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Formation of an (α-pyrone)Fe(CO)$_3$ Complex in the Reaction of a *tert*-Butyl-Substituted (Alkynylcarbene)iron(0) Complex with Cyclohexadiene

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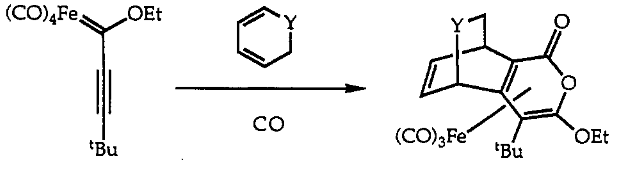
Summary: *(η^4-α-pyrone)Fe(CO)$_3$ complexes (**2**) are formed in the reactions of [(3,3-dimethylbutynyl)ethoxymethylene]Fe(CO)$_4$ (**1a**) with 1,3-cyclohexadiene, 1,3-cycloheptadiene, and cycloheptatriene under CO pressure. However, an (η^4-vinylketene)iron complex (**3**) is formed as the major product in the reaction of [((trimethylsilyl)ethynyl)ethoxymethylene]Fe(CO)$_4$ (**1b**) with cyclohexadiene.*

Many interesting and valuable reactions have been devised by using various Fischer carbene complexes,[1] including those having alkenyl or alkynyl substituents at the carbene carbons.[2] Recently, we have reported the synthesis of (alkynylcarbene)iron(0) complexes **1** and the formation of (η^1-vinylcarbene)- and (η^3-vinylcarbene)iron(0) complexes via [2 + 4] cycloaddition between the alkynyl moieties and 1,3-dienes in the reactions of **1** with cyclopentadiene and linear 1,3-dienes.[3]

Herein we describe the results observed in reactions of **1** with 1,3-cyclohexadiene, 1,3-cycloheptadiene, and cycloheptatriene. Unexpectedly, the reactions of *tert*-butyl-substituted alkynylcarbene complex **1a** with the cyclic compounds led to the formation of (η^4-α-pyrone)Fe(CO)$_3$ complexes **2** (Scheme I),[2a,4] which seems to involve rearrangement of the *tert*-butyl group at the stage of (η^3-vinylcarbene)iron(0) complexes when the [2 + 4] cycloaddition is assumed as the initial step.

Results and Discussion

Scheme I



1a

2a : Y = -CH$_2$-
b : Y = -CH$_2$CH$_2$-
c : Y = -CH=CH-

The reaction between **1a** and 1,3-cyclohexadiene at 70 °C under CO pressure (120 psi) gave the 1:1 adduct **2a** in 63% yield. Reduced CO pressure lowered the yield of **2a** and produced a number of side products. The compound **2a** was isolated by column chromatography (silica gel, hexane/ethyl acetate) as a yellow solid and recrystallized from ether/hexane at −20 °C. The structure of **2a** was elucidated by X-ray crystallography (Figure 1). The structure reveals the (η^4-α-pyrone)Fe(CO)$_3$ framework formed through [2 + 4] cycloaddition, two CO insertions, and migration of the ethoxy group.

The reactions of **1a** with 1,3-cycloheptadiene and cycloheptatriene under CO pressure proceeded in a fashion similar to that of **1a** with 1,3-cyclohexadiene, and the corresponding (η^4-α-pyrone)Fe(CO)$_3$ complexes **2b,c** were formed in 57% and 59% yields, respectively. Noticeably, only one regioisomer was obtained in the reaction of **1a** and cycloheptatriene.[5]

In the meantime the three compounds **3–5** were isolated by column chromatography on silica gel as the major products in the reaction of trimethylsilyl-substituted alkynylcarbene complex **1b** with 1,3-cyclohexadiene (Scheme II). The compound **3** is a vinylketene complex and is slowly hydrolyzed in the presence of silica gel to give the (bicyclo[2.2.2]octa-2,5-diene)Fe(CO)$_3$ complex **5**.[3a] The compound **4** is a regioisomer of **5**, which would be formed from an intermediate analogous to **3** by hydrolysis during reaction or chromatographic separation.[6] Application of CO pressure slightly lowered the yields of the above products, instead of giving an (η^4-α-pyrone)Fe(CO)$_3$ complex.

The mechanism for the formation of pyrones **2** has not been established. However, a pathway can be outlined for **2a** on the basis of known facts (Scheme III). The η^3-vinylcarbene complex **6** is suggested as the key intermediate.[7] Then, migratory CO insertion into the carbene carbon of **6** leads to formation of the η^4-vinylketene complex **7**. The (η^4-ethoxycarbonyl–vinylketene)Fe(CO)$_3$

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1993.

[1] For reviews, see: (a) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1990; Vol. 5. (b) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1. (c) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587–608.

