Synthesis, Characterization, and Reactions of $(C_5H_5)(CO)_2Fe{=}C(CH_3)_2^+$ and $(C_5H_5)(CO)_2Fe{=}CH{-}CH{=}C(CH_3)_2^+$

Charles P. Casey,* William H. Miles, and Hideyuki Tukada

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received July 26, 1984*

Abstract: Reaction of either $C_5H_5(CO)_2FeC(CH_3){=}CH_2$ (**4**) or $(C_5H_5)(CO)_2FeC(OCH_3)(CH_3)_2$ (**3**) with HBF_4 in ether at −23 °C gives $(C_5H_5)(CO)_2Fe{=}C(CH_3)_2{}^+BF_4^-$ (**1a**). At −11 °C, **1a** rearranges to $(C_5H_5)(CO)_2Fe(CH_2{=}CHCH_3)^+BF_4^-$ (**10**). Reaction of **1a** at −20 °C with $P(OCH_3)_3$ gives $(C_5H_5)(CO)_2FeC[P(OCH_3)_3](CH_3)_2{}^+BF_4^-$ (**11**). **1a** reacts with isobutylene to give 1,1,2,2-tetramethylcyclopropane. Reaction of $(C_5H_5)(CO)[P(C_6H_5)_3]FeC(CH_3){=}CH_2$ (**9**) with HBF_4 produces $(C_5H_5)(CO)[P(C_6H_5)_3]Fe{=}C(CH_3)_2{}^+BF_4^-$ (**12a**), which is stable indefinitely as a solid at room temperature. Reaction of $(C_5H_5)(CO)_2FeCH{=}CH{-}C(CH_3)_2OH$ (**14**) with HBF_4 in diethyl ether at −23 °C gives vinyl carbene complex $(C_5H_5)(CO)_2Fe{=}CH{-}CH{=}C(CH_3)_2{}^+$ (**2**), which was identified by low-temperature ^1H and ^{13}C NMR spectroscopy. The reaction of **2** with isobutylene gives 2,2-dimethyl-1-(2-methyl-1-propenyl)cyclopropane (**15**) in 56% yield. Cyclooctene reacts with **2** to give *syn*-9-(2-methyl-1-propenyl)bicyclo[6.1.0]nonane in 37% yield. The reaction of **2** with styrene gives *cis*- and *trans*-1-phenyl-2-(2-methyl-1-propenyl)cyclopropane, *cis*- and *trans*-**19**, in a 1:2 ratio in 45% yield. The unusual selectivity for formation of *trans*-**19** is due to the isomerization of the initially formed $(C_5H_5)(CO)_2Fe^+$ complex of *cis*-**19** to the corresponding complex of *trans*-**19**.

The facile isomerization of traditional carbene and carbenoid reagents underscores the need for the development of new cyclopropanating agents. Electrophilic transition-metal carbene complexes[1] have generated considerable interest due to their reactivity with alkenes to give cyclopropanes.[2-13] Several of these electrophilic carbene complexes have been shown to be synthetically useful cyclopropanating reagents.[3,6-8]

Although the methylidene complex $(C_5H_5)(CO)_2Fe{=}CH_2^+$ is too unstable to observe by ^1H NMR even at low temperatures,[14] it readily reacts in situ with alkenes to give cyclopropanes in high yields.[2,3] The thermally stable, crystalline $(C_5H_5)(CO)_2FeCH_2S(CH_3)_2{}^+BF_4^-$ developed by Helquist[3] is the most convenient precursor of methylidene complex $(C_5H_5)(CO)_2Fe{=}CH_2^+$. Methylidene complexes of tungsten and molybdenum, such as the spectroscopically observed $(C_5H_5)(CO)_2[P(C_6H_5)_3]Mo{=}CH_2^+$ and $(C_5H_5)(CO)_2[P(C_6H_5)_3]W{=}CH_2^+$, also appear to have potential in methylene transfer reactions.[4]

Benzylidene complexes $(CO)_5W{=}CHC_6H_5$[5] and $(C_5H_5)(CO)_2Fe{=}CHC_6H_5^+$ [6] react with alkenes to give high yields of phenyl-substituted cyclopropanes. Cyclopropanation by these reagents proceeds with high cis or syn stereoselectivity. The successful reaction of these benzylidene complexes with alkenes has prompted the exploration of other substituted transition-metal carbene complexes. Brookhart[7] and Helquist[8] have reported the successful ethylidene transfer reaction of $(C_5H_5)(CO)_2Fe{=}CHCH_3{}^+$ with alkenes. As in the case of benzylidene complex $(C_5H_5)(CO)_2Fe{=}CHC_6H_5^+$, there is a high cis or syn stereoselectivity.

In light of these results, we undertook research directed toward the synthesis of a dimethylcarbene complex which would serve as a reagent for the synthesis of *gem*-dimethylcyclopropanes and of a vinylcarbene complex that would serve as a reagent for the synthesis of vinylcyclopropanes related to chrysanthemic acid. Here we present a full account of the synthesis, characterization, and reactivity of dimethylcarbene complex $(C_5H_5)(CO)_2Fe{=}C(CH_3)_2{}^+$ (**1**), and of the vinylcarbene complex $(C_5H_5)(CO)_2Fe{=}CH{-}CH{=}C(CH_3)_2{}^+$ (**2**). Preliminary reports of our results[10,12] and the related studies of Helquist[11,13] have appeared.

Results

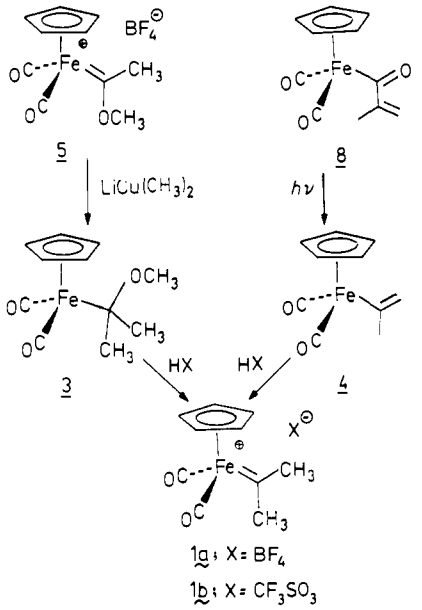
Precursors of Dimethylcarbene Complexes. There are three general routes to electrophilic carbene complexes which are not stabilized by an α-heteroatom: (1) the addition of electrophiles to MCRR'X systems,[2-10,12] (2) protonation or alkylation of vinyl metal complexes,[9-11,13] and (3) α-hydrogen abstraction from metal-alkyl systems.[4,15] For the synthesis of dimethylcarbene complex **1**, we investigated the synthesis and reactivity of ether complex $(C_5H_5)(CO)_2FeC(CH_3)_2(OCH_3)$ (**3**) and vinyl complex $(C_5H_5)(CO)_2FeC(CH_3){=}CH_2$ (**4**). The α-hydrogen abstraction of $(C_5H_5)(CO)_2FeCH(CH_3)_2$ appeared improbable; studies have shown that the reaction of the $(C_5H_5)(CO)_2Fe$ alkyl complexes with hydrogen abstracting reagents leads to β-hydrogen abstraction,[16] with few exceptions.[17,18]

The synthesis of ether precursor **3** centered around the addition of methyl organometallic reagents to $(C_5H_5)(CO)_2Fe{=}C(CH_3)(OCH_3)^+BF_4^-$ (**5**). Alkoxycarbene complex **5** was prepared by the addition of $(CH_3)_3O^+BF_4^-$ to acyl complex $(C_5H_5)(CO)_2FeCOCH_3$ (**6**); the $CF_3SO_3^-$ and PF_6^- salts of $(C_5H_5)(CO)_2Fe{=}C(CH_3)(OCH_3)^+$ have been previously reported.[7,9] In

(1) For recent reviews see: Casey, C. P. In "Reactive Intermediates"; Jones, M.; Moss, R. A., Eds.; Wiley: New York, 1981; Vol. II, Chapter 4.
(2) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044.
(3) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473.
(4) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760.
(5) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.
(6) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099. Brookhart, M.; Humphrey, M. B.; Kratzer, H. J.; Nelson, G. O. *Ibid.* **1980**, *102*, 7802.
(7) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.
(8) Kremer, K. A. M.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 1862.
(9) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31.
(10) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761.
(11) Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119.
(12) Casey, C. P.; Miles, W. H. *Organometallics* **1984**, *3*, 808.
(13) Kuo, G.-H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806.
(14) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203.
(15) Wong, W.-K.; Tam, W.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5440. Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.
(16) Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963**, *1*, 58. Bly, R. S.; Silverman, G. S.; Hossain, M. M.; Bly, R. K. *Organometallics* **1984**, *3*, 642.
(17) Sanders, A.; Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 5430.
(18) Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604.

0002-7863/85/1507-2924$01.50/0

principle, the reaction of methyl organometallic reagents with **5** can give **3**, deprotonation product $(C_5H_5)(CO)_2FeC(OCH_3){=}CH_2$ (**7**), or demethylation product **6**. We have observed all three modes of reaction with various methyl organometallic reagents. Reaction of **5** with CH_3Li in CH_2Cl_2 at −78 °C gave a 1:1 mixture of addition product **3** and deprotonation product **7**; reaction of **5** with CH_3MgI gave predominately demethylation product **6**; and reaction of **5** with $LiCu(CH_3)_2$ in CH_2Cl_2–$(CH_3CH_2)_2O$ at −78 °C gave ether precursor complex **3** (45–50% isolated yield) and small, variable amounts of **7**.



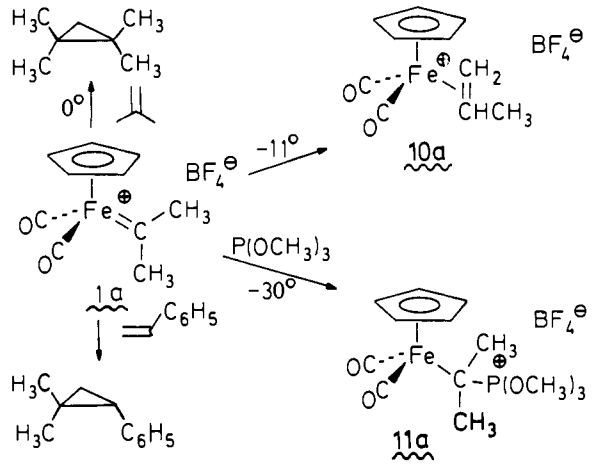
Unexpectedly, ether complex **3** is thermally unstable and eliminates CH_3OH to produce vinyl complex $(C_5H_5)(CO)_2FeC(CH_3){=}CH_2$ (**4**). Thermolysis of **3** in benzene at 60 °C for 8 h gave **4** in 80% yield. Vinyl complex **4** is more conveniently prepared in two steps by the reaction of metacryloyl chloride and $(C_5H_5)(CO)_2Fe^-Na^+$ which produces acyl complex $(C_5H_5)(CO)_2FeCOC(CH_3){=}CH_2$ (**8**) (64%) followed by photolysis of **8** which produces **4** (69%) and some $[(C_5H_5)(CO)_2Fe]_2$.

