# Photochemical Reactions of Diiron $\mu$-Alkenylidene Complexes with Hydrogen, Trialkylsilanes, and Diazo Compounds: Cleavage to Alkenes, Vinylsilanes, and Allenes

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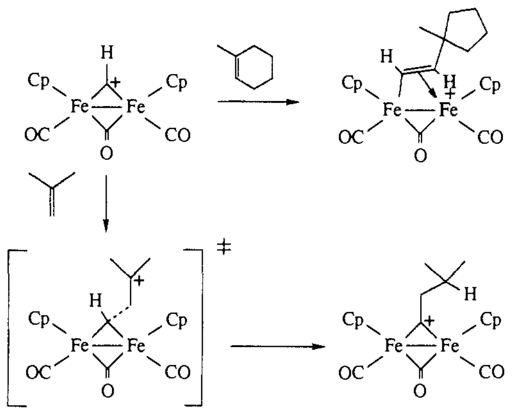
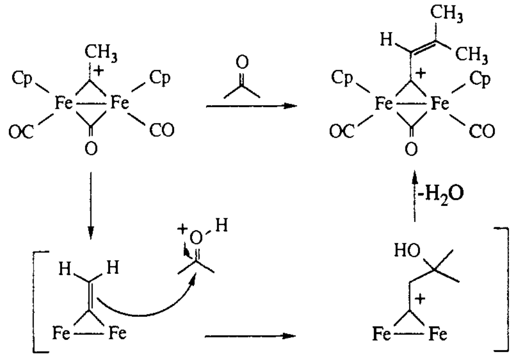
**Abstract**: Photolysis of the $\mu$-ethenylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-CO})(\mu\text{-C=CH}_2)$ (**1**) in the presence of ethyl diazoacetate produces the $\mu$-allene complex $[C_5H_5(CO)Fe]_2(\mu\text{-CH}_2\text{=C=CHCO}_2\text{CH}_2\text{CH}_3)$ (**4**) in 48% yield. Similarly, photolysis of the $\mu$-propenylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-CO})(\mu\text{-C=CHCH}_3)$ (**2**) with ethyl diazoacetate produced an 82:18 mixture of two diastereomers of the allene complex $[C_5H_5(CO)Fe]_2(\mu\text{-CH}_3\text{CH=C=CHCO}_2\text{CH}_2\text{CH}_3)$ (**6k** and **6t**). When this mixture of isomers was heated at 60 °C, the mixture was completely converted to the minor kinetic isomer **6t**. Allene complexes were also formed from the photochemical reactions of $\mu$-alkenylidene diiron compounds with (trimethylsilyl)diazomethane and methyl 2-diazopropionate. The synthesis of $\mu$-allene complexes required light and was inhibited by CO. Free allenes released from the diiron complexes under a variety of conditions including oxidation with $O_2$ and thermolysis under CO. Photolysis of $[C_5H_5(CO)Fe]_2(\mu\text{-CO})[\mu\text{-C=C(CH}_3)\text{CH}_2\text{CH}_3]$ (**3**) under a hydrogen atmosphere gave 2-methyl-1-butene (22%) and 2-methylbutane (48%). Photolysis of $\mu$-alkenylidene complex **3** with trimethylsilane gave a 1:1 mixture of isomers of $CH_3CH_2(CH_3)C\text{=CHSi(CH}_3)_3$ in 100% yield. Photolysis of $[C_5H_5(CO)Fe]_2(\mu\text{-CO})(\mu\text{-C=CH}_2)$ in the presence of $^{13}CO$ led to initial incorporation of $^{13}CO$ at a terminal position (>15:1 terminal:bridge $^{13}CO$). At longer photolysis times, $^{13}CO$ label was incorporated into the bridging position also. On the basis of the kinetics of $^{13}CO$ incorporation, a triply bridged intermediate $[C_5H_5Fe]_2(\mu\text{-CO})_2(\mu\text{-C=CH}_2)$ is proposed. This same intermediate is probably involved in photochemical reactions with diazo compounds, silanes, and $H_2$.

During the last several years, we have developed a number of new carbon–carbon bond forming reactions based on the unique reactivity of the $[C_5H_5(CO)Fe]_2(\mu\text{-CO})(\mu\text{-CR})$ framework. The diiron $\mu$-methylidyne complex $[C_5H_5(CO)Fe]_2(\mu\text{-CO})(\mu\text{-CH})^+PF_6^-$ adds the C–H bond of the methylidyne group across the double bond of many different alkenes to produce $\mu$-alkylidyne complexes.[1,2] For some alkenes, reaction with **1** leads directly to $\mu$-alkenyl products.[3] Both of these reactions involve an initial nucleophilic interaction of the alkene with the methylidyne carbon.

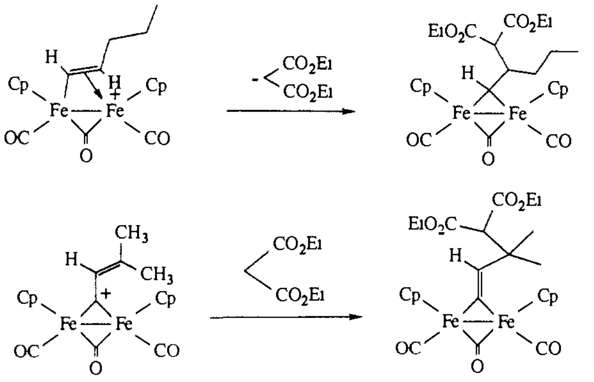


A second carbon–carbon bond forming reaction occurs between cationic $\mu$-alkylidyne compounds such as $[C_5H_5(CO)Fe]_2(\mu\text{-CO})(\mu\text{-CCH}_3)^+BF_4^-$ and aldehydes or ketones in which a condensation produces vinyl carbyne complexes.[4] The first step in this reaction is a proton transfer from the $\mu$-alkylidyne complex to the oxygen of the aldehyde or ketone. This activates the aldehyde or ketone for nucleophilic attack by the $\mu$-alkenylidene intermediate.

A third class of carbon–carbon bond forming reactions occurs between cationic diiron complexes and carbon nucleophiles. We



have found that both vinylcarbyne[5] and $\mu$-alkenyl[6] complexes react with nucleophiles to produce neutral $\mu$-alkenylidene and $\mu$-alkylidene complexes, respectively.



Interconversions between many of these different types of bridging complexes have been observed. Cationic $\mu$-alkylidyne diiron complexes are readily deprotonated by base to yield $\mu$-alkenylidene complexes.[1,7] In this reaction, the proton is removed from the carbon atom adjacent to the cationic bridging carbon.

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[1] Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950–4951.

[2] Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S. R.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043–4053.

[3] Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Colborn, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 4053–4059.

[4] Casey, C. P.; Konings, M. S.; Palermo, R. E.; Colborn, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 5296–5297.

[5] Casey, C. P.; Konings, M. S.; Marder, S. R. *J. Organomet. Chem.* **1988**, *345*, 125–134.

[6] Casey, C. P.; Vosejpka, P. C. *Organometallics* **1988**, *7*, 934–936.

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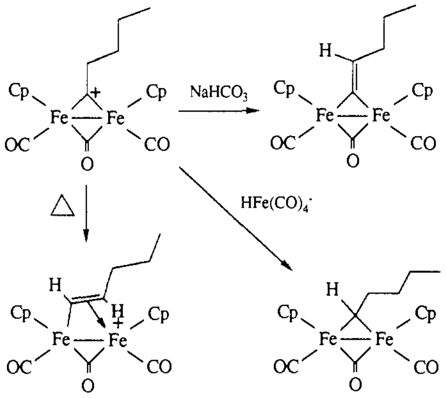
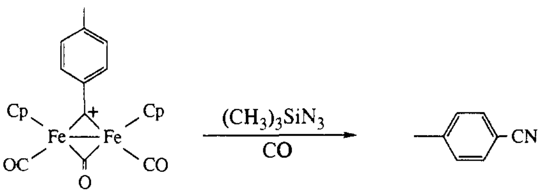
Treatment of these neutral compounds with strong acid cleanly regenerates the μ-alkylidyne complex.[7,8] When μ-alkylidyne diiron complexes are heated in solution or in the solid state, they undergo a 1,2 hydrogen shift to give μ-alkenyl complexes.[9] μ-Alkylidyne complexes are converted to neutral μ-alkylidene complexes upon treatment with hydride sources such as $HFe(CO)_4^-$.[7,10]

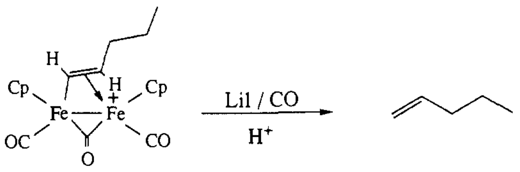


One of our long-term goals is to employ this new chemistry of diiron compounds in organic synthesis. To take advantage of the many types of transformations that diiron complexes undergo, we need to develop efficient methods for the cleavage of the bridging organic ligand from the diiron framework. Our initial attempts to cleave diiron compounds centered on cationic μ-alkylidyne and μ-alkenyl complexes.

Releasing the organic fragment from a μ-alkylidyne complex with the newly formed carbon–carbon bond intact requires the delivery of three new valences and a negative charge to the bridging carbon atom. We found that azide ion acts as such a reagent.[11] Treatment of μ-alkylidyne complexes with trimethylsilyl azide under a CO atmosphere gave nitriles.