[2] For examples and leading references, see: (a) Mitsudo, T.; Watanabe, H.; Sasaki, T.; Takegami, Y.; Watanabe, Y.; Kafuku, K.; Nakatsu, K. *Organometallics* **1989**, *8*, 368–378. (b) Alcock, N. W.; Richards, C. J.; Thomas, S. E. *Organometallics* **1991**, *10*, 231–238. (c) Bao, J.; Dragisich, V.; Wenglowsky, S.; Wull, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 9873. (d) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 9855. (e) Duetsch, M.; Lackmann, R.; Stein, F.; de Meijere, A. *Synlett* **1991**, 324. (f) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 6419. (g) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550. (h) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7565.

[3] (a) Park, J.; Kang, S.; Whang, D.; Kim, K. *Organometallics* **1992**, *11*, 1738. (b) Park, J.; Kang, S.; Whang, D.; Kim, K. *Organometallics* **1991**, *10*, 3413. (c) Park, J.; Kang, S.; Whang, D.; Kim, K. *Taehan Hwahakhoe Chi* **1992**, *36*, 770.

[4] For examples of (η^4-α-pyrone)Fe(CO)$_3$ complexes, see: (a) Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *J. Am. Chem. Soc.* **1984**, *106*, 5363. (b) Semmelhack, M. F.; Park, J. *Organometallics* **1986**, *5*, 2550. (c) Mitsudo, T.; Ogino, Y.; Komiya, Y.; Watanabe, H.; Watanabe, Y. *Organometallics* **1983**, *2*, 1202.

[5] The regiochemistry of **2c** was analyzed by NOE measurement between the bridgehead methine proton (δ 3.67 ppm) and methyl protons of the *tert*-butyl group (δ 1.33 ppm).

[6] A vinylketene complex, which has a structure similar to that of **7** in Scheme III, can be suggested.

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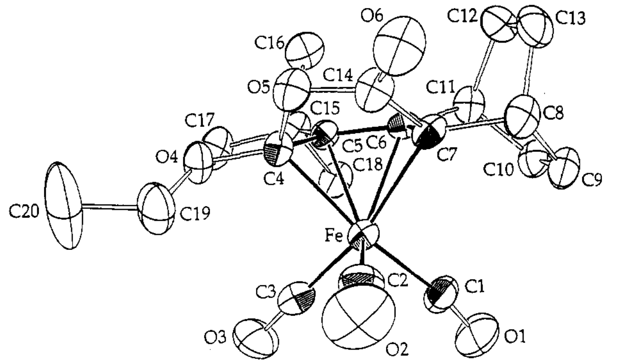

Figure 1. Structure of **2a** with the atom-labeling scheme.

complex **9** is given by the ethoxy migration in **7** and subsequent second migratory CO insertion into the carbene carbon of the (η^3-ethoxycarbonyl–vinylcarbene)Fe(CO)$_3$ complex **8**. The isomeric (η^4-ethoxycarbonyl–vinylketene)-Fe(CO)$_3$ complex **10**, which is the obvious precursor of **2a**, is formed by the second ethoxy migration in **9**.

Intermediates related to **6**–**8** have been known for the formation of (6-alkoxy-η^4-α-pyrone)Fe(CO)$_3$ complexes.[2a,4a] Also, the equilibrium between **10** and **9** is supported by the observation of thermal interconversion between two isomeric (6-ethoxy-η^4-α-pyrone)Fe(CO)$_3$ complexes through migration of the ethoxy groups.[4a] In fact, at a higher reaction temperature (135 °C) the complex **11**, which would be formed from **9** by coordination of the internal carbon–carbon double bond, was obtained as the major product in 43% yield with **2a** in 18% yield.

Experimental Section

General Comments. Solvents were all reagent grade and were further purified by standard techniques. The iron(0) alkynylcarbene complexes were prepared by the method described previously.[3a]

All reactions and manipulations were carried out on a dual manifold providing vacuum and dry argon. For reactions involving CO pressure, a Parr pressure reactor (Model No. 4561) was used. Purification of crude reaction mixtures was carried out by means of either recrystallization or flash column chromatography using mixtures of degassed hexane and ethyl acetate as the eluents and silica gel (Merck: silica gel 60, 40–63 μm particle size) as the stationary phase.

IR spectra were recorded on a Bomem Michelson 100 FT-IR spectrometer using a matched NaCl solution cell of 0.5-mm path length. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ASPECT 300 spectrometer. Chemical shifts are reported in ppm downfield from TMS but were measured relative to the residual ^{1}H in the solvent. Electron impact mass spectra were recorded on a Kratos 25-RAF. Melting points were measured on a Thomas Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were conducted by Korea Basic Science Center, Seoul, Korea.