In anticipation that phosphine-substituted dimethylcarbene complex $(C_5H_5)[P(C_6H_5)_3](CO)Fe{=}C(CH_3)_2^+$ (**12**) would be more stable than dimethylcarbene complex **1**, we prepared vinyl complex $(C_5H_5)[P(C_6H_5)_3](CO)FeC(CH_3){=}CH_2$ (**9**). Reger[19] had previously prepared vinyl complex **9** by the addition of hydride to allene complex $(C_5H_5)[P(C_6H_5)_3](CO)Fe(CH_2{=}C{=}CH_2)^+BF_4^-$. We prepared **9** by the photolysis of either acyl complex **8** or vinyl complex **4** in the presence of triphenylphosphine. Our attempts to prepare the methyl ether complex $(C_5H_5)[P(C_6H_5)_3](CO)FeC(CH_3)_2(OCH_3)$ by the photolysis of **3** and $P(C_6H_5)_3$ gave only $[(C_5H_5)(CO)_2Fe]_2$.

Generation and Characterization of Dimethylcarbene Complex 1. We failed in our initial experiments to cleanly generate and observe dimethylcarbene complex **1** by the addition of $HBF_4{\cdot}(CH_3CH_2)_2O$ or CF_3SO_3H to alkoxyiron complex **3** or vinyliron complex **4** in CH_2Cl_2. A multiplicity of signals in the ^1H NMR was observed even at low temperature. The successful isolation of thermally unstable **1** relied on the precipitation of **1** from $(CH_3CH_2)_2O$ as it was formed at low temperature. In a typical experiment, $HBF_4{\cdot}(CH_3CH_2)_2O$ was added to vinyl complex **4** or alkoxyiron complex **3** in $(CH_3CH_2)_2O$ at −23 °C to give a yellow precipitate identified as $(C_5H_5)(CO)_2Fe{=}C(CH_3)_2^+BF_4^-$ (**1a**). The precipitate was washed with $(CH_3CH_2)_2O$ at −23 °C, pumped dry at −23 °C, dissolved in CD_2Cl_2 at −23 °C, and then observed by low-temperature ^1H NMR. In a similar manner, $(C_5H_5)(CO)_2Fe{=}C(CH_3)_2^+CF_3SO_3^-$ (**1b**) was prepared by addition of CF_3SO_3H to ether solutions of **3** or **4** at −78 °C.

The ^1H NMR of **1a** in CD_2Cl_2 at −40 °C consists of two singlets, one for the cyclopentadienyl ring protons at δ 5.66 (5 H) and the other for the methyl protons at δ 3.73 (6 H). Our spectra also had signals due to small amounts of $(CH_3CH_2)_2O$ and of propene complex $(C_5H_5)(CO)_2Fe(CH_3CH{=}CH_2)^+BF_4^-$ (**10a**). A similar ^1H NMR spectrum was observed for **1b**. The greater solubility of **1b** allowed us to obtain a ^{13}C NMR at −60 °C. In the ^{13}C NMR spectrum of **1b**, the carbene carbon resonance appeared far downfield at δ 419.0.

Solutions of dimethylcarbene complex **1a** decompose at −11 °C in CD_2Cl_2 with a half-life of about 70 min to give $(C_5H_5)(CO)_2Fe(CH_3CH{=}CH_2)^+BF_4^-$ (**10a**)[20] in nearly quantitative yield (101 ± 5%) as indicated by ^1H NMR. In a preparative reaction, propene complex **10a** was isolated in 78% yield. Carbene complex **1a** is more stable as a solid than in solution. Whereas solid **1a** underwent only 50% decomposition to **10a** in 20 min at room temperature, a CH_2Cl_2 solution of **1a** was completely converted to **10a** within several minutes at room temperature.



Carbene complexes **1a** and **1b** were further characterized by trapping with $P(OCH_3)_3$ to give stable phosphonium salts. The addition of excess $P(OCH_3)_3$ to a CD_2Cl_2 solution of **1a** at −23 °C led to the immediate disappearance of signals assigned to **1a** and appearance of new signals assigned to phosphonium complex $(C_5H_5)(CO)_2FeC(CH_3)_2P(OCH_3)_3^+BF_4^-$ (**11a**). In a preparative experiment, phosphonium complex **11a** was isolated in 70% yield. The addition of nucleophiles to the carbene carbon atom of metal–carbene complexes is a characteristic reaction of electrophilic carbene complexes and is particularly useful for characterization of unstable carbene complexes such as **1**.[1]

Reactions of 1 with Alkenes. We have found that the reaction of dimethylcarbene complex **1a** with reactive alkenes such as isobutylene and styrene gives moderate yields of *gem*-dimethylcyclopropanes. The reaction of **1a**, prepared and isolated at −40 °C, with a sixfold excess of isobutylene at 0 °C in CH_2Cl_2 gave 1,1,2,2-tetramethylcyclopropane in 20% GC yield. Similarly, the reaction of isolated **1a** with excess styrene gave 1,1-dimethyl-2-phenylcyclopropane in 45% GC yield. However, the reaction of isolated **1a** with 1-octene did not give 1,1-dimethyl-2-hexylcyclopropane (<0.5% by GC).

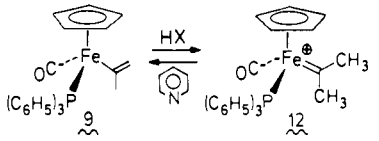
To gain insight into the reason for the low yield of cyclopropanes, the reaction of **1a** with isobutylene was monitored by ^1H NMR. When isobutylene (0.2 M, 1.5 equiv) was added to a 1.4:1 mixture of carbene complex **1a**:propene complex **10a** in CH_2Cl_2, two competing reactions were observed at 0 °C. The formation of 1,1,2,2-tetramethylcyclopropane (33% yield based on **1a**) and an increase in the amount of propene complex **10a** were observed. The rapid competing decomposition of **1a** to propene complex **10a** is therefore responsible for the low yields of cyclopropanes in the reactio ıs of **1a** with alkenes.

In the cyclopropane forming reactions of $(CO)_5W{=}CHC_6H_5$ with alkenes, isobutylene was 625 times more reactive than 1-butene and styrene was 73 times more reactive than 1-butene.[5] Since the decomposition of **1** is competitive with the reaction of

(19) Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *171*, 73.
(20) Faller, J. W.; Johnson, B. T. *J. Organomet. Chem.* **1975**, *88*, 101.

1 with isobutylene, it is not surprising that **1** did not react with 1-octene to produce a cyclopropane. It is anticipated that only very nucleophilic alkenes such as isobutylene will react with **1** to give cyclopropanes. Helquist[1] has reported that 1-decene and **1a** give a "low yield" of cyclopropane product.

Synthesis and Characterization of $C_5H_5[P(C_6H_5)_3](CO)Fe{=}C(CH_3)_2^+$ (12). We anticipated that the substitution of a phosphine ligand in place of a carbon monoxide ligand would enhance the thermal stability of a dimethylcarbene complex, since $(C_5H_5)[P(C_6H_5)_3](CO)Fe{=}CHCH_3^+$ is substantially more kinetically stable than $(C_5H_5)(CO)_2Fe{=}CHCH_3^+$.[7,9] Protonation of vinyl complex **9** with $HBF_4{\cdot}(CH_3CH_2)_2O$ in $(CH_3CH_2)_2O$ at 0 °C gave dimethylcarbene complex $(C_5H_5)[P(C_6H_5)_3](CO)Fe{=}C(CH_3)_2^+BF_4^-$ (**12a**) which was isolated at room temperature. Complex **12a** is stable as a solid and decomposes very slowly in CD_2Cl_2 solution at room temperature and rapidly at 88 °C. The corresponding triflate salt $(C_5H_5)[P(C_6H_5)_3](CO)Fe{=}C(CH_3)_2^+CF_3SO_3^-$ (**12b**) was also prepared by the addition of CF_3SO_3H to vinyl complex **9** in $(CH_3CH_2)_2O$ at 0 °C. Although **12b** is stable as a solid, it decomposes faster than **12a** in CD_2Cl_2 with a half-life of 15 min at 40 °C. The decomposition of **12a** and **12b** are complex, and the products were not identified.



9 12

The ^1H NMR of **12a** consists of a singlet at δ 3.13 for the two methyl groups of the carbene ligand, a singlet at δ 5.13 for the C_5H_5 ligand, and a multiplet at δ 7.5 for the aromatic protons. The equivalence of the methyl groups of **12a** indicates that there is rapid rotation about the $Fe{=}CMe_2$ bond. In the ^{13}C NMR of **12b** (CD_2Cl_2, −20 °C), a doublet (J = 18 Hz) was observed at δ 406.5 for the carbene carbon coupled to phosphorus; the methyl groups are NMR equivalent and gave rise to a single resonance at δ 59.1.

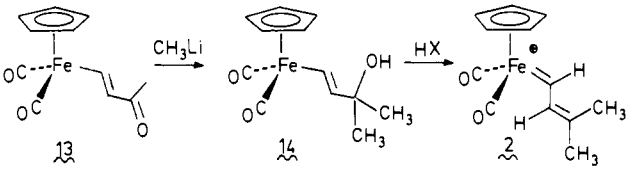
Carbene complexes **12a** and **12b** are very acidic. The addition of pyridine to a $(CH_3CH_2)_2O$ slurry of **12b** at room temperature regenerated vinyl complex $(C_5H_5)[P(C_6H_5)_3](CO)FeC(CH_3){=}CH_2$ (**9**) in 78% yield.

Although the rate of decomposition of phosphine substituted carbene complex **12** is greatly diminished relative to the related dicarbonyl carbene complex **1**, the reactivity of **12** toward alkenes is diminished to an even greater extent. When isobutylene (4.6 equiv) and **12a** were heated in CD_2Cl_2 at 88 °C for 3 h, no 1,1,2,2-tetramethylcyclopropane was observed by ^1H NMR.

Precursors of Vinylcarbene Complex $(C_5H_5)(CO)_2Fe{=}CH{-}CH{=}C(CH_3)_2^+$ (2). There are several potential routes to vinylcarbene complex **2**. Previous work by Giering[21] indicated that α-hydride abstraction from $(C_5H_5)(CO)_2FeCH_2{-}CH{=}C(CH_3)_2$ would not be a viable route to vinylcarbene complex **2**. Helquist[13] has independently developed a route to **2** based on the protonation of dienyliron complexes. We have developed a route to vinyl carbene complex **2** based on the addition of an electrophile to a $(C_5H_5)(CO)_2Fe{-}CH{=}CH{-}C(CH_3)_2X$ system.

