Cp), 69.3 (=CH–), 29.7 (≥CH), 38.0, 36.5, 35.1, 33.7, 28.7, 28.3 (>CH_2's). Anal. Calcd for $C_{17}H_{19}F_3FeO_5S$: C, 45.55; H, 4.27. Found: C, 45.23; H, 4.01.

Conversion of 23c into (η^2-3-Homoadamantene)dicarbonyl(η^5-cyclopentadienyl)iron(II) Triflate (31$^+$Tf$^-$) Using Trimethylsilyl Triflate. To a solution containing 0.120 g (0.337 mmol) of **23c** in 3 mL of dichloromethane at −78 °C was added by syringe 0.13 mL of trimethylsilyl triflate (0.141 g, 0.673 mmol). The reaction mixture was stirred at −78 °C for 10 min and then at 0 °C for another 10 min. After the volume had been reduced under vacuum to ~1 mL, 5 mL of diethyl ether was added. The resulting yellow precipitate was washed well with diethyl ether at −78 °C and dried under vacuum. The yield of **31**$^+$Tf$^-$ was 0.115 g (72%): mp 82–84 °C dec; IR (CH_2Cl_2) 2030, 2010 cm^{-1} (C≡O); ^{1}H NMR (CD_2Cl_2) δ 5.48 (s, 5 H, Cp), 4.63 (m 1 H, =$CHCH_2$–), 2.90–1.45 (m, 15 H, >CH_2's and ≥CH's); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 210.2, 207.6 (–C≡O's), 101.4 (>C=), 89.7 (Cp), 66.1 (=CH–), 35.0, 29.9, 29.3 (≥CH's), 48.6, 43.3, 41.9, 36.1, 36.0, 31.4, 30.7 (>CH_2's). Crystalline **31**$^+$Tf$^-$ is apparently not very stable thermally; three unsuccessful attempts were made to determine its carbon and hydrogen content. Anal. Calcd for $C_{19}H_{21}F_3FeO_5S$: C, 48.12; H, 4.46. Found: C, 43.60 ± 3.60; H, 4.36 ± 0.35. The unit-mass FAB mass spectrum of **31**$^+$ shows *m/e* 325 ($[C_{18}H_{21}FeO_2]^+$), 297 ($[C_{17}H_{21}FeO]^+$), and 269 ($[C_{16}H_{21}Fe]^+$).

Attempted Conversion of 26$^+BF_4^-$ to 3 Using Sodium Iodide. A 55-mg (0.14 mmol) sample of **26**$^+BF_4^-$ in ~0.4 mL of perdeuterioacetone was combined in an NMR tube at ambient temperature with excess sodium iodide (~30 mg, 0.2 mmol). The reaction was monitored by $^{13}C\{^1H\}$ NMR. No decomplexation was observed after pulsing overnight at probe temperature nor after the sample had been heated for 6 h at 45 °C.[51]

Conversion of 26$^+BF_4^-$ to 3 Using Trimethylamine Oxide. A solution of 108 mg (0.28 mmol) of **13**$^+BF_4^-$ in 1.3 mL of dichloromethane was cooled to −78 °C, and 23 mg (0.31 mmol) of triethylamine oxide was added.[52] The mixture was warmed to −20 °C. After 1 h at this temperature, the reaction mixture was separated by GLPC on a 20% Carbowax 20M, 10% KOH on Chromasorb W column using norcamphor as an internal standard. The IR, ^{1}H NMR, and ^{13}C NMR spectra of the collected material (75% GLPC yield) are identical with those reported previously for authentic 1-bicyclo[3.3.1]octene.[95] Catalytic hydrogenation (Pd/C) produces a saturated hydrocarbon whose $^{13}C\{^1H\}$ NMR spectrum[95] and mass spectral fragmentation pattern[53] are virtually identical with those of authentic bicyclo[3.3.1]octane.

η^1-(1-Bicyclo[3.2.1]octylcarbinyl)dicarbonyl(η^5-cyclopentadienyl)iron (28). To a stirred solution of 100 mg (0.32 mmol) of **18a** in 5 mL of THF at 0 °C was added 2.0 mL of 0.97 M BH_3/THF in THF. The mixture was allowed to warm to ambient temperature and stirred for 12 h. Excess hydride was decomposed by the addition of 1 mL of methanol. The solvent was evaporated under reduced pressure and the residue was chromatographed on alumina using pentane as eluent to give 75 mg (79%) of yellow crystals: mp 30–31 °C; IR (CH_2Cl_2) 2015, 1940 cm^{-1} (C≡O); ^{1}H NMR ($CDCl_3$) δ 4.72 (s, Cp), 2.4–0.4 (m, 15 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, −5 °C) δ 218.7 (C≡O), 85.6 (Cp), 48.3 (>C<), 36.5 (≥CH), 49.3, 40.4, 37.7, 32.0, 30.0, 20.6, 16.4 (>CH_2's); MS *m/e* $[M]^{\cdot+}$, calcd for $C_{16}H_{20}FeO_2$ 300.0813, found 300.0807; MS *m/e* $[M - CO]^{\cdot+}$, calcd for $C_{15}H_{20}FeO$ 272.0864, found 272.0852; MS *m/e* $[M - 2CO]^{\cdot+}$, calcd for $C_{14}H_{20}Fe$ 244.0914, found 244.0909.