Reaction of 1a with Cyclohexadiene at 70 °C. 1,3-Cyclohexadiene (1.0 mL, 10 mmol) was added to a solution of **1a** (157 mg, 0.51 mmol) in THF (15 mL). The mixture was transferred to a pressure vessel filled with CO. After the CO pressure was raised to 120 psi, the mixture was heated at 75 °C for 21 h. Then, the reaction mixture was transferred to a Schlenk flask and concentrated under vacuum. The residue was chromatographed (15:1 hexane/EtOAc) to give **2a** (133 mg, 0.32 mmol; 63%) as a yellow solid. Anal. Calcd for $C_{20}H_{22}O_6Fe$: C, 58.09; H, 5.35. Found: C, 57.97; H, 5.40. Mp: 118–119 °C. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2053 (s), 1987 (s), 1728 (m). ^{1}H NMR (C_6D_6, ppm): δ 5.88 (ddd, J = 7.0, 7.0, 1.4 Hz, 1 H, $-\mathrm{CH{=}C}H-$), 5.80 (dd, J = 7.0, 7.0 Hz, 1 H, $-\mathrm{C}H\mathrm{{=}CH}-$), 3.98 (dt, J = 9.2, 7.1 Hz, 1 H, $-\mathrm{OC}H_2\mathrm{CH_3}$), 3.74 (br d, J = 5.8 Hz, 1 H, $-\mathrm{C}H-$), 3.64 (m, 1 H, $-\mathrm{C}H-$), 3.40 (dt, J = 9.2, 7.1 Hz, 1 H, $-\mathrm{OC}H_2\mathrm{CH_3}$), 1.95–1.80 (m, 1 H, $-\mathrm{C}H_2\mathrm{CH_2}-$), 1.33 (s, 9 H, $-\mathrm{C(C}H_3)_3$), 1.23–1.03 (m, 3 H, $-\mathrm{C}H_2\mathrm{C}H_2-$), 0.98 (dd, J = 7.0, 7.0 Hz, 3 H, $-\mathrm{OCH_2C}H_3$). ^{13}C NMR (C_6D_6, ppm): δ 207.2 (Fe—CO), 166.7 ($-C{=}$O), 136.7 ($-C{=}$C$-$), 135.9 ($-$C$=C-$), 124.4, 119.4, 90.8, 67.7 (4 sp^2 carbons i the pyrone ring), 68.4 ($-\mathrm{O}C\mathrm{H_2CH_3}$), 36.1 ($-CH-$), 35.9 ($-CH-$), 33.9 ($-C\mathrm{(CH_3)_3}$), 32.2 ($-\mathrm{C(}C\mathrm{H_3)_3}$), 24.1 ($-C\mathrm{H_2CH_2}-$), 24.0 ($-\mathrm{CH_2}C\mathrm{H_2}-$), 14.8 ($-\mathrm{OCH_2}C\mathrm{H_3}$). MS (EI): *m/z* 414 (M$^+$, 1), 386 (4), 358 (49), 330 (71), 302 (86), 274 (83), 230 (72), 56 (100).

Reaction of 1a with 1,3-Cyclohexadiene at 135 °C. The compounds **2a** (76 mg, 18%) and **11** (168 ng, 43%) were obtained from the reaction of **1a** (314 mg, 1.05 mmol) and 1,3-cyclohexadiene (1.0 mL, 10 mmol) under CO pressure (80 psi) at 135 °C for 30 min. Data for **11** are as follows. Anal. Calcd for $C_{19}H_{22}O_5$-Fe: C, 59.06; H, 5.70. Found: C, 59.25; H, 5.73. Mp: 91–92 °C. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2019 (s), 1966 (s), 1774 (m), 1695 (m). ^{1}H NMR (C_6D_6, ppm): δ 4.06 (dd, J = 5.6, 5.6 Hz, 1 H, $-\mathrm{C}H\mathrm{{=}CH}-$), 3.92–3.76 (m, 2 H, $-\mathrm{OC}H_2\mathrm{CH_3}$), 3.65 (ddd, J = 7.0, 7.0, 2.5 Hz, 1 H, $-\mathrm{C}H-$), 3.39 (dddd, J = 5.4, 2.6, 2.6, 2.6 Hz, 1 H, $-\mathrm{C}H-$), 3.19 (ddd, J = 7.3, 5.6, 2.1 Hz, 1H, $-\mathrm{CH{=}C}H-$), 1.40–0.68 (m, 4 H, $-\mathrm{C}H_2\mathrm{C}H_2-$), 1.30 (s, 9H, $-\mathrm{C(C}H_3)_3$), 0.94 (dd, J = 7.1, 7.1 Hz, 3 H, $-\mathrm{OCH_2C}H_3$). ^{13}C NMR (C_6D_6, ppm): δ 227.8 (O$=C=$C$-$), 216.3 (Fe–CO), 215.1 (Fe–CO), 171.5 ($-C\mathrm{O_2Et}$), 84.4, 78.2, 48.8 (3 sp^2 carbons in the vinylketene moiety), 78.8 ($-C{=}$C$-$), 70.0 ($-$C$=C-$), 60.8 ($-\mathrm{O}C\mathrm{H_2CH_3}$), 35.7 ($-CH-$), 34.9 ($-CH-$), 32.4 ($-C\mathrm{(CH_3)_3}$), 31.3 ($-\mathrm{C(}C\mathrm{H_3)_3}$), 25.9 ($-C\mathrm{H_2CH_2}-$), 23.1 ($-\mathrm{CH_2}C\mathrm{H_2}-$), 13.9 ($-\mathrm{OCH_2}C\mathrm{H_3}$). MS (EI): *m/z* 358 (M$^+$ – CO, 14), 330 (100), 302 (72), 274 (36), 230 (65), 189 (36), 84 (62).