We synthesized the precursor complex *trans*-$(C_5H_5)(CO)_2Fe{-}CH{=}CH{-}C(CH_3)_2OH$ (**14**) in two steps from $[(C_5H_5)(CO)_2Fe]_2$. The addition of $(C_5H_5)(CO)_2Fe^-Na^+$ to 4-chlorobut-3-en-2-one[22] gave *trans*-$(C_5H_5)(CO)_2Fe{-}CH{=}CHCOCH_3$ (**13**) in 54% yield, as described by Nesmeyanov.[23] Addition of CH_3Li to the ketone group of **13** gave *trans*-$(C_5H_5)(CO)_2Fe{-}CH{=}CH{-}C(CH_3)_2OH$ (**14**) in 62% yield as a pure red oil.

Generation and Characterization of Vinylcarbene Complex 2. Addition of $HBF_4{\cdot}(CH_3CH_2)_2O$ to an ether solution of tertiary



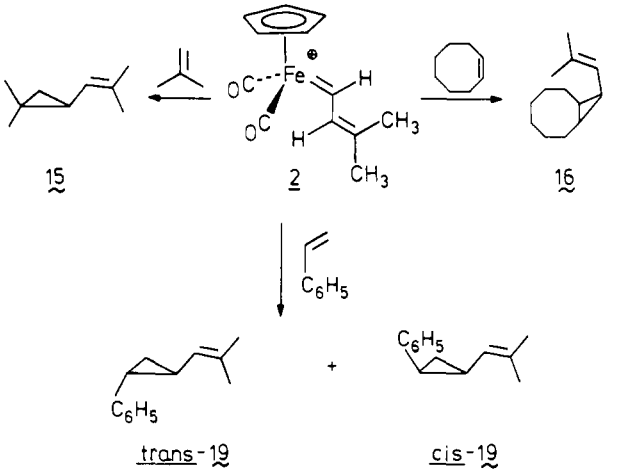
13 14 2

allylic alcohol **14** at −15 °C led to the precipitation of $C_5H_5(CO)_2Fe{=}CH{-}CH{=}C(CH_3)_2^+BF_4^-$ (**2**) as a red-orange solid which was washed with ether at −15 °C and dried under vacuum at −15 °C. **2** is unstable at room temperature but was fully characterized spectroscopically by low-temperature NMR.

In the ^1H NMR of **2** in CD_2Cl_2 at −55 °C, the proton on the carbene carbon appears as a doublet at δ 15.96 (J = 14.7 Hz) coupled to the vinyl proton at δ 8.21 (d, J = 14.7 Hz). In the coupled ^{13}C NMR of **2** at −60 °C, the carbene carbon appears as a doublet (J_{CH} = 148 Hz) at δ 316.7. The vinyl carbon which is bonded to the two methyl groups appears as a singlet at δ 178.7, and the other vinyl carbon appears as a doublet at δ 154.0 (J_{CH} = 159 Hz).

Carbene complex **2** is stable in solution at −55 °C for several hours but decomposes upon warming to room temperature. Our attempts to monitor the decomposition of **2** by ^1H NMR were frustrated by extensive line broadening.

Reaction of 2 with Alkenes. Isolated vinylcarbene complex **2** reacts with alkenes to give moderate yields of vinylcyclopropane iron complexes from which the vinylcyclopropane can be released by treatment with NaI in acetone.[24] In a preparative reaction, a CH_2Cl_2 solution of vinylcarbene complex **2** and 3 equiv of isobutylene were stirred at −23 °C for 45 min and then warmed to room temperature. The volatile fraction was transferred under high vacuum, and NaI in acetone was added to the remaining solid to free the complexed 2,2-dimethyl-1-(2-methyl-1-propenyl)-cyclopropane (**15**). The volatile fraction of the acetone solution was also transferred under high vacuum. Gas-chromatographic analysis of the combined volatile fractions indicated 56% yield of **15** which was isolated by preparative gas chromatography.



15 2 16

trans-19 cis-19

Reaction of vinylcarbene complex **2** with 3 equiv of cyclooctene followed by workup with NaI in acetone and isolation by silica gel chromatography and Kugelrohr distillation gave *syn*-9-(2-methyl-1-propenyl)bicyclo[6.1.0]nonane (**16**) in 37% yield. A single isomer was seen by gas chromatography on several columns, and **16** appeared pure by both ^1H and ^{13}C NMR. The syn stereochemistry of **16** was conclusively established by ozonolysis to give *syn*-bicyclo[6.1.0]nonane-9-carboxylic acid[25] (*syn*-**17**). Authentic samples of isomerically pure *syn*-**17** and *anti*-**17** were prepared by saponification of the known ethyl esters.[25]

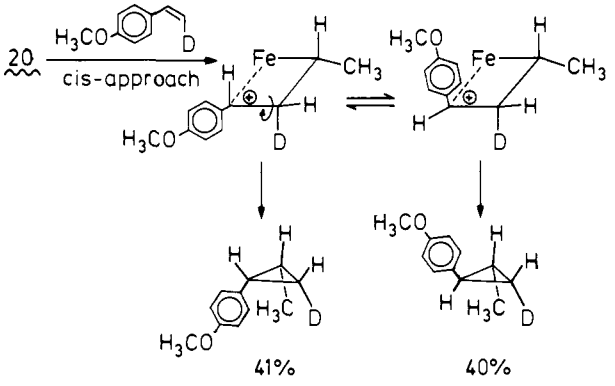
In the reaction of vinyl carbene complex **2** with 3 equiv of styrene, a 2:1 mixture of *trans*-:*cis*-1-phenyl-2-(2-methyl-1-propenyl)cyclopropane (*trans*-**19** and *cis*-**19**) was formed in 45%

(21) Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V.; Sanders, A. *J. Organomet. Chem.* **1974**, *65*, C57.
(22) Catch, J. R.; Elliott, D. F.; Hey, D. H.; Jones, E. R. J. *J. Chem. Soc.* **1948**, 278.
(23) Nesmeyanov, A. N.; Rybin, L. V.; Rybinskaya, M. I.; Ystynyuk, Y. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1967**, *37*, 1505.
(24) Rosan, A.; Rosenblum, M.; Tancrede, J. *J. Am. Chem. Soc.* **1973**, *95*, 3062.
(25) Dauben, W. G.; Michno; D. M. *J. Am. Chem. Soc.* **1981**, *103*, 2284.

yield. Pure samples of *trans*-**19** and *cis*-**19** were obtained by preparative gas chromatography, and the stereochemistry of each isomer was conclusively established by measurement of ^1H NMR coupling constants of the cyclopropyl hydrogens. In a related experiment, reaction of styrene with vinylcarbene complex **2** generated in situ by addition of $(C_6H_5)_3C^+PF_6^-$ to a methylene chloride solution of allylic alcohol **4** led to the isolation of a 3:1 mixture of *trans*- and *cis*-**19** in 47% yield.

The selective formation of a trans cyclopropane from styrene is surprising in view of the normally high cis or syn selectivity of cyclopropane formation from iron carbene complexes.[6-8] Moreover, Helquist[13] has reported the selective formation of *cis*-**19** in 15% yield from reaction of styrene and $(C_5H_5)[P(OCH_3)_3](CO)Fe{=}CH{-}CH{=}C(CH_3)_2^+$ which is a close analogue of our vinylcarbene complex **2**. The anomalous trans selectivity we observed for **2** prompted us to carry out several control experiments.

The possibility that trans cyclopropane is formed via initial cis approach of styrene followed by rotation about the former alkene carbon–carbon double bond in a cationic intermediate was investigated since Brookhart[26] has demonstrated that a similar process occurs in the selective formation of trans cyclopropane from reaction of *p*-methoxystyrene with $C_5H_5(CO)_2Fe{=}CHCH_3^+$ (**20**). Brookhart found that **20** reacts with *cis*-β-deuteriostyrene to give a 6.5:1 mixture of cis and trans cyclopropanes both of which have retained the cis relationship between D and C_6H_5. In contrast, the more nucleophilic alkene *cis*-β-deuterio-*p*-methoxystyrene reacts with **20** to give a 1.1:1.0 mixture favoring a trans cyclopropane in which the initial cis relationship between D and $C_6H_4OCH_3$ has been largely inverted to trans. Brookhart rationalized these results by postulating cis approach of β-deuterio-*p*-methoxystyrene to **20** to give a cationic intermediate stabilized by the *p*-methoxy substituent that can undergo bond rotation before ring closure to give cyclopropane.



If the reaction of **2** with styrene proceeds by a mechanism similar to that suggested by Brookhart, the large amount of *trans*-**19** formed could be attributed to bond rotation in an intermediate cation. This same bond rotation would lead to loss of stereochemistry when *cis*-2-deuterio-1-phenylethylene is used as the substrate.

The reaction of **2** with *cis*-$CHD{=}CHC_6H_5$ gave a 2:1 ratio of deuteriocyclopropanes *trans*-**19**-*d* and *cis*-**19**-*d* in 51% yield. ^1H NMR of pure *trans*-**19**-*d* and of pure *cis*-**19**-*d* isolated by preparative gas chromatography indicated complete *retention* of the stereochemistry (>90%) between deuterium and the phenyl ring. These results rule out a mechanism analogous to that of Brookhart.[25]

The possibility that *cis*-**19** is isomerized or selectively destroyed by adventitious acid was briefly investigated. Treatment of a 1:2 mixture of *cis*-:*trans*-**19** with 0.1 equiv of $HBF_4{\cdot}(CH_3CH_2)_2O$ in CH_2Cl_2 led to selective destruction of *trans*-**19**; after 1 h, the 50% cyclopropane remaining had a cis:trans ratio 3:1. Thus, acid selectively destroys *trans*-**19** and cannot be responsible for the high trans:cis isomer ratios observed.

We next checked for possible isomerization of the iron complex of *cis*-**19** to the corresponding iron complex of *trans*-**19** as a possible source of the unusual observed trans selectivity. To test this possibility, we independently prepared the iron complex of *cis*-**19**. Reaction of *cis*-**19** (90% cis) with $(C_5H_5)(CO)_2Fe^+BF_4^-$, prepared from $(C_5H_5)(CO)_2FeI$ and $AgBF_4$ in CH_2Cl_2, gave vinylcyclopropane complex **21** which was isolated in 75% crude yield and washed with ether. This olefin complex was decomposed by treatment with NaI in acetone to regenerate vinylcyclopropane in 43% yield. The reisolated cyclopropane was a 3.5:1 mixture of *trans*- and *cis*-**19**. The absolute amount of *trans*-**19** increased by a factor of 2.4, indicating that a cis to trans isomerization had taken place and not merely the selective destruction of *cis*-**19**.

