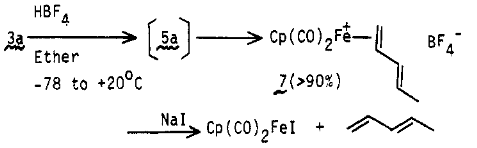
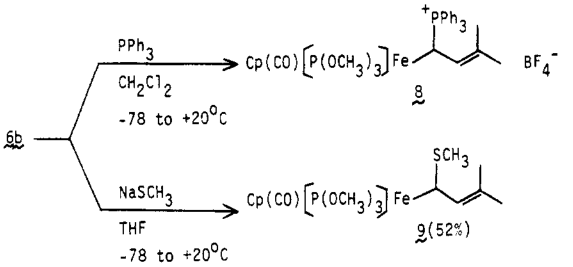
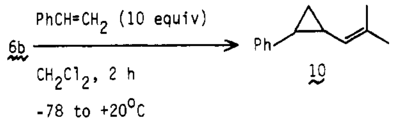


(6)



(7)



(8)

overall yield from **4b**. Cyclopropanation also occurs when the sulfide **9** is converted into a sulfonium salt[8,9] through use of trimethyloxonium tetrafluoroborate in the presence of styrene.

In conclusion, we have developed a convenient route to allylidene complexes of iron that exhibit potentially useful reactivity. Applications of these complexes are being pursued in our laboratory.

Acknowledgment. We are grateful to Professor C. P. Casey and Dr. W. H. Miles (University of Wisconsin) for informing us of their concurrent studies. We also acknowledge the generous financial support provided by the National Science Foundation (Grant CHE 8120466) and the donors of the Petroleum Research Fund, administered by the American Chemical Society. The Nicolet 300-MHz NMR spectrometer used in this work was purchased in part with funds provided by the NSF Instrumentation Program (Grant 8114412).

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(26) *cis*-**10**: ^{1}H NMR (CDCl$_3$) δ 7.01-7.41 (m, 5 H), 4.51 (d, J = 8.8 Hz, 1 H), 2.28 (m, 1 H), 1.87 (m, 1 H), 1.71 (s, 3 H), 1.56 (s, 3 H), 1.26 (m, 1 H), 0.87 (m, 1 H); ^{13}C NMR (CDCl$_3$) δ 139.3, 132.7, 128.9, 127.8, 125.5, 122.9, 25.6, 22.8, 18.3 (probably two overlapping peaks), 12.4.

Synthesis and Characterization of $(C_5H_5)(CO)_2Fe{=}CHCH{=}C(CH_3)_2^+$ and Its Reaction with Alkenes To Give Vinylcyclopropanes

Charles P. Casey* and William H. Miles

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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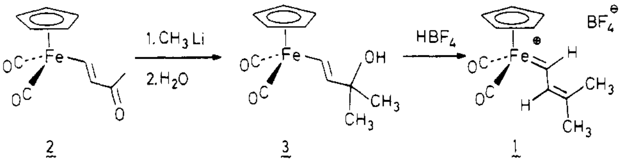
Summary: Reaction of $(C_5H_5)(CO)_2FeCH{=}CHC(CH_3)_2OH$ (**3**) with HBF$_4$ in diethyl ether at −23 °C gives the vinylcarbene complex $(C_5H_5)(CO)_2Fe{=}CHCH{=}C(CH_3)_2^+$, **1**, which was identified by low-temperature ^{1}H and ^{13}C NMR spectroscopy. The reaction of **1** with isobutylene gives 2,2-dimethyl-1-(2-methyl-1-propenyl)cyclopropane (**4**) in 56% yield. Cyclooctene reacts with **1** to give *cis*-9-(2-methyl-1-propenyl)bicyclo[6.1.0]nonane in 37% yield. The reaction of **1** with styrene gives *cis*- and *trans*-1-phenyl-2-(2-methyl-1-propenyl)cyclopropane in a 1:2 ratio in 45% yield.

