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(η^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.

Acknowledgment. We appreciate the financial support of the National Science Foundation, initially in the form of an EPSCOR grant to the University of South Carolina and later as a research grant to the principal investigator as well as funds provided to the Department of Chemistry (CHE-8411172) for the purchase of the Bruker ASPECT 3000 multinuclear NMR spectrometer, and that of the National Institutes of Health in the form of an Instrumentation grant (1-510-RR02849) to the Chemistry Department for the purchase of an accurate-mass, double-focusing, VG 70SQ mass spectrometer and data analysis system.

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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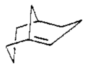
Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received November 3, 1987*

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 $[(CO)_2(\eta^5\text{-}C_5H_5)Fe(\textit{exo}\text{-}\eta^2\text{-}2\text{-bicyclo}[3.2.1]\text{octene-1-“CH”})]^+$ (**22**$^+$: **a**, “CH” = ^{12}C^{1}H; **b**, “CH” = ^{13}C^{1}H; **c**, “CH” = ^{12}C^{2}H), 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{^{1}H} 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 $\{(CO)_2(\eta^5\text{-}C_5H_5)\text{-}Fe[\textit{endo}\text{-}$ and $\textit{exo}\text{-}\eta^2\text{-}2\text{-}(1\text{-}[^{13}C]\text{bicyclo}[3.2.1]\text{octenes})]\}^+$ (**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(η^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-

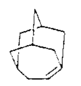
(1)

adamantene (**3**).[1] These three bridgehead olefins have estimated



1

2



3

"olefin strains" (OS, kcal/mol) of 15.2, 19.2, and 20.2, respectively.[2] In the idiom of Maier and Schleyer, **1** is "isolable" and **2** and **3** are "observable". In an effort to extend our method to the formation of Fp-complexed bridgehead olefins that fall into the "unstable" category (OS > 21), we have attempted the synthesis of a $[\mathrm{Fp}(\eta^2\text{-1-bicyclooctene})]^+$ by the intramolecular rearrangement of $[\mathrm{Fp}(\eta^1\text{-1-norbornylmethylidene})]^+$ (**11⁺**). Herein, we describe the results of our study, which include an example of transition-metal alkylidene to alkylidene isomerization without loss of a ligand, formation of a metallocyclic intermediate or oxidative insertion/reductive elimination, and evidence of diastereotopic facial interconversion in a cationic $\mathrm{Fp}(\eta^2\text{-olefin})$ complex.

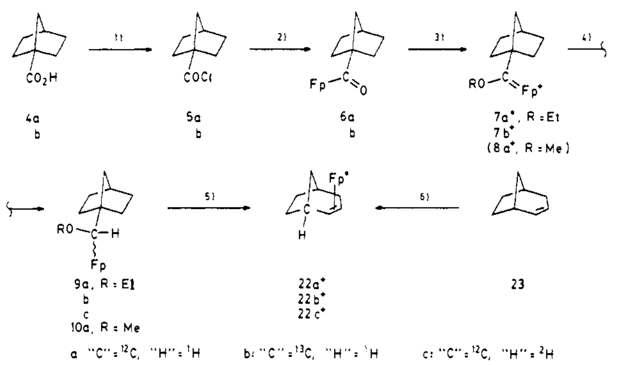
Results

The required starting materials, **9** and **10**, were prepared in the manner described earlier.[3,4] from the known 1-norbornanecarboxylic and -[^{13}C]carboxylic acids, **4a**[5,6] and **4b**,[7] respectively (Scheme I).

When protonated at 25 °C with $\mathrm{HBF_4}$ in $\mathrm{CH_2Cl_2/Ac_2O/HOAc}$ or $\mathrm{CH_2Cl_2/Et_2O}$[8,9] or when treated with trimethylsilyl triflate,[10] **9a** and **10a** are each converted rapidly and essentially quantitatively to a cationic olefin complex, **22a⁺**, identical with that prepared by direct complexation of bicyclo[3.2.1]oct-2-ene (**23**). From the known steric bias of bicyclo[3.2.1]oct-2-enes for exo addition[11,12] and from a comparison of the 400-MHz ^{1}H NMR spectra of **22a⁺**[3] and **23**[3] with the 60-MHz spectra of norbornene[13] and its *exo*-Fp⁺ complex,[14] we formulate **22a⁺** as the exo complex. No other free nor complexed olefin could be detected at room temperature. When **7a⁺** is reduced with borodeuteride and the resulting **9c** is similarly protonated, >90% of the incorporated deuterium appears at the allylic bridgehead, C(1), of the product, **22c⁺** (Scheme I). Likewise, when starting material containing >95% ^{13}C at the promethylidene position, i.e. **9b**, is protonated at 25 °C, the only observable product by ^{13}C NMR is **22b⁺** (Scheme I).

The peregrination of the promethylidene carbon of **9b** during the rearrangement can be followed by ^{13}C{^{1}H} NMR. Typical sequential spectra that result when a $\mathrm{CD_2Cl_2}$ solution of **9b** is mixed with an approximately 2-fold excess of $\mathrm{HBF_4/Et_2O}$ at −89 °C are recorded in Figure 1. Gated decoupling indicates that each of the ^{13}C-enriched carbons, i.e. those responsible for the resonances at 394, 78, 38, and 34 ppm, is bonded to a single hydrogen. We interpret these data as outlined in Scheme II. The low-field resonance of the initial intermediate at 394 ppm is characteristic of the methylidene carbon of a cationic Fe(II) alkylidene[15] while the unperturbed doublet of the coupled spectrum ($^1J_{\mathrm{CH}}$ = ~143 Hz) indicates this carbon to be monosubstituted and devoid of β-hydrogens.[16] Thus, the initial intermediate, formed when **9b** is protonated, is surely the cationic alkylidene **11b⁺**. Several such iron(II) alkylidenes have been prepared and observed in a similar manner.[8,17-20] Judging from its chemical shift, the 78 ppm resonance of the second intermediate (cf. Figure 1) could, a priori, be due to the vinyl carbon, C(2), of a π-complexed bridgehead olefin,[1,21] **15b⁺**–**17b⁺**, or to the "allylic" bridgehead, C(1), of the rearranged alkylidene,[22] **19b⁺**. We attribute it to the latter because the chemical shift of the associated Cp carbons (93.0), Figure 1, is consistent with the Cp ring resonances of related $[\mathrm{Fp}(\eta^1\text{-alkylidenes})]^+$[25] but not with those of

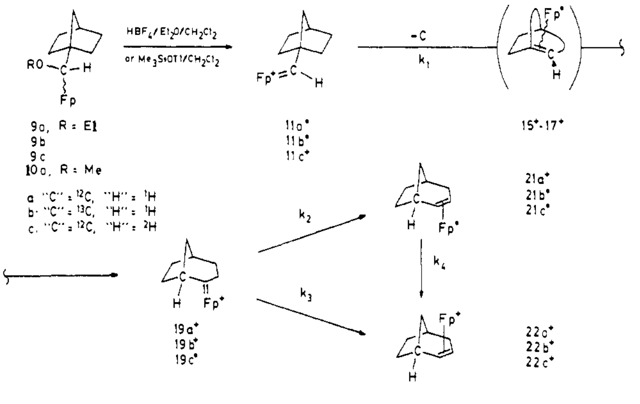
Scheme I



a "C" = ^{12}C, "H" = ^{1}H b: "C" = ^{13}C, "H" = ^{1}H c: "C" = ^{12}C, "H" = ^{2}H

1) $(\mathrm{COCl})_2$ 2) KFp 3) $\mathrm{Et_3O^+BF_4^-}$ or MeOTf 4) $\mathrm{NaBH_4/MeOH/MeO^-}$ or $\mathrm{NaBD_4/MeOD/MeO^-}$
5) $\mathrm{HBF_4/Et_2O/CH_2Cl_2}$ or $\mathrm{Me_3SiOTf/CH_2Cl_2}$ 6) $\mathrm{Fp^+/CH_2Cl_2}$

Scheme II



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[1] Bly, R. S.; Hossain, M. M.; Lebioda, L.; Raja, M. *J. Am. Chem. Soc.*, companion paper in this issue.

[2] Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

[3] (a) Bly, R. S.; Silverman, G. S. *Organometallics* **1984**, *3*, 1765. (b) We thank John R. Lever (Undergraduate Research Report, Department of Chemistry, University of South Carolina, 1975) for the original preparation of **6a**.

[4] Bly, R. S.; Hossain, M. M.; Lebioda, L. *J. Am. Chem. Soc.* **1985**, *107*, 5549.

[5] Boehme, W. R. *J. Am. Chem. Soc.* **1959**, *81*, 2762.

[6] Kwart, H.; Null, G. *J. Am. Chem. Soc.* **1959**, *81*, 2765.