Discussion

Conformation of the Carbene Ligand in 1 and 12. The conformation of the carbene ligand in $(C_5H_5)(CO)_2Fe$ complexes has been a matter of interest in both experimental[14,15] and theoretical studies.[27] Molecular orbital calculations for $Cp(CO)_2Fe{=}CH_2^+$ indicate that the lowest energy conformation has the H–C–H plane of the carbene ligand perpendicular to the plane of the cyclopentadienyl ring. This conformation maximizes the back-bonding of the d orbitals to the carbene ligand and carbonyl ligands. If dimethylcarbene complex **1** has a similar conformation, its methyl groups would be nonequivalent. We believe that the observation of only one signal in both the ^1H and ^{13}C NMR for the two methyl groups is due to fast rotation about the Fe–carbene carbon bond (<10 kcal/mol). However, we cannot exclude the possibility that **1** exists in a conformation in which the methyl groups are equivalent; in such a conformation, the dihedral angle between the plane of the carbene ligand and the Cp–Fe axis is approximately 90°. Brookhart[14] observed two signals for the methylene protons of carbene complex $(C_5H_5)[P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2]Fe{=}CH_2^+$ in the ^1H NMR only at low temperature; the barrier to rotation about the Fe–carbene bond (10.4 kcal/mol) was determined by variable-temperature ^1H NMR. Replacement of the phosphine ligands with carbon monoxide ligands would decrease back-bonding from the metal center to the carbene ligand and would result in a weaker Fe–carbene bond and a lower rotational barrier about the Fe–carbene carbon bond.

In the case of phosphine-substituted dimethylcarbene complex **12**, the methyl groups are nonequivalent for any given conformation of the complex due to the proximity of the asymmetric iron center. Rotation about the Fe–carbene carbon bond exchanges the environment of the methyl groups and is responsible for the observation of only one signal for the methyl groups in the ^1H and ^{13}C NMR. Maximum back-bonding from the d orbitals to the carbene ligand in **12** is achieved by a conformation in which the (CH_3)–C–(CH_3) of the carbene ligand and the Fe—C≡O are all in the same plane.

^{13}C NMR Chemical Shifts of Carbene Carbons. The carbene carbon atom of metal carbene complexes gives rise to a characteristic low-field resonance in the ^{13}C NMR spectrum. The enormous downfield chemical shifts of metal carbene complexes in the ^{13}C NMR must be due to more than just the charge on the carbene carbon since organic carbonium ions do not exhibit comparable downfield chemical shifts.[28]

The cause of the large downfield chemical shifts of carbene carbons in the ^{13}C NMR has been the subject of recent calculations by Fenske,[29] who has ascribed a major role to the paramagnetic contribution to the chemical shift. In eq 1, the index (*i*) refers to occupied orbitals and the index (*j*) refers to unoccupied or virtual orbitals. The angular momentum operator L_m and the operator L_m/R^3 couple the virtual and occupied orbitals. $\Delta E(i$

(26) Brookhart, M.; Kegley, S. E.; Husk, G. R. *Organometallics* **1984**, *3*, 650.

(27) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

(28) Farnum, D. G. *Adv. Phys. Org. Chem.* **1975**, *11*, 123.

(29) Fenske, R. F. In "Organometallic Compounds: Synthesis, Structure and Theory"; Shapiro, B. L., Ed.; Texas A&M University Press: College Station, Texas 1983.

Table I. ^{13}C NMR Chemical Shifts of the Carbene Carbon for (Cyclopentadienyl)iron Carbene Complexes

iron carbene complex	chemical shift (δ)
$(C_5H_5)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Fe{=}CH_2^+$ [14]	317.5
$(C_5H_5)[P(C_6H_5)_3](CO)Fe{=}CHCH_3^+$ [7]	380.0
$(C_5H_5)[(C_6H_5)_3](CO)Fe{=}CHCH_2CH_3^+$ [7]	383.2
$(C_5H_5)(CO)_2Fe{=}C(CH_3)_2^+$ (**1**)	419.0
$(C_5H_5)[P(C_6H_5)_3](CO)Fe{=}C(CH_3)_2^+$ (**12**)	406.5
$(C_5H_5)(CO)_2Fe{=}CHC_6H_5^+$ [6]	342.4
$(C_5H_5)[P(C_6H_5)_3](CO)Fe{=}CHC_6H_5^+$ [6]	341.2
$(C_5H_5)(CO)_2Fe{=}CH{-}CH{=}C(CH_3)_2^+$ (**2**)	316.7
$(C_5H_5)[P(OCH_3)_3](CO)Fe{=}CH{-}CH{=}C(CH_3)_2^+$ [13]	314.3
$(C_5H_5)(CO)_2Fe{=}CHOCH_3^+$ [18]	321.9
$(C_5H_5)(CO)_5Fe{=}C(CH_3)(OCH_3)^+$ (**5**)	336.0

$\rightarrow j$) is the energy separation between the filled orbital, ϕ_i, and the virtual orbital, ϕ_j.

$$\sigma_p = \frac{2e^2}{3m^2c^2} \sum_{i=1}^{N} \sum_{j=N+1}^{\infty} \frac{\langle \phi_i | \vec{L}_m / R_M^3 | \phi_j \rangle \cdot \langle \phi_j | \vec{L}_m | \phi_i \rangle}{\Delta E(i \rightarrow j)} \quad (1)$$

Large contributions from the σ_p term can arise for several reasons. As the energy between the virtual and filled orbitals (ΔE) decreases, the σ_p term increases. The σ_p term becomes larger as the orbitals become localized on the ^{13}C in question due to the dependence on the $1/R^3$ term. The angular momentum operator is maximized when the virtual and filled orbitals are orthogonal, a geometry inherent in metal carbene complexes.

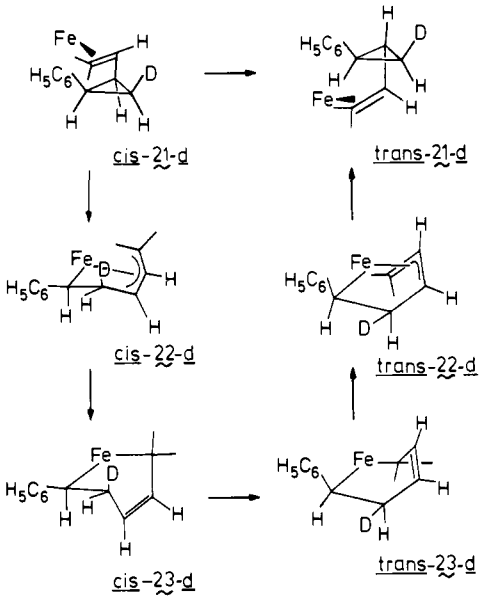
The chemical shifts for the carbene carbon of some iron carbene complexes are given in Table I. The large downfield chemical shift of the carbene carbon of **1** reflects the large σ_p contribution. Calculations[29] have shown that the virtual orbital (LUMO) is localized on the carbene carbon for carbene complexes such as $(C_5H_5)(CO)_2Fe{=}CH_2^+$ and that there is a relatively small energy gap between this LUMO and the Fe–carbene carbon σ-bonding filled orbitals. The large chemical shift difference between the carbene carbons of **1** (δ 419.0) and $(C_5H_5)(CO)_2Fe{=}CHOCH_3^+$ (δ 336.0) is due to the fact that the electron-donating methoxy substituent on the carbene ligand raises the energy of the LUMO centered on the carbene carbon and thus gives rise to a larger ΔE. The vinyl substituent on the carbene ligand in vinylcarbene complex **2** acts in a similar manner; in addition, the LUMO is delocalized into the vinyl group. The ^{13}C chemical shift of the γ-carbon atom of **2** ($Fe{=}C_\alpha H{-}C_\beta H{=}C_\gamma(CH_3)_2$) does not exhibit a large downfield shift (δ 178.8); C_γ is too far away from the localized Fe–carbene carbon σ-bonding filled orbital to experience a large σ_p contribution to its chemical shift.

Trans Selectivity in the Reaction of 2 with Styrene. In order to account for the trans selectivity observed in the reaction of vinylcarbene complex **2** with styrene, there are three major points which must be addressed. (1) The related carbene complexes $(C_5H_5)(CO)_2Fe{=}CHCH_3^+$ and $(C_5H_5)(CO)_2Fe{=}CHC_6H_5^+$ react with alkenes to give cis or syn cyclopropanes in high yields. Vinylcarbene complex **2** and cyclooctene gave exclusively *syn*-**16**. The cis selectivity observed for these cyclopropanating reagents is thought to arise from the directing effects of the bulky cyclopentadienyl ligand. (2) The addition of **2** to *cis*-$CHD{=}CHC_6H_5$ was stereospecific; retention of the stereochemistry between the deuterium and phenyl ring is maintained in both *cis*- and *trans*-**19**. (3) We have observed isomerization of complexed *cis*-**19** to complexed *trans*-**19** under the reaction conditions.

We feel that these points are best explained by the following scenario: reaction of **2** and styrene leads preferentially to *cis*-**19** which is coordinated by $(C_5H_5)(CO)_2Fe^+$ as *cis*-**21**; a subsequent rearrangement of coordinated *cis*-**21** produces coordinated *trans*-**21**. This rearrangement must maintain the stereochemistry between the phenyl ring and the deuterium in the case of the vinylcyclopropane products derived from *cis*-$CHD{=}CHC_6H_5$.

We presently favor the mechanism shown in Scheme I for the isomerization of vinyl cyclopropane complex *cis*-**21** to *trans*-**21**. Five steps are involved: (1) ring opening of *cis*-**21** to π-allyl complex *cis*-**22**, (2) isomerization to σ-allyl complex *cis*-**23**, (3) ring flip to σ-allyl complex *trans*-**23**, (4) isomerization to π-allyl complex *trans*-**22**, and (5) ring closure to alkene complex *trans*-**21**. Cyclopentadienyl ring slippage may be required to avoid 20 electron π-allyl intermediates.

Scheme I



This mechanism accomplishes the required cis–trans isomerization of vinylcyclopropane **19** while maintaining the cis relationship between the deuterium and phenyl ring of *cis*-**19**-*d* and *trans*-**19**-*d*. The mechanism in Scheme I can be tested by labeling one of the methyl groups. Isomerization of *cis*-**19** which has a CD_3 group cis to the alkene proton should give *trans*-**19** which has a CD_3 group trans to the alkene proton.[30]

Improved Reagents for Cyclopropanation. The inefficient transfer of the dimethylcarbene ligand of **1** to alkenes due to β-hydrogen migration severely limits the synthetic utility of **1**. Replacement of one of the carbon monoxide ligands of **1** with the electron-donating triphenylphosphine ligand gave the stabilized dimethylcarbene complex **12** which was totally unreactive toward isobutylene. The successful development of a dimethylcarbene transfer reagent may have to rely on new cyclopropanating reagents in the tungsten and molybdenum series. The successful methylidene transfer reaction of $(C_5H_5)[P(C_6H_5)_3](CO)_2W{=}CH_2^+$ and $(C_5H_5)[P(C_6H_5)_3](CO)_2Mo{=}CH_2^+$ to alkenes developed by Brookhart[4] offers a starting point for the development of new reagents.