Electrophilic transition-metal carbene complexes, including $(CO)_5W{=}CHC_6H_5$[2] and $(C_5H_5)(CO)_2[P(C_6H_5)_3]Mo{=}CH_2^+$,[3] have been shown to be useful cyclopropanating reagents.[1] The most efficient and best studied reagents are the $(C_5H_5)(CO)_2Fe{=}CRR'^+$ complexes investigated by Pettit,[4] Brookhart,[5,6] Helquist,[7-9] Cutler,[10] and ourselves.[11] In an effort to develop a 3-methylbut-2-en-1-ylidene cyclopropanating reagent useful in the preparation of chrysanthemic acid derivatives,[12] we have studied the synthesis and reactions of $C_5H_5(CO)_2Fe{=}CHCH{=}C(CH_3)_2^+$ (**1**).[13]

There are two efficient general syntheses of electrophilic metal carbene complexes: (1) the addition of an electrophile to a M-CHR-X (X = OR, SR, Cl) derivative[2-8,10,11] and (2) the addition of acids to vinylmetal complexes.[9-11] In the accompanying communication, Helquist[14] reports a synthesis of vinylcarbene complexes based on the protonation of dienyliron complexes. We have independently developed a route to **1** based on the addition of an electrophile to a $FeCH{=}CHC(CH_3)_2X$ system. $C_5H_5(CO)_2FeCH{=}CHCOCH_3$, **2**, was prepared in 54% yield by reaction of $Na^+C_5H_5Fe(CO)_2^-$ (120 mmol) with 4-chlorobut-3-en-2-one (130 mmol)[15] as previously described by Nesmeyanov.[16] Addition of CH$_3$Li (13.8 mmol) to the ketone group of **2** (12.2 mmol) gave $C_5H_5(CO)_2FeCH{=}CHC(CH_3)_2OH$, **3**,[17] in 62% yield as a pure red oil after aqueous workup and alumina chromatography.



Addition of HBF$_4$ in diethyl ether (0.3 mmol) to an ether solution of tertiary allylic alcohol **3** (0.29 mmol) at −23 °C led to the precipitation of $C_5H_5(CO)_2Fe{=}CHCH{=}C(CH_3)_2^+BF_4^-$ (**1**), as a red-orange solid which was washed

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(17) **3**: ^{1}H NMR (C$_6$D$_6$, 270 MHz) δ 6.70 (d, J = 15.8 Hz, 1 H), 6.00 (d, J = 15.8 Hz, 1 H), 4.05 (s, 5 H), 1.34 (s, 6 H), 1.31 (s, 1 H, exchange with D$_2$O); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 15.04 MHz) δ 216.5, 153.1, 121.9, 85.2, 72.8, 30.7; IR (CH$_2$Cl$_2$) 3585, 2006, 1958 cm^{-1}; exact mass (30 eV) 262.0291, calcd for C$_{12}$H$_{14}$FeO$_3$ 262.0292.

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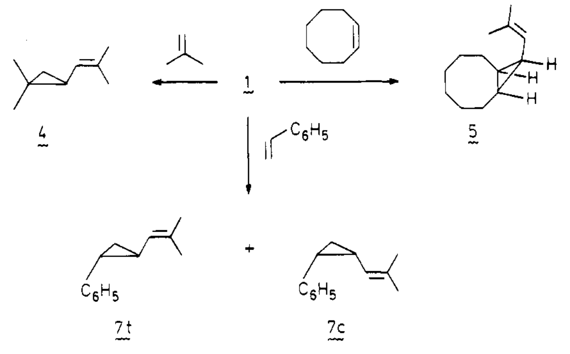
with ether at −23 °C and dried under vacuum at −23 °C. **1** is unstable at room temperature but was fully characterized spectroscopically by low-temperature NMR.[18]

In the ^{1}H NMR of **1** in CD_2Cl_2 at −50 °C, the proton on the carbene carbon and the vinyl proton appear as two doublets at δ 15.96 and 8.21, respectively. In the ^{13}C NMR of **1** at −50 °C, the carbene carbon appears at δ 315.5 and the vinyl carbons appear at δ 177.9 and 155.3. Solutions of **1** in CD_2Cl_2 are stable for hours at −50 °C but decompose on warming to room temperature. We have not succeeded in isolating the decomposition products.

