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Reactions between Iron(0) Alkynylcarbene Complexes and Cyclopentadiene: Formation of Iron(0) η^1-Vinylcarbene Complexes and Their Facile Thermal Transformation into the Corresponding (η^3:η^1-Allylacyl)iron(II) Complexes

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[(3-*tert*-Butylnorbornadienyl)ethoxymethylene]$Fe(CO)_4$, the iron(0) η^1-vinylcarbene complex **2**, is obtained from the reaction of [(3,3-dimethylbutynyl)ethoxymethylene]$Fe(CO)_4$ (**1a**) with cyclopentadiene at 25 °C. Complex **2** transforms into the η^3:η^1-allylacyl complex **4a** via a CO insertion reaction at the original carbene carbon by heating at 50 °C for 1 h. However, direct formation of η^3:η^1-allylacyl complexes is observed in reactions of cyclopentadiene with other alkynylcarbene complexes, **1b** (R = $SiMe_3$), **1c** (R = cyclohexyl), **1d** (R = *n*-propyl), and **1e** (R = phenyl), at 25 °C.

Considerable interest has been focused on the chemistry of transition-metal vinylcarbene complexes. They have been involved as key species in a number of noticeable reactions such as alkyne polymerization,[1] the Diels–Alder reaction,[2] formation of bicyclic lactones via a van Halban–White type double-cyclization,[3] and reactions of alkynes with metal carbene complexes,[4] including the Dötz reaction.

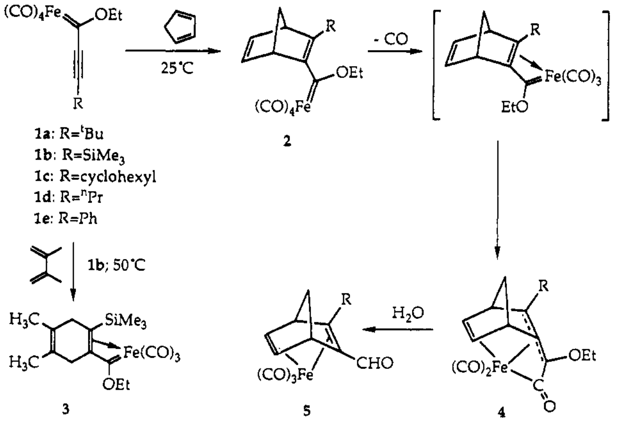
There are two types of metal vinylcarbene complexes: η^1- and η^3-types.[5] However, to our knowledge, there is no previous examples of iron(0) η^1-vinylcarbene complexes, although iron(II) η^1-vinylcarbene complexes are known.[6] Recently, we have reported the synthesis of iron(0) alkynylcarbene complexes and formation of the η^3-vinylcarbene complex **3** in the reaction of the trimethylsilyl-substituted alkynylcarbene complex **1b** with 2,3-dimethyl-1,3-butadiene.[7]

Herein we describe the formation of the iron(0) η^1-vinylcarbene complex **2** in the reaction of the *tert*-butyl-substituted alkynylcarbene complex **1a** with cyclopentadiene and the facile thermal transformation of **2** into the η^3:η^1-allylacyl complex **4a** of which the molecular structure is elucidated by X-ray crystallography (Scheme I).

Experimental Section

General Comments. Solvents were all reagent grade and were further purified by standard techniques. Ethanefluorosulfonate was prepared by using literature procedures.[8] The iron(0) alkynylcarbene complexes were prepared by the method described previously.[7]

Scheme I



All reactions and manipulations were carried out on a dual manifold providing vacuum and dry argon. Purification of crude reaction mixtures was carried out by means of either recrystallization or the 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 Perkin-Elmer 843 or a Bomem Michelson 100 FT-IR spectrometer using a matched NaCl solution cell of 0.5-mm path length. ^1H 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 ^1H 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 Cyclopentadiene at 25 °C. Cyclopentadiene (3.20 mL, 39.4 mmol) was added to a solution of **1a** (225 mg, 0.74 mmol) in THF (10 mL) at 25 °C. After being stirred for 6 h at 25 °C, the mixture was concentrated under vacuum. The residue was chromatographed (hexane/ethyl acetate = 100/1) to give 260 mg (92%) of **2** as a brown oil. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2050 (s), 2009 (m), 1977 (m), 1947 (vs). ^1H NMR (C_6D_6, ppm): δ 6.82 (m, 1 H, $-CH{=}C\mathit{H}-$), 6.77 (m, 1 H, $-C\mathit{H}{=}CH-$), 4.22 (br q, J = 6.4 Hz, 2 H, $-OC\mathit{H}_2CH_3$), 3.46 (br s, 1 H, $-C\mathit{H}CH_2CH-$), 3.31 (br s, 1 H, $-CHCH_2C\mathit{H}-$), 2.15 (br s, 1 H, $-CHC\mathit{H}_2CH-$), 1.69 (d, J = 6.2 Hz, 1 H, $-CHC\mathit{H}_2CH-$), 1.00 (s, 9 H, $-C(C\mathit{H}_3)_3$), 1.00 (t, J = 6.9 Hz, 3 H, $-OCH_2C\mathit{H}_3$). ^{13}C NMR (C_6D_6, ppm): δ 328.5 ($Fe{=}\mathit{C}-$), 214.9 (Fe–CO), 150.6 ($={\mathit{C}}-C(CH_3)_3$), 143.4 ($={\mathit{C}}-$