[7] Barfield, M.; Brown, S. E.; Canada, E. D., Jr.; Ledford, N. D.; Marshall, J. L.; Walter, S. R.; Yakali, E. *J. Am. Chem. Soc.* **1980**, *102*, 3355.

[8] Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044.

[9] Green, M. L. H.; Ishaq, M.; Whiteley, R. N. *J. Chem. Soc. A* **1967**, 1508.

[10] (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.

[11] Sauers, R. R.; How, H. M.; Feilich, H. *Tetrahedron* **1965**, *21*, 983.

[12] Goering, H. L.; Kantner, S. S. *J. Org. Chem.* **1984**, *49*, 422.

[13] Pouchert, C. J.; Campbell, J. R. *Aldrich Library of NMR Spectra*; Aldrich Chemical Co.: Milwaukee, WI, 1974; Vol. 1, p 45.

[14] Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 3495.

[15] Cf.: Reference 1, footnote 61 and reference cited therein.

[16] Wehrli, F. W.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*; Heyden: London, 1980; p 50 ff, and reference cited therein.

[17] Casey, C. P.; Miles, W. H.; Tukada, H. *J. Am. Chem. Soc.* **1985**, *107*, 2924.

[18] Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203.

[19] Brookhart, M.; Humphrey, M. B.; Kratzer, H. J.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099.

[20] Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31.

[21] Godleski, S. A.; Valpey, R. S.; Grundlach, K. B. *Organometallics* **1985**, *4*, 296.

[22] $\delta(\mathrm{C}_\beta)$: (a) $[\mathrm{Cp(diphos)Fe{=}C_\alpha HC_\beta Me_3}]^+$, 63;[23] (b) $[\mathrm{Fp{=}C_\alpha H\text{-}C_\beta HCH_2CH_2}]^+$, 62;[24] (c) $[\mathrm{Fp{=}C_\alpha(C_\beta H_3)_2}]^+$, 61.4;[17] (d) $[\mathrm{(CO)Cp(PPh_3)\text{-}Fe{=}C_\alpha(C_\beta H_3)_2}]^+$, 59.4;[17] (e) $[\mathrm{(CO)Cp(PPh_3)Fe{=}C_\alpha HC_\beta H_2CH_3}]^+$, 48;[10b] (f) $[\mathrm{(CO)Cp(PPh_3)Fe{=}C_\alpha HC_\beta H_3}]^+$, 51.0.[10b]

[23] Davison, A.; Seleque, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2455.

[24] Brookhart, M.; Studabaker, W. B.; Husk, G. R. *Organometallics* **1985**, *4*, 943.

[25] δ(Cp): (a) $[\mathrm{Fp{=}CMe_2}]^+$, 93.4;[17] (b) $[\mathrm{Fp{=}CH}(c\text{-}\mathrm{C_3H_5})]^+$, 92;[24] (c) $[\mathrm{Fp{=}CHPh}]^+$, 93.2.[26]

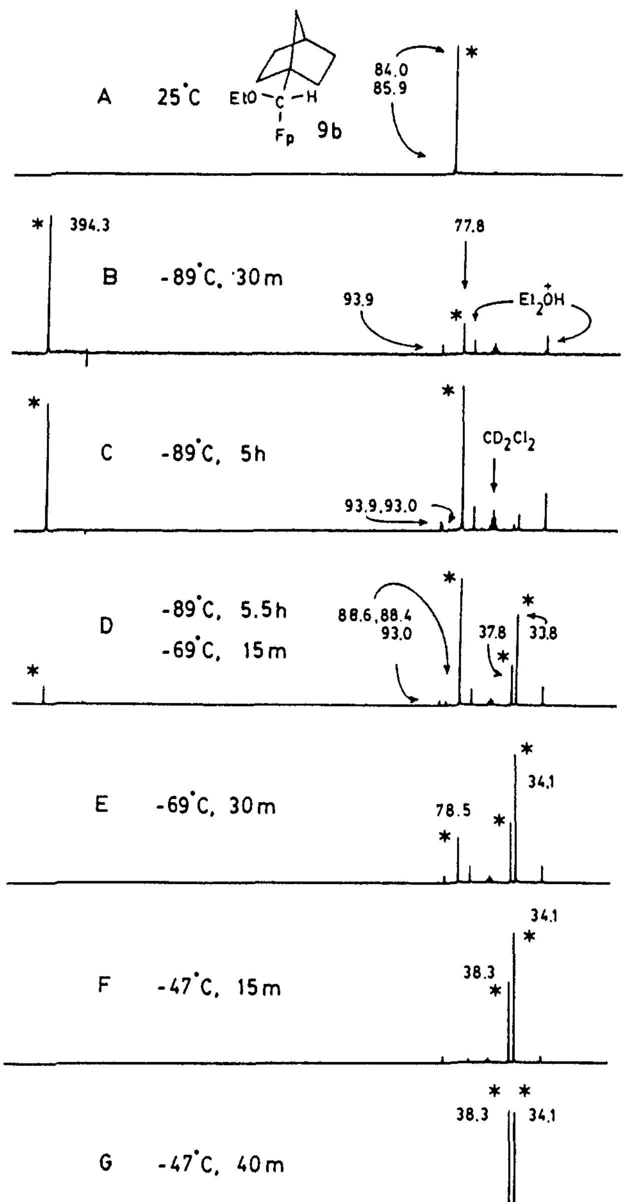

Figure 1. Sequential $^{13}C\{^1H\}$ NMR spectra of **9b** ("C" = ^{13}C, "H" = ^1H) and HBF_4/Et_2O in CD_2Cl_2. The resonances of the ^{13}C-enriched carbons are indicated with an asterisk (*); other indicated but unidentified resonances are due to magnetically equivalent, unenriched, cyclopentadienyl ring carbons: (A) **9b** only, 25 °C; (B) **9b** + H^+, 30 min after mixing at -89 °C; (C) at -89 °C, 5 h after mixing; (D) after ~5.5 h at -89 °C and ~15 min at -69 °C; (E) after ~5.5 h at -89 °C and ~30 min at -69 °C; (F) after ~5.5 h at -89 °C, ~30 min at -69 °C, and ~15 min at -47 °C; (G) after ~5.5 h at -89 °C, ~30 min at -69 °C, and ~40 min at -47 °C; (H) after removing the NMR tube from the cooled probe, warming it by hand for ~1 min, and reinserting it in the probe at -47 °C. The spectrum is that of **22b**$^+$ ("C" = ^{13}C, "H" = ^1H).

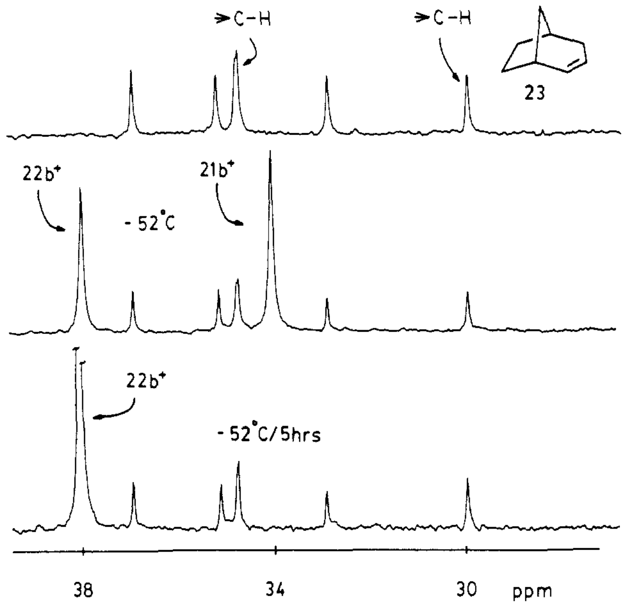

Figure 2. Sequential $^{13}C\{^1H\}$ NMR spectra: (top) bicyclo[3.2.1]oct-2-ene, (**23**); (middle) **23**, **21b**$^+$, and **22b**$^+$ shortly after mixing at -52 °C (note the ^{13}C-labeled bridgehead carbons of **21b**$^+$ and **22b**$^+$ at ~34 and ~38 ppm, respectively); (bottom) **23**, **21b**$^+$, and **22b**$^+$ 5 h after mixing at -52 °C (note that the 34 ppm resonance is no longer evident while the relative intensities of the carbon resonances of unenriched **23** are unchanged).

