Synthesis and Ring-Opening Reactions of α-Fluoro-Substituted Cyclopropanes σ-Bonded to Iron

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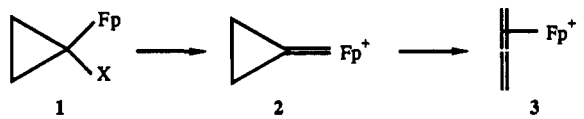
Dicarbony(η^5-cyclopentadienyl)(1-fluoro-2,3-dimethylcyclopropyl)iron (**17**) and dicarbonyl(η^5-cyclopentadienyl)(7-fluoro-7-bicyclo[4.1.0]heptyl)iron (**23**) have been synthesized as the first examples of α-halocyclopropyl σ complexes of iron. The monocyclic complex (**17**) is thermally unstable above 0 °C. Attempts to purify it by chromatography over silica gel led to clean ring opening to an alcohol (**20**) that is believed to have resulted from initial silica gel induced ring opening to an allene complex followed by reaction with water. Reaction of **17** with BF_3 leads cleanly to the allene complex **21**, and photolysis gives the centrally substituted π-allyl complex **29**. The latter ring opening is stereospecific, is facilitated by the α-fluorine, and occurs disrotatorily away from the metal. The bicyclic complex **23** is similar to **17** in that it also reacts essentially instantaneously with BF_3 to give the corresponding allene complex but is different in that it is much more photostable. This is consistent with the mechanism proposed for opening of **17** to **29**, since applying the same mechanism to the opening of a bicyclic complex with the stereochemistry pictured in **23** would lead to a prohibitively strained π-allyl complex.

Introduction

Access to complexes of Fp^- [Fp = dicarbonyl(η^5-cyclopentadienyl)iron] or other transition metals σ-bonded to cyclopropanes substituted on the α-carbon with a halogen atom would be desirable for two reasons. First, since halides can be readily abstracted by appropriate electrophiles, such complexes could serve as precursors to rare cyclopropylidene complexes **2** that may react further to



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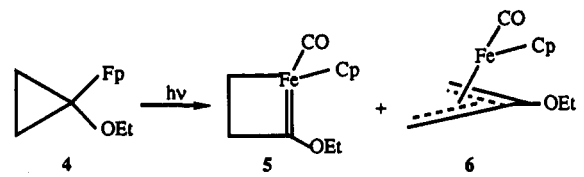
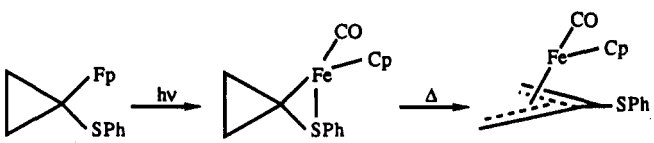
give allene complexes **3**.[1,2] Second, it would be interesting to compare their chemistry with α-alkoxy, α-thiophenyl, and unsubstituted cyclopropyl Fp–σ complexes. For instance, photolysis of the α-ethoxy Fp–σ complex **4** leads



4 5 6

primarily to α-elimination of carbon to give the ring-expanded carbene complex **5** with a slower side reaction of ring opening to the π-allyl complex **6**.[3] Photolysis of the α-thiophenylcyclopropyl Fp–σ complex **7** leads to the



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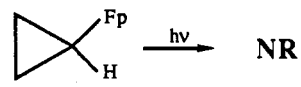
chelate **8** which, upon warming, rearranges to its π-allyl isomer **9**.[3c] And, finally, photolysis of the unsubstituted Fp cyclopropyl complex **10** shows no reaction.[3] It would therefore be interesting to see where an α-halogen stands in this spectrum of reactions.



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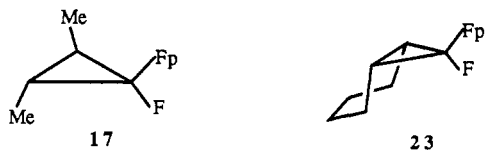
At this time, we report preparation of **17** and **23**, the first examples of α-halocyclopropyl σ complexes of iron (and possibly of any transition metal) and preliminary studies of some of their chemistry.



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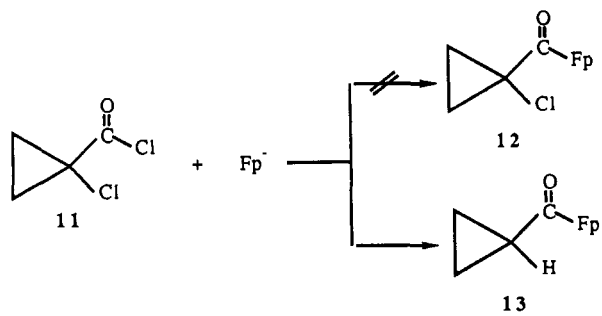
Results and Discussion

Our efforts to prepare α-halocyclopropyl complexes of dicarbonyl(η^5-cyclopentadienyl)iron began some years ago when we attempted to prepare α-chlorocyclopropylacyl Fp complex **12** for decarbonylation studies.[4] At that time, we found that treatment of the acyl halide **11** with Fp^- led



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exclusively to reduction to give only the unsubstituted acyl complex **13**. Since it was known at that time that reaction of Fp^- with a 1,1-dichlorocyclopropane led to reduction rather than substitution,[5] attempts to prepare metal-sub-