The cyclopropanation of alkenes by vinyl carbene complexes to give vinyl cyclopropanes in the $(C_5H_5)(CO)_2Fe$ system is very promising. Although the yields of vinyl cyclopropanes are modest for the reaction of **2** with alkenes due to side reactions, vinylcyclopropanating reagents based on the $(C_5H_5)(CO)_2Fe$ system may provide the most expedient preparation of vinyl cyclopropanes directly from alkenes.

Experimental Section

General Data. All reactions were carried out under an atmosphere of dry nitrogen with dry, degassed solvents. ^1H NMR spectra were recorded on a JOEL-MH-100, Bruker WH-270, or WP-200 spectrometer; ^{13}C NMR spectra were recorded on a JOEL FX-200 or FX-60 spectrometer. Infrared spectra were recorded on a Beckman 4230 infrared spectrometer. Mass spectra were recorded on an AEI-MS-902 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Labs (Woodside, NY).

$(C_5H_5)(CO)_2Fe{=}C(CH_3)(OCH_3)^+BF_4^-$ (**5**). $(CH_3)_3O^+BF_4^-$ (3.40 g, 23.0 mmol) was added to $(C_5H_5)(CO)_2FeCOCH_3$ (5.00 g, 22.7 mmol)

(30) An alternate mechanism suggested by a referee involves abstration of an allylic cyclopropyl hydride from carbon 1 of *cis*-**19** by $Cp(CO)_2Fe^+$. The resulting $Cp(CO)_2FeH$ can then donate hydride to the opposite face of the intermediate cyclopropyl cation to produce *trans*-**19**. The CD_3 labeling experiments can distinguish between this mechanism and that proposed in Scheme I.

in CH_2Cl_2 (150 mL) at room temperature. The resulting mixture was stirred for 12 h. The solvent was reduced to 50 mL, and diethyl ether (150 mL) was added to precipitate a fluffy, yellow solid, which was washed with diethyl ether to give pure **5** (6.54 g, 95%), mp 141–143 °C. For **5**: ^1H NMR (CD_2Cl_2, 100 MHz) δ 5.36 (s, 5 H, C_5H_5), 4.60 (s, 3 H, OCH_3), 3.15 (s, 3 H, CH_3); $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 15.04 MHz, 0.02 M $Cr(acac)_3$) δ 336.0 (Fe=C), 209.7 (CO), 89.2 (C_5H_5), 87.1 (OCH_3), 68.7 (CH_3); IR (CH_2Cl_2) 2060 (s), 2014 (s) cm^{-1}.

$(C_5H_5)(CO)_2FeC(CH_3)_2(OCH_3)$ (3). Lithium dimethylcuprate, prepared by the addition of CH_3Li (58 mL, 1.50 *M*, 88 mmol) to CuI (8.38 g, 44.0 mmol) in diethyl ether (75 mL) at 0 °C, and **5** (12.2 g, 40.0 mmol) were stirred in CH_2Cl_2 (250 mL) at −78 °C for 0.5 h and then warmed to 0 °C. Solvent was removed under vacuum at 0 °C. The residue was washed with pentane (3 × 150 mL, 1 × 500 mL), and the combined extracts were evaporated under vacuum at 10–20 °C to give crude poduct which was redissolved in pentane (50 mL) and filtered through activated alumina (5 g). Removal of solvent gave **3** (5.45 g, 49%) as a red solid, contaminated by a small amount of $(C_5H_5)(CO)FeC(OCH_3){=}CH_2$. Small batches of **3** were purified by filtering through small plugs of alumina to give **3** as a yellow solid, mp 85 °C dec. For **3**: ^1H NMR (C_6D_6, 270 MHz) δ 4.18 (s, 5 H, C_5H_5), 3.12 (s, 3 H, OCH_3), 1.67 (s, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 15.04 MHz) δ 219.0 (CO), 89.2 (Fe–C), 87.2 (C_5H_5), 52.1 (OCH_3), 39.1 (CH_3); IR ($CHCl_3$) 2000 (s), 1944 (s) cm^{-1}. **3** was too unstable to obtain an elemental analysis and did not have a parent peak in the mass spectrum.

$(C_5H_5)(CO)_2FeCOC(CH_3){=}CH_2$ (8). $ClCOC(CH_3){=}CH_2$ (11.0 mL, 113 mmol) was added to $(C_5H_5)(CO)_2Fe^-Na^+$ (100 mmol) in tetrahydrofuran (250 mL) at 0 °C over 0.5 h. The reaction mixture was warmed to room temperature, and the volatiles were removed under water aspirator vacuum. The resulting oily mixture was washed with methylene chloride (3 × 75 mL; 10 mL of H_2O added to facilitate separation of the salt and the organic phase), and the combined extracts were filtered through an alumina plug. Solvent was evaporated under vacuum, and the crude product was distilled (bp 88–92 °C (10^{-2} mm)) to give **8** (10.54 g, 70%), mp 24–28 °C. For **8**: ^1H NMR ($CDCl_3$, 100 MHz) δ 5.37 (br s, 1 H, =CH), 5.28 (s, 1 H, =CH), 4.83 (s, 5 H, C_5H_5), 1.75 (s, 3 H, CH_3); $^{13}C\{^1H\}$NMR (C_6D_6, 15.04 MHz, 0.07 M $Cr(acac)_3$) δ 251.7 (FeCO), 215.0 (CO), 157.8 (=CH_2), 119.1 (−*C*CH_3), 86.4 (C_5H_5), 18.9 (CH_3); IR ($CHCl_3$) 2007 (s), 1967 (s), 1624 (w), 1597 (m) cm^{-1}; MS (30 eV) *m/e* 245.9979 (M^+), calcd for $C_{11}H_{10}FeO_3$ 245.9979.

$(C_5H_5)(CO)_2FeC(CH_3){=}CH_2$ (4). A solution of **8** (13.6 g, 55.0 mmol) in toluene–hexane (25–75, 100 mL) was photolyzed with a 450-W medium-pressure mercury lamp for 2 h. Solvent was evaporated under vacuum, and the crude product was distilled (bp 39–42 °C (10^{-3} mm)) to give **4** (8.07 g, 67%), mp 28–31 °C. For **4**: ^1H NMR (C_6D_6, 270 MHz) δ 5.87 (q, *J* = 1.3 Hz, 1 H, =CH), 5.19 (s, 1 H, =CH), 4.09 (s, 5 H, C_5H_5), 2.18 (s, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 15.04 MHz) δ 216.8 (CO), 152.3 (Fe—C=), 125.4 (=CH_2), 85.5 (C_5H_5), 39.2 (CH_3); IR ($CHCl_3$) 2005 (s), 1961 (s), 1581 (w) cm^{-1}; MS (30 eV) *m/e* 218.0029 (M^+), calcd for $C_{10}H_{10}FeO_2$ 218.0029.

Vinyl complex **4** was also prepared by the thermolysis of **3**. A solution of **3** (5.45 g, 21.8 mmol) in benzene (150 mL) was heated at 60–65 °C for 8 h. Solvent was evaporated under vacuum, and the red, oily mixture was distilled (bp 50–55 °C (10^{-3} mm)) to give vinyl complex **4** (3.80 g, 80%).

$(C_5H_5)(CO)_2Fe{=}C(CH_3)_2^+BF_4^-$ (1a). Addition of $HBF_4{\cdot}(CH_3CH_2)_2O$ (0.010 mL, 0.8 mmol) to **4** (0.010 g, 0.46 mmol) in diethyl ether (2 mL) at −23 °C led to the immediate precipitation of carbene complex **1a**. The reaction mixture was stirred for 10 min at −23 °C, solvent was decanted, and yellow **1a** was washed with diethyl ether (2 × 10 mL) at −23 °C. The solvent was evaporated under vacuum at −23 °C, CD_2Cl_2 was vacuum transferred into the flask at −23 °C, and the low-temperature ^1H NMR spectra of the light orange solution was taken. For **1a**: ^1H NMR (CD_2Cl_2, 270 MHz, −40 °C) δ 5.66 (s, 5 H, C_5H_5), 3.73 (s, 6 H, CH_3); IR (CH_2Cl_2, −10 °C) 2076 (s), 2031 (s) cm^{-1}.

Carbene complex **1a** was also prepared by the addition of $HBF_4{\cdot}(CH_3CH_2)_2O$ (0.010 mL, 0.8 mmol) to **3** (0.010 g, 0.040 mmol) in diethyl ether at −23 °C and was isolated and observed as described above.

$(C_5H_5)(CO)_2Fe{=}C(CH_3)_2^+CF_3SO_3^-$ (1b). The addition of CF_3SO_3H (0.080 mL, 0.9 mmol) to **4** (0.20 g, 0.85 mmol) in diethyl ether (10 mL) at −78 °C led to the immediate precipitation of carbene complex **1b**. The reaction mixture was stirred for 15 min at −78 °C, solvent was decanted, and yellow **1b** was washed with diethyl ether (2 × 25 mL) at −78 °C. Solvent was evaporated under vacuum at −15 °C, CD_2Cl_2 (1.6 mL) was vacuum transferred into the flask at −78 °C, and the low-temperature ^{13}C NMR spectrum was taken. For **1b**: ^1H NMR (CD_2Cl_2, 270 MHz, −40 °C) δ 5.66 (s, 5 H, C_5H_5). 3.69 (s, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 50.1 MHz, −60 °C) δ 419.0 (Fe=C), 206.8 (CO), 93.4 (C_5H_5), 61.4 (CH_3); IR (CH_2Cl_2, −10 °C) 2062 (s), 2015 (s) cm^{-1}.

$(C_5H_5)(CO)_2Fe(CH_2{=}CHCH_3)^+BF_4^-$ (10a). Addition of $HBF_4{\cdot}(CH_3CH_2)_2O$ (0.21 mL, 1.0 mmol) to **4** (0.127 g, 0.63 mmol) in diethyl ether (5 mL) at −23 °C led to the immediate precipitation of carbene complex **1a**. Solvent was decanted and yellow **1a** was washed with diethyl ether (2 × 10 mL) and dried under vacuum, all at −23 °C. Methylene chloride (0.5 mL) was added, the mixture was stirred for 1 h at room temperature, and diethyl ether (10 mL) was added. Solvent was decanted from the yellow precipitate which was washed with diethyl ether. The yellow powder was dried under vacuum and identified as propene complex **10a** (0.150 g, 78%). For **10a**: ^1H NMR ($(CD_3)_2CO$, 100 MHz) δ 5.75 (s, 5 H, C_5H_5), 5.30 (m, 1 H, $CHCH_3$), 4.01 (d, *J* = 8 Hz, 1 H, proton trans to methyl in $=CH_2$), 3.59 (d, *J* = 14 Hz, 1 H, proton cis to methyl in $=CH_2$), 1.85 (d, *J* = 6 Hz, 3 H, CH_3).