Reaction of 1a with 1,3-Cycloheptadiene. The compound **2b** (206 mg, 0.48 mmol; 57%) was obtained as a brown solid from **1a** (257 mg, 0.84 mmol) and 1,3-cycloheptadiene (2.0 mL, 18 mmol) via a procedure similar to that described for **2a**. Anal. Calcd for $C_{21}H_{24}O_6Fe$: C, 58.90; H, 5.65. Found: C, 58.85; H, 5.61. Mp: 127–128 °C. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2051 (s), 2001 (w), 1972 (s), 1722 (m). ^{1}H NMR (C_6D_6, ppm): δ 5.88–5.72 (m, 2 H, $-\mathrm{C}H\mathrm{{=}CH}-$), 4.05 (dt, J = 9.2, 7.0 Hz, $-\mathrm{OC}H_2\mathrm{CH_3}$), 3.51–3.38 (m, 2 H, $-\mathrm{C}H-$ and $-\mathrm{OC}H_2\mathrm{CH_3}$), 3.06–2.98 (m, 1 H, $-\mathrm{C}H-$), 2.29–2.17 (m, 1 H, $-\mathrm{C}H_2\mathrm{CH_2CH_2}-$), 1.48–1.22 (m, 5 H, $-\mathrm{C}H_2\mathrm{C}H_2\mathrm{C}H_2-$), 1.33 (s, 9 H, $-\mathrm{C(C}H_3)_3$), 1.02 (dd, J = 7.0, 7.0 Hz, 3 H, $-\mathrm{OCH_2C}H_3$). ^{13}C NMR (C_6D_6, ppm): δ 209.7 (Fe—CO), 167.5 ($-C{=}$O), 135.4 ($-C{=}C-$), 124.3, 117.8, 91.3, 68.9 (4 sp^2 carbons in the pyrone ring), 68.3 ($-\mathrm{O}C\mathrm{H_2CH_3}$), 35.51 ($-CH-$), 35.47 ($-CH-$), 34.6 ($-C\mathrm{(CH_3)_3}$), 32.9 ($-\mathrm{C(}C\mathrm{H_3)_3}$), 26.1 ($-\mathrm{CH_2}C\mathrm{H_2CH_2}-$), 23.4 ($-C\mathrm{H_2CH_2CH_2}-$), 23.1 ($-\mathrm{CH_2CH_2}C\mathrm{H_2}-$), 14.8 ($-\mathrm{OCH_2}C\mathrm{H_3}$). MS (EI): *m/z* 400 (M$^+$ – CO, 1), 372 (9), 344 (27), 316 (36), 288 (22), 260 (77), 231 (85), 203 (30), 131 (100).

Reaction of 1a with 1,3,5-Cycloheptatriene. The compound **2c** (255 mg, 0.60 mmol; 59%) was obtained as an orange solid from **1a** (312 mg, 1.02 mmol) and 1,3,5-cycloheptatriene (2.0 mL, 19 mmol) via a procedure similar to that described for **2a**. Anal. Calcd for $C_{21}H_{22}O_6Fe$: C, 58.90; H, 5.65. Found: C, 58.85; H, 5.61. Mp: 146–150 °C. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2055 (s), 1989 (s), 1725 (m). ^{1}H NMR (C_6D_6, ppm): δ 6.03 (ddd, J = 8.4, 7.3, 1.4