(1) Cohen, L.; Kennedy, D.; Magatti, C. V.; Sanders, A.; Giering, W. P. *J. Organomet. Chem.* **1974**, *65*, C57.
(2) Lisko, J. R.; Jones, W. M. *Organometallics* **1985**, *4*, 612.
(3) (a) Lisko, J. R.; Jones, W. M. *Organometallics* **1985**, *4*, 944. (b) Conti, N. J.; Jones, W. M. *Organometallics* **1988**, *7*, 1666. (c) Conti, N. J.; Crowther, D. J.; Tivakornpannarai, S.; Jones, W. M. *Organometallics* **1990**, *9*, 175.
(4) Manganiello, F. J.; Christensen, L. W.; Jones, W. M. *J. Organomet. Chem.* **1982**, *235*, 327.
(5) (a) Marten, D. F.; Dehmlow, E. V.; Hanlon, D. J.; Hossain, M. B.; Van der Helm, D. *J. Am. Chem. Soc.* **1981**, *103*, 4940. (b) Marten, D. F.; Wilburn, S. M. *J. Organomet. Chem.* **1983**, *251*, 71.

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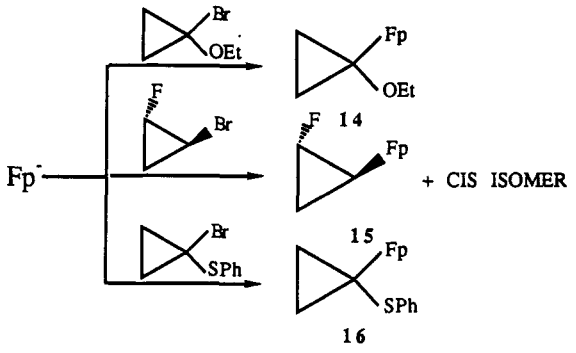
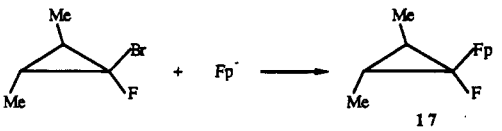
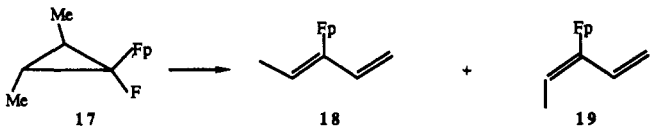
stituted α-halocyclopropanes were abandoned. However, when we discovered that Fp^--substituted cyclopropanes (e.g. **14–16**) could be conveniently prepared by direct



substitution of halide on the ring[3] (believed to go by a single electron-transfer process), we were encouraged to revisit reaction of Fp^- with geminal dihalocyclopropanes as a possible source of the desired complexes. From Marten's[5] results, it was clear that *gem*-dichlorocyclopropanes could not be used for this purpose and it was anticipated that the corresponding dibromides may be reduced even more readily. Indeed, the only product isoolated (in high yield) from reaction of a variety of *gem*-dibromocyclopropanes with Fp^- was the oxidation product Fp_2; no trace of the desired σ complexes could be detected. The exceptional strength of the C–F bond suggested that an α-fluorocyclopropyl bromide might more closely resemble the α-bromoether. *trans*-1-Bromo-1-fluoro-2,3-dimethylcyclopropane was therefore prepared, and indeed, reaction with Fp^- in THF gave 33% of the desired σ complex **17** as air-sensitive reddish yellow crystals that are reasonably stable at −30 °C but decompose rapidly if allowed to warm above 0 °C.

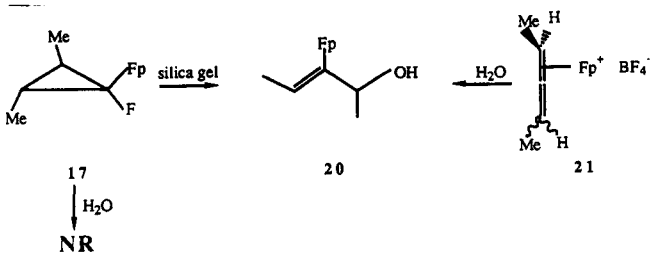


The products of the thermal decomposition of **17** varied in unpredictable ways. However, we were successful in isolating a mixture of frequently recurring products in an essentially 1:1 ratio which, on the basis of ^1H and ^{13}C spectra, are tentatively assigned the dehydrohalogenated isomeric structures **18** and **19**. Attempts to separate these



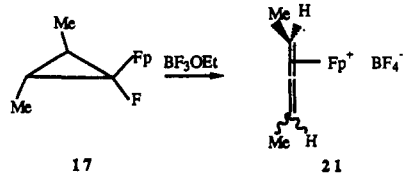
isomers were unsuccessful although careful chromatography led to partial enrichment which permitted unique assignment of both ^1H and ^{13}C NMR resonances.

Attempts to purify **17** by chromatography on silica gel led to complete reaction to give the alcohol **20** as a single stereoisomer. This was reproducible; and, indeed, it was

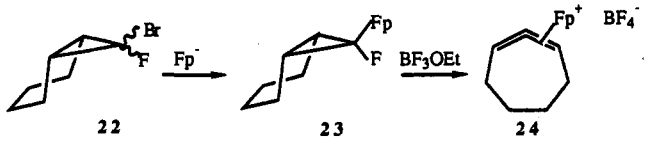


found that, although **17** is inert to water, simply stirring it with silica gel leads to quantitative conversion to **20**. Conversion of **17** to **20** probably arises from initial silica gel induced ring opening to allene **21** followed by attack of water on the terminal carbon of the complexed double bond.[6] To test this as a viable possibility, authentic allene complex **21**[7] was treated with water and found to give **20**, again as a single stereoisomer, in 78% isolated yield. At this time we cannot unequivocally assign a stereochemistry to **20**. However, Rosenblum[8] has found that attack of water on the Fp^+ complex of 2,3-propadiene occurs exclusively on the stereoisomer with the methyl group on the noncomplexed double bond endo to the iron. A similar mechanism for reaction of **21** with water would lead to the stereoisomer pictured in **20**.