Reaction of 1a and $(CH_3)_2C{=}CH_2$. Complex **1a**, prepared from $HBF_4{\cdot}(CH_3CH_2)_2O$ (0.52 mL, 4.3 mmol) and **4** (0.90 g, 4.1 mmol) at −40 °C, was dried under vacuum at −40 °C. Isobutylene (1.3 g, 24 mmol) and CH_2Cl_2 (10 mL) were added to **1a** at −40 °C, and the reaction mixture was warmed to 2 °C over 50 min. All volatile material was vacuum transferred. Analysis by ^1H NMR indicated a 20% yield of 1,1,2,2-tetramethylcyclopropane[31] which was isolated by preparative gas chromatography (UCON-5/HB-280X, 60 °C). For tetramethylcyclopropane: ^1H NMR ($CDCl_3$, 100 MHz) δ 0.98 (s, 12 H, CH_3), 0.02 (s, 2 H, CH_2). 1,1,2,2-Tetramethylcyclopropane was independently synthesized from tetramethylethylene by the Simmons–Smith reaction.[31]

Reaction of 1a with $C_6H_5CH{=}CH_2$. Complex **1a**, prepared from $HBF_4{\cdot}(CH_3CH_2)_2O$ (0.10 mL, 8 mmol) and **4** (0.14 g, 0.64 mmol) at −40 °C, was dried under vacuum at −40 °C, and styrene (0.9 mL, 7.8 mmol) and methylene chloride (1.5 mL) were added at −65 °C. The reaction mixture was allowed to warm to room temperature over 1 h. Hexane (30 mL) was added to precipitate iron complexes. Solvent was decanted, the precipitates were washed with hexane (2 × 5 mL), and the combined washes were dried (K_2CO_3). Analysis of the solution by gas chromatography (SE-30, 133 °C; dodecane as internal GC standard) indicated a 45% yield of 1,1-dimethyl-2-phenylcyclopropane, which was isolated as pure material by preparative gas chromatography (SE-30, 135 °C). ^1H NMR ($CDCl_3$, 100 MHz) δ 7.3 (m, 5 H, C_6H_5), 1.90 (dd, *J* = 8, 6 Hz, 1 H, CHC_6H_5), 1.24 (s, 3 H, CH_3), 0.82 (m, 2 H, CH_2), 0.80 (s, 3 H, CH_3). 1,1-Dimethyl-2-phenylcyclopropane was independently synthesized from $C_6H_5COCH{=}C(CH_3)_2$, hydrazine hydrate, and KOH.[5]

$(C_5H_5)(CO)_2FeC(CH_3)_2[P(OCH_3)_3]^+BF_4^-$ (11a). Carbene complex **1a** (1.37 mmol), prepared from **4** (0.30 g, 1.37 mmol) and $HBF_4{\cdot}(CH_3CH_2)_2O$ (0.30 mL, 2.4 mmol) and isolated at −23 °C as previously described, was slurried in CH_2Cl_2 (5 mL) at −78 °C, and $P(OCH_3)_3$ (0.17 mL, 1.4 mmol) was added. The reaction mixture was warmed to −23 °C and then cooled again to −78 °C, and diethyl ether (25 mL) was added to precipitate yellow phosphonium complex **11a** [0.47 g, 70%, mp 58 °C dec] which was washed with ether and dried under vacuum. For **11a**: ^1H NMR (CD_2Cl_2, 270 MHz) δ 4.98 (s, 5 H, C_5H_5), 4.16 (d, *J* = 10.5 Hz, 9 H, OCH_3), 1.47 (d, *J* = 22.0 Hz, 6 H, $C(CH_3)_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 15.04 MHz) δ 214.9 (CO), 86.3 (C_5H_5), 58.7 (d, J_{CP} = 10 Hz, OCH_3), 30.0 ($C(CH_3)_2$), 10.3 (d, J_{CP} = 100 Hz, FeC); IR (CH_2Cl_2) 2023 (s), 1984 (s) cm^{-1}.

$(C_5H_5)(CO)_2FeC(CH_3)_2[P(OCH_3)_3]^+CF_3SO_3^-$ (11b). Carbene complex **1b** (3.6 mmol) was prepared from CF_3SO_3H (0.32 mL, 3.7 mmol) and **4** (0.80 g, 3.6 mmol) in diethyl ether (50 mL) at −78 °C. $P(OCH_3)_3$ (0.46 mL, 4.0 mmol) was added to the slurry of carbene complex **1b** in diethyl ether at −78 °C. The reaction mixture was stirred at room temperature for 3 h. The fluffy yellow carbene complex was converted to a more granular yellow solid during this procedure. Solvent was decanted, and yellow **11b** was washed with diethyl ether (2 × 50 mL) to give **11b** (1.49 g, 83%) as a yellow powder, mp 100 °C dec. For **11b**: ^1H NMR (CD_2Cl_2, 270 MHz) δ 4.99 (s, 5 H, C_5H_5), 4.17 (d, *J* = 10.2 Hz, 9 H, OCH_3), 1.48 (d, *J* = 22.0 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 15.04 MHz) δ 215.0 (CO), 86.4 (C_5H_5), 58.9 (d, J_{CP} = 10 Hz, OCH_3), 30.1 (d, J_{CP} = 2 Hz, $C(CH_3)_2$), 10.4 (d, J_{CP} = 99 Hz, FeC); IR (CH_2Cl_2) 2023 (s), 1980 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{20}F_3FeO_8PS$: C, 34.16; H, 4.09. Found: C, 34.03; H, 4.27.

$(C_5H_5)[P(C_6H_5)_3](CO)FeC(CH_3){=}CH_2$ (9). A solution of **4** (1.30 g, 5.93 mmol) and $P(C_6H_5)_3$ (1.54 g, 5.87 mmol) in toluene–hexane (8–92, 60 mL) was photolyzed with a 450-W medium-pressure mercury lamp for 1.25 h. Upon cooling the mixture to −20 °C, **9** (2.06 g, 65%) crystallized, was washed with hexane, and was dried under vacuum (mp 128 °C dec. lit.[19] mp 129–130 °C)).

9 was also prepared by photolysis of $P(C_6H_5)_3$ (1.59 g, 6.06 mmol) and **8** (1.50 g, 6.07 mmol) in hexane–benzene (95–5, 60 mL) with a 450-W medium-pressure mercury lamp for 2.5 h. Following chromatography (80–20 hexane–ether, activity III alumina) and trituration with

(31) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256.

hexane, slightly impure **9** (1.39 g, 51%) was isolated.

$(C_5H_5)[P(C_6H_5)_3](CO)Fe{=}C(CH_3)_2{}^+CF_3SO_3^-$ (12b). Addition of triflic acid (0.31 mL, 3.5 mmol) to **9** (0.50 g, 3.30 mmol) in diethyl ether (50 mL) at 0 °C led to the precipitation of yellow microcrystalline **12b** (1.68 g, 83%) which was washed with diethyl ether and dried under vacuum, mp 100 °C dec. For **12b**: ^1H NMR (CD_2Cl_2, 100 MHz) δ 7.5 (m, 15 H, C_6H_5), 5.14 (d, J = 1.2 Hz, 5 H, C_5H_5), 3.14 (s, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 50.1 MHz, −20 °C, 0.07 M $Cr(acac)_3$) δ 406.5 (d, J = 18 Hz, Fe=C), 213.9 (d, J = 26 Hz, CO), 132.4 (d, J = 10 Hz, ortho or meta), 131.6 (para), 130.5 (d, J = 52 Hz, ipso), 128.9 (d, J = 10 Hz, ortho or meta), 91.7 (C_5H_5), 59.1 (CH_3); IR (CH_2Cl_2) 1992 (s) cm^{-1}.

$(C_5H_5)[P(C_6H_5)_3](CO)Fe{=}C(CH_3)_2{}^+BF_4^-$ (12a). Addition of $HBF_4{\cdot}(CH_3CH_2)_2O$ (0.50 mL, 4.0 mmol) to **9** (0.55 g, 1.21 mmol) in diethyl ether (25 mL) at 0 °C gave yellow microcrystalline **12a** (0.61 g, 93%), mp 140 °C dec. For **12a**: ^1H NMR (CD_2Cl_2, 270 MHz) δ 7.5 (m, 15 H, C_6H_5), 5.13 (s, 5 H, C_5H_5), 3.13 (s, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 50.1 MHz, 0 °C, 0.07 M $Cr(acac)_3$) δ 407.5 (br s, Fe=C), 214.2 (d, J = 29 Hz, CO), 132.6 (d, J = 8 Hz, ortho or meta), 131.8 (para), 130.9 (d, J = 52 Hz, ipso), 129.2 (d, J = 8 Hz, ortho or meta), 91.8 (s, C_5H_5), 59.4 (s, CH_3); IR (CH_2Cl_2) 1993 (s) cm^{-1}. Anal. Calcd for $C_{27}H_{26}BF_4FeOP$: C, 60.04; H, 4.85; P, 5.73. Found: C, 60.09; H, 5.01; P, 5.85.

Deprotonation of $(C_5H_5)[P(C_6H_5)_3](CO)Fe{=}C(CH_3)_2{}^+CF_3SO_3^-$ (12b). A slurry of **12b** (0.20 g, 0.34 mmol) in diethyl ether (10 mL) was stirred with pyridine (0.05 mL, 6 mmol) for 0.5 h. The resulting orange solution was decanted, and the solid residue was washed with diethyl ether (2 × 10 mL). The solvent was removed from the combined organic phases to give pure **9** (0.11 g, 74%).