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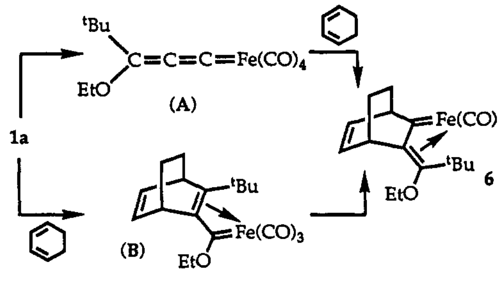
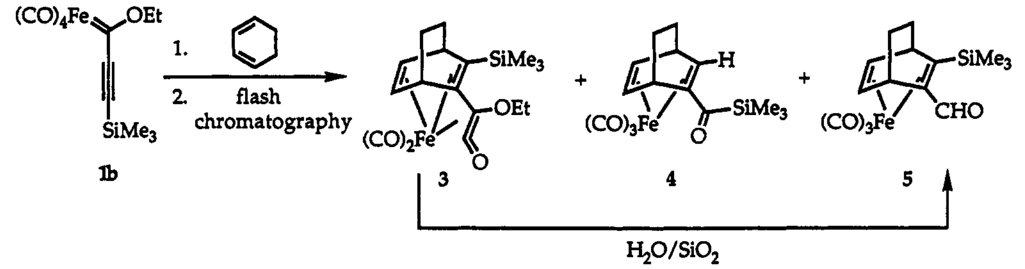
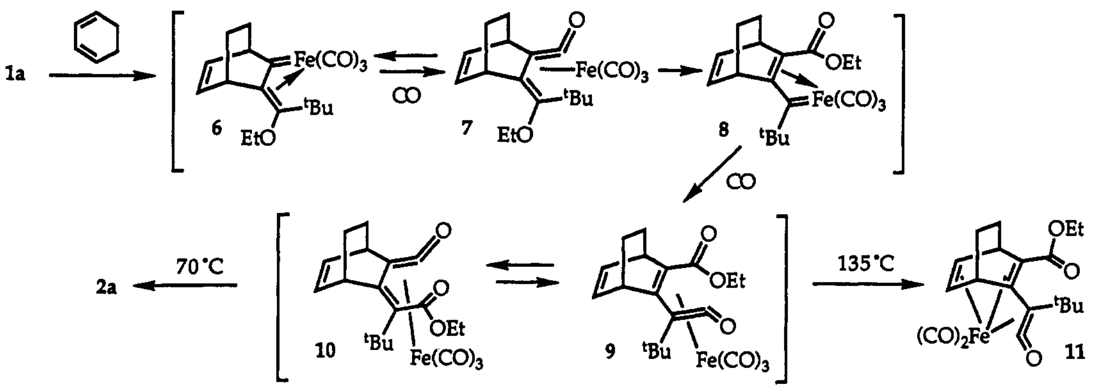
(7) One of the reviewers pointed out the possibility that the formation of the intermediate **6** would proceed via migration of the ethoxy group in **1a**, which gives the ferrabutatriene complex **A**. However, we could not observe the products that can be formed from **A** in reactions of **1** with cyclopentadiene and various linear 1,3-dienes under similar conditions. While a mechanism involving **A** cannot be ruled out completely, it is also possible that migration of the *tert*-butyl group proceeds after the [2 + 4] cycloaddition, which gives the η^3-vinylcarbene complex **B**.



Scheme II



Scheme III



Hz, 1 H, -CHC*H*=CHCH-), 5.72 (dd, J = 7.5, 7.5 Hz, 1 H, -CHCH=C*H*CH-), 5.61 (dddd, J = 10.8, 8.1, 2.3, 2.3 Hz, 1 H, -CHC*H*=CHCH$_2$-), 5.07 (ddd, J = 10.7, 3.8, 3.8, 1 H, -CHCH=C*H*CH$_2$-), 4.01 (dt, J = 9.2, 7.0, 1 H, -OC*H*$_2$CH$_3$), 3.67 (dd, J = 7.5, 7.5 Hz, 1 H, -C*H*-), 3.41 (dt, J = 9.2, 7.0, 1 H, -OC*H*$_2$CH$_3$), 3.17 (dddd, J = 19.2, 4.3, 4.1, 2.2 Hz, 1 H, -CHCH=CHC*H*$_2$-), 3.03–2.98 (m, 1 H, -C*H*-), 1.84 (ddd, J = 19.3, 5.7, 2.8 Hz, 1 H, -CHCH=CHC*H*$_2$-), 1.33 (s, 9 H, -C(C*H*$_3$)$_3$), 0.99 (dd, J = 7.0, 7.0 Hz, 3 H, -OCH$_2$C*H*$_3$). ^{13}C NMR (C$_6$D$_6$, ppm): δ 209.5 (Fe—*C*O), 167.2 (-*C*=O), 137.2 (-*C*=C-), 132.0 (-*C*=C-), 130.7 (-*C*=C-), 126.6 (-*C*=C-), 124.3, 120.3, 90.3, 66.3 (4 sp^2 carbons in the pyrone ring), 65.3 (-O*C*H$_2$CH$_3$), 35.9 (-*C*H-), 34.9 (-*C*H-), 34.1 (-*C*(CH$_3$)$_3$), 32.9 (-C(*C*H$_3$)$_3$), 27.4 (-CH=CH*C*H$_2$), 14.7 (-OCH$_2$*C*H$_3$). MS (EI): m/z 426 (M$^+$, 4), 398 (9), 370 (6), 342 (23), 314 (22), 286 (20), 258 (43), 242 (34), 166 (89), 136 (100).