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C=Fe), 141.8 (–*C*H=*C*H–), 75.5 (–O*C*H$_2$CH$_3$), 58.5 (–*C*HCH$_2$CH–), 53.2 (–CHCH$_2$*C*H–), 34.1 (–CH*C*H$_2$CH–), 29.6 (–*C*(CH$_3$)$_3$), 28.4 (–C(*C*H$_3$)$_3$), 14.2 (–OCH$_2$*C*H$_3$). MS (EI): *m/z* 372 (M$^+$, 2), 344 (11), 316 (21), 288 (32), 260 (79), 203 (86), 121 (100), 56 (71).

Reaction of 1a with Cyclopentadiene at 45 °C. Cyclopentadiene (5.0 mL, 61.5 mmol) was added to a solution of **1a** (450 mg, 1.47 mmol) in THF (10 mL) at 25 °C. After being stirred for 4 h at 45 °C, the mixture was concentrated under vacuum. The residue was chromatographed (silica gel; hexane/ethyl acetate = 30/1) to give 283 mg (56%) of **5a** as a brown oil and 170 mg (37%) of **4a** as a yellow powder. For X-ray crystallography yellow crystals of **4a** were afforded by recrystallization from pentane at –78 °C. Anal. Calcd for **4a**: C, 59.30; H, 5.86. Found: C, 59.37; H, 5.76. Mp: 48–49 °C. IR (CH$_2$Cl$_2$, cm^{-1}): ν_{CO} 2009 (s), 1956 (s), 1728 (m). ^{1}H NMR (C$_6$D$_6$, ppm): *δ* 4.21 (m, 1 H, –OC*H*$_2$CH$_3$), 3.94 (m, 1 H, –OC*H*$_2$CH$_3$), 3.83 (br s, 1 H, –C*H*=CH–), 3.75 (m, 1 H, –CH=C*H*–), 3.64 (t, *J* = 5.0 Hz, 1 H, –C*H*CH$_2$CH–), 2.88 (br s, 1 H, –CHCH$_2$C*H*–), 1.27 (m, 2 H, –CHC*H*$_2$CH–), 1.17 (t, *J* = 7.0 Hz, 3 H, –OCH$_2$C*H*$_3$), 0.80 (s, 9 H, –C(C*H*$_3$)$_3$). ^{13}C NMR (C$_6$D$_6$, ppm): *δ* 232.8 (–C=*C*=O), 217.6 (Fe—*C*O), 212.7 (–*C*O), 104.1 (–*C*=C=O), 75.6 (=*C*—C—OEt), 68.0 (–O*C*H$_2$CH$_3$), 65.2 (–*C*HCH$_2$*C*H–), 64.8 (=*C*—C(CH$_3$)$_3$), 51.6 (–CH*C*H$_2$CH–), 49.5 (–CH=*C*H–), 43.5 (–*C*H=CH–), 35.0 (–*C*(CH$_3$)$_3$), 30.9 (–C(*C*H$_3$)$_3$), 15.5 (–OCH$_2$*C*H$_3$). MS (EI): *m/z* 344 (M$^+$, 22), 316 (51), 288 (52), 260 (100), 214 (48), 203 (97), 186 (19). Anal. Calcd for **5a**: C, 56.99; H, 5.10. Found: C, 56.95; H, 5.10. Mp: 83–84 °C. IR (CH$_2$Cl$_2$, cm^{-1}): ν_{CO} 2038 (s), 2014 (w), 1960 (s), 1625 (m). ^{1}H NMR (C$_6$D$_6$, ppm): *δ* 9.46 (s, 1 H, –C*H*O), 3.99 (br s, 1 H, –C*H*CH$_2$CH–), 3.29 (m, 1 H, –C*H*=CH–), 3.02 (m, 1 H, –CH=C*H*–), 2.76 (br s, 1 H, –CHCH$_2$C*H*–), 0.90 (s, 9 H, –C(C*H*$_3$)$_3$), 0.74 (d, *J* = 9.6 Hz, 1 H, –CHC*H*$_2$CH–), 0.69 (d, *J* = 9.6 Hz, 1 H, –CHC*H*$_2$CH–). ^{13}C NMR (C$_6$D$_6$, ppm): *δ* 214.0 (Fe—*C*O), 188.2 (–*C*HO), 67.1 (=*C*—C(CH$_3$)$_3$), 57.1 (–*C*HCH$_2$CH–), 55.8 (–CHCH$_2$*C*H–), 54.8 (–CH*C*H$_2$CH–), 49.4 (–*C*H=CH–), 47.0 (=*C*—CHO), 41.2 (–CH=*C*H–), 35.5 (–*C*(CH$_3$)$_3$), 31.2 (–C(*C*H$_3$)$_3$). MS (EI): *m/z* 316 (M$^+$, 8), 288 (7), 260 (35), 232 (48), 216 (100), 186 (29).