The isolated vinylcarbene complex **1** reacts with alkenes to give moderate yields of (vinylcyclopropane)iron complexes from which the vinylcyclopropane product can be released by treatment with NaI in acetone.[19] Isobutylene (1.35 mmol) was condensed into a CH_2Cl_2 solution of vinylcarbene iron complex **1** (0.45 mmol)[20] at −78 °C. The reaction mixture was stirred for 45 min at −23 °C and then for 1 h at room temperature. The volatile fraction of the solution was transferred under high vacuum, and NaI in acetone (0.47 mmol in 1 mL) was added to the remaining solid to free the complexed 2,2-dimethyl-1-(2-methyl-1-propenyl)cyclopropane (**4**). The volatile fraction of the acetone solution was transferred under vacuum and combined with the previous volatile fraction. The yield of **4** was 56% as determined by gas chromatography, and pure **4** was isolated by preparative gas chromatography.[21]



Reaction of **1** (2.37 mmol in 10 mL of CH_2Cl_2) with cyclooctene (7.1 mmol) followed by workup with NaI in acetone and isolation by silica gel chromatography and Kugelrohr distillation gave *cis*-9-(2-methyl-1-propenyl)bicyclo[6.1.0]nonane (**5**) in 37% yield. A single isomer was seen by gas chromatography on several columns, and *cis*-**5** appeared pure by both ^{1}H and ^{13}C NMR.[23] The cis stereochemistry of **5** was conclusively established by ozonolysis to give *cis*-bicyclo[6.1.0]nonane-9-carboxylic acid (**6**)[24] whose stereochemistry was established by Eu shift studies on the related ethyl esters.[25,26] The selective formation of *cis*-cyclopropanes from electrophilic metal carbene complexes is a common phenonmenon.[2,5–7]

In the reaction of **1** (2.37 mmol in 10 mL of CH_2Cl_2) with styrene (6.9 mmol), we were surprised to find that a 2:1 mixture of *trans*- and *cis*-1-phenyl-2-(2-methyl-1-propenyl)cyclopropane, **7t** and **7c**, was formed in 45% yield. Pure samples of **7t** and **7c** were obtained by preparative gas chromatography, and the stereochemistry of each isomer was conclusively established by measurement of ^{1}H NMR coupling constants of the cyclopropyl hydrogens.[27] The unexpected selectivity for formation of *trans*-cyclopropane is particularly surprising since Helquist has found cis selectivity in the reaction of styrene with the closely related complex $(C_5H_5)[P(OCH_3)_3](CO)Fe{=}CHCH{=}CH(CH_3)_2{}^+$.[14]

Although the moderate yields of vinylcyclopropanes obtained here have been encouraging, we have not yet been successful in the synthesis of chrysanthemic acid derivatives. The reaction of **1** with $(CH_3)_2C{=}CHCH_2OSi(CH_3)_2C(CH_3)_3$ did not lead to detectable (<1%) yields of vinylcyclopropane products.

Acknowledgment. We would like to express our appreciation to Professor Paul Helquist for keeping us informed of his related studies. Helpful discussions with Hideyuki Tukada and research support from the National Science Foundation are gratefully acknowledged.

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(18) The ether wash contained no nonvolatile material and ^{1}H NMR indicated >95% purity for **1**. **1**: ^{1}H NMR (CD_2Cl_2, 270 MHz) δ 15.96 (d, J = 14.7 Hz, 1 H), 8.21 (d, J = 14.7 Hz, 1 H), 5.66 (s, 5 H), 2.22 (s, 6 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 15.04 MHz) δ 315.5, 207.1, 177.9, 153.3, 91.9, 29.9, 23.4.

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(20) **1** was prepared by the addition of HBF_4 (0.45 mmol) in diethyl ether to a diethyl ether solution of **3** (0.45 mmol).

(21) 2,2-Dimethyl-1-(2-methyl-1-propenyl)cyclopropane was isolated by preparative gas chromatography (SE-30) and identified by spectral and chromatographic comparison with an authentic sample.[22] **4**: ^{1}H NMR (C_6D_6, 270 MHz) δ 4.96 (dm, J = 8.1 Hz, 1 H), 1.69 (br s, 3 H), 1.67 (d, J = 1.5 Hz, 3 H), 1.29 (ddd, J = 8.6, 8.1, 4.6 Hz, 1 H), 1.04 (s, 3 H), 1.02 (s, 3 H), 0.63 (dd, J = 8.6, 4.6 Hz, 1 H), 0.22 (t, J = 4.6 Hz, 1 H); $^{13}C\{^1H\}$ NMR (C_6D_6, 15.04 MHz) δ 132.4, 125.3, 27.6, 26.0, 24.6, 22.9, 21.4, 18.6, 18.2.