The only other cleavage reaction of diiron complexes we have reported involves the conversion of cationic diiron μ-alkenyl complexes to alkenes. Treatment of μ-alkenyl complexes with lithium iodide and strong acid under an atmosphere of CO gave free alkenes in moderate yields.[12]

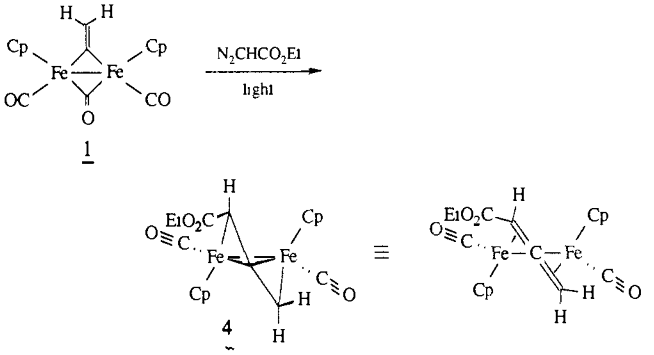


In a determined effort to develop additional cleavage reactions for diiron complexes, we began a study of the reactions of neutral μ-alkenylidene complexes. This class of compounds was chosen because they are readily prepared by several synthetic routes outlined above and because they require the delivery of only two valences and no charge to release a neutral organic molecule.

Here we report that photolysis of neutral μ-alkenylidene diiron complexes in the presence of trapping agents leads to organic products incorporating the bridging organic ligand. The use of $H_2$ or trialkylsilanes as the trapping agent produces alkenes or vinylsilanes. When a diazo compound is used as a trap, diiron μ-allene complexes are produced which can subsequently be cleaved to free allenes.

## Results

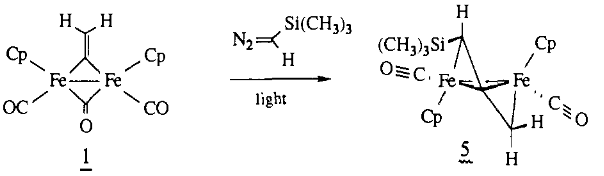
**Synthesis of μ-$\eta^2,\eta^2$-Allene Complexes.** A dark red solution of μ-alkenylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ (**1**) and excess ethyl diazoacetate was photolyzed for 3.5 h in toluene at 0 °C. Evaporation of solvent and chromatography of the residue gave the dark green μ-allene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CH_2{=}C{=}CHCO_2CH_2CH_3)$ (**4**) in 48% yield.[13]



The structure of **4** was established spectroscopically. In the $^1H$ NMR spectrum in acetone-$d_6$, the three unique protons on the coordinated allene appear as separate doublets of doublets at δ 3.29 ($J$ = 1.2, 2.3 Hz), 3.49 ($J$ = 2.3, 4.1 Hz), and 3.84 ($J$ = 1.2, 4.1 Hz); the inequivalent cyclopentadienyl groups appear at δ 4.28 and 4.39. The IR spectrum of **4** has two bands at 1974 (s) and 1921 (s) $cm^{-1}$ that establish the presence of two terminal carbonyl groups and the absence of a bridging carbonyl group. The loss of a bridging CO ligand in the conversion of **1** to **4** provides a convenient means of monitoring these reactions by IR spectroscopy.

Hoel has reported the X-ray crystal structure of the unsubstituted μ-allene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CH_2{=}C{=}CH_2)$.[14] In this structure, there is a $C_2$ axis passing through the center allene carbon and the midpoint of the iron–iron vector. The three-carbon allene unit sits above the iron–iron axis in a criss-cross arrangement. This geometry allows interaction of one π-bond of the allene with one iron center and of the second π bond of the allene with the second iron center. The hydrogens on the allene occupy two different positions. On each terminal carbon of the allene, one C–H bond is approximately alligned with the $C_2$ axis of the framework (axial) and the other C–H bond is approximately perpendicular to the $C_2$ axis (equatorial). For the carboethoxy substituted allene complex **4**, there are two possible isomers, one with the ester in an axial position and one with the ester in an equatorial position. Only a single isomer was observed for **4**.

μ-Alkenylidene complex **1** also reacted with (trimethylsilyl)diazomethane under photolytic conditions to produce the green μ-allene complex $[C_5H_5(CO)Fe]_2[\mu\text{-}CH_2{=}C{=}CHSi(CH_3)_3]$ (**5**) in 70% yield. The formation of **5** required photolysis and was



inhibited by carbon monoxide. In a $^1H$ NMR experiment in benzene-$d_6$, three aliquots of a solution of μ-alkenylidene complex

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(8) Dawkins, G. M.; Green, M.; Jeffrey, J. C.; Sambale, C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 499–506.

(9) Casey, C. P.; Marder, S. R.; Adams, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 7700–7705.

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(11) Casey, C. P.; Woo, L. K. *J. Organomet. Chem.* **1987**, *328*, 161–168.

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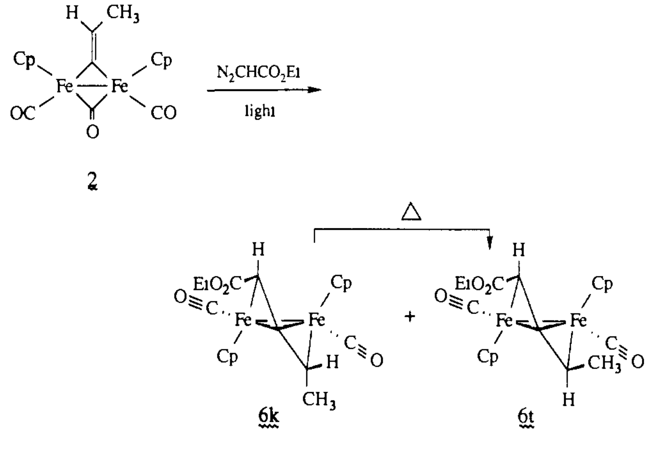
(13) A communication has appeared: Casey, C. P.; Austin, E. A. *Organometallics* **1986**, *5*, 584–585.

(14) Hoel, E. L.; Ansell, G. B.; Leta, S. *Organometallics* **1986**, *5*, 585–587.

**1** and (trimethylsilyl)diazomethane were added to NMR tubes. Tube one was exposed to light, tube two was placed under a CO atmosphere and exposed to light, and tube three was held in the dark as a control. Only the μ-alkenylidene complex in tube one reacted with (trimethylsilyl)diazomethane to form μ-allene complex **5**. The diiron and diazo compounds in tubes two and three were unchanged.

The μ-1-propenylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_3)$ (**2**) reacted with ethyl diazoacetate to give a 82:18 mixture of stereoisomeric μ-allene complexes $[C_5H_5(CO)Fe]_2(\mu\text{-}CH_3CH{=}C{=}CHCO_2CH_2CH_3)$, **6k** and **6t**, in 43% yield. The IR spectrum of the mixture of **6k** and **6t** showed two terminal CO bands at 1945 (s) and 1916 (s) $cm^{-1}$ and a carboethoxy band at 1684 (m) $cm^{-1}$.

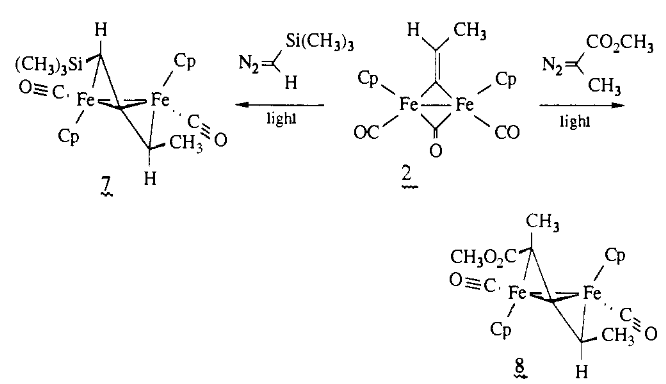


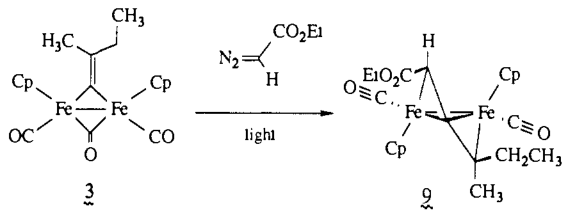
The initial 82:18 mixture of allene complexes **6k**:**6t** is kinetically determined. When an isolated sample containing a 82:18 ratio of **6k**:**6t** was heated overnight at 62 °C in benzene-$d_6$, the mixture was completely converted to the thermodynamically more stable isomer **6t** which was the minor kinetically formed isomer. This thermal isomerization was not inhibited by the presence of added carbon monoxide.

The μ-allene complex **6** has five chiral centers which gives rise to 16 possible diastereomers. If the diiron portion of the molecule has the configuration observed in the X-ray crystal structure of the unsubstituted μ-allene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CH_2{=}C{=}CH_2)$,[14] the number of possible diastereomers is reduced to four. These isomers result from two possible configurations at the carboethoxy-substituted carbon and at the methyl-substituted carbon of the complexed allene. Because of the large difference between the $^1H$ NMR chemical shifts of the methyl groups ($\Delta\delta = 0.41$) of **6k** and **6t** and the small difference in the chemical shifts of the ester groups, we suggest that the two observed diastereomers have the same configuration at the ester-substituted carbon and opposite configurations at the methyl-substituted carbon. Because the axial site appears to be less sterically crowded than the equatorial position, the large ester substituent is suggested to occupy an axial position in both **6t** and **6k**.

Photolysis of a dark red solution of μ-alkenylidene complex **2** and (trimethylsilyl)diazomethane in $CH_2Cl_2$ gave the green μ-allene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CH_3CH{=}C{=}CHSi(CH_3)_3)$ (**7**) in 55% yield as a 6:1 mixture of isomers. In contrast to the isomerization of the initially formed μ-allene complex **6k**, no change in the ratio of the isomers of **7** was observed upon heating at 62 °C. Photolysis of a solution of **2** and methyl 2-diazopropionate led to the formation of green trisubstituted μ-allene complex $[C_5H_5(CO)Fe]_2[\mu\text{-}CH_3CH{=}C{=}C(CH_3)CO_2CH_3]$ (**8**) in 19% yield as a 9:1 mixture of isomers after chromatography on alumina.