Reaction of 1b with Cyclopentadiene. Cyclopentadiene (1.80 mL, 61.5 mmol) was added to a solution of **1b** (348 mg, 1.08 mmol) in THF (10 mL) at 25 °C. After being stirred for 2 h at 25 °C, the mixture was concentrated under vacuum. The residue was chromatographed (hexane/ethyl acetate = 8/1) to give 156 mg (41%) of **4b** as a golden yellow oil and 106 mg (30%) of **5b** as a yellow powder. High-resolution MS (EI) Calcd for **4b**: *m/z* 360.0479. Found: 360.0466. IR (CH$_2$Cl$_2$, cm^{-1}): ν_{CO} 2011 (s), 1957 (s), 1733, (m). ^{1}H NMR (C$_6$D$_6$, ppm): *δ* 4.06 (dq, *J* = 10.3, 7.3 Hz, 1 H, –OC*H*$_2$CH$_3$), 3.78 (dq, *J* = 10.3, 7.3 Hz, 1 H, –OC*H*$_2$CH$_3$), 3.79 (broad s, 1 H, –C*H*CH$_2$CH–), 3.69–3.63 (m, 2 H, –C*H*=C*H*–), 2.55 (broad s, 1 H, –CHCH$_2$C*H*–), 1.26 (d, *J* = 9.3 Hz, 1 H, –CHC*H*$_2$CH–), 1.20 (d, *J* = 9.3 Hz, 1 H, –CHC*H*$_2$CH–), 1.08 (t, *J* = 7.1 Hz, 3 H, –OCH$_2$C*H*$_3$), –0.04 (s, 9 H, –Si(C*H*$_3$)$_3$). ^{13}C NMR (C$_6$D$_6$, ppm): *δ* 231.6 (–C=*C*=O), 216.9 (Fe—*C*O), 212.6 (Fe—*C*O), 102.5 (–*C*=C=O), 86.6 (–*C*=C—Si), 66.9 (–*C*HCH$_2$CH–), 66.3 (–CHCH$_2$*C*H–), 65.3 (–O*C*H$_2$CH$_3$), 53.3 (–CH*C*H$_2$CH–), 48.9 (–H*C*=CH–), 42.1 (–HC=*C*H–), 32.3 (–C=*C*—Si), 15.4 (–OCH$_2$*C*H$_3$), –0.1 (Si(*C*H$_3$)). MS (EI): *m/z* 388 (M$^+$, 0.8), 360 (12), 332 (40), 304 (39), 276 (96), 219 (100). Anal. Calcd for **5b**: C, 50.62; H, 4.85. Found: C, 50.30; H, 4.62. Mp: 78–80 °C. IR (CH$_2$Cl$_2$, cm^{-1}): ν_{CO} 2042 (s), 2008 (w), 1974 (s), 1647 (m). ^{1}H NMR (C$_6$D$_6$, ppm): *δ* 9.10 (s, 1 H, –C*H*O), 3.73 (broad s, 1 H, –C*H*CH$_2$CH–), 3.16 (m, 1 H, –C*H*=CH–), 2.93 (m, 1 H, –CH=C*H*–), 2.58 (broad s, 1 H, –CHCH$_2$C*H*–), 0.70 (d, *J* = 9.6 Hz, 1 H, –CHC*H*$_2$CH–), 0.67 (d, *J* = 9.6 Hz, 1 H, –CHC*H*$_2$CH–), 0.06 (s, 9 H, –Si(C*H*$_3$)$_3$). ^{13}C NMR (C$_6$D$_6$, ppm): *δ* 213.4 (Fe—*C*O), 189.4 (–*C*HO), 56.6 (–*C*HCH$_2$CH–), 55.3 (–CHCH$_2$*C*H–), 54.5 (–C=*C*—Si), 53.8 (–CH*C*H$_2$CH–), 48.4 (–*C*H=CH–), 39.8 (–CH=*C*H–), 33.1 (–C=*C*–CHO), 0.2 (–Si(*C*H$_3$)$_3$). MS (EI): *m/z* 332 (M$^+$, 0.6), 304 (2.7), 276 (15), 248 (27), 66 (100).