Reaction of 25a$^+BF_4^-$ and Lithium Triethylborohydride. Fluoroboric acid etherate (0.4 mL) was added with stirring to a precooled (−100 °C) solution containing 0.026 g (0.076 mmol) of **20a** and **21a**. After 25 min, a 0.9-mL portion of 1 M lithium triethylborohydride in THF was added

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(94) For reasons that we do not presently understand, many of the resonances in the previously reported $^{13}C\{^1H\}$ NMR spectrum of this carbene[60] are "twinned". Such twins do not appear in the present spectrum.

(95) Becker, K. B. *Helv. Chim. Acta* **1977**, *60*, 81.

7730 *J. Am. Chem. Soc.* **1988**, *110*, 7730–7737

slowly and allowed to react for 20 min. Excess hydride was decomposed by adding 0.05 mL of degassed methanol. The solvent was removed under reduced pressure. The residue was digested with pentane and chromatographed on alumina to give 0.013 g (57%) of **28**, spectrally identical with that prepared by direct reduction of **18a**.

Kinetic Determinations. In a typical kinetic run a standard 5-mm NMR tube was loaded under an atmosphere of He with 3–5 mg of **23a** and **24a**, **23b**, **23c**, or $FpCH(OCH_3)C(CH_3)_3$,[70] capped with a rubber no-air stopper, and cooled in liquid nitrogen. A solution of HBF_4/Et_2O in CD_2Cl_2 was prepared in a separate container by adding ~0.6 mL of CD_2Cl_2 to 10 mL of HBF_4/Et_2O using a vacuum line. This acid solution was transferred, via syringe, into the chilled NMR tube where it freezes on the cold wall above the Fp methoxyalkyl. Except in the case of $FpCH(OCH_3)C(CH_3)_3$, the NMR tube was transferred momentarily to a dry ice/isopropyl alcohol bath at −78 °C to thaw and to mix the contents (and thus to generate the $Fp(\eta^1$-alkylmethylidene) tetrafluoroborate) and then inserted quickly into the precooled probe of the NR-80 spectrometer.

The rate of rearrangement of the cationic alkylidene to the corresponding π-complex was followed by monitoring the decrease in integrated area of the alkylmethylidenic proton signal $[(Fp{=}CHR)^+]$ at δ 17.9 (**25a**), 17.9 (**25b**), 17.8 (**25c**), or 18.1 $\{[Fp{=}CHC(CH_3)_3]^+\}$, respectively. A typical kinetic run consisted of 10–30 individual points and gave a first-order plot, which was linear (r^2 = 0.91–0.99) over about 75% reaction (after which the integrated areas of the methylidene hydrogen resonances become too small to determine reproducibly). The temperature of the probe was determined before and after each kinetic run by a calibrated thermocouple immersed in a standard 5-mm NMR tube containing ethylene glycol. Runs in which the before and after temperature readings differed by a degree or more were discarded. Activation parameters were calculated from the observed first-order rate constants and temperatures of individual runs in the usual manner by plotting $\ln (k_1/T)$ vs $1/T$.[96] They are summarized in Table II together with the first-order rate constants of each 1-polycycloalkylmethylidene extrapolated to −95 °C for comparison with that of $[Fp{=}CHC(CH_3)_3]^+$, which could be measured only at that temperature.

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Supplementary Material Available: Listings of atomic positional and thermal parameters (10 pages). Ordering information is given on any current masthead page.

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[96] Cf.: Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 117–118.

$[Fp\text{-}\eta^1\text{-}1\text{-norbornylmethylidene}]^+$ to $[Fp\text{-}\eta^2\text{-}(2\text{-bicyclo}[3.2.1]\text{octene})]^+$ Rearrangement. Iron(II) Alkylidene to Iron(II) Alkylidene Isomerization via Ligand Rearrangement