***trans*-$(C_5H_5)(CO)_2FeCH{=}CHC(CH_3)_2OH$ (14).** A solution of CH_3Li (9.2 mL, 14 mmol, 1.50 M in diethyl ether) and $(C_5H_5)(CO)_2Fe{-}CH{=}CHCOCH_3$, (**13**)[23] (3.00 g, 12.2 mmol) in diethyl ether (125 mL) was stirred for 1 h at 0 °C and then quenched with H_2O (0.5 mL). The ether layer was evaporated, and the oily residue was extracted with toluene (3 × 75 mL). The combined extracts were concentrated and chromatographed (activity III alumina; hexane, diethyl ether) to give **14** as a red oil (1.98 g, 62%). For **14**: ^1H NMR (C_6D_6, 270 MHz) δ 6.70 (d, J = 15.8 Hz, 1 H, FeCH=C), 6.00 (d, J = 15.8 Hz, 1 H, C=CH=C), 4.05 (s, 5 H, C_5H_5), 1.34 (s, 6 H, CH_3), 1.31 (s, 1 H, exchange with D_2O, OH). $^{13}C\{^1H\}$ NMR (C_6D_6, 15.04 MHz) δ 216.5 (CO), 153.1 (Fe—C=), 121.9 (FeCH=*C*), 85.2 (C_5H_5), 72.8 (C-OH), 30.7 (CH_3); IR (CH_2Cl_2) 3685 (w), 2006 (s), 1958 (s) cm^{-1}; MS (30 eV) *m/e* 262.0291 (M^+), calcd for $C_{12}H_{14}O_3Fe$ 262.0292.

$(C_5H_5)(CO)_2Fe{=}CHCH{=}C(CH_3)_2{}^+BF_4^-$ (2). Addition of $HBF_4{\cdot}(CH_3CH_2)_2O$ (40 μL, 0.32 mmol) to **14** (0.090 g, 0.34 mmol) in diethyl ether (2 mL) at −15 °C gave **2** as an orange precipitate, which was washed with diethyl ether and dried under vacuum, all at −15 °C. Dry orange **2** was dissolved in CD_2Cl_2 at −78 °C, and ^1H and ^{13}C NMR were taken at low temperature. For **2**: ^1H NMR (CD_2Cl_2, 270 MHz, −55 °C) δ 15.96 (d, J = 14.7 Hz, 1 H, Fe=CH), 8.21 (d, J = 14.7 Hz, 1 H, —CH=C), 5.66 (s, 5 H, C_5H_5), 2.22 (s, 6 H, CH_3); ^{13}C NMR (CD_2Cl_2, 50.1 MHz, −60 °C) δ 316.7 (d, J = 148 Hz, Fe=CH), 207.8 (s, CO), 178.8 (s, =*C*(CH_3)$_2$), 154.0 (d, J = 159 Hz, —CH=), 92.1 (d, J = 182 Hz, C_5H_5), 29.9 (q, J = 130 Hz, CH_3), 23.4 (q, J = 130 Hz, CH_3); both ^1H and ^{13}C NMR had small peaks due to $(CH_3CH_2)_2O$; IR (CH_2Cl_2), −10 °C) 2065 (s), 2022 (s) cm^{-1}.

2,2-Dimethyl-1-(2-methyl-1-propenyl)cyclopropane (15). Isobutylene (135 mmol) and methylene chloride (1 mL) were vacuum transferred at −78 °C onto complex **2**, prepared from $HBF_4{\cdot}O(CH_2CH_3)_2$ (54 μL, 0.45 mmol) and **14** (0.117 g, 0.45 mmol) in diethyl ether (3 mL) at −23 °C. The reaction mixture was stirred at −23 °C for 45 min and warmed to room temperature, and the volatile material was removed under vacuum. The residue was stirred with NaI (0.70 g, 0.47 mmol) in acetone (1 mL) for 15 min, and the volatile material was again removed under vacuum. Octane (50 μL for use as an internal GC standard) was added to the combined distillates. Gas chromatography (SE-30) indicated a 56% yield of **15** based on **14**. The cyclopropane was isolated by preparative gas chromatography (SE-30, 100 °C) and compared with an authentic sample.[32] For **15**: ^1H NMR (C_6D_6, 270 MHz) δ 4.96 (br d, J = 8.1 Hz, 1 H, CH=C), 1.69 (br s, 3 H, CH_3), 1.67 (d, J = 1.5 Hz, 3 H, CH_3), 1.29 (ddd, J = 8.6, 8.1, 4.6 Hz, 1 H, C*H*—CH=), 1.04 (s, 3 H, CH_3), 1.02 (s, 3 H, CH_3), 0.63 (dd, J = 8.6, 4.6 Hz, 1 H, syn-H of CH_2), 0.22 (t, J = 4.6 Hz, 1 H, anti-H of CH_2); $^{13}C\{^1H\}$ 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.

***syn*-9-(2-Methyl-1-propenyl)bicyclo[6.1.0]nonane (16).** Complex **2**, prepared from $HBF_4{\cdot}O(CH_2CH_3)_2$ (0.28 mL, 2.3 mmol) and **14** (0.62 g, 2.37 mmol) at −15 °C, was stirred with cyclooctene (0.92 mL, 0.78 g, 7.1 mmol) in 10 mL of CH_2Cl_2 for 30 min at −15 °C. Solvent was evaporated under vacuum, NaI (0.35 g, 2.3 mmol) in acetone (5 mL) was added, and after stirring for 15 min at room temperature, solvent was evaporated under vacuum. The oily residue was washed with hexane, the hexane washes were chromatographed (silica gel, hexane), and the isolated oil was further purified by Kugelrohr distillation 90 °C (0.1 mm)) to give **16** (0.157 g, 37%). For **16**: ^1H NMR (C_6D_6, 270 MHz) δ 5.14 (dm, J = 7.8 Hz, 1 H, =CH), 1.75 (s, 3 H, CH_3), 1.70 (s, 3 H, CH_3), 1.28–1.70 (m, 13 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; MS (70 eV) *m/e* 178.1722 (M^+), calcd for $C_{13}H_{22}$ 178.1722.

Ozonolysis of 16. Ozone was bubbled through a solution of **16** (0.070 g, 0.4 mmol) in acetic acid (3 mL) and formic acid (1.5 mL) for 30 min. H_2O_2 (30%) (1 mL) was added, and the reaction mixture was refluxed for 2 h. After the mixture was cooled, water (5 mL) was added and ether (2 × 40 mL) was used to extract *syn*-**17** (0.050 g, 75%), which was isolated as a white solid, mp 140–143 °C. For *syn*-**17**: ^1H NMR (C_6D_6, 270 MHz) δ 12.26 (br s, 1 H, OH), 1.93 (m, 2 H), 1.10–1.65 (m, 11 H), 0.80 (m, 2 H).

Ethyl *syn*- and *anti*-bicyclo[6.1.0]nonane-9-carboxylate (*syn*- and *anti*-18) were prepared as described previously[25] by reaction of $N_2CH{-}CO_2CH_2CH_3$ (21.0 mL, 0.20 mol) with cyclooctene (39 mL, 0.30 mol) and $CuSO_4$ (4.79 g, 30 mmol) at 100 °C. *syn*- and *anti*-**18** (22.1 g, 56%) were isolated by distillation (bp 85–88 °C (0.8 mm)) and separated by gas chromatography (QF-1, 210 °C). For *syn*-**18**: ^1H NMR (C_6D_6, 270 MHz) δ 4.00 (q, J = 7.1 Hz, 2 H, OCH_2), 2.14 (m, 2 H), 1.1–1.7 (m, 11 H), 0.99 (t, J = 7.1 Hz, 3 H, OCH_2CH_3), 0.85 (m, 2 H). For *anti*-**18**: ^1H NMR (C_6D_6, 270 MHz) δ 4.01 (q, J = 7.1 Hz, 2 H, OCH_2), 1.81 (m, 2 H), 1.0–1.5 (m, 11 H), 0.99 (t, J = 7.1 Hz, 3 H, OCH_2CH_3), 0.74 (m, 2 H). The resonance due to the proton attached to carbon 9 of the ethyl ester of *anti*-**18** 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.

***cis*-Bicyclo[6.1.0]nonane-9-carboxylic Acid (*syn*-17).**[25] *syn*-**18**, (0.050 g, 0.25 mmol) was hydrolyzed by treatment with NaOH solution (0.12 g NaOH/2 mL H_2O) at 70 °C for 20 h. Workup gave pure *syn*-**17** (0.030 g, 71%), mp 140–142 °C.

***anti*-Bicyclo[6.1.0]nonane-9-carboxylic Acid (*anti*-17).** *anti*-**18** (0.17 g, 0.87 mmol) was hydrolyzed by treatment with NaOH solution (0.30 g of NaOH/5 mL of H_2O) at 70 °C for 40 h. Workup gave pure *anti*-**17** (0.11 g, 75%), mp 133–135 °C. For *anti*-**17**: ^1H NMR (C_6D_6, 270 MHz) δ 13.2 (br s, 1 H, OH), 1.72 (m, 2 H), 1.0–1.5 (m, 11 H), 0.66 (m, 2 H).

***cis*- and *trans*-2-Phenyl-1-(2-methyl-1-propenyl)cyclopropane (*cis*- and *trans*-19).** Vacuum dried complex **2**, prepared from $HBF_4{\cdot}O(CH_2CH_3)_2$ (0.28 mL, 2.3 mmol) and **14** (0.62 g, 2.37 mmol) in diethyl ether (10 mL) at −15 °C, was stirred with styrene (0.79 mL, 0.72 g, 6.9 mmol) in 10 mL of methylene chloride for 30 min at −15 °C. Workup as described for **16** gave *cis*- and *trans*-**19** (0.19 g, 45% based on **4**) isolated by Kugelrohr distillation ((0.5 mm) 90 °C). *cis*- and *trans*-**19** (*cis*-**19**–*trans*-**19**, 1–2) were separated by preparative gas chromatography (20% OV-255, 180 °C). For *cis*-**19**: ^1H NMR ($(CD_3)_2CO$, 270 MHz) δ 7.2 (m, 5 H, C_6H_5), 4.52 (dm, J = 8.7 Hz, 1 H, CH=), 2.28 (dt, J = 6.2, 8.6 Hz, 1 H, C*H*C_6H_5), 1.89 (m, 1 H, C*H*—C=), 1.67 (d, J = 1.1 Hz, 3 H, CH_3), 1.50 (d, J = 0.9 Hz, 3 H, CH_3), 1.21 (dt, J = 4.7, 8.6 Hz, 1 H, anti-H of CH_2), 0.89 (dt, J = 4.8, 6.0 Hz, 1 H, syn-H of CH_2); $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 50.1 MHz) δ 140.4, 132.9, 129.6, 128.6, 126.3, 124.2, 25.7, 23.5, 19.1, 18.3, 12.7; MS (70 eV) *m/e* 172.1252 (M^+), calcd for $C_{13}H_{16}$ 172.1252. For *trans*-**19**: ^1H NMR ($(CD_3)_2CO$, 270 MHz) δ 7.2 (m, 5 H, C_6H_5), 4.77 (dm, J = 8.7 Hz, 1 H, CH=), 1.81 (ddd, J = 4.5, 5.5, 8.5 Hz, 1 H, C*H*C_6H_5), 1.73 (m, 1 H, C*H*—C=), 1.68 (d, J = 1.2 Hz, 3 H, CH_3), 1.67 (s, CH_3), 1.16 (ddd, J = 4.6, 5.5, 8.7 Hz, 1 H, proton of CH_2 syn to C_6H_5), 0.94 (ddd, J = 4.5, 5.6, 8.5 Hz, 1 H, proton of CH_2 syn to vinyl group); $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 15.04 MHz) δ 143.5, 131.5, 128.7, 127.1, 126.1, 125.8, 25.6, 25.5, 23.8, 18.5, 17.6; MS (70 eV) *m/e* 172.1252 (M^+), calcd for $C_{13}H_{16}$ 172.1252.

cis- and *trans*-**19** were also synthesized by generating carbene complex **2** in situ. $(C_6H_5)_3C^+PF_6^-$ (0.97 g, 2.50 mmol), **4** (0.65 g, 250 mmol), and styrene (0.83 mL, 0.76 g, 7.3 mmol) were stirred in methylene chloride (20 mL) at −15 °C for 0.5 h. Workup as before gave *cis*- and *trans*-**19** (1–3, 0.20 g, 47%).