Reaction of 1c with Cyclopentadiene, Followed by Hydrolysis. Cyclopentadiene (5.0 mL, 61.5 mmol) was added to a solution of **1c** (251 mg, 0.76 mmol) in THF (10 mL) at 25 °C. After the mixture was stirred for 90 min at 25 °C, 0.1 mL of degassed water was added. The mixture was stirred at 25 °C for 12 h and concentrated under vacuum. The residue was chromatographed (hexane/ethyl acetate = 8/1) to give 104 mg (40%) of **5c** as a yellow solid. Anal. Calcd for **5c**: C, 59.67; H, 5.30. Found: C, 59.57; H, 5.56. Mp: 97–98 °C. IR (CH$_2$Cl$_2$, cm^{-1}): ν_{CO} 2040 (s), 1971 (s), 1954 (s), 1635 (m). ^{1}H NMR (C$_6$D$_6$, ppm): *δ* 9.13 (s, 1 H, –C*H*O), 3.48 (br s, 1 H, –C*H*CH$_2$CH–), 3.20 (dd, *J* = 3.5, 3.7 Hz, 1 H, –C*H*=CH–), 2.98 (dd, *J* = 3.5, 3.7 Hz, 1 H, –CH=C*H*–), 2.82 (br s, 1 H, –CHCH$_2$C*H*–), 2.20–0.85 (m, 11 H, –C*H*(C*H*$_2$)$_5$), 0.73 (d, *J* = 9.5 Hz, 1 H, –CHC*H*$_2$CH–), 0.66 (d, *J* = 9.5 Hz, 1 H, –CHC*H*$_2$CH–). ^{13}C NMR (C$_6$D$_6$, ppm): *δ* 213.7 (Fe—*C*O), 189.6 (–*C*HO), 60.3 (=*C*—CH(CH$_2$)$_5$), 55.5 (–*C*HCH$_2$CH–), 54.8 (–CHCH$_2$*C*H–), 53.5 (–CH*C*H$_2$CH–), 45.2 (=*C*—CHO), 40.9 (–*C*H=CH–), 39.6 (–CH=*C*H–), 34.9 (–*C*H(CH$_2$)$_5$), 26.8 (–CH(*C*H$_2$)$_5$), 26.5 (–CH(*C*H$_2$)$_5$), 26.3 (–CH(*C*H$_2$)$_5$) MS (EI): *m/z* 342 (M$^+$, 9), 314 (13), 286 (46), 258 (100), 192 (33).

Reaction of 1d with Cyclopentadiene, Followed by Hydrolysis. Cyclopentadiene (5.0 mL, 61.5 mmol) was added to a solution of **1d** (126 mg, 0.43 mmol) in hexane (10 mL) at 25 °C. After the mixture was stirred for 3 h at 25 °C, 0.1 mL of degassed water was added. The mixture was stirred at 25 °C for 10 h and concentrated under vacuum. The residue was chromatographed (hexane/ethyl acetate = 8/1) to give 68 mg (52%) of **5d** as a yellow oil. Anal. Calcd for **5d**: C, 55.63; H, 4.64. Found: C, 55.58; H, 4.66. IR (CH$_2$Cl$_2$, cm^{-1}): ν_{CO} 2040 (s), 1960 (s), 1953 (s), 1639 (m). ^{1}H NMR (C$_6$D$_6$, ppm): *δ* 9.05 (s, 1 H, –C*H*O), 3.48 (br s, 1 H, –C*H*CH$_2$CH–), 3.16 (br s, 1 H, –C*H*=CH–), 2.98 (m, 1 H, –CH=C*H*–), 2.62 (br s, 1 H, –CHCH$_2$C*H*–), 1.89 (m, 1 H, –C*H*$_2$CH$_2$CH$_3$), 1.65 (m, 1 H, –C*H*$_2$CH$_2$CH$_3$), 1.34 (m, 1 H, –CH$_2$C*H*$_2$CH$_3$), 1.07 (m, 1 H, –CH$_2$C*H*$_2$CH$_3$), 0.72 (m, 5 H, –CH$_2$CH$_2$C*H*$_3$ and –CHC*H*$_2$CH–). ^{13}C NMR (C$_6$D$_6$, ppm): *δ* 213.6 (Fe—*C*O), 189.3 (–*C*HO), 55.2 (–*C*HCH$_2$CH–), 54.1 (=C^{n}Pr), 53.5 (–CHCH$_2$*C*H–), 52.7 (–CH*C*H$_2$CH–), 48.3 (–*C*H=CH–), 47.9 (=*C*—CHO), 41.0 (–CH=*C*H–), 34.7 (–*C*H$_2$CH$_2$CH$_3$), 24.1 (–CH$_2$*C*H$_2$CH$_3$), 14.1 (–CH$_2$CH$_2$*C*H$_3$). MS (EI): *m/z* 302 (M$^+$, 13), 274 (21), 246 (49), 218 (71), 190 (80), 162 (65), 134 (42), 84 (100).