[Fp(η^2-olefins)]$^+$ (Cp C's = ~89 ppm)[27] and because of the detection in a comparable variable-temperature experiment using unlabeled starting material (**9a**) of a low-field, methylidene carbon resonance at 420 ppm[15] whose intensity rises and falls in concert with that of the 78 ppm peak. No resonance attributable to a bridgehead-olefin π-complex is observed.[1] The 34 ppm resonance is due to the third and final intermediate observable in the conversion of **11b**$^+$ to **22b**$^+$. Because the Cp carbons, the two nonequivalent, unlabeled vinyl carbons, and the labeled carbon of this intermediate exhibit chemical shifts that are very similar to those of the final product, **22b**$^+$, and because the $^1J_{CH}$'s of the labeled positions are experimentally identical in the two materials, we attribute the 34 ppm resonance to the enriched allylic bridgehead of the isomeric π-complex *endo*-**21b**$^+$.[28] As the spectra of Figure 1 reveal, at reduced temperatures it and **22b**$^+$ (38 ppm) are formed simultaneously in an ~3:1 ratio from rearranged alkylidene **19b**$^+$. At higher temperatures this third intermediate isomerizes smoothly into the final π-complex, **22b**$^+$. When the isomerization of **21b**$^+$ in the presence of a severalfold excess of unlabeled **23** is monitored at -52 °C by $^{13}C\{^1H\}$ NMR, the intensity of the allylic bridgehead resonance of **23** at 35.1 ppm is unchanged as the comparable resonance of **21b**$^+$ at 34.1 ppm is converted monotonically into the allylic bridgehead resonance of the final π-complex, **22b**$^+$, at 38.0 ppm (Figure 2).

From variable-temperature $^{13}C\{^1H\}$ NMR spectra comparable to those of Figure 1, first-order rate constants and crude activation parameters can be determined for the individual steps of the rearrangement outlined in Scheme II. These are summarized in Table I.

The presence both of the initial and of the rearranged alkylidene, postulated above on the basis of spectral data, can be confirmed chemically. As an electrophilic alkylidene the initial intermediate, **11**$^+$, should react rapidly with both neutral and anionic nucleophiles.[17,20,29-31] Thus, acidifying **9a** at -78 °C, stirring at this

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[26] Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099.

[27] Cf: Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic: London, 1981; Table 2.14D, 219 ff, and references cited therein.

[28] The "allylic" carbons of [Fp(η^2-olefins)]$^+$ characteristically appear between 28.9 and 45.1 ppm in the ^{13}C NMR. Cf.: (a) Cutler, A.; Ehntholt, D.; Lennon, P.; Nicholas, K.; Rosenblum, M. *J. Am. Chem. Soc.* **1975**, *97*, 3149. (b) Laycock, D. E.; Baird, M. C. *Inorg. Chim. Acta* **1980**, *42*, 263.

[29] Dotz, K. H. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, FRG, 1983; pp 204–208.

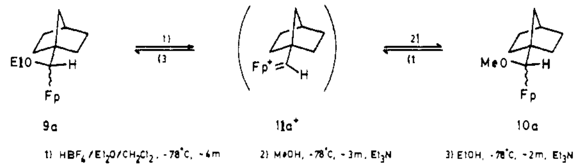
[30] Kreissl, F. R. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, FRG, 1983, pp 153–160, and references cited therein.

Table I. Rate and Activation Parameters of the Isomerizations of $[\mathrm{Fp}\text{-}\eta^1\text{-norbornylmethylidene}]^+$ (**11**$^+$) and Its Progeny, $[\mathrm{Fp}\text{-}\eta^1\text{-(2-bicyclo[3.2.1]octylidene)}]^+$ (**19**$^+$) and $[\mathrm{Fp}\text{-}endo\text{-}\eta^2\text{-(2-bicyclo[3.2.1]octene)}]^+$ (**21**$^+$)

temp, °C	10^5k_1,[a] s^{-1}	$10^5(k_2 + k_3)$,[b] s^{-1}	10^5k_4,[c] s^{-1}
−46			23
−57			1.7
−60			(0.8)
−77		24[d]	
−78	(35)	(24)	(0.0052)
−80		21	
−83	16	4.6	
−86	4.9	1.9[d]	
−88	4.0		
	3.7[e]		
−92	2.0		
−95	(0.83)		
$\delta(H^*)$, kcal/mol	15	22	23
$\delta(S^*)$, eu	2.3	38	25
$\delta(G^*)$, kcal/mol	14 (−95 °C)	14 (−78 °C)	18 (−78 °C)
r^2	0.91	0.93	

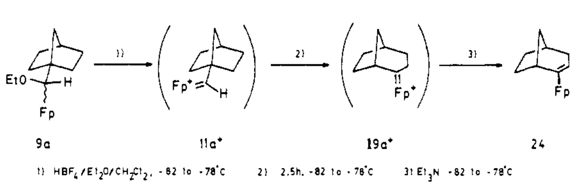
[a] Rate of disappearance of the 394 ppm resonance of **11b**$^+$ unless otherwise indicated. [b] Rate of disappearance of the 78 ppm resonance of **19b**$^+$ after **11b**$^+$ constitutes <2% of the total organometallic unless otherwise specified. [c] Rate of disappearance of the 34 ppm resonance of **21b**$^+$ after **19b**$^+$ constitutes <2% of the total organometallic. [d] Rate of disappearance of the Cp resonance of **19a**$^+$ at 90 ppm when **11a**$^+$ constitutes <2% of the total organometallic. [e] Rate of disappearance of the Cp resonance of **11a**$^+$ at 94 ppm.

temperature for 5 min (~0.24 $t_{1/2}$ of **11a**$^+$), quenching with excess methanol, and neutralizing the reaction mixture with excess triethylamine replace the ethoxyl of **9a** with methoxyl (eq 2).



(2)

Methoxy can be exchanged for ethoxy in a similar manner. The rearranged, cationic alkylidene, **19**$^+$, is expected to have characteristically acidic β-hydrogens[17,31] and thus to deprotonate readily in base. Stirring protonated **9a** at −82 to −78 °C for 2.5 h—at which time the reaction mixture is estimated from kinetic data to consist of about 70% **21a**$^+$ and **22a**$^+$, 30% **19a**$^+$, and <0.5% **11a**$^+$—adding excess triethylamine, and stirring at −78 °C for an additional 2 h produce a neutral yellow oil identified as (η^1-2-bicyclo[3.2.1]oct-2-enyl)dicarbonyl (η^5-cyclopentadienyl)iron (**24**) by spectral comparison with an authentic sample (cf. the Experimental Section; eq 3). A control experiment indicates that neither of the η^2-olefin complexes reacts with triethylamine under these conditions.



(3)

Discussion

Like other cationic $[\mathrm{Fp}\text{-}\eta^1\text{-(1-polycycloalkylmethylidenes)}]^+$, **11**$^+$ apparently ring enlarges via a transition state which develops early and localizes considerable charge at the pro bridgehead, β-carbon.[1] The rearrangement rate of the initial alkylidene, extrapolated to −95 °C and corrected statistically for the fact that the same intermediate can be formed from two conformers, falls near, but not on, the plot of −log k_1(corr.) vs δSE developed previously to rationalize the relative reactivities of $[\mathrm{Fp}(\eta^1\text{-}tert\text{-alkyl-type methylidenes})]^+$, which isomerize to stable and/or detectable $[\mathrm{Fp}(\eta^2\text{-trialkyl-type ethenes})]^{+\,1,32-35}$ (cf. Figure 3). Thus, the ring enlargement of **11**$^+$ bears some similarity to those reported previously in that it probably also occurs via a bridgehead-cation-like, rate-limiting transition state.

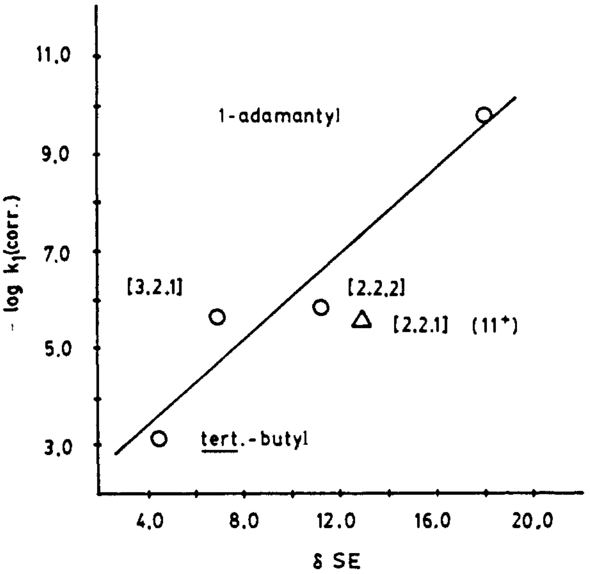
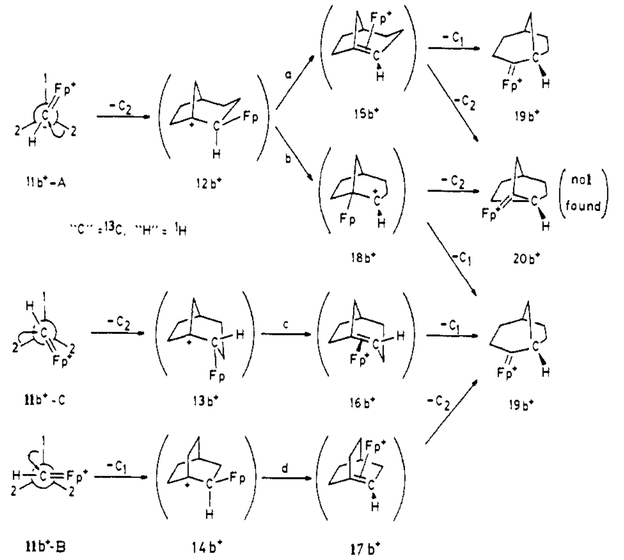