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Abstract: 1-Norbornane[^{12}C]carboxylic (**4a**) and -[^{13}C]carboxylic (**4b**) acids are converted to the corresponding Fp 1-alkoxy-1-norbornylmethylidene tetrafluoroborates, $[(CO)_2(\eta^5\text{-}C_5H_5FeC_\alpha H)(OR)(1\text{-}C_7H_{11})]^+BF_4^-$ (**7**: **a**, R = C_2H_5; C_α = ^{12}C; **b**, R = C_2H_5, C_α = ^{13}C or **8a**, R = CH_3, C_α = ^{12}C), by sequential treatment with $(COCl)_2$, $(CO)_2(\eta^5\text{-}C_5H_5)FeK$, and $(C_2H_5)_3O^+BF_4^-$ or $(CH_3)_3O^+BF_4^-$. Reduction of the alkoxymethylidenes with $NaBH_4$ or $NaBD_4$ in basic solution provides the alkoxyalkyls $(CO)_2(\eta^5\text{-}C_5H_5)FeC_\alpha R'(OR)(1\text{-}C_7H_{11})$ (**9**: **a**, R = C_2H_5, C_α = ^{12}C, R′ = ^{1}H; **b**, R = C_2H_5, C_α = ^{13}C, R′ = ^{1}H; **c**, R = C_2H_5, C_α = ^{12}C, R′ = ^{2}H and **10a**, R = CH_3, C_α = ^{12}C, R′ = ^{1}H). At 25 °C in CH_2Cl_2 **9a–c** and **10a** are converted quantitatively in <1 min to $[(CO)_2(\eta^5\text{-}C_5H_5)Fe(exo\text{-}\eta^2\text{-}2\text{-bicyclo}[3.2.1]\text{octene-1-“CH”})]^+$ (**22**$^+$: **a**, “CH” = $^{12}C^1H$; **b**, “CH” = $^{13}C^1H$; **c**, “CH” = $^{12}C^2H$), salts of $\mathbf{BF_4^-}$ or $\mathbf{CF_3SO_3^-}$ by $HBF_4/(C_2H_5)_2O$ or $CH_3OSO_2CF_3$. As the temperature of a mixture of **9b** and $HBF_4/(C_2H_5)_2O$ in CD_2Cl_2 is gradually raised from −89 to +25 °C while being monitored by $^{13}C\{^1H\}$ NMR, the initially formed $[(CO)_2(\eta^5\text{-}C_5H_5)Fe{=}^{13}CH(1\text{-}C_7H_{11})]^+$ (**11b**$^+$) is observed to rearrange (k_1) to $\{(CO)_2(\eta^5\text{-}C_5H_5)Fe[\eta^1\text{-}2\text{-}(1\text{-}[^{13}C]\text{bicyclo}[3.2.1]\text{octylidene})]\}^+$ that in turn isomerizes ($k_2 + k_3$) into an ~3:1 mixture of $\{(CO)_2(\eta^5\text{-}C_5H_5)\text{-}Fe[endo\text{- and } exo\text{-}\eta^2\text{-}2\text{-}(1\text{-}[^{13}C]\text{bicyclo}[3.2.1]\text{octenes})]\}^+$ (**21b**$^+$ and **22b**$^+$), respectively. As the temperature increases above about −60 °C, **21b**$^+$ begins to isomerize (k_4) at an appreciable rate to the ultimate product, **22b**$^+$$BF_4^-$. The first-order rate constants of these isomerizations are measured at several temperatures and extrapolated for comparison to −78 °C: $k_1 = 3.5 \times 10^{-4}\ s^{-1}$; $k_2 + k_3 = 2.4 \times 10^{-4}\ s^{-1}$; $k_4 = 5.2 \times 10^{-8}\ s^{-1}$. Protonation of **9a** in CD_2Cl_2 at −78 °C with $HBF_4/(C_2H_5)_2O$ followed by dilution 5 min later with CH_3OH produces **10a**. A comparable sequence converts **10a** to **9a**. Protonation of **9a** in CD_2Cl_2 at −78 °C followed by addition of $(CH_3)_3N$ at that temperature 2.5 h later produces $(CO)_2(\eta^5\text{-}C_5H_5)Fe(\eta^1\text{-}2\text{-bicyclo}[3.2.1]\text{oct-2-ene})$ (**24**). Protonation of **24** in CD_2Cl_2 with $HBF_4/(C_2H_5)_2O$ re-forms **19a**$^+$. The rearrangement of **21b**$^+$ to **22b**$^+$ in the presence of excess unlabeled 2-bicyclo[3.2.1]octene (**23**) causes no dilution or scrambling of the ^{13}C label in **22b**$^+$. The rearrangement of **11a**$^+$ to **19b**$^+$, which involves a β- to α-carbon shift followed by a retro β- to α-carbon shift without breaking the original methylidene C–H bond, is the first example of a transition-metal alkylidene to alkylidene rearrangement that does not involve loss of a ligand, formation of a metallocycle, or oxidative insertion/reductive elimination.

In the preceding paper we describe a new method for the synthesis of cationic dicarbonyl (η^5-cyclopentadienyl)iron(II), i.e. Fp, (η^2-1-polycycloalkenes), viz. ring enlargement of cationic $Fp(\eta^1$-1-norpolycycloalkylmethylidenes) (eq 1) and display its utility by preparing $[Fp(\eta^2\text{-olefin})]^+$ complexes of (*Z*)-bicyclo[3.3.1]oct-1-ene (**1**), bicyclo[3.2.2]oct-1-ene (**2**), and 3-homo-