direct route to its diisopropyl ester.[16] Mixing with an equimolar amount of (*R,R*)-2,3-butanediol and distilling yielded **2**: bp 68–70 °C (5 torr); $[\alpha]^{25}{}_{546}$ +10.2° (*c* 3.5, toluene) (hydrolyzed rapidly by atmospheric moisture).[17] To make **4a**, 5 mmol of **2** in 10 mL of THF was cooled to −78 °C and 5 mmol of Grignard or lithium reagent (purity checked by titration) was added dropwise. After the solution was stirred 5 min, ~480 mg (3.5 mmol) of anhydrous zinc chloride[1] was added and the mixture was kept at 20 °C overnight (except for R = Ph, 2 h at −30 to +20 °C). The solvent was evaporated under vacuum, and the residue was triturated with 3 × ~50 mL of petroleum ether. The solution was stirred with 10 g of anhydrous magnesium sulfate, filtered, and concentrated to yield **4a**, which showed only minor impurities in the NMR. Treatment of **4a** with an equivalent of optically pure (+)-pinanediol[1] in hexane followed by chromatography[1] (no isomer separation) yielded **4b** on which the isomer ratios were determined (Table I).

**Acknowledgment.** We thank the National Institutes of Health for Grant GM27109, the National Science Foundation for Grant CHE-8025229, and the Boeing Corp. for a gift in support of departmental purchase of the Nicolet NT-200 200-MHz NMR instrument.

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[15] The reaction mixture[14] was extracted with butanol/ether and distilled; bp 68–70 °C (0.1 torr).

[16] Brown, H. C.; Cole, T. E. *Organometallics* **1983**, *2*, 1316–1319.

[17] Satisfactory analyses for all elements except O were obtained.

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# Generation and Reactions of Allylidene Complexes of the ($\eta^5$-Cyclopentadienyl)dicarbonyliron and ($\eta^5$-Cyclopentadienyl)(trimethyl phosphite)carbonyliron Systems

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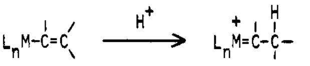
*Received November 28, 1983*

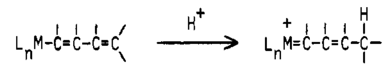
*Summary:* A series of four dienyliron complexes, $Cp(CO)(L)FeCH{=}CHC(R^1){=}CHR^2$ [L = CO or $P(OCH_3)_3$; $R^1$ = H, $R^2$ = $CH_3$ or $R^1$ = $CH_3$, $R^2$ = H], is prepared by acylation of $[Cp(CO)_2Fe]Na$ with the appropriate dienoyl chlorides followed by photochemical decarbonylation and, when desired, ligand exchange of carbon monoxide by trimethyl phosphite. Treatment of these complexes with strong acid at low temperature produces the corresponding cationic allylidene complexes $[Cp(CO)(L)Fe{=}CHCH{=}C(R^1)CH_2R^2]^+$, which have been characterized by NMR and by their reaction behavior. Included among their reactions are rearrangement to an $\eta^2$-diene complex, nucleophilic addition of triphenylphosphine and of sodium methylmercaptide, and alkene cyclopropanation.

Transition-metal carbene complexes are now recognized as possible intermediates in many metal-promoted reactions,[1] including the cyclopropanation, metathesis,[2] and polymerization of alkenes[3] as well as Fischer–Tropsch syntheses.[4] Carbene complexes of the ($\eta^5$-cyclopentadienyl)dicarbonyliron system were first reported by Pettit[5] and by Green[6] several years ago and since that time have been studied extensively by several other groups.[7] With the goal of developing routes to alkylidene complexes in general, we have previously reported methylene,[8] ethylidene,[9] and isopropylidene complexes[10] in this series of iron compounds. We now wish to describe an entry into the corresponding *allylidene* (or vinylcarbene) complexes.[11]

The protonation of alkenylmetal complexes to produce the corresponding carbene complexes (eq 1) has been reported for various metals including the above-mentioned iron system.[12,13] This reaction serves as the basis of one of the routes to iron alkylidenes developed previously by us[10] and by Casey.[14] Analogous reactions of alkynylmetal compounds afford vinylidene complexes.[15] Continuing this analogy, one may expect the protonation of dienyl complexes to form allylidene complexes (eq 2) which are somewhat less common but potentially quite useful.[16] Indeed, this reaction forms the basis of the present report.



$$L_nM-C=C \xrightarrow{H^+} L_n\overset{+}{M}=C-\overset{H}{C}- \qquad (1)$$



$$L_nM-C=C-C=C \xrightarrow{H^+} L_n\overset{+}{M}=C-C=C-\overset{H}{C}- \qquad (2)$$

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[1] For some recent reviews of transition-metal carbene complexes see: (a) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. (b) Cardin, D. J.; Norton, R. J. *Organomet. Chem.* **1982**, *10*, 213. See also the earlier volumes of this series. (c) Casey, C. P. In "Reactive Intermediates"; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2, pp 135–174.