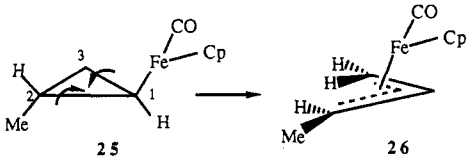
As mentioned in the introduction, one reason for interest in an α-halocyclopropyl Fp complexes is their potential as precursors to complexes of cyclopropylidenes and allenes. Indeed, treatment of **17** with BF_3 etherate led to instan-



taneous precipitation of a yellow solid that is identical with the known flurorborate salt of **21**.[7] Application of this reaction to the preparation of otherwise inaccessible allene complexes is currently under active investigation. For example, reaction of Fp^- with a mixture of syn and anti isomers of 7-bromo-7-fluorobicyclo[4.1.0]heptane (**22**) gives **23**, which reacts smoothly with BF_3 to give known **24**.[9]



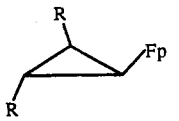
The stereochemistry of the ring opening of the 16-electron carbonyl(η^5-cyclopentadienyl)iron complex of *trans*-2-methylcyclopropane **25** has recently been found



to occur exclusively as depicted.[3c] To explain this, a disrotatory opening of the cyclopropane ring was proposed in which the electron pair of the C2–C3 bond essentially displaces the carbonyl(η^5-cyclopentadienyl)iron moiety with possible "d" orbital assistance from the iron.[3c] However, although a disrotatory opening was assumed, it could not be confirmed by the reported experiments. In principle, this should be easily accomplished by examining the stereochemistry of the products from the opening of a *trans*-2,3-disubstituted cyclopropyl complex, since disrotatory and conrotatory openings would give products

(6) Cf.: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 842–848.
(7) Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2161.
(8) Klemarczyk, P.; Rosenblum, M. *J. Org. Chem.* **1978**, *43*, 3488.
(9) (a) Manganiello, F. J.; Oon, S. M.; Radcliffe, M. D.; Jones, W. M. *Organometallics* **1985**, *4*, 1069. (b) Oon, S. M.; Koziol, A.; Palenik, G. J.; Jones, W. M. *J. Chem. Soc., Chem. Commun.* **1987**, 491. (c) Oon, S. M.; Jones, W. M. *Organometallics* **1988**, *7*, 2172.

with different stereochemistry. Unfortunately, and consistent with the fickle nature of many 16-electron cyclopropyl systems,[3c,10] brief photolysis of **27** (R = Et) gave no reaction,[11] while extended photolysis (30 h) of **27** (R = Me) gave 40% ferrocene and 50% starting material.



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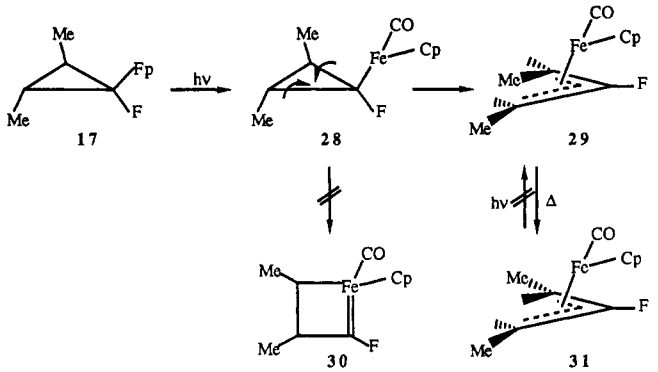
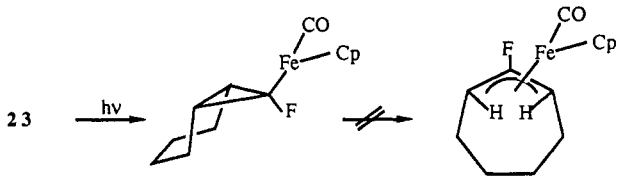
In earlier work we found that π-donors α to the Fp moiety in cyclopropyl σ complexes facilitate ring opening to π-allyl complexes.[3c] In addition, it is known that fluorine substituted at C1 weakens the C2–C3 bond of a cyclopropane.[12] It was, therefore, our hope that the α-fluoro substituent would facilitate ring opening of **28** to **29**



without diverting the reaction to the carbene complex **20**, as has been found with the alkoxy substituent.[3,13] This turned out to be the case. Photolysis of **17** leads cleanly to the π-allyl complex **29**; at concentrations comparable to **27** (R = Me), $t_{1/2}$ for **17** is approximately 18 h. Furthermore, it was found that when **29** was warmed, it slowly isomerized to its thermodynamically more stable isomer **31**, which did not isomerize back to **29** under the original photolysis conditions. This confirms that **29** is the kinetic product of the ring-opening process and further confirms that, as presumed, the ring opening to the π-allyl complex **28** is a disrotatory process.