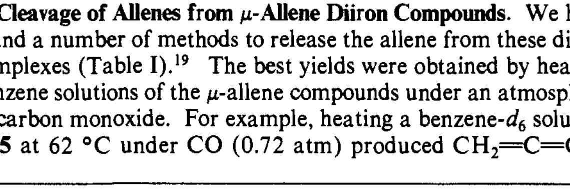
Photolysis of the disubstituted μ-alkenylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CH_3)CH_2CH_3]$ (**3**) and ethyl diazoacetate gave the μ-allene complex $[C_5H_5(CO)Fe]_2[\mu\text{-}CH_3CH_2(CH_3)C{=}C{=}CHCO_2CH_2CH_3]$ (**9**) in 46% yield as a 3:2 mixture of isomers.





Unlike the unsubstituted and monosubstituted μ-alkenylidene complexes **1** and **2**, the disubstituted μ-alkenylidene compound **3** failed to react with (trimethylsilyl)diazomethane to give a μ-allene complex. When a red solution of **3** and (trimethylsilyl)diazomethane was photolyzed in $CH_2Cl_2$ at 0 °C, no color change to the characteristic green of a μ-allene complex was observed. The IR spectrum of the crude reaction mixture showed a band at 1774 (s) $cm^{-1}$ for a bridging CO and two bands at 1973 (s) and 1934 (m) $cm^{-1}$ in the terminal CO region. Chromatography of the reaction mixture gave a small amount of a red solid. The $^1H$ NMR of this material showed singlets at δ 1.60, 4.89, and 0.25. From these spectroscopic data, the compound was identified as the μ-alkylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHSi(CH_3)_3]$ (**10**).

The photolysis of (trimethylsilyl)diazomethane and $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)_2$ (**12**) also led to the formation of μ-alkylidene complex **10** in 29% yield. The reaction of **12** with ethyl diazoacetate at low temperature to give μ-alkylidene products has been reported by Herrmann.[15] Small amounts of **10** were also seen in the syntheses of μ-allene complexes **5** and **7**.



The photochemical reaction of diiron μ-alkenylidene complexes with various diazo compounds has proven to be an effective way to prepare diiron μ-allene complexes. Related dimanganese,[16] dimolybdenum,[17] diruthenium,[18] and diiron[14] complexes are known.

**Cleavage of Allenes from μ-Allene Diiron Compounds.** We have found a number of methods to release the allene from these diiron complexes (Table I).[19] The best yields were obtained by heating benzene solutions of the μ-allene compounds under an atmosphere of carbon monoxide. For example, heating a benzene-$d_6$ solution of **5** at 62 °C under CO (0.72 atm) produced $CH_2{=}C{=}CH$-

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(15) Herrmann, W. A.; Plank, J.; Bernal, I.; Creswick, M. *Z. Naturforsch.* **1980**, *35b*, 680–688.

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(18) Knox, S. A. R.; Doherty, N. M., private communication.

(19) For examples of allene syntheses, see: (a) Lang, R. W.; Hansen, H.-J. *Helv. Chim. Acta* **1980**, *63*, 438–455. (b) Danheiser, R. L.; Carini, D. J.; Kwasigroch, C. A. *J. Org. Chem.* **1986**, *51*, 3870–3878. (c) Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935–947.

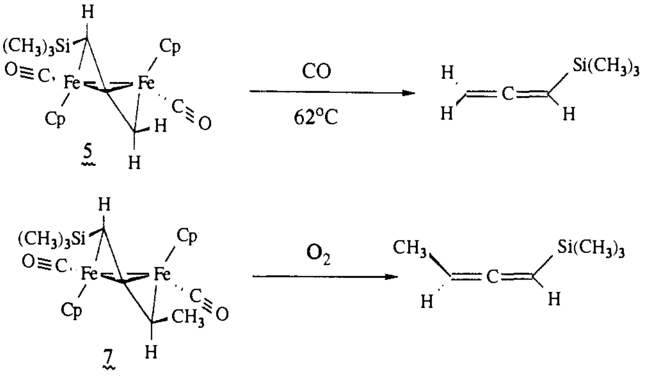
Table I. Percentage Yields of Allenes from Cleavage Reactions of μ-Allene Complexes[a]

| | | reaction conditions | | | |
|---|---|---|---|---|---|
| μ-allene complex | allene produced | CO/ 62 °C | $O_2$ | CO/ $h\nu$ | $CD_3CN$/ 65 °C |
| **4** | $CH_2{=}C{=}CHCO_2R$ | 78 | 70 | 36[b] | *d* |
| **5** | $CH_2{=}C{=}CHSiR_3$ | 94 | 61 | 83 | 66 |
| **6** | $MeCH{=}C{=}CHCO_2R$ | 69[c] | 65 | | |
| **7** | $MeCH{=}C{=}CHSiR_3$ | 86 | 57 | 94 | *d* |
| **8** | $MeCH{=}C{=}C(Me)CO_2R$ | 91 | 64 | | |
| **9** | $MeEtC{=}C{=}CHCO_2R$ | 97 | 56 | | |

[a] NMR yields vs an internal standard. [b] 44% of **4** remained. [c] 20% of **6** remained. [d] No free allene seen by $^1H$ NMR.

$Si(CH_3)_3$ (94%) and $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)_2$ (**12**) (92%) with $t_{1/2}$ = 45 min. Complexes **4**, **7**, **8**, and **9** behaved similarly and decomposed under CO to give free allenes and **12**. Compound **6** also reacted with CO to give free allene, but it did so much more slowly ($t_{1/2}$ = 5 days) than all the other μ-allene complexes.

Dioxygen was also found to be an effective cleavage reagent for μ-allene complexes. For example, when a solution of **7** was exposed to $O_2$ (0.68 atm) overnight, allene $CH_3CH{=}C{=}CHSi(CH_3)_3$ (57%) and ferrocene (10%) were produced. In a preparative scale experiment, a pure sample of $CH_2{=}C{=}CHSi(CH_3)_3$ was isolated by preparative gas chromatography from the reaction of **5** with oxygen in pentane. This cleavage method worked well for all of the μ-allene complexes reported here.



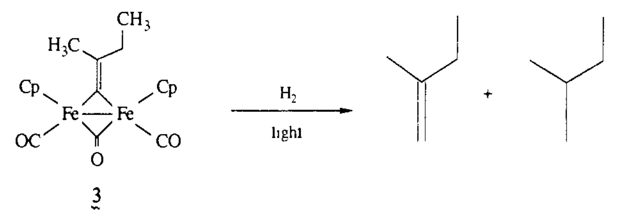
Photolysis of the μ-allene complexes in the presence of CO also led to release of the allene ligand. Under these conditions, trimethylsilyl-substituted μ-allene complexes **5** and **7** both were converted to **12** and the respective free allene with a time for half reaction of about 3 h. Ester-substituted allenes such as **4** reacted much more slowly ($t_{1/2}$ = 4 days) to give **12** and free substituted allenes.

Finally, the μ-allene complex **5** reacted with acetonitrile to produce an allene. When a solution of **5** was heated in $CD_3CN$ for 4 h, the allene $CH_2{=}C{=}CHSi(CH_3)_3$ was formed in 66% yield. Neither **4** nor **7** gave an allene when heated in $CD_3CN$.

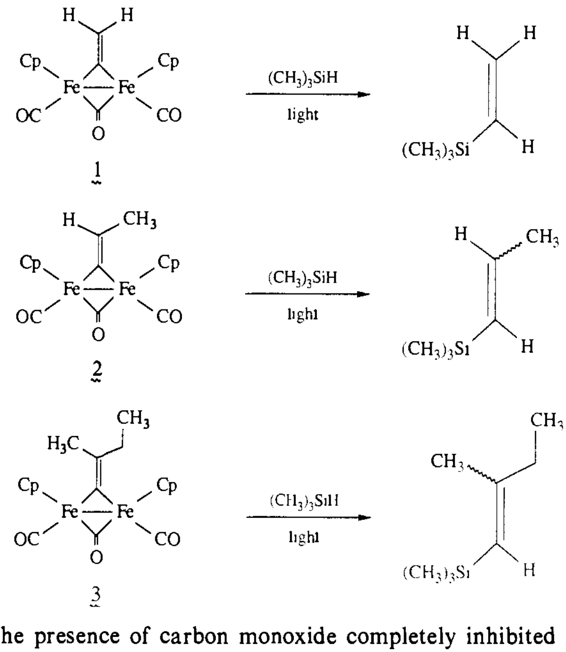
We have found that heating solutions of μ-allene diiron compounds under a CO atmosphere provides the most convenient method for release of the free allene.

**Cleavage of μ-Alkenylidene Complexes with Hydrogen or Trialkylsilanes.** When solutions of μ-alkenylidene compounds **1**, **2**, **3**, or $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHCH_2CH_2CH_3)$ (**11**) were photolyzed under a hydrogen atmosphere, mixtures of the expected alkene and the hydrogenated alkane were obtained. The iron-containing products were the iron dimer **12**, the iron tetramer $[C_5H_5(CO)Fe]_4$ (**13**),[20] and unidentified insoluble species. For example, photolysis of a solution of μ-alkenylidene diiron compound **3** in benzene-$d_6$ under $H_2$ for 10 h gave 2-methylbutane (48%), 2-methyl-1-butene (22%), **12** (46%), and **13** (24%).

The production of substantial amounts of alkane was observed in the reactions of each of the μ-alkenylidene compounds. The formation of alkanes is probably the result of hydrogenation of initially formed alkenes. The secondary hydrogenation of an initially formed alkene is supported by the observation that 1-hexene was hydrogenated to hexane when 1-hexene and **11** were photolyzed under a $H_2$ atmosphere. The secondary hydrogenation of initially formed alkenes to alkanes was partially suppressed at lower temperature. When a solution of **11** was photolyzed under $H_2$ at 0 °C for 6 h, 44% 1-pentene and only 13% pentane were observed by gas chromatography.