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(23) *cis*-**5**: ^{1}H NMR (C_6D_6, 270 MHz) δ 5.14 (dm, J = 7.8 Hz, 1 H), 1.75 (s, 3 H), 1.70 (s, 3 H), 1.28–1.70 (m, 11 H), 1.10 (m, 2 H), 0.74 (m, 2 H); $^{13}C\{^1H\}$ NMR (C_6D_6, 15.04 MHz) δ 133.8, 120.6, 30.4, 27.4, 26.2, 23.3, 21.1, 18.9, 17.9; exact mass (70 eV) 178.1722; calcd for $C_{13}H_{22}$ 178.1722.

(24) *cis*-**6**: ^{1}H NMR (C_6D_6, 270 MHz) δ 12.26 (br s, 1 H), 1.93 (m, 2 H), 1.10–1.65 (m, 11 H), 0.80 (m, 2 H). The ^{1}H NMR spectra of *cis*-**6** from ozonolysis of *cis*-**5** was identical with the ^{1}H NMR spectra of *cis*-**6** prepared by the saponification of the pure ethyl ester of *cis*-**6**. *trans*-**6** was prepared by saponification of the pure ethyl ester of *trans*-**6**. *trans*-**6**: ^{1}H NMR (C_6D_6, 270 MHz) δ 13.2 (br s, 1 H), 1.72 (m, 2 H), 1.0–1.5 (m, 11 H), 0.66 (m, 2 H).

(25) Ethyl *cis*- and *trans*-bicyclo[6.1.0]nonane-9-carboxylate[26] were separated by preparative gas chromatography (QF-1). Ethyl ester of *trans*-**6**: ^{1}H NMR (C_6D_6, 270 MHz) δ 4.01 (q, J = 7.1 Hz, 2 H), 1.81 (m, 2 H), 1.0–1.5 (m, 11 H), 0.99 (t, J = 7.1 Hz, 3 H), 0.74 (m, 2 H). The resonance due to the proton attached to carbon 9 of the ethyl ester of *trans*-**6** was shifted to δ 2.92 by 15 mol % $Eu(fod)_3$ shift reagent (0.004 M in C_6D_6) and appeared as a triplet with J = 4.6 Hz, unambiguously establishing the trans stereochemistry. Ethyl ester of *cis*-6: ^{1}H NMR (C_6D_6, 270 MHz) δ 4.00 (q, J = 7.1 Hz, 2 H), 2.14 (m, 2 H), 1.1–1.7 (m, 11 H), 0.99 (t, J = 7.1 Hz, 3 H), 0.85 (m, 2 H).

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(27) GC separation was achieved with a 20% OV-225 column at 180 °C. *cis*-**7**: ^{1}H NMR ($(CD_3)_2CO$, 270 MHz) δ 7.2 (m, 5 H), 4.52 (dm, J = 8.7 Hz, 1 H), 2.28 (ddd, J = 6.2, 8.6, 8.6 Hz, 1 H), 1.89 (m, 1 H), 1.67 (d, J = 1.1 Hz, 3 H), 1.50 (d, J = 0.9 Hz, 3 H), 1.21 (ddd, J = 4.7, 8.6, 8.6 Hz, 1 H), 0.89 (ddd, J = 4.8, 6.0, 6.0 Hz, 1 H); exact mass (70 eV) 172.1252, calcd for $C_{13}H_{16}$ 172.1252. *trans*-**7**: ^{1}H NMR ($(CD_3)_2CO$, 270 MHz) δ 7.2 (m, 5 H), 4.77 (dm, J = 8.7 Hz, 1 H), 1.81 (m, 1 H), 1.73 (m, 1 H), 1.68 (d, J = 1.2 Hz, 3 H), 1.67 (s, 3 H), 1.16 (ddd, J = 8.7, 5.5, 4.6 Hz, 1 H), 0.94 (ddd, J = 8.5, 5.6, 4.5 Hz, 1 H); exact mass (70 eV) 172.1252, calcd for $C_{13}H_{16}$ 172.1252.

Reactions of $M_2(CO)_8(\mu\text{-}PPh_2)_2$ (M = Mo or W) with BR_3H^- and LiR Nucleophiles. Proton-Induced Cleavage of M–(μ-PPh_2) Bonds in Binuclear Anionic Complexes

Shin-Guang Shyu and Andrew Wojcicki*

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received January 13, 1984

Summary: Reactions of $M_2(CO)_8(\mu\text{-}PPh_2)_2$ (**2**, M = Mo or W) with 1 equiv of $M'BR_3H$ (M' = Li or K; R = Et or *sec*-Bu) in THF proceed to $[\overline{(CO)_4M(\mu\text{-}PPh_2)M}(CO)_4$-