Figure 3. Plot of δSE, the difference in strain energy of the R of $[(\mathrm{CO})_2(\eta^5\text{-}C_5H_5)\mathrm{Fe}{=}\mathrm{CHR}]^+$ and the rearranged, 2-Fp-substituted cation vs the negative logarithm of the statistically corrected (see text[1]) first-order rate constant, k_1(corr.), of the rearrangement at −95 °C. The line shown is that of the original correlation.[1]

Scheme III



Though the initial step in the ring enlargement of **11**$^+$, i.e. k_1, involves the same sort of β- to α-carbon shift observed in other cationic Fp(1-polycycloalkylmethylidenes), the developing bridgehead cation in this case is *not* trapped as a stable $[\mathrm{Fp}(\eta^2\text{-1-homopolycycloalkene})]^+$ but rearranges further.[1] At −92 °C the first intermediate observable by $^{13}C\{^1H\}$ NMR (cf. Figure

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[31] Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119.

[32] (a) Even though we do not know which of three possible intermediates is formed, vide supra, it is likely that only one is actually produced, hence we divide k_1, extrapolated to −95 °C (Table I), by 3. (b) δSE = SE$^+$, the ~SE of either 1-bicyclo[3.2.1]- or -[2.2.2]octyl cation estimated as described previously,[33-35] minus the SE of norbornane[2] = 28 − 15 = 13.

[33] Cf.: Reference 1, Table II and appended footnotes.

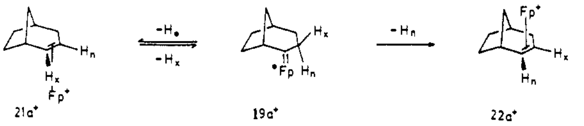
[34] Gleicher, G. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 582.

[35] Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3189.

[36] Brookhart, M.; Timmers, D.; Tucker, J. R.; Williams, G. D.; Husk, G. R.; Brunner, H.; Hammer, B. *J. Am. Chem. Soc.* **1983**, *105*, 6721, and references cited therein.

[37] Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

Scheme IV



1) is not one of the expected [Fp-(η^2-1-bicyclooctene)]$^+$ complexes (**15**$^+$–**17**$^+$) but rearranged alkylidene,**19**$^+$. Our label studies indicate that the original methylidene carbon, C_α, becomes the bridgehead carbon, C(1), of **19**$^+$ and that the original C_α–H bond is not broken during the rearrangement. Thus **19**$^+$ is formed, not by the shift of a C(2) hydrogen to the bridgehead of the ring-enlarged intermediate but rather by the shift of a bridgehead-bound carbon to C(2) (Scheme III).

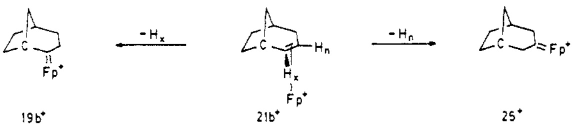
We do not know the identity of the putative intermediate bridgehead cation and/or bridgehead-olefin π-complex formed in the rearrangement of **11**$^+$. The SE's of the ametallic [2.2.2] and [3.2.1] bridgehead cations are too similar—27.8 and 28.4, respectively[35]—to distinguish by means of a linear free energy correlation between log k_1(corr.) and δSE (cf. Figure 3). Unless the barriers to rotation about the C_α–C_β bond of alkylidene **11**$^+$ are unexpectedly high[10,18,36,37] or the SE's of Fp-complexed bridgehead cations **12**$^+$–**14**$^+$ unexpectedly dissimilar, the preferred bridgehead-olefin complex should be **15**$^+$, for (*Z*)-1-bicyclo[3.2.1]octene is predicted to be 12–13 kcal/mol more stable than either the (*E*) isomer or 1-bicyclo[2.2.2]octene.[2] However, the conversion of **15b**$^+$ to rearranged alkylidene **19b**$^+$ requires either a synperiplanar shift of the methano bridge carbon to C(2) or the transfer of the iron moiety to C(1) followed by a shift of methano bridge carbon C(7) to the now positively charged C(2) of **18b**$^+$. Alternately, the intermediate formation of either of the presumably less stable olefin complexes **16b**$^+$ and **17b**$^+$ could yield the observed alkylidene, **19b**$^+$, by shifting an antiperiplanar methano or ethano bridge, respectively (cf. Scheme III). Because it is probably the lower energy route, path b may be preferred even though it implies the formation of an additional unobserved intermediate, viz. **18**$^+$, presumably unstabilized by the vicinal iron(II) moiety.

If Fp effectively migrates to an adjacent carbon during the isomerization of **11**$^+$ to **19**$^+$, why does not hydrogen? Perhaps in the putative bridgehead-cation intermediate **12**$^+$ or **13**$^+$, the hydrogen is forced by the bulky, geminal Fp into an axial position in which its bond to carbon is essentially orthogonal to the empty bridgehead orbital.

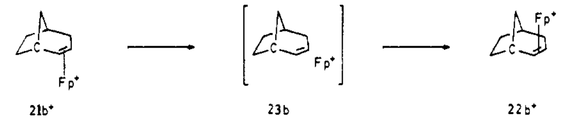
The rearranged alkylidene itself is not stable at reduced temperature but shifts β-hydrogen to form a pair of diastereomeric, η^2-(2-bicyclo[3.2.1]octene) complexes, the *endo*-**21**$^+$ and the *exo*-**22**$^+$ (Scheme II). At reduced temperatures the ratio of **21**$^+$ to **22**$^+$ is kinetically determined. As expected[38] the *exo*-hydrogen migrates more rapidly than the endo, about 3 times as fast between -92 and -80 °C. At higher temperatures the less stable endo complex, **21**$^+$, is converted at a perceptible rate ($t_{1/2} \approx 24$ h at -60 °C; Table I) to the more stable exo complex, **22**$^+$. No endo complex can be detected in the reaction mixture at ambient temperature.

The further isomerization of **19**$^+$ to a temperature-dependent mixture of **21**$^+$ and **22**$^+$ looks like a classic case of kinetic vs thermodynamic control (Scheme IV), provided, of course, that the exo C(3) hydrogen shift is reversible. The rearrangement of **11b**$^+$ to **19b**$^+$ (Scheme II) incorporates in a "formal" sense a retro β- to α-carbon shift, but, to our knowledge, the comparable retro hydrogen shift (Scheme IV) has not been observed;[39-44] i.e. [Fp(η^2-alkenes)]$^+$ are not known to rearrange to [Fp(η^1-alkylidenes)]$^+$.

Scheme V



Scheme VI



Aside from the question of reversibility, a problem with this interpretation is that, if the C(2) hydrogen of **21b**$^+$ migrates to C(3) to reform **19b**$^+$, the C(3) hydrogen would be expected also to migrate at a comparable rate to produce **25**$^+$, which having C_s local symmetry, would permit the ^{13}C label to scramble between the two bridgeheads of **22**$^+$ (Scheme V). The ^{13}C NMR spectrum of **22b**$^+$ indicates that such ^{13}C scrambling does not occur; the label is confined to C(1).

A possible alternative path for the isomerization of **21**$^+$ to **22**$^+$ that does not require a retro β- to α-hydrogen shift is outlined in Scheme VI. It involves dissociation of **21**$^+$ into **23** and Fp$^+$ followed by their recombination to produce **22**$^+$. Such a path has been suggested previously by Brookhart, Tucker, and Husk[10b] to rationalize the epimerization of [Cp(CO)(PPh$_3$)Fe(η^2-CH$_3$CH=CH$_2$)]$^+$ that occurs above about -40 °C and by us[45] to explain the formation of [Fp(*exo*-η^2-norbornene)]$^+$ when Fp(*endo*-η^1-2-norbornane) reacts with triphenylmethyl tetrafluoroborate in dichloromethane at 25 °C. The fact that we are unable to trap any of the dissociated Fp$^+$ before it recombines with **23b** to form **22b**$^+$ (cf. Figure 2) may indicate that if dissociation–recombination occurs, it does so in a solvent cage. Our present data do not permit us to distinguish the alternate possibilities outlined in Schemes IV and V.