In an attempt to produce more highly functionalized organic products, we examined the photochemical reaction of μ-alkenylidene complexes with trialkylsilanes.[21] Photolysis of the μ-alkenylidene complexes **1**, **2**, and **3** in the presence of trimethylsilane produced vinylsilanes.[22] When a solution of **1** and trimethylsilane in benzene-$d_6$ was photolyzed for 6 h, the vinyl silane $(CH_3)_3SiCH{=}CH_2$ was formed in 70% yield. The soluble iron products from all the trialkylsilane cleavage reactions were identified by $^1H$ NMR as **12** (49–53%) and **13** (24–37%). Photolysis of μ-alkenylidene compound **2** with trimethylsilane for 3 h gave a 6:1 mixture of (*trans*-:*cis*-1-propenyl)trimethylsilane ($CH_3CH{=}CHSi(CH_3)_3$) in 77% yield. Similarly, photolysis of **3** and trimethylsilane for 2 h gave an essentially quantitative yield (100%) of a 1:1 mixture of (*Z*)-:(*E*)-(2-methyl-1-butenyl)trimethylsilane ($CH_3CH_2(CH_3)C{=}CHSi(CH_3)_3$).



The presence of carbon monoxide completely inhibited the formation of vinyl silanes under these conditions. When identical solutions of compound **2** and trimethylsilane were photolyzed with and without CO, vinylsilane was formed only in the absence of CO.

Photolysis was required for the cleavage of μ-alkylidene complexes with hydrogen and with trialkylsilanes. Thermolysis of μ-alkenylidene complexes in the presence of hydrogen or trialkylsilanes led only to cis–trans equilibration of the μ-alkylidene

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(20) (a) King, R. B. *Inorg. Chem.* **1966**, *5*, 2227–2230. (b) Neuman, M. A.; Trinh-Toan; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 3383–3388.

(21) For an example of photocatalyzed hydrosilation of alkenes see: Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 344–358.

(22) For syntheses of vinyl silanes see: (a) Petrov, A. D.; Mironov, V. F.; Glukhovtsev, V. G. *Zh. Obshch. Khim.* **1957**, *27*, 1535–1539. (b) Benkeser, R. A.; Hickner, R. A. *J. Am. Chem. Soc.* **1958**, *80*, 5298–5300. (c) Seyferth, D.; Vick, S. C. *J. Organomet. Chem.* **1978**, *144*, 1–12. (d) Boeckman, R. K.; Blum, D. M.; Ganem, B.; Halvey, N. *Org. Synth.* **1978**, *58*, 152. (e) Cunico, R. F.; Han, Y.-K. *J. Organomet. Chem.* **1979**, *174*, 247–262. (f) Westmijze, H.; Kleijn, H.; Vermeer, P. *J. Organomet. Chem.* **1984**, *276*, 317–323.

Table II. Photochemical $^{13}$CO Incorporation into **1**

| | *cis*-**1** | | | | *trans*-**1** | | | | combined *cis*- and *trans*-**1** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| time, min | % *cis*-**1**$^a$ | % $^{13}$CO$^b$ terminal | % $^{13}$CO$^b$ bridge | t/b$^c$ | % *trans*-**1**$^b$ | % $^{13}$CO$^b$ terminal | % $^{13}$CO$^b$ bridge | t/b$^c$ | % $^{13}$CO$^b$ terminal | % $^{13}$CO$^b$ bridge | % $^{13}$CO$^b$ total | t/b$^c$ |
| 0 | 70.5 | 0 | 0 | | 29.5 | 0 | 0 | | 0 | 0 | 0 | |
| 10 | 72.2 | 7.2 | 0.2 | 36 | 27.8 | 7.2 | 0.3 | 24 | 7.2 | 0.2 | 7.4 | 36 |
| 20 | 69.3 | 21.9 | 0.8 | 27 | 30.7 | 15.7 | 0.3 | 52 | 20.0 | 0.6 | 21.2 | 34 |
| 30 | 74.2 | 29.8 | 1.6 | 19 | 25.8 | 26.4 | 1.2 | 22 | 28.9 | 1.5 | 30.4 | 19 |
| 50 | 72.3 | 42.9 | 3.3 | 13 | 27.7 | 38.8 | 3.0 | 13 | 41.8 | 3.2 | 44.9 | 13 |
| 80 | 74.6 | 62.1 | 7.9 | 7.8 | 25.4 | 58.8 | 7.4 | 7.9 | 61.3 | 7.8 | 69.0 | 7.8 |

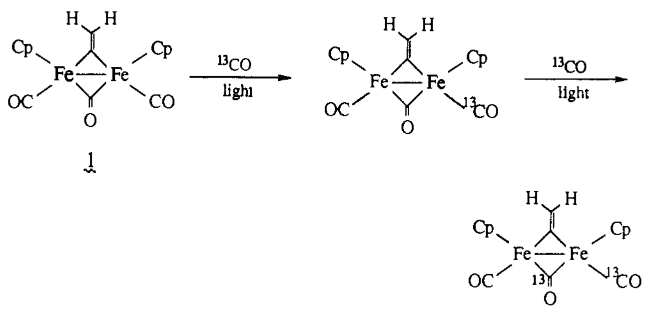
[a] Ratio of *cis*-**1**:*trans*-**1** determined by integration of Cp resonances; estimated error ±2%. [b] Excess over natural abundance; estimated errors are ±5% of value for terminal $^{13}$CO; estimated percentage errors for excess bridge $^{13}$CO are large at low <1.0% $^{13}$CO incorporation due to subtraction of natural abundance (e.g., 1.4 ± 0.2 − 1.1 = 0.4 ± 0.2). [c] Ratio of excess terminal $^{13}$CO:excess bridge $^{13}$CO.

complexes. For example, when a solution of **2** and trimethylsilane in benzene-$d_6$ was heated at 62 °C, 100% of both starting materials remained after 93 h.

**Photochemical $^{13}$CO Incorporation in $\mu$-Ethenylidene Complex 1.** The photochemical incorporation of $^{13}$CO into $\mu$-alkenylidene complexes was studied to gain information about the primary photochemical process involved in the photoinduced cleavage reactions of these compounds. A THF solution of a 2.4:1 mixture of *cis*- and *trans*-**1** under 1 atm of 99.5% $^{13}$CO was photolyzed at 15 °C. Aliquots were periodically withdrawn over 80 min and were analyzed by $^{13}$C NMR spectroscopy at 20 °C with Cr(acac)$_3$ and a 4.7 s relaxation delay to achieve accurate integrations. Control experiments demonstrated that thermal $^{13}$CO incorporation did not occur even when THF solutions of **1** were heated at 62 °C for 80 min and that thermal cis–trans isomerization of **1** did not occur at the temperature of the photolysis (15 °C) or $^{13}$C NMR analysis (20 °C, 30 min).[23]

The data summarized in Table II indicate that initial incorporation of $^{13}$CO occurs highly selectively at the terminal CO position of both *cis*- and *trans*-**1**. For example, after 20 min 21.9% $^{13}$CO was incorporated into the terminal position of *cis*-**1** but only 0.8% was incorporated into the bridging position. Because of the small amount of incorporation into the bridging position there are substantial errors in the ratio of terminal:bridge $^{13}$CO incorporation, but the ratio is certainly high (27 ± 7 for *cis*-**1** at 20 min). At longer photolysis times, $^{13}$CO incorporation into the bridging position became more extensive, and the ratio of terminal:bridge $^{13}$CO incorporation decreased. After 80 min, 62.1% $^{13}$CO was incorporated into the terminal position and 7.9% into the bridging position of *cis*-**1** and the ratio of terminal:bridge $^{13}$CO incorporation dropped to 7.8 ± 0.5. During the course of this $^{13}$CO exchange experiment, the ratio of *cis*-**1** to *trans*-**1** increased from about 70:30 to 75:25 as a photostationary state was approached.

In Figure 1, the percent $^{13}$CO label incorporated into the bridging site of **1** is plotted versus the total percent $^{13}$CO incorporated into **1**. The pronounced upward curvature of the plot is qualitatively consistent with a mechanism in which $^{13}$CO initially enters only the terminal position of **1** and in which reaction of terminal $^{13}$CO labeled **1** undergoes a second reaction that places some label in the bridging site.



We have developed a model that explains initial incorporation of $^{13}$CO exclusively into terminal sites and incorporation of $^{13}$CO into bridging sites after two sequential $^{13}$CO exchange events. Photolysis of **1** is suggested to proceed by ejection of a terminal carbonyl group and generation of a coordinatively unsaturated intermediate. The two requirements for the intermediate are (1) that it react with $^{13}$CO to give exclusively terminal $^{13}$CO labeled **1** and (2) that the two CO ligands in the intermediate must either be equivalent by symmetry or by reason of rapid site exchange.

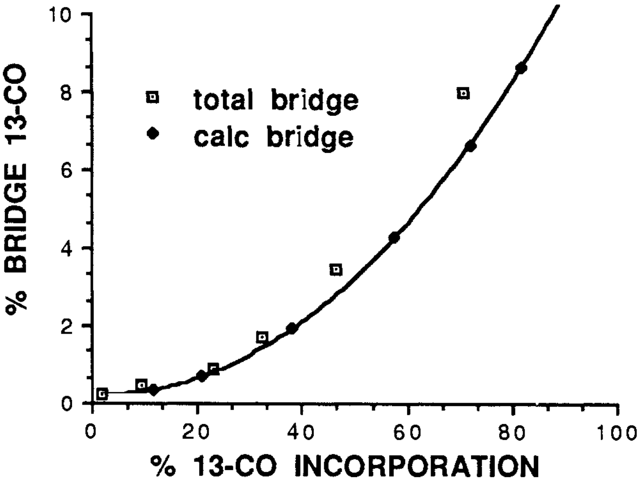


Figure 1. The combined percent $^{13}$CO in the bridging positions of *cis*- and *trans*-**1** is plotted versus the combined percent $^{13}$CO incorporation into both the terminal and bridging positions of *cis*- and *trans*-**1**. The line was calculated by using the model described in the text.