Reaction of 1b with Cyclohexadiene. Cyclohexadiene (3.0 mL, 30 mmol) was added to a solution of **1b** (428 mg, 1.33 mmol) in THF (15 mL) under an argon atmosphere. After being stirred at 50 °C for 24 h, the mixture was concentrated under vacuum. The residue was chromatographed to give 177 mg (37%) of **3** as an orange oil and 65 mg (14%) of **4** as a yellow solid. Data for **3** are as follows. IR (CH$_2$Cl$_2$, cm^{-1}): ν_{CO} 2008 (s), 1954 (s), 1738 (m). ^{1}H NMR (C$_6$D$_6$, ppm): δ 4.08–3.97 (m, 2 H, -OC*H*$_2$CH$_3$ and -C*H*-), 3.76 (dt, J = 10.1, 7.1 Hz, 1 H, -OC*H*$_2$CH$_3$), 3.66 (dd, J = 5.4, 5.4 Hz, 1 H, -C*H*=CH-), 3.40 (ddd, J = 7.0, 5.4, 1.8 Hz, -CH=C*H*-), 2.29 (dddd, J = 5.6, 2.8, 2.8, 2.8 Hz, 1 H, -C*H*-), 1.45–0.65 (m, 4 H, -C*H*$_2$C*H*$_2$-), 1.06 (dd, J = 7.0, 7.0 Hz, 3 H, -OCH$_2$C*H*$_3$), 0.07 (s, 9 H, -Si(C*H*$_3$)$_3$). ^{13}C NMR (C$_6$D$_6$, ppm): δ 231.8 (Fe—*C*(O)-), 213.2 (Fe—*C*O), 211.2 (Fe—*C*O), 105.8, 89.1, 39.6 (3 sp^2 carbons in the vinylketene moiety), 74.5 (-*C*H=CH-), 68.8 (-CH=*C*H-), 65.4 (-O*C*H$_2$CH$_3$), 37.2 (-*C*H-), 32.6 (-*C*H-), 27.3 (-*C*H$_2$CH$_2$-), 23.2 (-CH$_2$*C*H$_2$-), 15.3 (-OCH$_2$*C*H$_3$), 0.6 (-Si(*C*H$_3$)$_3$). MS (EI): m/z 374 (M$^+$, 2), 346 (16), 318 (40), 290 (100), 260 (55), 233 (20), 204 (22). Data for **4** are as follows. Anal. Calcd for C$_{15}$H$_{18}$O$_4$FeSi: C, 52.03; H, 5.24. Found: C, 51.90; H, 5.31. Mp: 124–125 °C. IR (CH$_2$Cl$_2$, cm^{-1}): ν_{CO} 2041 (s), 1980 (s), 1967 (s), 1653 (m). ^{1}H NMR (C$_6$D$_6$, ppm): δ 3.03 (d, J = 1.5 Hz, 1 H, -C(O)C=C*H*-), 2.96 (ddd, J = 7.1, 7.1, 1.5 Hz, 1 H, -C*H*=CH-), 2.72 (ddd, J = 7.1, 7.1, 1.6 Hz, 1 H, -CH=C*H*-), 2.62–2.56 (m, 1 H, -C*H*CH$_2$CH$_2$CH-), 2.51 (dd, J = 7.5, 7.5 Hz, 1 H, -CHCH$_2$CH$_2$C*H*-), 1.41–1.38 (m, 1 H, -CHC*H*$_2$CH$_2$CH-), 1.18–1.13 (m, 1 H, -CHC*H*$_2$CH$_2$CH-), 0.77–0.68 (m, 2 H, -CHCH$_2$C*H*$_2$CH-), -0.21 (s, 9 H, -Si(C*H*$_3$)$_3$). ^{13}C NMR (C$_6$D$_6$, ppm): δ 214.2 (Fe—*C*O), 193.2 (-*C*HO), 70.1 (-CH=*C*H-), 65.9 (-CH=*C*H-), 47.2 (-*C*H=CC=O), 43.9 (-*C*H-), 39.7 (-CH=*C*O=O), 31.1 (-*C*H-), 28.7 (-CH*C*H$_2$CH$_2$CH-), 24.4 (-CHCH$_2$*C*H$_2$CH-), -0.13 (-Si(*C*H$_3$)$_3$). MS (EI): m/z 346 (M$^+$, 6), 318 (12), 290 (60), 262 (64), 232 (20), 206 (20), 134 (100).