Reaction of 1e with Cyclopentadiene, Followed by Hydrolysis. At –78 °C, to a solution of iron pentacarbonyl (0.40 mL, 3.0 mmol) in ether (20 mL) was added dropwise (phenylethynyl)lithium, generated by treatment of a solution of phenylacetylene (0.33 mL, 3.0 mmol) in ether (10 mL) with ^{n}BuLi (1.8 mL, 2.9 mmol; 1.60 M in hexane) at 78 °C for 30 min. After 1 h at 78 °C, the solution was warmed to 25 °C over ca. 2 h, HMPA (5 mL) was added, and the deep brown solution was recooled to –78 °C. Ethanefluorosulfonate (1.20 mL, 12.9 mmol) was added dropwise to the mixture at –78 °C with stirring. After being stirred at –78 °C for 4 h, the reaction mixture was warmed slowly to 25 °C. To the reaction mixture, containing 1e, was added cyclopentadiene (10.0 mL, 123 mmol) at 25 °C. After being stirred for 3 h at 25 °C, the mixture was partitioned between hexane and saturated aqueous sodium bicarbonate. Then, the organic layer was washed with water and aqueous sodium chloride, dried over magnesium sulfate and concentrated under vacuum. Yellow crystals (501 mg, 50%) of **4e** were obtained by crystallization of the residue from ether/hexane at –20 °C. An orange oil (70 mg, 100%) of **5e** was obtained by treatment of a solution of 4e (72 mg, 0.21 mmol) in hexane (10 mL) with 0.1 mL of degassed water at 25 °C for 10 h and subsequent removal of volatiles from the reaction mixture under vacuum. Anal. Calcd for **4e**: C, 62.66; H, 4.43. Found: C, 62.76; H, 4.39. Mp: 119–120 °C. IR (CH$_2$Cl$_2$, cm^{-1}): ν_{CO} 2012 (s), 1961 (s), 1750 (s). ^{1}H NMR (C$_6$D$_6$, ppm): *δ* 7.00–6.80 (m, 5 H, –C$_6$*H*$_5$), 4.11 (dq, *J* = 10.1, 7.0 Hz, 1 H, –OC*H*$_2$CH$_3$), 3.90–3.80 (m, 3 H, –OC*H*$_2$CH$_3$, –C*H*=CH–, and –C*H*CH$_2$CH–), 3.70 (m, 1 H, –CH=C*H*–), 3.11 (m, 1 H, –C*H*CH$_2$CH–), 1.23 (m, 2 H, –CHC*H*$_2$CH–), 1.13 (t, *J* = 7.0 Hz, 3 H, –OCH$_2$C*H*$_3$). ^{13}C NMR (C$_6$D$_6$, ppm): *δ* 232.5 (–C=*C*=O), 217.9 (Fe—*C*O), 213.0 (Fe—*C*O), 129.1 (–*C*$_6$H$_5$), 128.0 (–*C*$_6$H$_5$), 126.6 (–*C*$_6$H$_5$), 102.8 (–*C*=C=O), 75.7 (=*C*—C=C=O), 68.4 (–O*C*H$_2$CH$_3$), 67.8 (–*C*HCH$_2$CH–), 66.1 (–CHCH$_2$*C*H–), 53.4 (=*C*—Ph), 52.3 (–*C*H=CH–), 52.0 (–CH=*C*H–), 43.6 (–CH*C*H$_2$CH–), 15.9 (–OCH$_2$*C*H$_3$). MS (EI): *m/z* 364 (M$^+$, 1), 336 (2), 308 (64), 280 (15), 252 (100), 223 (23). Anal. Calcd for **5e**: C, 60.75; H, 3.60. Found: C, 59.47; H, 3.89. IR (C$_6$D$_6$, cm^{-1}): ν_{CO} 2045 (s), 1980 (s), 1955 (s), 1647 (m). ^{1}H NMR (C$_6$D$_6$, ppm): *δ* 9.29 (s, 1 H, –C*H*O), 7.30–6.85 (m, 5 H, –C$_6$*H*$_5$), 3.63 (br s, 1 H, –C*H*CH$_2$CH–), 3.36 (m, 1 H, –C*H*—CH–), 3.07 (m, 1 H, –CH—C*H*–), 3.00 (m, 1 H, –CHCH$_2$C*H*–), 0.87 (d, *J* = 9.5 Hz, 1 H, –CHC*H*$_2$CH–), 0.69 (d, *J* = 9.5 Hz, 1 H, –CHC*H*$_2$CH–). ^{13}C NMR (C$_6$D$_6$, ppm): *δ* 212.4 (Fe—*C*O), 188.1 (–*C*HO), 140.5 (–*C*$_6$H$_5$), 130.3 (–*C*$_6$H$_5$), 128.8 (–*C*$_6$H$_5$), 127.0 (–*C*$_6$H$_5$), 56.1 (–*C*H=CH–), 54.5 (–*C*HCH$_2$CH–), 54.3 (–CHCH$_2$*C*H–), 53.6 (=*C*—Ph), 46.1 (=