This model quantitatively predicts the rate of $^{13}$CO incorporation into the bridging site. Photolysis of terminal $^{13}$CO labeled **1** would lead to expulsion of $^{13}$CO or $^{12}$CO with equal probability. If $^{12}$CO is ejected, the resulting intermediate has symmetry-related $^{12}$CO and $^{13}$CO groups. When a second $^{13}$CO reacts with this intermediate, the new $^{13}$CO will enter a terminal site but the $^{13}$CO present in the intermediate will end up in the terminal and bridging sites of **1** with equal probability. Thus the rate of incorporation of $^{13}$CO into a bridging site of terminal labeled **1** is one quarter the rate of incorporation of $^{13}$CO into unlabeled **1**. Figure 1 shows the close agreement between the observed and calculated extent of incorporation of $^{13}$CO into the bridging position as a function of total $^{13}$CO incorporation. The experimental points show somewhat higher incorporation of $^{13}$CO into the bridging position than calculated from our model. This is probably due to the fact that we did not include corrections for dilution of the $^{13}$CO pool that occurs as the reaction progresses. In view of the nearly quantitative agreement between our model and the observed rate of $^{13}$CO incorporation into the bridging site, it is very unlikely that a second type of photochemical process not involving $^{13}$CO dissociation is responsible for our results. The quantum yield for such a nondissociative $^{13}$CO isomerization would have to be precisely one-half the quantum yield for $^{13}$CO incorporation.

## Discussion

The cis–trans isomerizations of $\mu$-ethenylidene compound **1**[24] and other bridged diiron[25,26] and diruthenium[27] compounds have

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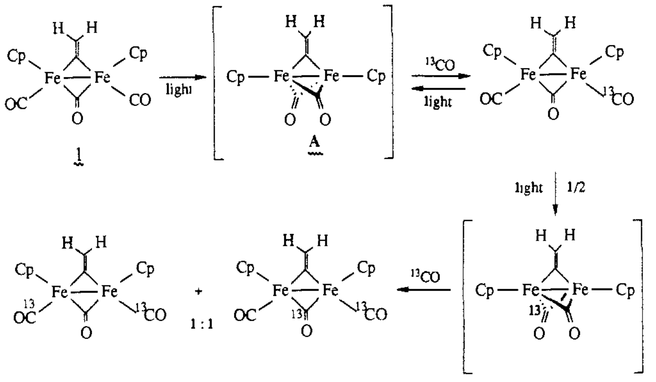
[23] Casey, C. P.; Austin, E. A., unpublished results.

[24] Dawkins, G. M.; Green, M.; Jeffery, J. C.; Sambale, C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 499–506.

been proposed to proceed via unbridging followed by rotation about the metal–metal bond and rebridging. A different class of intermediate with a site of coordinative unsaturation is required to explain the $^{13}CO$ exchange and cleavage reactions of μ-alkenylidene compounds reported here.

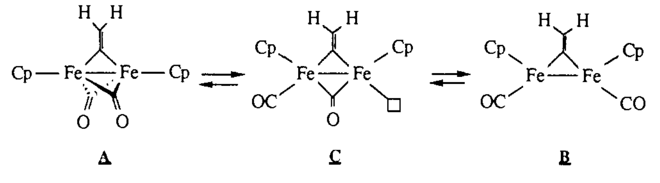
A number of possible formulations of the coordinatively unsaturated intermediate are consistent with our results. The prime candidate for the unsaturated intermediate is the triply bridged structure A that might be formed by the loss of a terminal CO, migration of the other terminal CO ligand to a bridging position, and movement of the Cp ligands to a position along the iron–iron axis. The related triply CO bridged complex $(C_5H_5Fe)_2(\mu\text{-}CO)_3$ has been observed in matrices at low temperature[28] as a product of the photolysis of $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)_2$ (**12**). The related pentamethylcyclopentadienyl compound $(C_5Me_5Fe)_2(\mu\text{-}CO)_3$ has been isolated.[29]

As $^{13}CO$ enters A at a terminal position, concurrent movement of one of the bridging CO's toward the opposite iron gives a μ-ethenylidene complex that contains label at a terminal position. Intermediate A accounts for the eventual appearance of label at the bridging position. Secondary photolysis of the initially formed terminal $^{13}CO$-labeled **1** could proceed by loss of $^{12}CO$ and formation of $^{13}CO$ bridge labeled A. Entry of a second $^{13}CO$ into a terminal position and unbridging of the unlabeled CO ligand provides a route to doubly labeled μ-ethenylidene complex **1** in which one $^{13}CO$ label occupies a bridging position and one $^{13}CO$ occupies a terminal position.

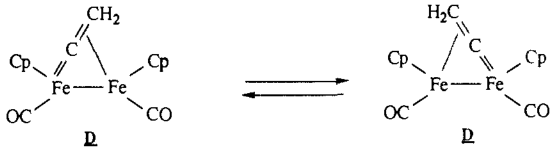


A second possible formulation of the symmetric intermediate is B in which both CO ligands are terminal. To be consistent with our results, B would have to be formed by loss of a terminal CO and migration of a bridging CO to a terminal position.

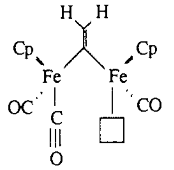
The unsymmetric intermediate C is also a viable candidate for the coordinatively unsaturated intermediate but only if it undergoes bridge–terminal CO exchange (possibly via A or B) more rapidly that it is trapped by $^{13}CO$.

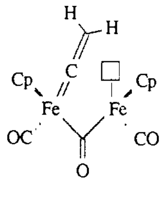


Similarly a side-on vinylidene structure D that is nominally coordinatively saturated is another candidate for the reactive intermediate. It could explain our results only if it were formed by loss of a terminal CO followed by rearrangement and if vinylidene migration from iron to iron via intermediate B is more rapid than trapping with $^{13}CO$. Knox has isolated the side-on dicoordinated vinylidene complex $[C_5Me_5(CO)_2Mo]_2(\mu\text{-}\eta^1,\eta^2\text{-}C{=}C{=}CH_2)$ and shown that it reacts with diazomethane to produce an allene complex.[17b]

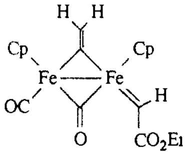


Our $^{13}CO$ incorporation results are inconsistent with structures such as E[30] and F[31] for the coordinatively unsaturated intermediate. E or F could incorporate $^{13}CO$ by an addition–elimination route that would place equal amounts of $^{13}CO$ at the bridging and terminal positions.


**E**


**F**

The reactions of μ-alkenylidene complexes **1**, **2**, **3**, and **11** with diazo compounds, dihydrogen, and trimethylsilane can all be explained by the intervention of a coordinatively unsaturated μ-alkenylidene intermediate generated by the photoinduced loss of CO. Oxidative addition to the vacant site of this coordinatively unsaturated intermediate followed by rearrangement and coupling lead to the observed products. For example, we propose that the diazo compound reacts with the coordinatively unsaturated intermediate to transfer a carboethoxycarbene to iron to produce diiron complex G that contains a bridging alkenylidene ligand and a terminal carbene ligand derived from the diazo compound. Coupling of the two carbene ligands of G then produces a diiron–allene complex. Similarly, the reactions of μ-alkenylidene complexes with $H_2$ and $HSiR_3$ are suggested to proceed via oxidative addition of $H_2$ or $HSiR_3$ to the coordinatively unsaturated intermediate followed by two reductive eliminations to produce alkenes or vinyl silanes.


**G**

## Summary

Diiron μ-alkenylidene complexes undergo a photochemically induced reaction with diazo compounds, hydrogen, or trialkylsilanes to give diiron μ-allene complexes, free alkenes, and vinylsilanes. From a study of the photochemical $^{13}CO$ incorporation we propose that the reaction proceeds through a coordinatively unsaturated intermediate, possibly the triply bridging complex $(C_5H_5Fe)_2(\mu\text{-}CO)_2(\mu\text{-}C{=}CH_2)$ (A). This intermediate can then oxidatively add the other reagents we have examined.

Two of these classes of cleavage reactions appear to be promising: the reaction of μ-alkenylidenes with trialkylsilanes to give vinyl silanes and the cleavage of μ-allene complexes to give allenes.

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(26) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417–1426.

(27) Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 861–862.

(28) (a) Hooker, R. H.; Mahmoud, K. A.; Rest, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1022–1024. (b) Hepp, A. F.; Blaha, J. P.; Lewis, C.; Wrighton, M. S. *Organometallics* **1984**, *3*, 174–177.

(29) Blaha, J. P.; Bursten, B. E.; Dewan, J. C.; Frankel, R. B.; Randolph, C. L.; Wilson, B. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 4561–4562.

(30) An intermediate similar to *E* has been proposed by Ziegler to explain the thermal cis–trans isomerization of $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$. Altbach, M. I.; Muedas, C. A.; Korswagen, R. P.; Ziegler, M. L. *J. Organomet. Chem.* **1986**, *306*, 375–383.

(31) An intermediate similar to *F* has been suggested by Gray in the photochemical reaction of $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)_2$ with phosphines. Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 6018–6021.

Our work on the cleavage of neutral diiron complexes by these and similar methods is continuing.