[2] For some reviews of alkene metathesis see: (a) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. (b) Cross, R. J. *Catalysis* **1982**, *5*, 382. See also the earlier volumes of this series.

[3] Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 2331.

[4] Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117.

[5] (a) Jolly, P. W.,; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. (b) Riley, P. E.; Capshew, C. E.; Pettit, R.; Davis, R. E. *Inorg. Chem.* **1978**, *17*, 408.

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

[7] For recent papers and other leading references in this area see: (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979. (b) Manganiello, F. J.; Radcliffe, M. D.; Jones, W. M. *J. Organomet. Chem.* **1982**, *228*, 273. (c) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.

[8] (a) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473. (b) O'Connor, E. J.; Helquist, P. *Ibid.* **1982**, *104*, 1869.

[9] Kremer, K. A. M.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 1862.

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

[11] We note the concurrent, related studies of Casey; see: Casey, C. P.; Miles, W. H. *Organometallics*, following paper in this issue.

[12] (a) Bell, R. A.; Chisholm, M. H. *Inorg. Chem.* **1977**, *16*, 698. (b) Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6157.

[13] (a) Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237. (b) Marten, D. F. *J. Org. Chem.* **1981**, *46*, 5422. (c) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31.

[14] Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761.

[15] (a) Bellerby, J. M.; Mays, M. J. *J. Organomet. Chem.* **1976**, *117* C21. (b) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763. (c) Adams, R. D.; Davison, A.; Selegue, J. P. *Ibid.* **1979**, *101*, 7232. (d) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471. (e) Selegue, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 119. (f) Selegue, J. P. *Organometallics* **1982**, *1*, 217.

[16] At issue in this approach is whether the protonation will occur at the β- or the δ-position of the dienyl ligand to give the desired allylidene complex or a 4-butylidene complex, respectively; see ref 23. For some examples of allylidene complexes of various metals see: (a) Fischer, E. O.; Kalder, H.-J.; Frank, A.; Koehler, F. H.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 623. (b) Doetz, K. H. *Chem. Ber.* **1977**, *110*, 78. (c) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282. (d) Wood, C. D.; McLain, S. J.; Schrock, R. R. *Ibid.* **1979**, *101*, 3210. (e) Nesmeyanov, A. N.; Petrovskaya, E. A.; Rybin, L. V.; Rybinskaya, M. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1979**, *28*, 1887. (f) Mitsudo, T.; Watanabe, H.; Watanabe, K.; Watanabe, Y.; Kafuku, K.; Nakatsu, K. *Chem. Lett.* **1981**, 1687. (g) Klimes, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 205. (h) McCullough, L. G.; Listemann, M. L.; Schrock, R. R.; Churchill, M. R.; Ziller, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 6729.

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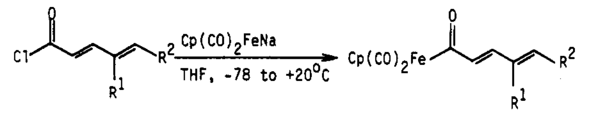
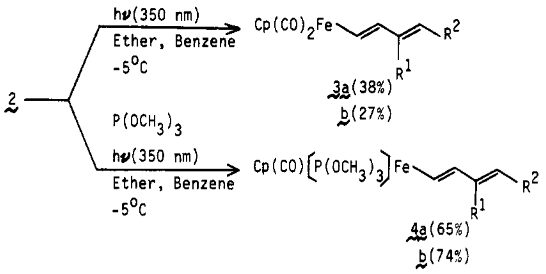
The requisite dienyl complexes were prepared by reaction of sodium cyclopentadienyldicarbonylferrate with the dienoyl chlorides **1**[17] to give the acyl complexes **2** (eq 3),[18]



(3)