Summary

The η^1-alkylidene/η^2-alkene isomerizations, which we report here, are probably more significant than the systems in which we observe them. The conversion of an η^2-alkene into an η^1-alkylidene by what we have termed a retro β- to α-hydrogen shift could conceivably be a source of catalyst in metathesis systems, which involve organometallic cocatalysts.[39-44] It has been suggested that this potentially important process has not yet been observed because the η^2-alkene complexes are normally considerably more stable than the isomeric η^1-alkylidenes.[29,30,42] The rearrangement of **11**$^+$ to **19**$^+$, which formally incorporates the carbon analogue of a retro β- to α-hydrogen shift, occurs quite readily here precisely because the putative intermediate would be highly strained and therefore less stable than the rearranged alkylidene **19**$^+$! It constitutes the first example we know in which one transition-metal alkylidene isomerizes to another without losing a ligand, forming a metallocyclic intermediate, or undergoing oxidative insertion/reductive elimination, and it establishes the formal reversibility of the β- to α-carbon shift discussed previously.[1]

Experimental Section

General Procedures. All operations were carried out under dry, oxygen-free nitrogen or helium atmospheres by standard Schlenk-line or drybox techniques. Unless otherwise specified ^{1}H NMR spectra were recorded on either a Varian EM-390 spectrometer at 90 MHz, an IBM NR-80 at 80 MHz, or a Bruker AM-300 at 300 MHz; the ^{13}C NMR

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(38) Cf.: (a) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 699. (b) Jones, A. J.; Huang, E.; Haseltine, R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1975**, *97*, 1133. (c) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M.; Anet, F. A. L. *J. Am. Chem. Soc.* **1982**, *104*, 7105.

(39) Calderon, N.; Ofstead, E. A.; Judy, W. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 401.

(40) Calderon, N.; Lawrence, P. J.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449.

(41) Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1982**, *1*, 1332.

(42) Miller, G. A.; Cooper, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 709.

(43) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 2605, and references cited therein.

(44) 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; pp 578–584.

(45) Bly, R. S.; Silverman, G. S.; Bly, R. K. *Organometallics* **1985**, *4*, 374.

spectra were recorded on the NR-80 at 20.13 MHz. Chemical shifts (δ) are reported downfield from TMS. Some of the ^{13}C assignments were made by the refocused "Insensitive Nucleus Enhancement through Polarization Transfer" (INEPT) technique[46] modified and made available to us by Dr. Ron Garber. 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 accurate-mass and the 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. For the FAB spectra, a *m*-nitrobenzyl alcohol matrix was employed; ions were generated from impact on the target matrix of a neutral argon atom derived from an Ar^+ ion beam at an accelerating potential of 8 kV. Microanalyses were performed by Atlantic Microlab, Inc., Alfred Bernhardt Mikroanalytisches Laboratorium, or Robertson Laboratory, Inc.

Solvents and Reagents. Reagent-grade benzene, diethyl ether (Et_2O), and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Reagent-grade dichloromethane was distilled under nitrogen from phosphorus pentoxide. Reagent-grade pentane was stirred overnight with concentrated sulfuric acid, washed with water, distilled from P_2O_5, stored over sodium ribbon, and redistilled 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-Norbornylcarbonyl)dicarbonyl(η^5-cyclopentadienyl)iron (6a). To a stirred solution of 1.17 g (7.41 mmol) of 1-norbornylcarbonyl chloride **5a**[5] in 20 mL of THF was added gradually at room temperature 1.60 g (7.41 mmol) of potassium dicarbonyl (η^5-cyclopentadienyl)ferrate (KFp).[47] The mixture was stirred for 16 h, the solvent was removed under reduced pressure, and the brown residual paste was digested with pentane and filtered through layers of sand and Celite. The pentane was removed, and the residue was dissolved in the minimum volume of benzene and chromatographed on alumina at 10 °C. The column was eluted with benzene to separate a dark band of Fp_2. Elution with ether gave 1.47 g (66%) of **6a**: mp 97–99 °C; IR (CH_2Cl_2) 2005, 1955 ($C\equiv O$), 1640 cm^{-1} ($>C{=}O$); ^{1}H NMR ($CDCl_3$) δ 4.80 (s, 5 H, Cp), 2.21 (br s, 1 H, $\geqslant$CH), 1.49 (m, 10 H, 5 $>CH_2$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 261.6 ($>C{=}O$), 215.0 ($-C\equiv O$), 86.1 (Cp), 75.3 ($-COC\leqslant$), 41.9 ($\geqslant$CH), 35.8 ($>C(7)H_2$), 32.3 ($>C(2,6)H_2$), 29.6 ($>C(3,5)H_2$). Anal. Calcd for $C_{15}H_{16}FeO_3$: C, 60.03; H, 5.37; O, 15.99. Found: C, 59.91; H, 5.41; O, 16.08.[3b]

The ^{13}C-labeled compound 6b was prepared similarly from 1-norbornane[^{13}C]carbonyl chloride (**5b**), which had, in turn, been prepared from the known 1-norbornane[^{13}C]carboxylic acid (**4b**)[7] and oxalyl chloride[48] and was used without isolation.

Dicarbonyl(η^5-cyclopentadienyl)[η^1-ethoxy(1-norbornyl)methylidene]iron Tetrafluoroborate ($7a^+BF_4^-$). A solution of 0.500 g (1.66 mmol) of **6a** and 0.543 g (2.86 mmol) of triethyloxonium tetrafluoroborate in 5 mL of CH_2Cl_2 was maintained at 35 °C. The reaction was monitored by periodically withdrawing small samples and comparing the relative intensities of the infrared absorptions at 1955 and 1640 cm^{-1}, the $C\equiv O$ and $C{=}O$ stretches, respectively, of **6a**, with a band at 2057 cm^{-1}, one of the $C\equiv O$ stretches of $7a^+BF_4^-$. After ~2 days no further increase of the product to starting material ratio could be observed. The solution was cooled and quickly washed with three ~5-mL portions of oxygen free water. Each time the upper, aqueous layer was withdrawn by syringe. After the final washing, the CH_2Cl_2 and remaining droplets of water were removed under vacuum. The residue was washed with two ~15-mL portions of cold ether and dried under vacuum to give 0.554 g (80%) of yellow, crystalline $7a^+BF_4^-$;[3a] IR (CH_2Cl_2) 2057, 2010 cm^{-1} ($C\equiv O$); ^{1}H NMR (CD_2Cl_2, −10 °C) δ 5.42 (s, 5 H, Cp), 5.30 (q, 2 H, J = 7.5 Hz, 2 H, $-OCH_2CH_3$), 2.40 (br s, 1 H, $\geqslant$CH), 1.90–1.32 (br m, 13 H, 5 CH_2 + $-CH_3$); ^{13}C{^{1}H} NMR (CD_2Cl_2, −10 °C) δ 342.9 ($Fp^+{=}C(OEt)-$), 209.4, ($C\equiv O$), 88.2 (Cp), 83.9, ($-OCH_2-$), 78.7 ($Fp^+{=}C(OEt)C\leqslant$), 44.7 ($\geqslant$CH), 37.3 (C(7)), 35.5 (C(2) & C(6)), 30.0 (C(3) & C(5), 14.7 ($-CH_3$). Anal. Calcd for $C_{17}H_{21}BF_4FeO_3$: C, 49.08; H, 5.09. Found: C, 49.10; H, 4.86. Some starting material, **6a**, (87 mg, 17%) was recovered from the ether washings.