## Experimental Section

**General.** $^1H$ NMR were obtained on Bruker WP200, WP270, or AM500 spectrometers. $^{13}C$ NMR were obtained on JEOL FX-200 (50.1 MHz) or Brucker AM500 (126 MHz) spectrometers with 0.07 M $Cr(acac)_3$ as a shiftless relaxation agent. Infrared spectra were measured on Beckman 4230 or Mattson Polaris infrared spectrometers. Mass spectra were determined on a Kratos MS-80.

Air-sensitive materials were manipulated in an inert-atmosphere glovebox or by standard high-vacuum and Schlenk techniques. Diethyl ether, THF, toluene, and hexane were distilled from purple solutions of sodium and benzophenone. $CH_2Cl_2$ and acetone were dried over $P_2O_5$ and $B_2O_3$, respectively. Chromatography was conducted on activity III alumina prepared by addition of 6% water by weight.

Photolyses were conducted in a Rayonet photochemical reactor equipped with 16 Sylvania F8T5 black light bulbs with maximum emission at 366 nm. Reaction solutions were contained in a jacketed Pyrex vessel.

**$[C_5H_5(CO)Fe]_2(\mu\text{-}CH_2{=}C{=}CHCO_2CH_2CH_3)$ (4).** A solution of **1** (202 mg, 0.57 mmol) and ethyl diazoacetate (370 $\mu$L, 0.40 g, 3.5 mmol) in dry, deoxygenated toluene (32 mL) was photolyzed at 0 °C. The reaction was followed by examining aliquots by IR spectroscopy and monitoring the disappearance of the bridging carbonyl band of **1**. After 3.5 h, the solvent and excess diazo compound were evaporated under high vacuum. Column chromatography (alumina, 2:1 hexane:$CH_2Cl_2$) of the residue gave **1** (10 mg, 5%) and green solid **4** (113 mg, 48%), mp (sealed capillary) 88–92 °C dec. $^1H$ NMR (acetone-$d_6$, 200 MHz) $\delta$ 4.39 (s, $C_5H_5$), 4.28 (s, $C_5H_5$), 4.06 (q, $J$ = 7.2 Hz, $OCH_2$), 3.84 (dd, $J$ = 1.2, 4.1 Hz, 1 H), 3.49 (dd, $J$ = 2.3, 4.1 Hz, 1 H), 3.29 (dd, $J$ = 1.2, 2.3 Hz, 1 H), 1.24 (t, $J$ = 7.2 Hz, $CH_3$). $^{13}C$ NMR (acetone-$d_6$, 50.1 MHz) $\delta$ 227.8 (CO), 226.5 (CO), 219.3 ($\mu$-C), 173.2 ($CO_2$), 83.9 (d, $J$ = 180 Hz, $C_5H_5$), 83.6 (d, $J$ = 176 Hz, $C_5H_5$), 59.9 (t, $J$ = 146 Hz, $\mathit{C}H_2CH_3$), 36.2 (t, $J$ = 150 Hz, $=CH_2$), 34.6 (d, $J$ = 168 Hz, $=\mathit{C}HCO_2$), 15.0 (q, $J$ = 128 Hz, $CH_3$). IR ($CH_2Cl_2$) 1947 (s), 1921 (s), 1693 (s) cm$^{-1}$. HRMS calcd for $C_{18}H_{18}Fe_2O_4$ 409.9904, found 409.9911.

**$[C_5H_5(CO)Fe]_2[\mu\text{-}CH_2{=}C{=}CHSi(CH_3)_3]$ (5).** A solution of **1** (194 mg, 0.55 mmol) and (trimethylsilyl)diazomethane (2.5 mL, 0.59 M in hexane, 1.48 mmol) in toluene (26 mL) was photolyzed at 0 °C for 4.5 h. Evaporation of solvent under high vacuum and chromatography (alumina, 6:1 hexane:$CH_2Cl_2$) of the residue gave $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHSi(CH_3)_3]$ (**10**) (12%) and green solid **5** (135 mg, 60%), mp (sealed capillary) 87–93 °C dec. $^1H$ NMR (acetone-$d_6$, 270 MHz) $\delta$ 4.29 (s, $C_5H_5$), 4.22 (s, $C_5H_5$), 3.40 (dd, $J$ = 1.6, 3.4 Hz, 1 H), 2.97 (t, $J$ = 3.4 Hz, 1 H), 2.70 (dd, $J$ = 1.5, 3.3 Hz), 0.14 (s, $Si(CH_3)_3$). $^{13}C$ NMR (acetone-$d_6$, 126 MHz) $\delta$ 228.8 (CO), 228.1 (CO), 222.8 ($\mu$-C), 83.4 (d, $J$ = 176 Hz, $C_5H_5$), 81.6 (d, $J$ = 174 Hz, $C_5H_5$), 37.1 (d, $J$ = 147 Hz, $=CH$), 28.9 (coupling not observed, $=CH_2$), –0.03 (q, $J$ = 121 Hz, $Si(CH_3)_3$). IR ($CH_2Cl_2$) 1929 (s), 1902 (vs) cm$^{-1}$. UV/vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\epsilon$) 230 (4.21), 368 (3.61), 490 (2.93), 620 (2.63). HRMS calcd for $C_{18}H_{22}Fe_2O_2Si$ 410.0081, found 410.0063.

**CO Inhibition of the Reaction of 1 and $(CH_3)_3SiCH{=}N_2$.** A solution of **1** (4.0 mg, 0.0011 mmol) and (trimethylsilyl)diazomethane (2.0 mg, 0.018 mmol) in benzene-$d_6$ (1.0 mL) was divided between three NMR tubes. Tube 1 was sealed under vacuum. Tube 2 was placed under CO (0.72 atm) and sealed. Tube 3 was sealed and wrapped in aluminum foil to exclude light. All the tubes were treated identically and exposed to laboratory fluorescent light and periodically monitored by $^1H$ NMR. Only tube 1 showed a reaction to give $\mu$-allene compound **4**. Neither tube 2 nor tube 3 showed any change throughout the course of the reaction.

**$[C_5H_5(CO)Fe]_2(\mu\text{-}CH_3CH{=}C{=}CHCO_2CH_2CH_3)$ (6).** A solution of **2** (211 mg, 0.58 mmol) and ethyl diazoacetate (370 $\mu$L, 0.40 g, 3.5 mmol) in THF (40 mL) was photolyzed at 15 °C for 4 h. Evaporation of solvent under high vacuum and chromatography (alumina, 5:2 hexane:$CH_2Cl_2$) of the residue gave green solid **6** (105 mg, 43%), mp (open capillary) 86–92 °C dec. $^1H$ NMR (acetone-$d_6$, 270 MHz) major isomer, $\delta$ 4.94 (dq, $J$ = 1.5, 6.4 Hz, $=C\mathit{H}CH_3$), 4.45 (s, $C_5H_5$), 4.38 (s, $C_5H_5$), 4.00 (q, $J$ = 7.2 Hz, $CO_2CH_2$), 2.95 (d, $J$ = 1.5 Hz, $=CHCO_2$), 2.09 (d, $J$ = 6.4 Hz, $CHC\mathit{H}_3$), 1.22 (t, $J$ = 7.2 Hz, $CH_3$); minor isomer (some resonances obscured), $\delta$ 4.35 (s, $C_5H_5$), 4.25 (s, $C_5H_5$), 3.02 (d, $J$ = 2.3 Hz, $=CHCO_2$), 1.68 (d, $J$ = 6.2 Hz, $CHC\mathit{H}_3$). $^{13}C\{^1H\}$ (acetone-$d_6$, 126 MHz) major isomer, $\delta$ 228.8 (CO), 224.9 (CO), 219.2 ($\mu$-C), 174.0 ($CO_2$), 84.6 ($C_5H_5$), 83.1 ($C_5H_5$), 59.7 ($CO_2\mathit{C}H_2$), 56.3 ($=\mathit{C}HCH_3$), 31.5 ($=\mathit{C}HCO_2$), 24.7 ($=CH\mathit{C}H_3$), 15.0 ($CH_3$); minor isomer, $\delta$ 228.2 (CO), 226.7 (CO), 215.7 ($\mu$-C), 173.3 ($CO_2$), 83.6 ($C_5H_5$), 83.5 ($C_5H_5$), 59.8 ($CO_2\mathit{C}H_2$), 54.0 ($=\mathit{C}HCH_3$), 32.3 ($=\mathit{C}HCO_2$), 24.6 ($=CH\mathit{C}H_3$), 15.0 ($CH_3$). IR ($CH_2Cl_2$) 1945 (s), 1916 (s), 1684 (m) cm$^{-1}$. HRMS calcd for $C_{19}H_{20}Fe_2O_4$ 424.0060, found 424.0042.

**$[C_5H_5(CO)Fe]_2[\mu\text{-}CH_3CH{=}C{=}CHSi(CH_3)_3]$ (7).** A solution of **2** (300 mg, 0.82 mmol) and (trimethylsilyl)diazomethane (3.0 mL, 0.59 M in hexane, 1.73 mmol) in $CH_2Cl_2$ (50 mL) was photolyzed at 0 °C for 3.5 h. Evaporation of solvent and flash chromatography (alumina, 9:1 hexane:$CH_2Cl_2$) of the residue gave green solid **7** (190 mg, 55%), mp (open capillry) 104–110 °C dec. $^1H$ NMR (acetone-$d_6$, 270 MHz) major isomer, $\delta$ 4.29 (s, $C_5H_5$), 4.21 (s, $C_5H_5$), 3.72 (dq, $J$ = 3.2, 6.3 Hz, $=C\mathit{H}CH_3$), 2.35 (d, $J$ = 3.2 Hz, $=CHSi$), 1.66 (d, $J$ = 6.3 Hz, $C_3$), 0.17 (s, $Si(CH_3)_3$); minor isomer (some resonances obscured), $\delta$ 4.48 (s, $C_5H_5$), 4.13 (s, $C_5H_5$), 1.99 (d, $J$ = 6.3 Hz, $CH_3$), 0.068 (s, $Si(CH_3)_3$). $^{13}C$ NMR (benzene-$d_6$, 126 MHz) major isomer, $\delta$ 228.7 (CO), 227.6 (CO), 218.6 ($\mu$-C), 82.8 (d, $J$ = 176 Hz, $C_5H_5$), 81.0 (d, $J$ = 176 Hz, $C_5H_5$), 45.4 (d, $J$ = 164 Hz, $=\mathit{C}HCH_3$), 34.5 (d, $J$ = 144 Hz, $=\mathit{C}HSi$), 25.7 (q, $J$ = 127 Hz, $CH_3$), 0.56 (q, $J$ = 118 Hz, $Si(CH_3)_3$). IR ($CH_2Cl_2$) 1923 (s), 1900 (vs) cm$^{-1}$. HRMS calcd for $C_{19}H_{24}Fe_2O_2Si$ 424.0237, found 424.0245.