**1a**, $R^1$=H, $R^2$=$CH_3$
**b**, $R^1$=$CH_3$, $R^2$=H

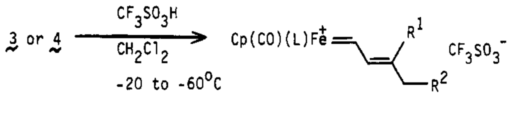
**2a**(80%)
**b**(91%)



(4)

**3a**(38%)
**b**(27%)

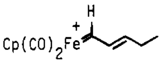
**4a**(65%)
**b**(74%)



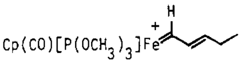
(5)

**5**, L=CO; **6**, L=P(OCH$_3$)$_3$

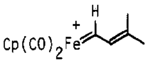
which were then subjected to photochemical decarbonylation[19] to afford the desired dienyl complexes **3**.[20] Alternatively, the latter step could be combined with ligand substitution[21] to give the monophosphite complexes **4** (eq 4).[22] According to plan, when these compounds are treated with acids at low temperature, allylidene complexes **5** and **6** (eq 5) are produced, as indicated by $^1$H NMR. The key chemical shifts for the carbene centers of these compounds are given below.[23] Of these four complexes, the best behaved is **6b**, which can be isolated as a yellow-orange, crystalline solid. For this compound, the $^{13}$C NMR spectrum reveals not only the expected low-field signal for the carbene center but also a rather large downfield shift of the γ-carbon at 162.3 ppm, which is suggestive of significant delocalization of positive charge within the allylidene unit.



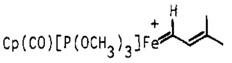
**5a**: $^1$H NMR (CD$_2$Cl$_2$, -100 °C) δ 17.16



**6a** (-80 °C): δ 16.75



**5b** (-60 °C): δ 15.88



**6b** (-45 °C): δ 16.03
$^{13}$C NMR δ 314.3

The reactions of these complexes are consistent with their indicated structures. For example, when a solution of **5a** and ether is allowed to warm above −60 °C, rearrangement[7c,10,13c,14] occurs to produce the 1,3-pentadiene complex **7** which was characterized spectroscopically[24] and by reaction with sodium iodide to release the free diene (eq 6). Triphenylphosphine and sodium methylmercaptide undergo nucleophilic addition to **6b** to give the phosphonium salt **8** and the sulfide **9**, respectively, the latter, at least, being obtained as a 4:1 mixture of diastereomers (eq 7).[25] Furthermore, **6b** reacts with a large excess of styrene to afford a 5:1 mixture of cis and trans disubstituted cyclopropanes **10**[26] (eq 8), albeit in only 15%

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(17) For preparation of **1a** see: (a) Lee, V. J.; Branfman, A. R.; Herrin, T. R.; Rinehart, K. L. *J. Am. Chem. Soc.* **1978**, *100*, 4225. (b) MacMillan, J. H.; Washburne, S. S. *J. Org. Chem.* **1973**, *38*, 2982. For preparation of **1b** and its carboxylic acid precursor see: (c) Sundberg, R. J.; Bukowick, P. A.; Holcombe, F. O. *J. Org. Chem.* **1967**, *32*, 2938. (d) Widmer, U.; Heimgartner, H.; Schmid, H. *Helv. Chim. Acta* **1978**, *61*, 815.

(18) **2a**: $^1$H NMR (CDCl$_3$) δ 5.74–6.55 (m, 4 H), 4.86 (s, 5 H), 1.82 (d, $J$ = 5.5 Hz, 3 H); IR (Nujol) 1960 and 2000 (FeC=O), 1648, (RC=O) cm$^{-1}$. **2b**: $^1$H NMR (CDCl$_3$) δ 6.38 (s, 2 H), 5.33 (br s, 2 H), 4.88 (s, 5 H), 1.85 (br s, 3 H); IR (Nujol) 1960 and 2008 (FeC=O), 1643 (RC=O) cm$^{-1}$.

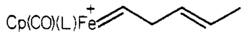
(19) For ferrate acylations and subsequent decarbonylations see: (a) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15. (b) Nesmeyanov, A. N.; Rybin, L. V.; Rybinskaya, M. I.; Kaganovich, V. S.; Petrovskii, P. V. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1971**, *20*, 2592. (c) Quinn, S.; Shaver, A. *Inorg. Chim. Acta* **1980**, *38*, 243. See also ref 14.