The ^{13}C-labeled carbene $7b^+BF_4^-$ was similarly prepared from **6b.**

Dicarbonyl(η^5-cyclopentadienyl)[η^1-ethoxy(1-norbornyl)carbinyl]iron (9a). To a stirred solution of 0.118 g (0.238 mmol) of carbene **7a** in 5 mL of CH_2Cl_2 at −78 °C was added dropwise by syringe 0.30 mL of a 1 M solution of lithium triethylborohydride in THF. The mixture was stirred at −78 °C for 1 h and then combined with ~20 mL of methanol to decompose excess hydride. The solvent was quickly removed at 10^{-3} Torr, and the residue was *immediately* extracted with pentane and chromatographed on alumina at 0 °C under a nitrogen atmosphere. The pentane eluent was removed at reduced pressure to give 71 mg (76%) of **9a**.[3a] In our hands, this compound, prepared as described, is a quixotically unstable yellow oil, which, when very pure, crystallizes slowly at −20 °C: IR (CH_2Cl_2) 1995, 1937 cm^{-1} ($C\equiv O$); ^{1}H NMR ($CDCl_3$, −10 °C) δ 5.10 (s, 1 H, FpCH(OEt)C$\leqslant$), 4.80 (s, 5 H, Cp), 3.57 (dq, $J_{ac} \approx 6.6$ Hz, $J_{ab} \approx 2$ Hz, 1 H, $\geqslant$C(*)OC*H*(*a*)H(b)CH(c)$_3$), 3.26 (dq, $J_{bc} \approx 6.6$ Hz, $J_{ba} \approx 2$ Hz, 1 H, $\geqslant$C(*)OCH(a)*H*(*b*)CH(c)$_3$), 2.11 (br s, 1 H, $\geqslant$CH), 1.9–0.9 (br m, ~10 H, 5 $>CH_2$, superimposed upon a triplet at 1.07, $J_{cb} \approx J_{ca} = 6.6$ Hz, ~3 H, $-CH_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, −20 °C) δ 218.9, 216.8 ($-C\equiv O$), 85.9 (Cp), 85.3 (Fp*C*H(OEt)C$\leqslant$), 65.8 ($-OCH_2Me$), 61.6 (FpCH(OEt)C$\leqslant$), 45.1 (C(7)), 36.6, 35.1 (C(2) & C(6)), 32.2 ($\geqslant$CH), 31.1, 30.4 (C(3) & C(5)), 15.4 ($-CH_3$); MS *m/e* 330 $[M]^{\bullet+}$, 302 $[M - CO]^{\bullet+}$ 274 $[M - 2CO]^{\bullet+}$ 153 $[M - Fp]^{\bullet+}$. Anal. Calcd for $C_{17}H_{22}FeO_3$: C, 61.84; H, 6.72. Found: C, 61.98; H, 6.48.

The ^{13}C-labeled ethoxycarbinyl 9b was similarly prepared from **7b**. Although a precise knowledge of the percent ^{13}C enrichment is not required for our application, we estimate from the relative areas of the unenriched Cp resonance at 84.9 ppm and the ^{13}C-enriched resonance of C(8) at 84.0 ppm in the ^{13}C{^{1}H} NMR of **9b** (Figure 1) that it contains at least 95% ^{13}C at the bridgehead-bonded carbinyl carbon.

Dicarbonyl(η^5-cyclopentadienyl)[η^1-ethoxydeuterio(1-norbornyl)carbinyl]iron (9c) was prepared in 62% yield in the same manner as **9a** with 0.141 g (0.34 mmol) of $7a^+BF_4^-$ dissolved in 5 mL of CH_2Cl_2 and a 0.4-mL aliquot of 1 M lithium triethylborodeuteride in THF (Aldrich, Super-Deuteride). Although a precise knowledge of the ^{2}H enrichment is not required for our application, we estimate from the relative intensities of the *m/e* 275 and 274 peaks ($M^{\bullet+}$ − 2CO) in the unit-mass mass spectrum of this material, run on the Finnigan at an ionization potential of 15 eV, that **9c** contains >95% ^{2}H. The ^{1}H NMR spectrum (CD_2Cl_2) of **9c** is identical with that of **9a**[3a] except for the absence of the singlet (due to the carbinyl hydrogen) at δ 5.10. Comparison of the peak areas of comparable resonances in the ^{1}H NMR spectra of **9a** and **9c** indicates no discernable deuterium at any of the remaining carbons of **9c**.

Dicarbonyl(η^5-cyclopentadienyl)[η^1-methoxy(1-norbornyl)carbinyl]iron (10a). To a solution of 0.325 g (1.083 mmol) of **6a** in 2 mL of dichloromethane was added 1.45 g (8.7 mmol) of methyl trifluoromethanesulfonate. The mxture was stirred at ambient temperature for 3 days. The resulting solution of methoxycarbene $8a^+$ was diluted to ~25 mL with dichloromethane and transferred to a dropping funnel.

A slurry of 0.75 g (20 mmol) of sodium borohydride and 1.9 g (35 mmol) of sodium methoxide in 25 mL of methanol was stirred at room temperature for 2 h, cooled in a dry ice/isopropyl alcohol bath, and combined, with rapid stirring during ~5 min, with the previously prepared dichloromethane solution of methoxycarbene $8a^+$. When the addition was complete, the cold bath was removed, and, after ~2 min, ~10 mL of degassed water was added. The dichloromethane 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 residue was chromatographed on Activity III alumina at 10 °C, eluting first with pentane and then with 5% ether/pentane. Vacuum evaporation of the solvent gave 0.307 g (86%) of a yellow solid: mp ~75 °C dec; IR (CH_2Cl_2) 1990, 1930 cm^{-1} ($C\equiv O$); ^{1}H NMR (CD_2Cl_2) δ 5.04 (s, $-CH(OCH_3)Fp$), 4.86 (s, Cp), 3.27 (s, $-OCH_3$), 2.12 (s, $\geqslant$CH, bridgehead), ~2.1–1.0 (m, 10 H); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 219.4, 217.3, 88.3, 86.3 (5 C), 62.1, 59.6, 45.1, 37.3, 35.4, 32.8, 31.5, and 30.8. Anal. Calcd for $C_{16}H_{20}FeO_3$: C, 60.78; H, 6.38. Found: C, 60.68; H, 6.28.

Reaction of Dicarbonyl(η^5-cyclopentadienyl)[η^1-ethoxy(1-norbornyl)carbinyl]iron (9a) and Tetrafluoroboric Acid at 25 °C: [*exo*-(η^2-Bicyclo[3.2.1]oct-2-ene)dicarbonyl(η^5-cyclopentadienyl)iron] Tetrafluoroborate ($22a^+BF_4^-$). A solution containing 0.13 g (0.4 mmol) of **9a** in 5 mL of CH_2Cl_2 was cooled in ice and slowly combined with ~0.6 mmol of HBF_4/Et_2O; the resulting solution was warmed to room temperature and allowed to stand for ~10 min. Most of the solvent was removed under reduced pressure, and the remaining 1–2 mL of solution was combined with ~5 mL of ether and cooled in dry ice. The solvent was removed by filtration (filter stick), and the residual solid was recrystallized from CH_2Cl_2/ether to produce 61 mg (0.16 mmol, 41%) of the yellow, crystalline tetrafluoroborate, mp 92.5–93.5 °C dec,[3a] whose physical and spectral properties are identical with those of $22a^+BF_4^-$, prepared by the reaction of Fp^+ and bicyclo[3.2.1]oct-2-ene (**23**), vide infra.

^{13}C- and ^{2}H-labeled Fp(η^2-olefin) tetrafluoroborates $22b^+$ and $22c^+$-BF_4^-, respectively, were prepared in a similar manner from the corresponding α-ethoxyalkyls **9b** and **9c**. Although a precise knowledge of the

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(46) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760.
(47) Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 285.
(48) Cf.: Wilt, J. W.; Parsons, C. T.; Schneider, C. A.; Schultenover, S. J.; Wagner., W. J. *J. Org. Chem.* **1968**, *33*, 694.

isotope enrichment is not required for our application, by comparing the intensities of the *m/e* 285 ($C_{15}H_{17}FeO_2^+$) and 286 ($C_{15}H_{18}FeO_2^{\cdot+}$) peaks in the unit-mass FAB mass spectrum of **22a**$^+BF_4^-$ with the corresponding *m/e* 286 and 287 peaks in the FAB mass spectra of **22b**$^+BF_4^-$ and of **22c**$^+BF_4^-$, we estimate that **22b**$^+$ contains >98% mono ^{13}C and **22c**$^+$ >94% mono ^2H. The $^{13}C\{^1H\}$ and $^1H\{^1H\}$ NMR spectra (CD_2Cl_2) of **22b**$^+BF_4^-$ and **22c**$^+BF_4^-$ confirm that the label is confined to a single bridgehead position, C(1), in each as evidenced by the enhancement or collapse (due to the loss of NOE at the deuteriated bridgehead), respectively, of the δ 38.8 resonance in the ^{13}C- or the ^2H-enriched material (cf. Figure 1).