Finally, photolysis of the norcarane complex **23** was compared with its 2,3-dimethylcyclopropyl congener **17**. This was of special interest because carbon–iron bond



breaking cannot be assisted by ring opening of the cyclopropane in a norcarane with the stereochemistry of **23**; disrotatory opening in a direction that could facilitate this process would necessarily give the *Z,Z* isomer of the π-allyl complex which would be prohibitively strained.[14] Indeed, **23** was much less photolabile than **17**; when the two were photolyzed at comparable concentrations, the norcarane showed no detectable reaction in the same time period that **17** showed about 50% conversion to the π-allyl complex **29**.

Experimental Section

Diethyl ether and tetrahydrofuran were distilled from Na and benzophenone ketyl; hexane was distilled from CaH_2; methylene chloride was distilled from P_2O_5; benzene was distilled from SilicaPent. The silica gel used was MCB 230–400 mesh and was degassed overnight (0.25 Torr, 25 °C) prior to use. All chromatographic separations were accomplished by the low-pressure flash chromatography method of Still.[15] Gas chromatography was performed on a Varian 3400 gas chromatograph. Photolysis was carried out by using a 450-W low-pressure Hg-Hanovia lamp in a Pyrex well. NMR spectra were taken on a Varian-XL 300 (300 MHz) or General Electrics-QE 300 (300 MHz) spectrometer. All spectra were recorded at room temperature unless otherwise specified. Mass spectra were run on an AEI MS-30 spectrometer. Atlantic Microlab, Inc., performed C and H analyses. Melting points (uncorrected) were obtained by using a Thomas-Hoover apparatus. All organometallic complexes were manipulated under nitrogen atmosphere (Schlenk line or glovebox). $CHBr_2F$ was purchased from PCR Inc. KFp was synthesized by the method described in the literature.[16]

Syntheses of 1,1-Dibromo-*trans*-2,3-dimethylcyclopropane and 1-Bromo-1-fluoro-*trans*-2,3-dimethylcyclopropane. Both compounds were prepared by the method of Skell and Garner.[17] They were purified by fractional distillation, while the 1-bromo-1-fluoro-*trans*-2,3-dimethylcyclopropane was additionally purified by preparative gas chromatography.

1-Bromo-1-fluoro-*trans*-2,3-dimethylcyclopropane: yield 48%; bp 45.0 °C/77 Torr; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.12–1.22 (m, 6 H), 1.02–1.12 (m, 1 H), 0.9–1.12 ppm (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 91.5 (d, $^1J_{CF}$ = 302.7 Hz, CF), 3.01 (d, $^2J_{CF}$ = 11.0 Hz, CH), 26.5 (d, $^2J_{CF}$ = 8.9 Hz, CH), 16.1 (s, trans CH_3), 11.4 ppm (d, $^3J_{CF}$ = 6.6 Hz, cis CH_3); ^{19}F NMR (282 MHz, $CDCl_3$, δ) −142.28 ppm (d, $^3J_{FHcis}$ = 19.8 Hz) [lit.[18] ^{19}F NMR (56.446 MHz, CCl_4, δ) −141.9 ppm (d, $^3J_{FH}$ = 21.2 Hz)].

1,1-Dibromo-*trans*-2,3-dimethylcyclopropane: yield 67.8%; bp 64.0 °C/23 Torr (lit.[17] bp 64.0 °C/23 Torr); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.3 (d, 6 H, CH_3), 1.1–1.2 ppm (m, 2 H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 40.8 (CBr_2), 32.3 (CH_3), 17.3 ppm (CH).

Synthesis of Dicarbonyl(η^5-cyclopentadienyl)(1-fluoro-*trans*-2,3-dimethylcyclopropyl)iron (17). To a stirred suspension of KFp (1.513 g, 7.0 mmol) in 50 mL of THF at −78 °C was added dropwise 1-bromo-1-fluoro-*trans*-2,3-dimethylcyclopropane (1.122 g, 6.7 mmol, 99.6% pure by GC) dissolved in 10 mL of THF via steel cannula under nitrogen. The mixture was stirred at −78 °C for 30 min. It was then allowed to warm to 0 °C and was stirred for an additional 3 h. The crude reaction mixture was filtered through Celite, the solvent removed, and the remaining amber oil extracted three times with hexane. After evaporation of hexane, 0.575 g (32.5%) of yellow to red crystals was obtained. During the filtration, extraction, and evaporation of solvents, flasks were never allowed to warm above 0 °C, since the compound is extremely thermally unstable: mp 38–41 °C dec.; ^{1}H NMR (300 MHz, C_6D_6, δ) 4.4 (s, 5 H, Cp), 1.4 (d, 3 H, CH_3), 1.0 (d, 3 H, CH_3), 0.7 (d of p, 1 H, $^3J_{HFcis}$ = 26.9 Hz, CH), 0.3 ppm (d of p, 1 H, $^3J_{HFtrans}$ = 8.4 Hz, CH); ^{13}C NMR (75 MHz, C_6D_6, δ) 217.2, 216.9 (M–CO), 93.3 (d, $^1J_{CF}$ = 284.0 Hz, CF), 85.8 (Cp), 30.4 (d, $^2J_{CF}$ = 9.1 Hz, CH), 27.4 (d, $^2J_{CF}$ = 9.6 Hz, CH), 17.9 (d, $^3J_{CFtrans}$ = 3.0 Hz, CH_3), 13.3 ppm (d, $^3J_{CFcis}$ = 11.6 Hz, CH_3); ^{19}F NMR (282 MHz, C_6D_6, δ) −123.1 ppm (d of d, $^3J_{FHcis}$ = 26.9 Hz,

(10) (a) Bruce, M. I.; Igbal, M. Z.; Stone, F. G. A. *J. Organomet. Chem.* **1969**, *20*, 161. (b) Brown, J. M.; Mertis, K. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1993. (c) Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1732. (d) Jones, N. L.; Ibers, J. A. *Organometallics* **1983**, *2*, 490. (e) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346.