(20) **3a**: $^1$H NMR (CDCl$_3$) δ 6.84 (d, $J$ = 15.3 Hz, 1 H), 6.31 (dd, $J$ = 15.3, 9.9 Hz, 1 H), 6.06 (dd, $J$ = 14.0, 9.9 Hz, 1 H), 5.29 (m, 1 H), 4.83 (s, 5 H), 1.71 (d, $J$ = 6.3 Hz, 3 H); $^{13}$C NMR (CD$_2$Cl$_2$) δ 216.4, 146.2, 136.1, 134.7, 119.8, 86.3, 18.0; IR (Nujol) 1964 and 1997 (FeC=O) cm$^{-1}$. **3b**: $^1$H NMR (CDCl$_3$) δ 7.02 (d, $J$ = 16.1 Hz, 1 H), 6.42 (d, $J$ = 16.1 Hz, 1 H), 4.84 (s, 5 H), 4.57 (br s, 2 H), 1.80 (m, 3 H); $^{13}$C NMR (CD$_2$Cl$_2$) δ 216.4, 147.8, 144.5, 134.0, 108.7, 86.4, 19.1; IR (Nujol) 1964 and 1995 (FeC=O) cm$^{-1}$. **3b** has been reported previously; see: Bauch, T. E.; Konowitz, H.; Kerber, R. C.; Giering, W. P. *J. Organomet. Chem.* **1977**, *131*, C7.

(21) Alway, D. G.; Barnett, K. W. In "Inorganic and Organometallic Photochemistry"; Wrighton, M. S., Ed.; American Chemical Society: Washington, 1978; *Adv. Chem. Ser. No. 168*, Chapter 7. See also ref 14.

(22) **4a**: $^1$H NMR (CD$_2$Cl$_2$) δ 7.14 (dd, $J$ = 15.7, 3.5 Hz, 1 H), 6.25 (ddd, $J$ = 15.7, 9.9, 2.6 Hz, 1 H), 6.01 (ddd, $J$ = 14.9, 9.9, 1.5 Hz, 1 H), 5.09 (dq, $J$ = 14.9, 6.6 Hz, 1 H), 4.62 (d, $J$ = 0.8 Hz, 5 H), 3.58 (d, $J$ = 11.3 Hz, 9 H), 1.68 (d, $J$ = 6.6 Hz, 3 H); IR (Nujol) 1932 (FeC=O) cm$^{-1}$. **4b**: $^1$H NMR (CD$_2$Cl$_2$) δ 7.47 (dd, $J$ = 16.2, 4.2 Hz, 1 H), 6.43 (dd, $J$ = 16.1, 2.8 Hz, 1 H), 4.65 (d, $J$ = 0.9 Hz, 5 H), 4.44 (br s, 2 H), 3.59 (d, $J$ = 11.3 Hz, 9 H), 1.81 (br s, 3 H); IR (Nujol) 1925 (FeC=O) cm$^{-1}$.

(23) For NMR data for related carbene complexes see: (a) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Organomet. Chem.* **1980**, *193*, C23. See also ref 7c, 10, and 14. We wish to note that in the cases of carbene complexes **5a** and **6a**, the presence of interfering peaks in the NMR spectra prevent us from ruling out the possibility of the following alternative structures resulting from protonation at the 2-positions of **3a** and **4a**:

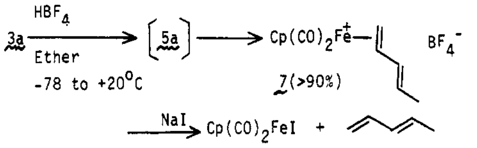


5a, L = CO
6a, L = P(OCH$_3$)$_3$

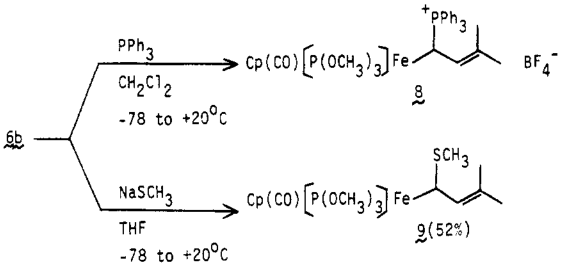
For the remaining two carbene complexes, better data are available. **5b**: $^1$H NMR (CD$_2$Cl$_2$) δ 15.88 (d, $J$ = 14.0 Hz, 1 H), 8.33 (d, $J$ = 14.3 Hz, 1 H), 5.66 (s, 5 H), 2.32 (br s, 6 H); **6b**: $^1$H NMR (CD$_2$Cl$_2$) 16.03 (d, $J$ = 13.8 Hz, 1 H; an upper limit for $J_{P-H}$ may be set at 1.7 Hz), 7.97 (d, $J$ = 13.8 Hz, 1 H), 5.39 (s, 5 H), 3.51 (d, $J$ = 11.5 Hz, 9 H), 1.99 (br s, 6 H); $^{13}$C NMR (CD$_2$Cl$_2$) δ 314.3 (d, $J$ = 33.5 Hz), 212.7 (d, $J$ = 46.9 Hz), 162.3, 152.0, 90.5 (remaining peaks obscured by solvent and other interfering signals). Although **6b** was the best behaved of these allylidene complexes, none of them, including **6b**, were stable at room temperature. Therefore, we have been unable to obtain further corraborating data (e.g., microanalyses), nor have we been able to determine the actual yields of these complexes. In the case of **6b**, though, we are at least able to set a lower limit for the yield at ca. 60% based upon NMR spectra and the subsequent conversion of **6b** into the isolable adduct **9**. Consistent with our findings is that Casey has also reported **5b** to be unstable at room temperature; see ref 11.

(24) **7**: $^1$H NMR (acetone-$d_6$) δ 5.51–6.10 (m, 3 H), 5.80 (s, 5 H), 3.83 (d, $J$ = 8.3 Hz, 1 H), 3.64 (d, $J$ = 14.4 Hz, 1 H), 1.85 (dd, $J$ = 6.5, 1.1 Hz, 3 H). Although **5b** also undergoes decomposition upon warming, we have not yet been able to identify the principal product of this reaction.

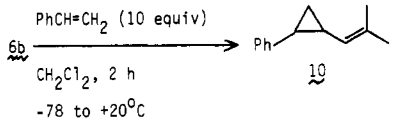
(25) **8**: $^1$H NMR (acetone-$d_6$) 7.70–7.93 (m, >15 H), 5.35 (m, 1 H), 4.29 (d, $J$ = 1.1 Hz, 5 H), 3.92 (d, $J$ = 10.9 Hz, 9 H), 3.70 (m, >1 H), 1.88 (d, $J$ = 4.6 Hz, 3 H), 1.67 (d, $J$ = 5.4 Hz, 3 H). **9**, diastereomer A: $^1$H NMR (acetone-$d_6$) 5.28 (d, $J$ = 12 Hz, 1 H), 4.70 (d, $J$ = 1 Hz, 5 H), 3.60 (d, $J$ = 11.2 Hz, 9 H), 3.15 (dd, $J$ = 12, 8 Hz, 1 H), 1.79 (s, 3 H), 1.66 (br s, 3 H), 1.51 (br s, 3 H). **9**, diastereomer B: $^1$H NMR same as that for A except for δ 3.70 (d, $J$ = 11.0 Hz, 9 H) and 1.82 (s, 3 H) in place of the peaks at δ 3.60 and 1.79.



(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.

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

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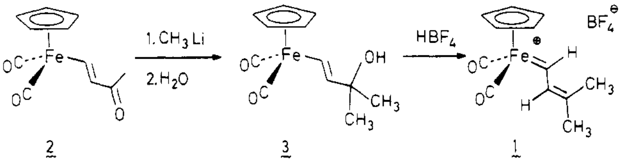
*Madison, Wisconsin 53706*

*Received December 21, 1983*

*Summary:* Reaction of (C$_5$H$_5$)(CO)$_2$FeCH=CHC(CH$_3$)$_2$OH (**3**) with HBF$_4$ in diethyl ether at −23 °C gives the vinylcarbene complex (C$_5$H$_5$)(CO)$_2$Fe=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)$_5$W=CHC$_6$H$_5$[2] and (C$_5$H$_5$)(CO)$_2$[P(C$_6$H$_5$)$_3$]Mo=CH$_2^+$,[3] have been shown to be useful cyclopropanating reagents.[1] The most efficient and best studied reagents are the (C$_5$H$_5$)(CO)$_2$Fe=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$_5$H$_5$(CO)$_2$Fe=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$_3$)$_2$X system. C$_5$H$_5$(CO)$_2$FeCH=CHCOCH$_3$, **2**, was prepared in 54% yield by reaction of Na$^+$C$_5$H$_5$Fe(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$_5$H$_5$(CO)$_2$FeCH=CHC(CH$_3$)$_2$OH, **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$_5$H$_5$(CO)$_2$Fe=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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