**$[C_5H_5(CO)Fe]_2[\mu\text{-}CH_3CH{=}C{=}C(CH_3)CO_2CH_3]$ (8).** A solution of **2** (205 mg, 0.56 mmol) and methyl 2-diazopropionate (520 $\mu$L, 4.9 mmol) in toluene (29 mL) was photolyzed at 0 °C. More methyl 2-diazopropionate (230 mL, 2.16 mmol) was added via syringe after 5 h. The reaction was stopped after 7 h and all solvent was evaporated. Chromatography (alumina, 2:1 hexane:$CH_2Cl_2$) of the residue gave green solid **8** (44 mg, 19%), mp (open capillary) 117–126 °C dec. $^1H$ NMR (acetone-$d_6$, 270 MHz) major isomer, $\delta$ 4.55 (s, $C_5H_5$), 4.19 (s, $C_5H_5$), 3.93 (q, $J$ = 6.5 Hz, CH), 3.66 (s, $CO_2CH_3$), 1.86 (s, $CH_3$), 1.52 (d, $CHC\mathit{H}_3$); minor isomer (some resonances obscured), $\delta$ 4.30 (s, $C_5H_5$), 3.75 (s, $C_5H_5$). $^{13}C\{^1H\}$ NMR (benzene-$d_6$, 126 MHz) $\delta$ 227.3 (CO), 225.9 (CO), 218.1 ($\mu$-C), 174.0 ($CO_2$), 84.1 ($C_5H_5$), 82.4 ($C_5H_5$), 50.9, 50.7 ($CO_2\mathit{C}H_3$, $=\mathit{C}HCH_3$), 48.7 ($=C$), 26.3 ($CH_3$), 24.8 ($CH_3$). IR ($CH_2Cl_2$) 1934 (s), 1910 (s), 1683 (m) cm$^{-1}$. HRMS calcd for $C_{19}H_{20}Fe_2O_4$ 396.0105, found 396.0103.

**$[C_5H_5(CO)Fe]_2[\mu\text{-}CH_3CH_2(CH_3)C{=}C{=}CHCO_2CH_2CH_3]$ (9).** A solution of **3** (440 mg, 1.12 mmol) and ethyl diazoacetate (450 $\mu$L, 0.488 mg, 4.3 mmol) in $CH_2Cl_2$ (75 mL) was photolyzed at 0 °C for 3 h. Evaporation of solvent under high vacuum and chromatography (alumine, 2:1 hexane:$CH_2Cl_2$) of the residue gave green solid **9** (230 mg, 46%), mp (open capillary) 86–90 °C dec. $^1H$ NMR (benzene-$d_6$, 500 MHz) major isomer, $\delta$ 4.28 (s, $C_5H_5$), 4.03 (q, $J$ = 7.5 Hz, $CO_2CH_2$), 3.87 (s, $C_5H_5$), 2.89 (s, $=CH$), 2.36 (dq, $J$ = 7.1, 14.3 Hz, $C\mathit{H}H$), 1.95 (dq, $J$ = 7.1, 14.3 Hz, $CH\mathit{H}$), 1.63 (s, $CH_3$), 1.54 (t, $J$ = 7.1 Hz, $CH_3$), 1.05 (t, $J$ = 7.5 Hz, ester $CH_3$); minor isomer (some resonances obscured), $\delta$ 4.29 (s, $C_5H_5$), 3.91 (s, $C_5H_5$), 2.25 (dq, $J$ = 7.4, 14.0 Hz, $C\mathit{H}H$), 2.07 (s, $CH_3$), 1.67 (dq, $J$ = 7.4, 14.0 Hz, $CH\mathit{H}$), 1.13 (t, $J$ = 7.4 Hz, $CH_3$). $^{13}C$ NMR (benzene-$d_6$, 126 MHz) major isomer, $\delta$ 228.7 ($\mu$-C), 224.0 (CO), 215.6 (CO), 173.5 ($CO_2$), 83.6 (d, $J$ = 176 Hz, $C_5H_5$), 82.8 (d, $J$ = 176 Hz, $C_5H_5$), 81.3 (s, $=C$), 59.4 (t, $J$ = 142 Hz, $CO_2\mathit{C}H_2$), 37.8 (t, $J$ = 135 Hz, $CH_2$), 31.3 (q, $J$ = 126 Hz, $C\mathit{C}H_3$), 28.7 (d, $J$ = 168 Hz, $=\mathit{C}H$), 15.3 (q, $J$ = 125 Hz, $CH_3$), 14.9 (q, $J$ = 130 Hz, $CH_3$); minor isomer (some resonance not observed), $\delta$ 224.5 (CO), 215.8 (CO), 83.2 (d, $J$ = 176 Hz, $C_5H_5$), 82.8 (coupling not resolved, $C_5H_5$), 80.1 (s, $=C$), 41.1 (t, $J$ = 126 Hz, $CH_2$), 29.8 (d, $J$ = 156 Hz, $=CH$), 28.6 (coupling not resolved, $CH_3$), 14.9 (coupling not resolved, $CH_3$), 12.4 (q, $J$ = 120 Hz, $CH_3$). IR ($CH_2Cl_2$) 1934 (s), 1909 (vs), 1683 (m) cm$^{-1}$. HRMS calcd for $C_{21}H_{24}Fe_2O_4$ 452.0373, found 452.0379.

**$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHSi(CH_3)_3]$ (10).** A solution of $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)_2$ (**12**) (300 mg, 0.85 mmol) and (trimethylsilyl)diazomethane (5.3 mL, 0.59 M in hexane, 3.1 mmol) in toluene (38 mL) was photolyzed at 0 °C for 4 h. Evaporation of solvent and chromatography (alumina, 4:1 hexane:$CH_2Cl_2$) of the residue gave red solid **10** (148 mg, 42%), mp (open capillary) 172–176 °C dec. $^1H$ NMR (acetone-$d_6$, 270 MHz) $\delta$ 11.60 (s, $\mu$-CH), 4.89 (s, $C_5H_5$), 0.25 (s, $Si(CH_3)_3$). $^{13}C$ NMR (benzene-$d_6$, 126 MHz) $\delta$ 270.5 ($\mu$-CO), 212.6 (CO), 159.8 (d, $J$ = 110 Hz, $\mu$-CH), 87.2 (d, $J$ = 178 Hz, $C_5H_5$), 3.4 (q, $J$ = 118 Hz, $Si(CH_3)_3$). IR ($CH_2Cl_2$) 1973 (s), 1934 (m), 1774 (s) cm$^{-1}$. HRMS calcd for $C_{17}H_{20}Fe_2O_3Si$ 411.9880, found 411.9887.

Anal. Calcd for $C_{17}H_{20}Fe_2O_3Si$: C, 49.55; H, 4.89. Found: C, 49.44; H, 4.94.

**Cleavage of 9 with CO.** **9** (7.0 mg, 0.015 mmol) and 4,4′-dimethylbiphenyl (4.0 mg, 0.022 mmol) as internal standard were dissolved in benzene-$d_6$ (0.53 mL) and sealed in an NMR tube under CO (0.72 atm). The solution was heated at 62 °C and monitored periodically by $^1H$ NMR. After 21 h, all of **9** had been converted to **12** (84%) and allene $CH_3CH_2(CH_3)C{=}C{=}CHCO_2CH_2CH_3$ (97%). $^1H$ NMR (benzene-$d_6$) $\delta$ 5.70 (q, $J$ = 2.9 Hz, 1 H), 4.05 (q, $J$ = 7.1 Hz, 1 H), 4.00 (q, $J$ = 7.1 Hz, 1 H), 1.72 (m, 2 H), 1.46 (d, $J$ = 2.9 Hz, 3 H), 0.96 (t, $J$ = 7.2 Hz, 3 H), 0.89 (t, $J$ = 7.4 Hz, 3 H). GC/MS calcd for $C_9H_{14}O_2$ 154.1, found 154.2.

**Cleavage of 7 with Oxygen.** **7** (6.0 mg, 0.014 mmol) and 4,4′-dimethylbiphenyl (3.0 mg, 0.016 mmol) as an internal standard were dissolved in benzene-$d_6$ (0.57 mL) and solution equally divided between two NMR tubes. Each was capped under $N_2$ and initial $^1$H NMR spectra were taken. Both samples were then degassed and sealed under $O_2$ (0.68 atm). After sitting overnight, $^1$H NMR showed the products to be ferrocene (10%) and the allene $CH_3CH{=}C{=}CHSi(CH_3)_3$ (57%). $^1$H NMR (benzene-$d_6$) $\delta$ 4.96 (dq, $J$ = 6.9, 4.1 Hz, 1 H), 4.72 (dq, $J$ = 6.9, 7.0 Hz, 1 H), 1.53 (dd, $J$ = 7.0, 4.1 Hz, 3 H), 0.12 (s, 9 H). GC/MS calcd for $C_7H_{14}Si$ 126.1, found 126.1.