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(14) Cf.: Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*; Plenum Press: New York, 1984; p 542.

(15) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(16) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L. *J. Organomet. Chem.* **1977**, *140*, C1.

(17) Skell, P. S.; Garner, A. Y. *J. Am. Chem. Soc.* **1956**, *78*, 3409.

(18) Seyferth, D.; Hopper, S. P. *J. Organomet. Chem.* **1973**, *51*, 77.

$^3J_{FHtrans}$ = 8.4 Hz); mass spectrum (chemical ionization) m/e 265 (MH^+), 245 (-HF), 217 (-HF, -CO), 177 (Fp^+); high-resolution calcd for $C_{12}H_{13}FFeO_2$ - (CO, HF) 216.023 75, found 216.024 58, deviation -3.4 ppm. Elemental analysis of this complex could not be done due to its decomposition above 0 °C.

Thermal Decomposition of Dicarbonyl(η^5-cyclopentadienyl)(1-fluoro-*trans*-2,3-dimethylcyclopropyl)iron. Title compound 17 spontaneously and rapidly decomposes above 0 °C. Decomposition products were chromatographed on a silica gel column using 5% ethyl acetate/hexane (v/v) as the eluent. The least polar yellow band was collected. After removal of solvent, a yellow oil was obtained. ^{1}H NMR spectroscopy shows that the product is a 1:1 mixture of two isomers 18 and 19 that could not be separated by column chromatography: ^{1}H NMR (300 MHz, C_6D_6, δ) *Z* isomer (18) 6.75 (d of d, 1 H), 6.52 (q, 1 H), 5.00 (d, 1 H), 4.80–4.85 (m, 1 H), 4.1 (s 5 H, Cp), 1.99 ppm (d, 3 H); ^{1}H NMR (300 MHz, C_6D_6, δ) *E* isomer (19) 6.65 (d of d, 1 H), 5.75 (q, 1 H), 4.85–4.95 (m, 2 H), 4.15 (s, 5 H, Cp), 1.9 ppm (d 3 H); ^{13}C NMR (75 MHz, C_6D_6, δ) *Z* isomer (18) 216.01 (Fe—CO), 153.59 (Fe—C=), 135.64, 109.23 (C=), 85.21 (Cp), 85.01 (C=), 20.67 ppm (CH_3); ^{13}C NMR (75 MHz, C_6D_6, δ) *E* isomer (19) 216.66 (Fe—CO), 146.10 (Fe—C=), 135.41, 110.92 (C=), 85.45 (Cp), 85.33 (C=), 18.16 ppm (CH_3).

Synthesis of Dicarbonyl(η^5-cyclopentadienyl)(4-hydroxy-2-penten-3-yl)iron (20). (a) From Dicarbonyl(η^5-cyclopentadienyl)(1-fluoro-*trans*-2,3-dimethylcyclopropyl)iron. A 0.106-g (0.40 mmol) sample of σ complex 17 was stirred with 3.0 g of silica gel in diethyl ether for 30 min, the solution was filtered, and the solvent was evaporated. The brown oil was flash chromatographed on silica gel with ethyl acetate as the eluent. The most polar red band was collected and the solvent evaporated. The resulting red oil was redissolved in 5 mL of hexane. When the solution was cooled to -78 °C, yellow crystals precipitated. After filtration, 0.053 g (50.5%) of yellow solid was obtained: mp 174–176 °C; ^{1}H NMR (300 MHz, C_6D_6, δ) 6.40 (q, 1 H, H—C=), 4.35 (m, 1 H, H—C—O, became q when water was added), 4.18 (s, 5 H, Cp), 1.75 (d, 3 H, H_3C—C=), 1.30 (d, 3 H, H_3C=C=O), 1.05 ppm (d, 1 H, -OH, disappeared when water was added); ^{13}C NMR (75 MHz, C_6D_6, δ) 217.0, 216.7 (M—CO), 150.5 (=C—Fp), 130.1 (=C—H), 85.5 (Cp), 81.0 (C—OH), 24.7, 20.3 ppm (CH_3); mass spectrum (chemical ionization) m/e 263 (MH^+), 245 ($-H_2O$), 217 ($-H_2O$, -CO), 189 ($-H_2O$, -2CO), 177 (Fp^+). Anal. Calcd for $C_{12}H_{14}O_3Fe$: C, 54.97; H, 5.39. Found: C, 54.93; H, 5.03.

(b) From Dicarbonyl(η^5-cyclopentadienyl)(η^2-1,3-dimethylallene)iron Tetrafluoroborate.[7] A 0.040-g (0.120 mmol) sample of the equilibrium mixture of the allene tetrafluoroborate 21 was dissolved in 10 mL of degassed water and stirred for 1 h. The water solution was extracted with benzene. After evaporation of solvent, 0.025 g (78.0%) of yellow solid remained. Its properties are the same as those of the compound described above.