An authentic sample of **[*exo*-(η^2-bicyclo[3.2.1]oct-2-ene)dicarbonyl(η^5-cyclopentadienyl)iron] tetrafluoroborate (22a$^+$BF$_4^-$)** was prepared with Reger's reagent.[49] To a solution of 0.508 g (4.7 mmol) of bicyclo[3.2.1]oct-2-ene (**23**) (Wiley Organics) in 2 mL of CH_2Cl_2 was added dropwise 8 mL of a 0.6 M solution of $Fp^+BF_4^-$ in CH_2Cl_2. The mixture was stirred for 3 h at ambient temperature, cooled to 0 °C, and diluted with 10 mL of Et_2O. The resulting yellow precipitate was isolated by filtration, washed with three 10-mL portions of ether, and recrystallized from 1:1 CH_2Cl_2/Et_2O. The product yield was 0.587 g (1.6 mmol, 34%): mp 92.5–93.5 °C dec; IR (CH_2Cl_2) 2079, 2038 cm^{-1} (C≡O); ^1H NMR (CD_2Cl_2) δ 5.50 [br s, ~5 H, Cp superimposed on an ~1 H m at ~5.4–5.5 due to Fp$^+$(η^2-(=C(3)HCH$_2$–)], 5.30 [s, 1 H, Fp$^+$(η^2-C(2)-*H*=)], 2.73 (m, 1 H, >C(1)*H*), 2.48 (perturbed d, 1 H, =CHC(4)*H*(endo)HCH<), 2.05–2.25 (m, 3 H, >C(5)*H* superimposed upon –C(6)H*H*(exo)C(7)H*H*(exo)–), ~1.86 (m, 2 H, –C(6)*H*(endo)CH(7)(endo)H–), 1.45 (m, 1 H, =CHC(4)H*H*(exo)CH<), 1.39 (br perturbed d, $J \approx 16$ Hz, 1 H, >C(8)*H*(anti)H), 0.58 (d, $J \approx 16$ Hz, 1 H, >C(8)H*H*(syn)); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, –10 °C) δ 211.1, 210.8 (–C≡O), 89.1 (Cp), 86.6 (–C(2)H=) 76.4 (=C(3)H–), 38.3 (C(1)H<), 35.1 (C(8)), 33.4 (C(4)), 32.5 (C(5)), 32.3, 30.5 (C(6) & C(7)). Anal. Calcd for $C_{15}H_{17}BF_4FeO_2$: C, 48.44; H, 4.61. Found: 48.09, H, 4.66, which is spectrally identical with that prepared from **9a**, vide supra.

Reaction of Dicarbonyl(η^5-cyclopentadienyl)[η^1-ethoxy(1-norbornyl)carbinyl]iron and Fluoroboric Acid Followed by Variable-Temperature ^{13}C{^{1}H} NMR. A freshly chromatographed, ~20-mg sample of **9b** was dissolved in ~0.2 mL of CD_2Cl_2 and transferred by syringe to a 5-mm NMR tube. The lower 1-in. portion of the tube was coated with a thin layer of the complex by slowly evaporating the solvent under reduced pressure while the tube was manually swirled. Helium was introduced, the sample tube was cooled in liquid nitrogen, and a solution containing ~0.18 mmol of HBF_4/Et_2O in 0.5 mL of CD_2Cl_2 was added by syringe and allowed to freeze (mp ~–95 °C) on the cold wall of the NMR tube. The tube was quickly capped under helium with a rubber septum and transferred from the liquid-nitrogen cold bath to a dry ice/isopropanol bath. The sample was allowed partially to thaw with swirling and shaking and then quickly inserted into the cold (~–89 °C) probe of the NR-80 spectrometer. (We estimate that less than 1 min elapsed between the start of thawing and the insertion of the tube into the spectrometer probe.) The spectrum of the mixture was determined periodically by scanning (500 scans/spectrum) ^{13}C in the 10 000-Hz window between –10 and 490 ppm. The peak positions and relative areas of the ^{13}C-enriched carbons of the organic ligand (δ ~394, 78, 38, and 34; cf. Figure 1) and the much weaker resonances of the magnetically equivalent, unenriched carbons of the Cp rings (δ ~94, 93, and 88) were recorded as the reaction progresses sequentially from starting material, **9b**, to final product, **22b**$^+$. The probe temperature was initially maintained at –89 °C or 5.5 h, raised to –69 °C, held there for ~30 min, and then raised to –47 °C. Finally, the sample was removed from the cooled probe, warmed to room temperature for ~1 min to complete the reaction, and reinserted in the –47 °C probe; the spectrum of the ultimate product, **22b**$^+$, was recorded.

Gated decoupling of the individual ^{13}C-enriched carbon resonances reveals each to be directly bonded to a single hydrogen; the $^1J_{CH}$'s are 143 Hz for –*CH*=Fp$^+$ of **11b**$^+$ and 141 Hz for the C(1)–H bridgeheads of **19b**$^+$, **21b**$^+$, and **22b**$^+$.

When the variable-temperature experiment is repeated with unlabeled **9a** and the changes in peak intensities with time are carefully noted, it is possible to assign with reasonable certainty many of the resonances of the unlabeled carbons as well. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, –88 °C) of alkylidene **11a**$^+$: δ 394.5 (–CH=Fe$^+$(CO)$_2$Cp), 205.7 (CO), 93.9 (Cp), 85.5 (C(1)?), 46.0, 39.9, 35.0 (2 C) and 30.3 (2 C). ^{13}C NMR (CD_2Cl_2, –88 °C) of alkylidene **19a**$^+$: δ 420.2 (>C=Fe$^+$(CO)$_2$Cp), 207.3, 206.8 (CO), 93.0 (Cp), 77.9 (C(1)), 63.8 (C(3)), 40.9, 40.2, 34.1, 30.6, 27.9; ^{13}C NMR (CD_2Cl_2, –76 °C) of endo π-complex **21a**$^+$: δ 212.3, 208.3 (CO), 89.2 (C(2)), 88.4 (Cp), 75.3 (C(3)), 37.5, 37.4, 34.0, 33.8 (C(1)), 31.7, 29.7.

Attempted Label-Dilution during the Isomerization of 21b$^+$ to 22b$^+$. A sample of ~20 mg of **9b** was allowed to react with excess HBF_4/Et_2O at ~–85 °C in the manner described. The progress of the rearrangement to mixed endo and exo π-complexes, **21b**$^+$ and **22b**$^+$, respectively, was followed by ^{13}C NMR. When the rearrangement as judged by the disappearance of the resonance at 78 ppm due to alkylidene **19b**$^+$ was ~90% complete, the sample was quickly transferred to a dry ice/isopropyl alcohol bath at –78 °C, combined with ~50 mg of unlabeled bicyclo[3.2.1]oct-2-ene (**23**) (Wiley Organics, Inc.), and reinserted in the spectrometer. The probe temperature was raised to –50 °C, and the spectrum was periodically determied (cf. Figure 2). Over the 5-h period during which the 34 ppm C(1)-bridgehead resonance of **21b**$^+$ is converted to the C(1)-bridgehead resonance of **22b**$^+$ at 38 ppm, the sum of these labeled-peak intensities remains essentially constant as do the individual intensities of the unlabeled bridgehead-carbon resonances of **23** at 30 and 34.8 ppm (cf. Figure 2).

Reaction of 10a and Trimethylsilyl Trifluoromethanesulfonate. A stirred solution of 0.060 g (0.19 mmol) of **10a** in 2 mL of CH_2Cl_2 was cooled in dry ice/isopropyl alcohol and combined with 0.1 mL of trimethylsilyl trifluoromethanesulfonate. A yellow solid formed immediately. As the reaction progressed, the amount of suspended material appeared first to diminish and then to increase in the latter stages. After 5 h the mixture was allowed to warm briefly to effect dissolution of the solid and then recooled to –78 °C and combined with ~15 mL of ether. The precipitated yellow product, 0.058 g (70%), was isolated by filtration. Its IR and $^{13}C\{^1H\}$ NMR spectra are similar to those of **22a**$^+BF_4^-$, prepared by treatment of **9a** with either trimethylsilyl trifluoromethanesulfonate or HBF_4.

The reaction of 9b and trimethylsilyl trifluoromethanesulfonate was followed by variable-temperature ^{13}C NMR spectroscopy at ~–80 °C as described for the reaction with HBF_4/Et_2O. The appearance and disappearance of enriched signals at 394, 78, 34, and 38 ppm could be observed as before, but their relative abundance could not be determined accurately because the triflates are less soluble than the tetrafluoroborates and precipitate from the solution under the conditions of the observation.

Interconversion of 9a and 10a. To a stirred solution of 61 mg (0.19 mmol) of **9a** in 1.5 mL of dichloromethane at –78 °C was added ~50 mg (0.3 mmol) of HBF_4/Et_2O. The reaction mixture was stirred for 5 min, combined with 0.1 mL of methanol, stirred for an additional 3 min, and then quenched with 0.1 mL of triethylamine. The solution was combined with 10 mL of cold pentane and chromatographed on a 1 × 10 cm column of alumina with pentane as the eluent. When the eluent was no longer colored, the solvent was removed under vacuum, and the dark yellow residue was rechromatographed on alumina with 5% ether/pentane. Evaporation of the solvent yielded 53 mg (90%) of complex **10b**.