Table I. Crystallographic Data for 4a

formula	$C_{17}H_{20}FeO_4$
fw	344.19
space group	$P2_1/n$ (No. 14)
a, Å	10.084 (3)
b, Å	12.084 (1)
c, Å	13.587 (6)
β, deg	99.94 (2)
V, Å^3	1630.8 (9)
Z	4
temp, °C	25
D(calcd), g cm^{-3}	1.400
cryst dimens, mm	0.20 × 0.25 ×0.45
radiation	Mo Kα_1 (0.709 26 Å)
linear abs coeff, cm^{-1}	9.3
take-off angle, deg	2.0
scan mode	$\omega/2\theta$
ω-scan width, deg	0.75 + 0.34 tan θ
2θ limit, deg	50
weighting scheme	$w = 4(F_o)^2/[\sigma(F_o)^2]^2$
no. of standard reflns	3
no. of data collcd	3012
no. of unique data	2616
no. of unique data with $I > 3\sigma(I)$	1374
no. of variables	199
GOF	0.55
R	0.065
R_w	0.074

C—CHO), 40.9 (-CHCH$_2$CH-). MS (EI): m/z 336 (M$^+$, 1), 308 (1), 280 (36), 252 (100), 226 (17), 196 (81).

X-ray Crystallography. A crystal of **4a** sealed in a capillary was mounted on 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 3 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 the empirical absorption corrections (based on the 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 an isotropic 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 9 for the non-hydrogen atoms and from the literature[10] for hydrogen. The positional and equivalent isotropic thermal parameters of the non-hydrogen atoms are listed in Table II.

Results and Discussion

The reaction between **1a** and cyclopentadiene at 25 °C leads to the formation of **2** in 92% yield. Spectroscopic analysis for **2** clearly shows the η^1-carbene–iron(0) functionality: The carbene carbon resonances are characteristically at 328.5 ppm,[11] and the IR spectrum is consistent with the formulation of **2** as a LFe(CO)$_4$ system by showing four strong absorptions at 2050, 2009, 1977, and 1947 cm^{-1} for the CO stretching.[12]

Table II. Positional Parameters and B_{eq} Values for Non-Hydrogen Atoms of 4a

atom	x	y	z	B_{eq}, Å^2
Fe	0.8296 (1)	0.2544 (2)	0.0116 (1)	3.60 (2)
O(1)	1.0754 (8)	0.245 (1)	−0.0747 (7)	8.4 (2)
O(2)	0.8279 (9)	0.0186 (7)	0.0568 (7)	6.9 (2)
O(3)	0.6971 (8)	0.2079 (6)	−0.1957 (5)	4.6 (2)
O(4)	0.7762 (8)	0.4603 (6)	−0.1302 (5)	4.5 (2)
C(1)	0.9771 (9)	0.251 (1)	−0.0396 (8)	4.6 (2)
C(2)	0.827 (1)	0.1117 (9)	0.0413 (7)	4.1 (2)
C(3)	0.7316 (8)	0.2552 (9)	−0.1153 (6)	3.2 (2)
C(4)	0.7198 (9)	0.3735 (8)	−0.0863 (7)	3.2 (2)
C(5)	0.703 (1)	0.3869 (8)	0.0139 (6)	3.3 (2)
C(6)	0.786 (1)	0.466 (1)	0.0868 (8)	4.8 (3)
C(7)	0.912 (1)	0.391 (1)	0.1164 (9)	6.5 (3)
C(8)	0.870 (1)	0.305 (1)	0.1698 (9)	6.0 (3)
C(9)	0.729 (1)	0.327 (1)	0.1799 (8)	5.4 (3)
C(10)	0.6593 (9)	0.2989 (9)	0.0711 (7)	3.4 (2)
C(11)	0.718 (1)	0.454 (1)	0.1790 (8)	5.9 (3)
C(12)	0.782 (1)	0.445 (1)	−0.2359 (7)	4.9 (3)
C(13)	0.647 (1)	0.450 (1)	−0.2980 (9)	6.5 (3)
C(14)	0.5189 (9)	0.245 (1)	0.0525 (7)	4.1 (2)
C(15)	0.423 (1)	0.314 (1)	0.1018 (9)	6.3 (3)
C(16)	0.524 (1)	0.128 (1)	0.1015 (9)	6.2 (3)
C(17)	0.459 (1)	0.227 (1)	−0.0569 (8)	6.0 (3)

[a] $B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j$.