Photolysis of Dicarbonyl(η^5-cyclopentadienyl)(1-fluoro-*trans*-2,3-dimethylcyclopropyl)iron. A 0.105-g (0.40 mmol) sample of the title compound 17 in 0.7 mL of benzene-d_6 was photolyzed in the ice bath for 35 h. The crude ^{1}H NMR spectrum shows two new methyl doublets assigned to the syn–anti dimethyl η^3-π-allyl complex. The crude mixture was chromatographed on silica gel, using hexane as eluent. The main, least polar, yellow band was collected. After removal of solvent, 0.038 g (40.1%) of yellow oil remained: ^{1}H NMR (300 MHz, C_6D_6, δ) 4.2 (d of q, 1 H, $^3J_{HF}$ = 18.9 Hz, syn C–H), 4.1 (s, 5 H, Cp), 1.9 (d or q, 1 H, $^3J_{HF}$ = 24.2 Hz, anti C–H), 1.7 (d, 3 H), 0.8 ppm (d, 3 H); ^{13}C NMR (75 MHz, C_6D_6, δ) 222.5 (M–CO), 140.0 (d, $^1J_{CF}$ = 243.3 Hz, CF), 81.1 (Cp), 42.6 (d, $^2J_{CF}$ = 13.2 Hz, CH), 37.5 (d, $^2J_{CF}$ = 10.3 Hz, CH), 19.8 (CH_3), 15.1 ppm (d, $^3J_{CF}$ = 3.9 Hz, CH_3); ^{19}F NMR (282 MHz, C_6D_6, δ) -143.9 ppm (t, $^3J_{HF}$ = 19.5 Hz); mass spectrum m/e 236 (M^+), 208 (-CO), 186 ($FeCp_2$).

Thermal Rearrangement of Syn-Anti Dimethyl η^3-π-Allyl Complex 29 to Syn–Syn Dimethyl η^3-π-Allyl Complex 31. A 0.030-g (0.11 mmol) sample of syn–anti dimethyl η^3-π-allyl complex 29 in 0.6 mL of benzene-d_6 was heated at 75 °C for 6 h. Approximately 90% of the complex rearranged to the syn–syn isomer 31. Even after 24 h at 75 °C the ratio did not change. After removal of solvent, a yellow oil remained: ^{1}H NMR (300 MHz, C_6D_6, δ) 4.05 (s, 5 H, Cp), 1.65 (d, 6 H), 1.29 ppm (d of q, 2 H, $^3J_{HF}$ = 17.7 Hz); ^{13}C NMR (75 MHz, C_6D_6, δ) 222.0 (M–CO), 140.5 (d, $^1J_{CF}$ = 245 Hz, CF), 80.8 (Cp), 37.6 (d, $^2J_{CF}$ = 10.3 Hz, CH), 15.5 ppm (CH_3); ^{19}F NMR (282 MHz, C_6D_6, δ) -159.5 ppm (t, $^3J_{HF}$ = 17.5 Hz); mass spectrum m/e 236 (M^+), 208 (-CO), 186 ($FeCp_2$); high-resolution calcd for $C_{11}H_{13}FFeO$ 236.029 98, found 236.029 66, deviation -1.3 ppm.

Synthesis of 1-Bromo-*trans*-2,3-dimethylcyclopropane. The compound was prepared by the reduction of the 1,1-dibromo-*trans*-2,3-dimethylcyclopropane with tri-*n*-butyltin hydride according to the method of Seyferth:[19] yield 74.5%; bp 112 °C/760 Torr; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 2.71–2.78 (d of d, 1 H, CHBr), 1.20 (d, 3 H, CH_3), 1.10 (d, 3 H, CH_3), 0.78 (d of p, 1 H), 0.65 ppm (p, 1 H) [lit.[20] ^{1}H NMR (60 MHz, CCl_4, δ) 2.69 (m, CHBr), 1.1–1.3 (m, CH_3)]; ^{13}C NMR (75 MHz, $CDCl_3$, δ) 31.0, 24.1, 19.1, 17.5, 15.5 ppm.

Synthesis of Dicarbonyl(η^5-cyclopentadienyl)(*trans*-2,3-dimethylcyclopropyl)iron (32). To a stirred suspension of KFp (0.97 g, 4.5 mmol) in 50 mL of THF at 0 °C was added 1-bromo-*trans*-2,3-dimethylcyclopropane (0.61 g, 4.1 mmol) dissolved in 10 mL of THF via steel cannula under nitrogen. The mixture was stirred at room temperature for 18 h, after which time the solvent was evaporated and the dark red paste was extracted two times with hexane. After evaporation of hexane, a small amount of yellow oil was obtianed (0.102 g, 10.1%). The oil was further purified by flash column chromatography on silica gel using hexane as the eluent: ^{1}H NMR (300 MHz, C_6D_6, δ) 4.15 (s, 5 H, Cp), 1.29 (d, 3 H, cis CH_3), 1.19 (d, 3 H, trans CH_3), 0.43–0.59 (m, 2 H), 0.18–0.26 ppm (m, 1 H); ^{13}C NMR (75 MHz, C_6D_6, δ) 215.4 (M–CO), 85.2 (Cp), 23.8, 22.1, 20.1, 18.9, 9.7 ppm; mass spectrum m/e 246 (M^+), 218 (-CO), 190 (-2CO); high-resolution calcd for $C_{12}H_{14}FeO_2$ 246.034 32, found 246.033 90, deviation -1.7 ppm.