**Cleavage of 7 with Carbon Monoxide and Light.** **7** (8.0 mg, 0.019 mmol) and 4,4′-dimethylbiphenyl (4.0 mg, 0.022 mmol) as an internal standard were dissolved in benzene-$d_6$ (0.69 mL) and sealed under CO (0.72 atm). Photolysis at 15 °C for 21 h gave **12** (91%), **13** (3%), and allene $CH_3CH{=}C{=}CHSi(CH_3)_3$ (94%).

**Cleavage of 5 with $CD_3CN$.** **5** (9.0 mg, 0.022 mmol) and 4,4′-dimethylbiphenyl (5.0 mg, 0.027 mmol) as an internal standard were dissolved in $CD_3CN$ (1.0 mL) and sealed under vacuum. Heating for 4 h at 65 °C caused complete conversion of starting material. $^1$H NMR showed the products to be ferrocene (35%), a peak at $\delta$ 4.94 assigned to $[(C_5H_5)(NCCH_3)Fe]_2(\mu\text{-}CO)_2$ (33%), and the allene $CH_2{=}C{=}CHSi(CH_3)_3$ (66%). $^1$H NMR ($CD_3CN$) $\delta$ 4.93 (t, $J$ = 7.2 Hz, 1 H), 4.31 (d, $J$ = 7.2 Hz, 2 H), 0.089 (s, 9 H).

**$CH_2{=}C{=}CHCO_2CH_2CH_3$.** $^1$H NMR (benzene-$d_6$) $\delta$ 5.56 (t, $J$ = 6.6 Hz, 1 H), 4.62 (d, $J$ = 6.6 Hz, 2 H), 3.97 (q, $J$ = 7.1 Hz, 2 H), 0.92 (t, $J$ = 7.0 Hz, 3 H). GC/MS calcd for $C_6H_8O_2$ 112.0522, found 112.0528.

**$CH_3CH{=}C{=}CHCO_2CH_2CH_3$.** $^1$H NMR (benzene-$d_6$) $\delta$ 5.62 (dq, $J$ = 6.8, 4.0 Hz, 1 H), 5.10 (dq, $J$ = 6.8, 7.3 Hz, 1 H), 4.04 (dq, $J$ = 6.4, 7.3 Hz, 1 H), 3.98 (dq, $J$ = 6.4, 7.3 Hz, 1 H), 1.19 (dd, $J$ = 4.0, 7.3 Hz, 3 H), 0.94 (t, $J$ = 7.3 Hz, 3 H). GC/MS calcd for $C_7H_{10}O_2$ 126.0678, found 126.0630.

**$CH_2{=}C{=}CHSi(CH_3)_3$.** $^1$H NMR (benzene-$d_6$) $\delta$ 4.88 (t, $J$ = 7.0 Hz, 1 H), 4.27 (d, $J$ = 7.0 Hz, 2 H), 0.084 (s, 9 H). GC/MS calcd for $C_6H_{12}Si$ 112.0705, found 112.0704.

**$CH_3CH{=}C{=}C(CH_3)CO_2CH_3$.** $^1$H NMR (benzene-$d_6$) $\delta$ 5.09 (qq, $J$ = 3.0, 7.1 Hz, 1 H), 3.40 (s, 3 H), 1.91 (d, $J$ = 3.0 Hz, 3 H), 1.40 (d, $J$ = 7.1 Hz, 3 H). GC/MS calcd for $C_7H_{10}O_2$ 126.1, found 126.1.

**Reaction of 11 with $H_2$ and Light.** **11** (250 mg, 0.63 mmol) and heptane (93 $\mu$L, 0.64 mmol) as an internal standard were dissolved in toluene (55 mL) and placed under a $H_2$ atmosphere. The solution was photolyzed at 0 °C and monitored by GC for the production of 1-pentene and pentane with a $AgNO_3$ column. The following yields were recorded, time (min) (% 1-pentene/% pentane): 40 (18/9), 120 (25/5), 170 (29/14), 215 (29/10), 270 (43/17), 325 (44/16), 385 (44/13).

**Reaction of 1 with Trimethylsilane.** **1** (9.0 mg, 0.026 mmol) and 4,4′-dimethylbiphenyl (5.0 mg, 0.027 mmol) as an internal standard were dissolved in benzene-$d_6$ (0.64 mL) and equally divided between two NMR tubes. Trimethylsilane (0.058 atm in 5.1 mL, 0.013 mmol) was added to each tube and the tubes were sealed. Photolysis of one tube for 6 h gave **12** (49%), **13** (24%), ferrocene (2%), and vinylsilane $(CH_3)_3SiCH{=}CH_2$ (70%). $^1$H NMR (benzene-$d_6$) $\delta$ 6.17 (dd, $J$ = 14.7, 20.1 Hz, 1 H), 5.91 (dd, $J$ = 3.9, 14.7 Hz, 1 H), 5.66 (dd, $J$ = 3.9, 20.1 Hz, 1 H), 0.049 (s, 9 H). GC/MS calcd for $C_5H_{12}Si$ 100.1, found 100.1.

**Reaction of 2 with Trimethylsilane.** **2** (11.0 mg, 0.030 mmol) and 4,4′-dimethylbiphenyl (7.0 mg, 0.038 mmol) as internal standard were dissolved in benzene-$d_6$ (0.79 mL) and divided between two NMR tubes. Trimethylsilane (0.066 atm in 5.1 mL, 0.015 mmol) was added to one tube and the tube was sealed. Photolysis for 3 h gave **12** (57%), **13** (32%), ferrocene (2%), and vinylsilane $(CH_3)_3SiCH{=}CHCH_3$ (77%) as a 6:1 mixture of trans and cis isomers. $^1$H NMR (benzene-$d_6$) trans: $\delta$ 6.01 (dq, $J$ = 18.3, 6.1 Hz, 1 H), 5.69 (dq, $J$ = 18.3, 1.6 Hz, 1 H), 1.69 (dd, $J$ = 6.1, 1.6 Hz, 3 H), 0.089 (s, 9 H); cis (some resonances obscured): $\delta$ 1.65 (dd, $J$ = 7.0, 1.6 Hz, 3 H), 0.15 (s, 9 H). GC/MS calcd for $C_6H_{14}Si$ 114.1, found 114.0.

**Reaction of 3 with Trimethylsilane.** **3** (9.0 mg, 0.023 mmol) and 4,4′-dimethylbiphenyl (4.0 mg, 0.022 mmol) as an internal standard were dissolved in benzene-$d_6$ (0.66 mL) and divided between two NMR tubes. Trimethylsilane (0.053 atm in 5.1 mL, 0.024 mmol) was added to both tubes and they were sealed. Photolysis of one tube for 2 h gave **12** (53%), **13** (37%), and vinylsilane $(CH_3)_3Si(CH_3)C{=}C(CH_3)CH_2CH_3$ (100%) as a 1:1 mixture of isomers that were indistinguishable by $^1$H NMR. $^1$H NMR (benzene-$d_6$) first isomer, $\delta$ 5.36 (q, $J$ = 1.1 Hz, 1 H), 1.97 (dq, $J$ = 1.1, 7.4 Hz, 2 H), 1.70 (s, 3 H), 0.94 (t, $J$ = 7.4 Hz, 3 H), 0.16 (s, 9 H); second isomer, $\delta$ 5.29 (q, $J$ = 1.5 Hz, 1 H), 2.07 (q, $J$ = 7.5 Hz, 2 H), 1.74 (d, $J$ = 1.2 Hz, 3 H), 0.96 (t, $J$ = 7.5 Hz, 3 H), 0.19 (s, 9 H). GC/MS calcd for $C_8H_{18}Si$ 142.1173, found 142.1192.

**Reaction of 2 with Trimethylsilane with and without CO.** **2** (4.0 mg, 0.011 mmol) and 4,4′-dimethylbiphenyl (3.0 mg, 0.016 mmol) as an internal standard were dissolved in benzene-$d_6$ (1.0 mL) and divided between two NMR tubes. Trimethylsilane (0.018 atm in 5.1 mL, 0.004 mmol) was added to each tube. One tube was sealed under vacuum and one under CO (0.72 atm). Both tubes were photolyzed for 3.5 h. $^1$H NMR of the tube with CO showed **2** (100%) and no vinylsilane. The tube without CO showed **12** (75%), **13** (20%), ferrocene (7%), and vinylsilane $(CH_3)_3SiCH{=}CHCH_3$ (90%) as a >9:1 mixture of trans:cis isomers.

**$^{13}$CO Incorporation into 1.** A solution of **1** (306 mg, 0.87 mmol) in THF (46 mL) was photolyzed under $^{13}$CO (99.5% $^{13}$C, 1 atm) at 15 °C for 80 min. Samples (5 mL) were withdrawn by syringe at 10, 20, 30, 50, and 80 min for analysis by $^{13}$C NMR. The solvent was removed from each aliquot and $Cr(acac)_3$ (15 mg) was added and the combined solids were dissolved in benzene-$d_6$ (0.30 mL). $^{13}$C NMR {$^1$H} data were gathered with use of a relaxation delay of 4.7 s to achieve accurate integrations for all the different carbons in the molecule. Data from $t$ = 0 spectra: $^{13}$C {$^1$H} NMR (benzene-$d_6$, 126 MHz) *cis*-**1**, $\delta$ 276.7 ($\mu$-C), 268.9 ($\mu$-CO), 211.4 (CO), 125.8 ($CH_2$), 87.7 ($C_5H_5$); *trans*-**1**, $\delta$ 279.0 ($\mu$-C), 269.5 ($\mu$-CO), 212.1 (CO), 125.4 ($CH_2$), 90.0 ($C_5H_5$).

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