Table I. Crystallographic Data for 2a

formula	C$_{20}$H$_{22}$FeO$_6$
fw	414.24
space group	$P\bar{1}$ (No. 2)
a, Å	8.059(3)
b, Å	8.773(2)
c, Å	15.085(3)
α, deg	88.96(1)
β, deg	78.12(2)
γ, deg	68.01(2)
V, Å^3	965.7(4)
Z	2
temp, °C	25
D(calcd), g cm^{-3}	1.426
crystal dimens, mm	0.30 × 0.35 × 0.40
radiation	Mo Kα (λ(Kα_1) = 0.709 26 Å)
linear abs coeff, cm^{-1}	8.11
takeoff angle, deg	2.0
scan mode	ω
ω-scan width, deg	0.9 + 0.34 tan θ
2θ limit, deg	50
no. of data collcd	3654
no. of unique data	3391
no. of unique data with $I > 3\sigma(I)$	2852
no. of variables	244
GOF	0.73
$R(F)$[a]	0.054
$R_w(F)$[b]	0.076

[a] $R = \sum||F_o| - |F_c||/|F_o|$. [b] $R_w = [\sum w(|F_0| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 4F_o^2/\sigma^2(F_o^2)$; $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{1/2}$.

Hydrolysis of 3. The solution of **3** (115 mg, 0.31 mmol) in hexane (10 mL) was added to a flask which was filled with degassed silica gel (500 mg) and water (0.1 mL). The suspension was stirred at 25 °C for 12 h. Then, the reaction product was extracted with a 4:1 hexane/EtOAc mixture. After volatiles were removed from the filtrate under vacuum, the residue was crystallized from ether at -78 °C to give 93 mg (94%) of **5** as an orange solid. Anal. Calcd for C$_{15}$H$_{18}$O$_4$FeSi: C, 52.05; H, 5.24. Found: C, 52.05; H, 5.47. Mp: 116–117 °C. IR (CH$_2$Cl$_2$, cm^{-1}): ν_{CO} 2037 (s), 1969 (s), 1653

Table II. Positional Parameters and B_{eq} Values for Non-Hydrogen Atoms of 2a

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Fe	0.1934(1)	0.47519(9)	0.31001(6)	2.23(2)
O(1)	–0.0371(7)	0.2757(6)	0.3486(4)	5.6(1)
O(2)	0.4721(8)	0.3173(8)	0.4151(4)	7.2(2)
O(3)	–0.0831(8)	0.6966(7)	0.4559(4)	5.8(2)
O(4)	0.2501(5)	0.7956(5)	0.3132(3)	2.95(9)
O(5)	0.4747(5)	0.5911(5)	0.2191(3)	2.94(9)
O(6)	0.6977(5)	0.3562(6)	0.1598(4)	4.5(1)
C(1)	0.0582(8)	0.3422(7)	0.3271(5)	3.4(1)
C(2)	0.3617(9)	0.3779(8)	0.3752(4)	3.7(2)
C(3)	0.0249(9)	0.6114(7)	0.3982(5)	3.5(1)
C(+)	0.2820(7)	0.6561(6)	0.2647(4)	2.3(1)
C(5)	0.1524(6)	0.6469(6)	0.2111(4)	2.0(1)
C(6)	0.2195(7)	0.4854(6)	0.1692(4)	2.1(1)
C(7)	0.3886(7)	0.3697(6)	0.1882(4)	2.4(1)
C(8)	0.4492(7)	0.2042(7)	0.1391(5)	3.0(1)
C(9)	0.2949(8)	0.1432(7)	0.1536(5)	3.2(1)
C(10)	0.1419(8)	0.2492(7)	0.1338(5)	3.1(1)
C(11)	0.1515(7)	0.4098(7)	0.1019(4)	2.7(1)
C(12)	0.3082(9)	0.3644(8)	0.0148(5)	3.8(2)
C(13)	0.4853(9)	0.2368(8)	0.0368(5)	3.9(2)
C(14)	0.5348(7)	0.4317(7)	0.1899(4)	3.0(1)
C(15)	–0.0254(7)	0.7880(6)	0.1974(4)	2.5(1)
C(16)	0.0092(9)	0.8303(8)	0.0982(5)	3.6(2)
C(17)	–0.0770(8)	0.9454(7)	0.2562(5)	3.6(2)
C(18)	–0.1903(7)	0.7329(7)	0.2209(5)	3.2(1)
C(19)	0.3441(9)	0.7742(8)	0.3876(5)	4.1(2)
C(20)	0.320(1)	0.938(1)	0.4232(6)	8.8(2)

[a] $B_{eq} = {}^4/_3 \sum_i \sum_j \beta_{ij} \mathbf{a}_i \mathbf{a}_j$.