Photolysis of Dicarbonyl(η^5-cyclopentadienyl)(*trans*-2,3-dimethylcyclopropyl)iron. A 0.095-g (0.39 mmol) sample of σ complex 32 in 0.7 mL of benzene-d_6 was photolyzed in the ice bath for 30 h. Reaction was periodically monitored by ^{1}H NMR spectroscopy. The major product formed was ferrocene. After 30 h there was still about 50% of unreacted σ complex; 40% was ferrocene and 10% was two other compounds containing Cp (5% each). They were expected to be ring-opened products. However, they were present in too small amount to be isolated by column chromatography. The only products isolated were the σ complex and ferrocene.

Synthesis of 7-Bromo-7-fluorobicyclo[4.1.0]heptane. This compound was prepared by the method of Skell and Garner.[17] The compound distills as a mixture of both isomers (endo/exo = 1.7 by the ^{19}F NMR spectrum) and was used without further separation: yield 42.5%; bp 60 °C/10 Torr (lit.[21] yield 44%; bp 44–47 °C/6 Torr; ratio of isomers = 1.7); ^{13}C NMR (75 MHz, $CDCl_3$, δ) major (endo) isomer 97.2 (d, $^1J_{CF}$ = 294.5 Hz, CF), 21.7 (d, $^2J_{CF}$ = 10.4 Hz, CH), 20.0 (d, $^3J_{CF}$ = 2.9 Hz, CH_2), 19.3 ppm (CH_2); ^{13}C NMR (75 MHz, $CDCl_3$ δ) minor (exo) isomer 85.3 (d, $^1J_{CF}$ = 305.4 Hz, CF), 23.2 (d, $^2J_{CF}$ = 10.0 Hz, CH), 20.8 (d, $^4J_{CF}$ = 1.8 Hz, CH_2), 17.2 ppm (d, $^3J_{CF}$ = 3.2 Hz, CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, δ) major (endo) isomer -118.7 ppm (t, $^3J_{HF}$ = 20.4 Hz); ^{19}F NMR (282 MHz, $CDCl_3$, δ) minor (exo) isomer -155.1 ppm.

Synthesis of Dicarbonyl(η^5-cyclopentadienyl)(7-fluoro-7-bicyclo[4.1.0]heptyl)iron (23). To a stirred suspension of KFp (1.00 g, 7.0 mmol) in 50 mL of THF at -78 °C was added 0.87 g (4.5 mmol) of 7-bromo-7-fluorobicyclo[4.1.0]heptane (unseparated mixture of isomers) dissolved in 10 mL of THF via steel cannula under nitrogen. The mixture was stirred at low temperature for 30 min. It was then allowed to warm to 0 °C and was stirred for an additional 3 h. The crude reaction mixture was filtered through Celite, the solvent removed, and the remaining red solid extracted three times with hexane. After evaporation of hexane, red crystals were obtained, which were additionally purified by recrystallization from hexane at -30 °C; 0.086 g (6.6%, assuming that both isomers reacted) of orange crystals was obtained: mp 71–73 °C; ^{1}H NMR (300 MHz, C_6D_6, δ) 4.24 (s, 5 H,

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Cp), 1.8-2.0 (m, 4 H, CH_2), 1.2-1.5 (m, 4 H, CH_2), 0.75 ppm (d of m, 2 H, $^3J_{HF}$ = 12.9 Hz); ^{13}C NMR (75 MHz, C_6D_6, δ) 216.45, 216.41 (M-CO), 99.5 (d, $^1J_{CF}$ = 150.0 Hz, CF), 85.9 (Cp), 23.3 (d, $^2J_{CF}$ = 12.0 Hz, CH), 22.66 (CH_2), 19.52 ppm (d, $^3J_{CF}$ = 7.2 Hz, CH_2); ^{19}F NMR (282 MHz, C_6D_6, δ) -144.6 ppm (t, $^3J_{HF}$ = 12.7 Hz); mass spectrum *m/e* 290 (M^+), 271 (-F), 262 (-CO), 242 (-CO, -HF), 234 (-2CO), 214 (-2CO, -HF), 140 ($FeCpF^+$), 121 ($FeCp^+$); high-resolution calcd for $C_{14}H_{15}FFeO_2$ - 2CO 234.050 71, found 234.050 10, deviation -2.6 ppm. Elemental analysis could not be obtained since the compound is slowly decomposing.

Photolysis of Dicarbonyl(η⁵-cyclopentadienyl)(7-fluoro-7-bicyclo[4.1.0]heptyl)iron. A 0.015-g (0.05 mmol) sample of norcaryl σ complex **23** in 0.6 mL of benzene-d_6 was photolyzed in the ice bath for 6 h. No changes were observed in the ^1H NMR spectrum.

Synthesis of Dicarbonyl(η⁵-cyclopentadienyl)(η²-1,3-dimethylallene)iron Tetrafluoroborate (21). To a stirred solution of 0.200 g (0.76 mmol) of σ complex **17** in 10 mL of diethyl ether at 0 °C was added 0.094 mL (0.76 mmol, 0.108 g) of freshly distilled BF_3OEt_2 via steel cannula under nitrogen. A yellow solid precipitated immediately. The solvent was evaporated, and the solid was recrystallized from methylene chloride/diethyl ether to give 0.221 g (87%) of a 1:2.4 equilibrium mixture of syn and anti isomers. Spectral data are in agreement with the compound described in the literature:[2,7] mp 156-159 °C dec.; ^1H NMR (300 MHz, CD_2Cl_2, δ) major (anti-3-methyl) isomer 6.2 (m, 1 H), 5.7 (s, 5 H, Cp), 4.4 (m, 1 H), 2.1 (d of d, 3 H), 1.65 ppm (d, 3 H); ^1H NMR (300 MHz, CD_2Cl_2, δ) minor (syn-3-methyl) isomer 6.7 (m, 1 H), 5.7 (s, 5 H, Cp), 4.3 (m, 1 H), 2.2 (d of d, 3 H), 1.6 ppm (d, 3 H).