Table III. Selected Bond Lengths (Å) and Angles (deg) for 4a

	Bond Lengths		
Fe–C(1)	1.75 (1)	C(4)–C(5)	1.41 (1)
Fe–C(2)	1.77 (1)	C(5)–C(6)	1.52 (1)
Fe–C(3)	1.843 (8)	C(5)–C(10)	1.43 (1)
Fe–C(4)	2.137 (9)	C(6)–C(7)	1.55 (2)
Fe–C(5)	2.05 (1)	C(6)–C(11)	1.54 (2)
Fe–C(7)	2.25 (1)	C(7)–C(8)	1.38 (1)
Fe–C(8)	2.20 (1)	C(8)–C(9)	1.48 (2)
Fe–C(10)	2.09 (1)	C(9)–C(10)	1.56 (1)
O(1)–C(1)	1.17 (1)	C(9)–C(11)	1.54 (2)
O(2)–C(2)	1.14 (1)	C(10)–C(14)	1.54 (1)
O(3)–C(3)	1.23 (1)	C(12)–C(13)	1.47 (2)
O(4)–C(4)	1.38 (1)	C(14)–C(15)	1.52 (2)
O(4)–C(12)	1.46 (1)	C(14)–C(16)	1.56 (2)
C(3)–C(4)	1.49 (1)	C(14)–C(17)	1.52 (1)
	Bond Angles		
C(1)–Fe–C(2)	96.5 (6)	C(1)–Fe–C(3)	88.9 (4)
C(1)–Fe–C(4)	98.8 (5)	C(1)–Fe–C(5)	126.8 (5)
C(1)–Fe–C(7)	91.4 (5)	C(1)–Fe–C(8)	111.6 (5)
C(1)–Fe–C(10)	88.9 (4)	C(2)–Fe–C(3)	101.1 (5)
C(2)–Fe–C(4)	140.6 (4)	C(2)–Fe–C(5)	136.3 (5)
C(2)–Fe–C(7)	126.2 (5)	C(2)–Fe–C(8)	93.1 (5)
C(2)–Fe–C(10)	96.8 (5)	C(3)–Fe–C(4)	43.3 (4)
C(3)–Fe–C(5)	77.0 (4)	C(3)–Fe–C(7)	132.2 (5)
C(3)–Fe–C(8)	153.6 (5)	C(3)–Fe–C(10)	91.0 (4)
C(4)–Fe–C(5)	39.3 (4)	C(4)–Fe–C(7)	89.6 (4)
C(4)–Fe–C(8)	114.3 (4)	C(4)–Fe–C(10)	72.3 (4)
C(5)–Fe–C(7)	65.1 (4)	C(5)–Fe–C(8)	77.4 (4)
C(5)–Fe–C(10)	40.4 (4)	C(7)–Fe–C(8)	36.1 (5)
C(7)–Fe–C(10)	78.6 (4)	C(8)–Fe–C(10)	65.0 (4)
C(4)–O(4)–C(12)	114.9 (8)	Fe–C(1)–O(1)	178 (1)
Fe–C(2)–O(2)	177 (1)	Fe–C(3)–O(3)	149.1 (9)
C(3)–C(4)–C(5)	113.1 (8)	C(4)–C(5)–C(10)	122.6 (9)
C(5)–C(6)–C(7)	97.8 (9)	C(8)–C(9)–C(10)	98.9 (9)
C(5)–C(10)–C(14)	125.7 (8)	C(9)–C(10)–C(14)	119.8 (9)
C(6)–C(11)–C(9)	93.4 (9)	C(10)–C(14)–C(16)	114.9 (8)

Even at 25 °C, **2** transforms slowly into **4a**. According to kinetic experiments with ^{1}H NMR spectroscopy[13] the transformation is fit for a unimolecular process, and the activation energy is estimated at 85 kJ/mol. However, for the η^1-vinylcarbene complexes expected in the reactions

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[9] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K.; 1974; Vol. IV.

[10] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

[11] This value is similar to that of [phenyl(ethoxy)methylene]Fe(CO)$_4$, and comparable to those of known η^1-carbene group 6 metal complexes. (a) Schnatter, W. Ph. D. Thesis, Princeton University, 1986. (b) Kreiter, C. G.; Formácek, V. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 141–142.