(s). ^{1}H NMR (C_6D_6, ppm): δ 9.02 (s, 1 H, –C*H*O), 3.98–3.93 (m, 1 H, $-C\mathit{H}CH_2CH_2CH-$), 3.09–3.04 (m, 1 H, –C*H*=CH–), 2.87–2.81 (m, 1 H, –CH=C*H*–), 2.76–2.71 (m, 1 H, $-CHCH_2CH_2C\mathit{H}-$), 0.98–0.91 (m, 1 H, $-CHC\mathit{H}_2CH_2CH-$), 0.84–0.70 (m, 2 H, $-CHCH_2C\mathit{H}_2CH-$), 0.09 (s, 9 H, $-Si(C\mathit{H}_3)_3$). ^{13}C NMR (C_6D_6, ppm): δ 214.0 (Fe—*C*O), 191.3 (–*C*HO), 62.5 (–CH=*C*H–), 61.2 (–CH=*C*H–), 58.9 (–C=*C*Si), 40.4 (–*C*=CSi), 37.1 ($-\mathit{C}HCH_2CH_2CH-$), 29.8 ($-CH\mathit{C}H_2CH_2CH-$), 27.2 ($-CHCH_2CH_2\mathit{C}H-$), 26.4 ($-CHCH_2\mathit{C}H_2CH-$), 1.4 ($-Si(\mathit{C}H_3)_3$). MS (EI): *m*/*z* 346 (M^+, 6), 318 (9), 290 (34), 262 (35), 234 (13), 218 (52), 163 (100).

X-ray Crystallography. A crystal of **2a** sealed in a capillary was mounted on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. Cell parameters and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $20.0 < 2\theta < 30.0°$. The crystallographic data and additional details of data collection are summarized in Table I. The intensities of three standard reflections, recorded every 3 h of X-ray exposure, showed no systematic changes. All the calculations were carried out with the Enraf-Nonius Structure Determination Package (SDP). The intensity data were corrected for Lorentz and polarization effects, and empirical absorption corrections (based on ψ scan) were also applied. The structure was solved by a combination of Patterson and difference Fourier methods and refined by full-matrix least-squares methods. All the non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were idealized (d(C–H) = 0.95 Å) and included in the calculations of the structure factors as fixed contributions. Each H atom was assigned a thermal parameter of 1.2 times that of the attached atom. The final cycle of refinement led to the *R* indices listed in Table I. The atomic scattering factors were taken from ref 8 for the non-hydrogen atoms and from ref 9 for hydrogen. The positional and equivalent isotopic thermal parameters of the non-hydrogen atoms are listed in Table II.

Table III. Selected Bond Lengths (Å) and Angles (deg) for 2a

Bond Lengths			
Fe–C(1)	1.855(8)	O(5)–C(14)	1.346(7)
Fe–C(2)	1.784(7)	O(6)–C(14)	1.217(6)
Fe-C(3)	1.773 (6)	C(4)–C(5)	1.471(9)
Fe–C(4)	2.025(6)	C(5)–C(6)	1.420(7)
Fe–C(5)	2.085(5)	C(6)–C(7)	1.443(7)
Fe–C(6)	2.094(5)	C(7)–C(14)	1.476(9)
Fe–C(7)	2.118(5)	C(9)–C(10)	1.324(8)
O(5)–C(4)	1.456(6)	C(12)–C(13)	1.544(9)
Bond Angles			
C(1)–Fe–C(2)	101.3(3)	C(3)–Fe–C(5)	95.0(2)
C(1)–Fe–C(3)	87.5(3)	C(3)–Fe–C(6)	129.3(2)
C(1)–Fe–C(4)	161.0(3)	C(3)–Fe–C(7)	165.2(3)
C(1)–Fe–C(5)	119.3(3)	C(4)–Fe–C(5)	41.9(2)
C(1)–Fe–C(6)	97.0(3)	C(5)–Fe–C(6)	39.7(2)
C(1)–Fe–C(7)	103.1(3)	C(6)–Fe–C(7)	40.1(2)
C(2)–Fe–C(3)	97.5(3)	C(4)–O(5)–C(14)	112.4(5)
C(2)–Fe–C(4)	97.7(3)	O(5)–C(4)–C(5)	116.2(4)
C(2)–Fe–C(5)	137.9(3)	C(4)–C(5)–C(6)	108.6(4)
C(2)–Fe–C(6)	130.3(2)	C(5)–C(6)–C(7)	116.8(5)
C(2)–Fe–C(7)	90.6(2)	C(6)–C(7)–C(14)	117.1(5)
C(3)–Fe–C(4)	91.0(3)	O(5)–C(14)–C(7)	114.7(4)

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Supplementary Material Available: Tables of anisotropic temperature factors, bond lengths, and bond angles for **2a** (4 pages). Ordering information is given on any current masthead page.

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