Synthesis of Dicarbonyl(η⁵-cyclopentadienyl)(η²-1,2-cycloheptadiene)iron Tetrafluoroborate (24). To a solution of 0.017 g (0.059 mmol) of norcaryl σ complex **23** in 10 mL of diethyl ether at 0 °C was added 7.27 μL (0.059 mmol) of freshly distilled BF_3OEt_2. A yellow precipitate appeared immediately. After the solvent was evaporated, a quantitative yield of a yellow solid was obtained. The product can be further purified by recrystallization from methylene chloride/diethyl ether. The compound has the same properties as **24** described in the literature:[9a] mp 145-148 °C dec.; ^1H NMR (300 MHz, CD_3NO_2, -20 °C, δ) 6.6 (m, 1 H, =C—H, free), 5.75 (s, 5 H, Cp), 4.3 (m, 1 H, =C-, complexed), 2.55 (m, 1 H), 2.35 (m, 2 H), 1.95 (m, 3 H), 1.6 (m, 1 H), 0.95 ppm (m, 1 H); ^{13}C NMR (75 MHz, CD_3NO_2, -20 °C, δ) 210.4, 207.4 (Fe—CO), 150.1 (=C=), 126.2 (-C=, free), 92.5 (Cp), 43.9 (-C=, complexed), 30.9, 30.8, 29.9, 29.5 ppm (CH_2).

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Effect of Allyl Methyl Substituents on the Preparation, Dynamics, and Reactivity of $(\eta^5\text{-}C_5Me_5)(allyl)ZrX_2$ Complexes (X = Cl, Br): Structure of $(\eta^5\text{-}C_5Me_5)(C_3H_5)ZrCl_2$ and $(\eta^5\text{-}C_5Me_5)(1,2\text{-}Me_2(butadiene))(\eta^2\text{-}CH_2PPh_2)Zr$. Dynamics of $(\eta^5\text{-}C_5Me_5)(2,3\text{-}Me_2(butadiene))(\eta^2\text{-}CH_2PPh_2)Zr$

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This paper deals with the effects of methyl substituents on the allyl ligand on the preparation, dynamics, and reactivity of compounds of the type Cp*(allyl)ZrX_2 (**1**: allyl = C_3H_5, X = Cl; **3**: allyl = 1,1,2-trimethylallyl, X = Br; **4**: allyl = 1,2,3-trimethylallyl, X = Br). Methyl substituents on the allyl ligand at the terminal positions leads to increased yields of these compounds via the reaction of allyl Grignards or allyl lithium with Cp^*ZrCl_3. Cyclic voltammetry reveals that **3** and **4** are more difficult to reduce than Cp_2ZrX_2 (X = Cl, Br). Nevertheless, compounds **3** and **4** are reduced by $K[CpM(CO)_2]$ (M = Fe, Ru) yielding $[MCp(CO)_2]_2$ and uncharacterizable oils instead of bimetallic compounds. The reaction of **3** and **4** with 2 equiv of $LiCH_2PPh_2$ gives $Cp^*(\eta^4\text{-}2,3\text{-}Me_2(butadiene))(\eta^2\text{-}CH_2PPh_2)Zr$ (**5**) and $Cp^*(\eta^4\text{-}1,2\text{-}Me_2(butadiene))(\eta^2\text{-}CH_2PPh_2)Zr$ (**6**). X-ray crystallography of **6** reveals that the CH_2PPh_2 is bound through both the P and C atoms (Zr-C, 2.346 (8) Å; Zr-P, 2.664 (2) Å) to yield a highly strained Zr-C-P ring. For **6**: cell constants a = 12.386 (5) Å, b = 12.778 (6) Å, c = 9.223 (4) Å, α = 109.26 (2)°, β = 91.52 (2)°, γ = 109.66 (2)°; space group $P\bar{1}$; R = 0.0626, R_w = 0.0607. Variable-temperature ^1H NMR studies of **5** revealed a dynamic process involving Zr-P bond rupture ($\Delta G^\ddagger$ = 38.9 ± 1.0 kJ/mol). Also isolated in small amounts were crystals of **1** suitable for an X-ray structure determination, which revealed a prone orientation for the $\eta^3\text{-}C_3H_5$ allyl ligand. For **1**: cell constants a = 9.726 (2) Å, b = 11.214 (2) Å, c = 13.262 (3) Å; space group *Pnam*; R = 0.0367, R_w = 0.0401. The ^1H NMR spectrum of **4** has revealed the presence of a second isomer in which one of the terminal allyl methyls assumes an anti orientation (the major isomer has both terminal methyls in the syn orientation). A variable-temperature ^1H NMR study of **4** revealed an $\eta^3\text{-}\eta^1$-allyl isomerization mechanism that leads to exchange between isomers ($\Delta G^\ddagger$ = 66.2 ± 1.0 kJ/mol).

Introduction

In an earlier paper we presented the preparation and the first structural and dynamic studies of compounds of the type $Cp^*(\eta^3\text{-allyl})ZrBr_2$ ($Cp^* = C_5Me_5$; allyl = 1,1,2-trimethyl (**3**) or 1,2,3-trimethyl (**4**)).[1] These complexes can be thought of as zirconocene dihalide analogues in which one Cp has been replaced with an allyl ligand. The

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