***cis*- and *trans*-19-*d*.** A CH_2Cl_2 solution of complex **2** (1.0 mmol), prepared from $HBF_4{\cdot}(CH_3CH_2)_2O$ (0.12 mL, 1.1 mmol) and **14** (0.26 g, 1.00 mmol) in diethyl ether (10 mL) at −15 °C, and *cis*-CHD=CHC_6H_5 (0.30 mL, 3.1 mmol) was stirred at −15 °C for 1 h. Workup with NaI as described earlier and column chromatography (hexane; silica gel) gave *cis*- and *trans*-**19**-*d* (1–2, 0.088 g, 51%) which were separated by preparative gas chromatography. For *cis*-**19**-*d*: ^1H NMR ($(CD_3)_2CO$, 270 MHz) δ 7.2 (m, 5 H, C_6H_5), 4.51 (dm, J = 8.7 Hz, 1

(32) Nelson, E. R.; Maienthal, M.; Lane, L. A.; Benderly, A. A. *J. Am. Chem. Soc.* **1957**, *79*, 3467.

H, CH=), 2.30 (t, J = 8.7 Hz, 1 H, CHC_6H_5), 1.89 (q, J = 8.7 Hz, 1 H, CH—C=), 1.66 (d, J = 0.9 Hz, 3 H, CH_3), 1.50 (d, J = 0.9 Hz, 3 H, CH_3), 1.20 (t, J = 8.5 Hz, 1 H, CHD). For *trans*-**19**-*d* ($(CD_3)_2SO$, 270 MHz) δ 7.2 (m, 5 H, C_6H_5), 4.73 (dm, J = 8.7 Hz, 1 H, CH=), 1.80 (dd, J = 4.3, 8.4 Hz, 1 H, CHC_6H_5), 1.69 (m, 1 H, CH—C=), 1.63 (br s, 6 H, CH_3), 0.92 (dd, J = 5.4, 8.5 Hz, 1 H, CHD).

Isomerization of *cis*-19. $(C_5H_5)(CO)_2FeI$ (0.043 g, 0.14 mmol) and $AgBF_4$ (0.030 g, 0.15 mmol) were stirred in 2 mL of CH_2Cl_2 for 30 min at room temperature. *cis*-**19** (0.025 g, 0.15 mmol; *cis*-**19**–*trans*-**19**, 9–1) was added to the dark solution containing precipitated AgI, and the mixture was stirred for 1 h. Diethyl ether (15 mL) was added to oil out the crude alkene complex $(C_5H_5)(CO)_2Fe$(*cis*- and *trans*-**19**)$^+BF_4^-$ (**21**), which was washed with diethyl ether (2 × 10 mL). The diethyl ether washes contained 5 mg of *cis*- and *trans*-**19** (2–1). Alkene complex **21** was dried under high vacuum for 1 h and became increasingly dark. NaI (21 mg, 0.15 mmol) in acetone (0.5 mL) was added to alkene complex **21**, and the mixture was stirred for 15 min. Chromatography (silica gel, hexane) gave **19**. Analysis by analytical gas chromatography (10% DEGS, 130 °C; heptadecane internal standard) indicated that 0.008 g of **19** (*cis*-**19**–*trans*-**19**, 1–3.5) was present.

Acknowledgment. Research support from the National Science Foundation is gratefully acknowledged. We thank Professor Paul Helquist for keeping us informed of his related studies.

Registry No. **1a**, 81939-62-0; **1b**, 95615-87-5; **2**, 89486-58-8; **3**, 81939-65-3; **4**, 95615-88-6; **5**, 81939-66-4; **6**, 12108-22-4; **7**, 82246-54-6; **8**, 81939-68-6; **9**, 70569-00-5; **10a**, 37668-14-7; **11a**, 81939-70-0; **11b**, 95615-89-7; **12a**, 81939-64-2; **12b**, 95615-90-0; **13**, 12288-63-0; **14**, 95721-03-2; **15**, 33422-32-1; **16**, 89486-60-2; *syn*-**17**, 89576-67-0; *anti*-**17**, 37151-61-4; *syn*-**18**, 53235-18-0; *anti*-**18**, 53276-22-5; *cis*-**19**, 89486-56-6; *trans*-**19**, 89486-57-7; *cis*-**19d**, 95615-94-4; *trans*-**19d**, 95615-95-5; *cis*-**21**, 95615-92-2; *trans*-**21**, 95721-05-4; $(C_5H_5)(CO)_2Fe^+BF_4^-$, 93757-32-5; $(C_5H_5)(CO)_2Fe^-Na^+$, 12152-20-4; $(C_5H_5)(CO)_2FeI$, 12078-28-3; $[(C_5H_5)(CO)_2Fe]_2$, 12154-95-9; $(C_5H_5)[P(C_6H_5)_3](CO)FeC(CH_3)_2(OCH_3)$, 95615-93-3; $ClCOC(CH_3)=CH_2$, 920-46-7; CH_3Li, 917-54-4; $N_2CHCO_2CH_2CH_3$, 623-73-4; *cis*-$CHD=CHC_6H_5$, 21370-59-2; MeI, 74-88-4; $C_6H_5COCH=C(CH_3)_2$, 5650-07-7; 1,1,2,2-tetramethylcyclopropane, 4127-47-3; 1,1-dimethyl-2-phenylcyclopropane, 7653-94-3; lithium dimethylcuprate, 15681-48-8; isobutylene, 115-11-7; styrene, 100-42-5; cyclooctene, 931-88-4; 4-chlorobut-3-en-2-one, 7119-27-9.

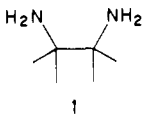
Stereoselective Synthesis of Vicinal Diamines from Alkenes and Cyanamide

Sang-Hun Jung[1] and Harold Kohn*

Contribution from the Department of Chemistry, University of Houston, Houston, Texas 77004. *Received October 5, 1984*

Abstract: A new procedure for the preparation of vicinal diamines is described beginning with unactivated olefins, cyanamide, and *N*-bromosuccinimide. Diamination proceeded stereospecifically and permitted access to nitrogen-unsubstituted diamines. With this procedure, 1-hexene (**2a**), 2-methylpropene (**2b**), *trans*-2-butene (**2c**), *trans*-4-octene (**2d**), *cis*-2-butene (**2e**), and cyclohexene (**2f**) were converted to the corresponding vicinal diamines in 47–71% overall yield. In the initial step, treatment of the alkene (**2**) with cyanamide (**3**) and *N*-bromosuccinimide (**4**) yielded the bromo cyanamide **5**. This adduct is then converted to the isourea salt **6** in situ with ethanolic hydrochloric acid. Treatment of **6** with mild bases (i.e., triethylamine, $NaHCO_3$) in select cases gave the 2-ethoxyimidazoline **8**. Alternatively, use of more basic conditions (i.e., sodium ethoxide, NaOH) led to ethyl aziridinecarboximidate **7** formation. The aziridine **7** could be stereospecifically transformed to the isomeric imidazoline **8** with nucleophilic catalysts (i.e., NaI, triethylamine–hydroiodide). Basic hydrolysis of the imidazoline **8** in the last step generated the desired vicinal diamine **1**. The mechanism and scope of each step in this diamination procedure are discussed.

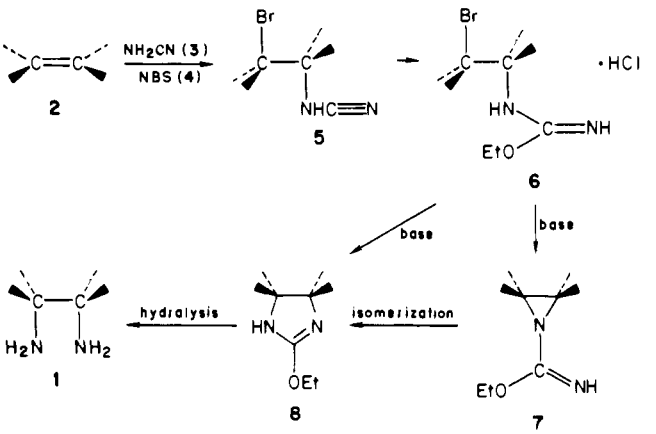
The vicinal diamine unit (**1**) is commonly observed in naturally occurring compounds and medicinal agents. Despite the importance of this functional group, few general diamination methods exist. This is astonishing in light of the many eloquent ways available for the synthesis of vicinal glycols,[2] vicinal halohydrins,[2] vicinal dihalides,[2] and vicinal oxyamino compounds.[3]



1

Conceptually, the simplest procedure for the generation of **1** is the ammonolysis of the corresponding vicinal dihalide.[4] Unfortunately, this method which was applied in the preparation of 1,2-diaminoethane yields predominantly elimination products in more complex systems.[5] As a result, a variety of other dis-

Scheme I. Synthesis of Vicinal Diamines



2 5 6 1 8 7

(1) Abstracted from: Jung, S. H. Ph.D. Dissertation, University of Houston, Houston, Texas, 1984. Additional structure proof, discussion, and experimental and spectral data may be found in this reference.

(2) Carey, F. A.; Sundberg, R. J. "Advanced Organic Chemistry, Part B, Reactions and Synthesis", 2nd ed.; Plenum Press: New York, 1983; Chapters 4 and 10.

(3) (a) Herranz, E.; Biller, S. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1978**, *100*, 3596–3598. (b) Patrick, D. W.; Truesdale, L. K.; Biller, S. A.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2628–2638. (c) Colvin, E. W.; Seebach, D. *J. Chem. Soc., Chem. Commun.* **1978**, 689–691. (d) Gasc, M. B.; Lattes, A.; Perie, J. J. *Tetrahedron* **1983**, *39*, 703–731.

(4) *Beilstein* **1922**, *4*, 230 and references therein.

0002-7863/85/1507-2931$01.50/0