[12] Fischer, E. O.; Beck, H.-J.; Kreiter, C. G.; Lynch, J.; Müller, J.; Winkler, E. *Chem. Ber.* **1972**, *105*, 162–172.

[13] The kinetic ^{1}H NMR experiment was carried out at 50 and 70 °C with a solution of **2** and **4a** (72.4 mg; the initial ratio = 91:9) in toluene-d_8 (0.45 mL) by analyzing integration ratios of the peak for the vinyl proton of **2** at 6.43 ppm to that of the methyne proton of **4a** at 3.00 ppm.

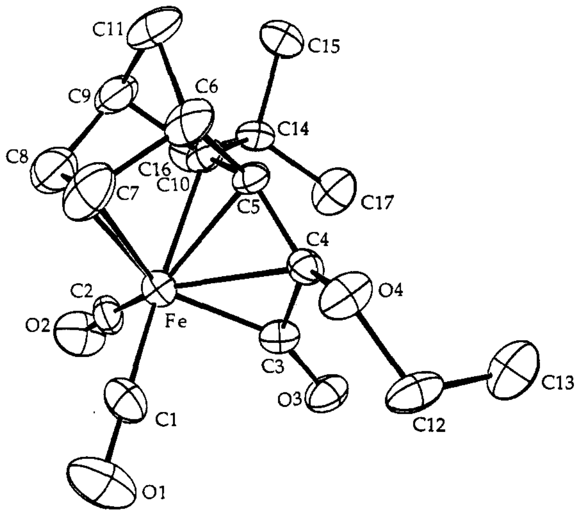

Figure 1. Structure of **4a** with the atom-labeling scheme.

of other alkynylcarbene complexes, **1b**–**1e**, with cyclopentadiene, the activation energies are apparently lower, and the corresponding CO insertion products, **4b**–**4e**, are given directly at 25 °C.

Among the CO insertion products, **4a** is crystallized from pentane at −78 °C. The molecular structure of **4a** is shown in Figure 1. The vinylketene ligand can be described as that of a (η^3-allyl + η^1-acyl)Fe(II) system rather than a (η^4-vinylketene)Fe(0) one:[14] The bond lengths C(4)–C(5) and C(5)–C(10) (1.41 and 1.43 Å) are in the range of those found in known (η^3-allyl)Fe complexes,[15] and the C(3)–C(4) bond length (1.49 Å) is similar to those of typical C(sp^2)–C(sp^2) single bonds. The Fe–C(3) bond length (1.834 Å) is much shorter than those of known (η^4-vinylketene)iron(0) complexes.[16] The C(7)–C(8) bond length (1.38 Å) is slightly longer than those of free alkenes, and this may implicate a weak metal–ligand back-bonding.[17]

The transformation appears to be initiated by decarbonylation accompanied with intramolecular coordination of the carbon–carbon double bond adjacent to the carbene carbon. Then, the CO insertion at the original carbene carbon is induced by the additional coordination of the remaining carbon–carbon double bond of the norbornadiene moiety (Scheme I). The additional coordination seems to be crucial for the CO insertion.[18] In reactions of the alkynylcarbene complexes with open-chain 1,3-dienes, η^3-vinylcarbene complexes (e.g., **3**) are produced rather than CO insertion products even at 50 °C.[7]

The η^3:η^1-allylacyl complexes, **4a**–**4e**, are reactive toward moisture. The hydrolysis products **5** result from treatment of solutions of **4** in hexane with a small amount of degassed water or during chromatographic separation. The formyl substituent of **5** is indicative of decarbonylation from the acyl moiety of **4** in the hydrolysis. However, the η^1-vinylcarbene complex **2** and the η^3-vinylcarbene complex **3** are stable against hydrolysis under the above conditions. The difference can be rationalized by the role of the internal carbon–carbon double bond like the C(7)–C(8) bond in **4a**, which is weakly coordinating and can be dissociated readily to induce decarbonylation, leading to formation of the corresponding η^3-vinylcarbene complex at the initial stage, but stabilize the hydrolysis products by forming (norbornadiene)Fe(CO)$_3$ derivatives.

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Registry No. **1a**, 136131-76-5; **1b**, 136131-77-6; **1c**, 136131-75-4; **1d**, 136131-71-0; **1e**, 136131-78-7; **2a**, 139583-34-9; **4a**, 139583-39-4; **4b**, 136154-77-3; **4e**, 139583-37-2; **5a**, 139583-40-7; **5b**, 136131-74-3; **5c**, 139583-35-0; **5d**, 139583-36-1; **5e**, 139583-38-3; cyclopentadiene, 542-92-7.

Supplementary Material Available: Tables of bond angles and anisotropic temperature factors for **4a** (2 pages); a listing of observed and calculated structure factors for **4a** (14 pages). Ordering information is given on any current masthead page.

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