In another experiment a solution of 69 mg (0.22 mmol) of **10a** in ~1.5 mL of CH_2Cl_2 was frozen in liquid nitrogen and combined with ~50 mg (0.3 mmol) of HBF_4/Et_2O. The mixture was allowed to thaw with swirling in a dry ice/isopropyl alcohol bath and, after ~2 min, was combined with 0.2 mL of ethanol, stirred for additional 3 min, and quenched with 0.1 mL of triethylamine. The reaction mixture was combined with 10 mL of pentane and chromatographed on alumina using 5% ether/pentane as eluent. After removal of the solvent, 66 mg (91%) of product **9a** was obtained.

Reaction of Alkylidene 19a$^+$ with Triethylamine. To a stirred solution of 65 mg (0.20 mmol) of **9a**$^+$ in 2 mL of CH_2Cl_2, cooled to ~–82 °C in an ethyl acetate/liquid nitrogen bath, was added 0.07 g (0.4 mmol) of HBF_4/Et_2O. After 2.5 h the mixture was slowly combined with 0.1 mL of triethylamine and kept in the cold bath for an additional 2 h. The solvent was removed under reduced pressure, and the residue was washed with pentane. The pentane washings were placed on an alumina column and eluted with pentane. Evaporation of the solvent yielded 0.016 g of a yellow oil, which, by $^{13}C\{^1H\}$ NMR analysis, was estimated to contain ~25 % **9a** and 75% (estimated yield 12 mg, 18%) of another product, spectrally identical with an authentic sample of η^1-(2-bicyclo[3.2.1]oct-2-enyl)dicarbonyl(η^5-cyclopentadienyl)iron (**24**) prepared in an alternative manner: IR (CH_2Cl_2) 1995, 1945 cm^{-1} (C≡O); ^1H 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 >CH's + 4 >CH$_2$'s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, –10 °C): δ 147.4, 131.8, 85.7 (Cp), 52.4, 42.4, 37.8, 33.8, 33.4 and 30.9. Anal. Calcd for $C_{15}H_{16}FeO_2$: C, 63.41; H, 5.68. Found: C, 63.47; H, 5.64. prepared in an alternate manner.[50] A $^{13}C\{^1H\}$ refocused INEPT[46] determination showed the δ 147.4 carbon to be quaternary, the δ 131.8, 52.4, and 33.8

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(49) Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *171*, 73.

(50) Bly, R. S.; Raja, M. *Abstracts of Papers*, 3rd Chemical Congress of North America & the 195th National Meeting of the American Chemical Society, Toronto, Canada, June 5–10, 1988; American Chemical Society: Washington, DC, 1988; INORG 732.

carbons to be >CH's, and the remainder to be $>CH_2$'s.

Stability of $22a^+$ in the Presence of Triethylamine. A solution of 40 mg (0.01 mmol) of complex $\mathbf{22a}^+$ in 0.5 mL of CH_2Cl_2 was combined with 0.06 mL of triethylamine at −78 °C and maintained at that temperature of 2 h. The solvent was removed, and the residue was washed with pentane; none dissolved. The ^1H NMR ($CDCl_3$) spectrum of the pentane-insoluble portion showed it to be unreacted starting material $\mathbf{22a}^+BF_4^-$.

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Fluorodestannylation. A Powerful Technique To Liberate Anions of Oxygen, Sulfur, Selenium, and Carbon[1]

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Abstract: Fluoride ions smoothly destannylate organotin chalcogenides to liberate nucleophilic chalcogenide ions; hence the first nucleophilic oxide (O^{2-}) and selenide (Se^{2-}) transfer agents are reported where the tin atom serves as a "group 16 (VIB) transfer agent". In the presence of crown ethers or ammonium salts, this process results in a new way to generate "naked" nucleophiles. Ethers and selenides are formed in good to excellent yield. In addition, a useful C–C bond-forming reaction has been developed by using alkyltins with aldehydes and acid chlorides in the presence of fluoride ion. Aspects concerning reactivity and mechanism are presented. Finally, the generality of the fluorodestannylation procedure and the differences with parallel silicon chemistry are detailed.

Considerable effort has been focused on desilylation reactions over the past decade;[2] far less attention has been accorded parallel work on organotin compounds. In 1985, Pearlman reported that fluoride ion could induce the formation of exocyclic double bonds from stannylated and hindered *sec*-alkyl sulfones.[3] The next year Danishefsky and Hungate published a fluorodestannylative procedure applied to a cyclic stannylene of use in an intramolecular O-alkylation.[4] Later in 1987, Ohno described selective O-monoalkylations of an *O*-stannylene acetal derived from a tartrate ester, using fluoride ion to promote the reaction.[5] None of the above procedures were extended beyond their specific synthetic context.

Our own work during this period involved the discovery of a fluorodestannylation reaction of organotin sulfides (**1**), permitting the preparation of a host of organosulfides in high yield under mild and neutral conditions[1] (eq 1). In addition, we found that cyanide ion performed comparably (cyanodestannylation).

$$\underset{\mathbf{1}}{R_3Sn{-}S{-}SnR_3} + 2R'{-}Br \xrightarrow[\text{(or } CN^-)]{F^-} R'{-}S{-}R' + 2R_3Sn{-}F \qquad (1)$$

We wish to report that fluoride ion combines with organotin oxides, -sulfides, and -selenides and organotins in general to liberate the corresponding anion (Scheme I, Table I). In the presence of appropriate electrophiles, ethers, thioethers, organic selenides, and carbon–carbon bonds are produced. Most of these reactions take place in neutral media, in contrast with many known procedures using strong bases.[6] The generality of these fluoride and cyanide effects demonstrates a significant new dimension in organotin chemistry.

Scheme I

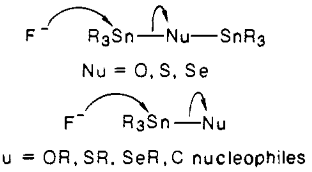

Table I. Tin Substrates under Investigation[a]

oxides	sulfides	selenides	organostannanes
$R_3Sn{-}O{-}SnR_3$	$R_3Sn{-}S{-}SnR_3$	$R_3Sn{-}Se{-}SnR_3$	R''_4Sn
$R_3Sn{-}OR'$	$R_3Sn{-}SR'$	$R_3Sn{-}SeR'$	$Bu_3Sn{-}R''$
	R_2SnS		$Bu_3Sn{-}C{\equiv}CH$

[a] R = aryl, alkyl; R′ = alkyl; R″ = allyl.

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(1) Organosulfur Chemistry. Part 55. Part 54: Harpp, D. N.; Gingras, M. *Tetrahedron Lett.* **1987**, *28*, 4373.

(2) Lalonde, M.; Chan, T. H. *Synthesis* **1986**, 817. Greene, T. W. *Protective Groups in Organic Synthesis*; Wiley: New York, 1981. Colvin, E. *Silicon in Organic Synthesis*; R. Krieger Publisher: Melbourne, FL, 1981.

(3) Pearlman, D. A.; Putt, S. R.; Fleming, J. A. *J. Org. Chem.* **1985**, *50*, 3622.

(4) Danishefsky, S.; Hungate, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 2486.

(5) Ohno, M.; Nagashima, N. *Chem. Lett.* **1987**, 141.

(6) Among them with sulfur: use of *t*-BuOK: Wilson, K. D.; Beak, P. *J. Org. Chem.* **1987**, *52*, 218; use of $NaBH_4$: Hopkins, P. B.; Holler, T. P.; Spaltenstein, A. *J. Org. Chem.* **1987**, *52*, 2977. Among them with oxygen: use of NaOH: Gokel, G. W.; Hernandez, J. C.; Viscariello, A. M.; Arnold, K. A.; Campana, C. F.; Echegoyen, L.; Fronczek, F. R.; Gandour, R. D.; Morgan, C. R.; Trafton, J. E.; Miller, S. R.; Minganti, C.; Eiband, D.; Schultz, R. A.; Tamminen, M. *J. Org. Chem.* **1987**, *52*, 2693; use of *t*-BuOK: Gupta, R. C.; Slawin, A. M. Z.; Stoodley, R. J.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1986**, 668; use of Grignard reagent: Marshall, J. A.; Lebreton, J.; DeHoff, B. S.; Jenson, T. M. *Tetrahedron Lett.* **1987**, *28*, 723. Among them in the formation of selenide ion (Se^{2-}): use of $NaBH_4$: Klayman, D. L.; Griffin, S. T. *J. Am. Chem. Soc.* **1973**, *95*, 197; use of $LiBHEt_3$: Gladysz, J. A.; Hornby, J. L.; Garbe, J. E. *J. Org. Chem.* **1978**, *43*, 1204; use of $NH_2NH_2/NaOH$: Syper, L.; Mlochowski, J. *Synthesis* **1984**, 439.

0002-7863/88/1510-7737$01.50/0