

Studies on Thermolysis of Isomerized Products of Olefin-Coordinated Alkoxycarbene Iron Complexes. Novel Thermolytic Products and Their Structures

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Heating a solution of the isomerized (butadiene)(alkoxycarbene)iron complexes $[\text{C}_4\text{H}_6(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{Ar}]$ (**1**, Ar = *o*-CH₃C₆H₄; **2**, Ar = *p*-CF₃C₆H₄) in benzene in a sealed tube at 70–80 °C for 70–72 h gave the H-migrating pyrolytic products $[\{(1-4-\eta)\text{-C}_4\text{H}_5\text{-C}(\text{H})(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{-CH}_3\text{-o}\}\text{Fe}(\text{CO})_3]$ (**15**) and $[\{(2-5-\eta)\text{-CH}_3\text{C}_4\text{H}_3(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CF}_3\text{-p}\}\text{Fe}(\text{CO})_3]$ (**16**), respectively. A similar thermolysis of $[\text{C}_4\text{H}_6(\text{CO})_2\{\text{P}(\text{OPh})_3\}\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CF}_3\text{-p}]$ (**3**), a $\text{P}(\text{OPh})_3$ adduct of **2**, yielded the analogous thermolytic product $[\{(2-5-\eta)\text{-CH}_3\text{C}_4\text{H}_3(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CF}_3\text{-p}\}\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}]$ (**17**). The ring-opened (cycloheptatriene)(alkoxycarbene)iron complex $[\text{C}_7\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}]$ (**4**) was heated similarly to give the conjugating polyolefin-coordinated tricarbonyliron compound $[\{(1-2-\eta):(7-8-\eta)\text{-C}_7\text{H}_8\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}\}\text{Fe}(\text{CO})_3]$ (**18**), while the thermal decomposition of the ring-opened norbornadiene alkoxycarbene complexes $[\eta^3\text{-C}_7\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{Ar}]$ (**5**, Ar = C₆H₅; **6**, Ar = *p*-CH₃C₆H₄; **7**, Ar = *o*-CH₃C₆H₄; **8**, Ar = *p*-CF₃C₆H₄) afforded the novel diiron dimers $[\{\text{Fe}(\mu\text{-CO})(\text{CO})(\eta^5\text{-C}_5\text{H}_4\text{-CH}_2\text{CH}_2\text{COAr})\}_2]$ (**19**, Ar = C₆H₅; **20**, Ar = *p*-CH₃C₆H₄) or C–C bond-breaking η^4 -olefin-coordinated tricarbonyliron complexes $[\{\eta^4\text{-C}_7\text{H}_8\text{C}(\text{OC}_2\text{H}_5)\text{Ar}\}\text{Fe}(\text{CO})_3]$ (**21**, Ar = *o*-CH₃C₆H₄; **22**, Ar = *p*-CF₃C₆H₄). The isomerized (limonene)(alkoxycarbene)iron complex $[\eta^3\text{-C}_{10}\text{H}_{16}(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5]$ (**9**) was thermally decomposed to produce the η^4 cyclic olefin coordinated tricarbonyliron complex $[\{\eta^4\text{-C}_{10}\text{H}_{15}\text{CH}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5\}\text{Fe}(\text{CO})_3]$ (**23**). Interestingly, the thermolysis of the (limonene)(alkoxycarbene)iron complex $[\eta^4\text{-C}_{10}\text{H}_{16}(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}]$ (**10**) can also give the analogous cyclic olefin coordinated tricarbonyliron complex $[\{\eta^4\text{-C}_{10}\text{H}_{15}\text{CH}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}\}\text{Fe}(\text{CO})_3]$ (**24**). The thermolysis of the isomerized 1,5-cyclooctadiene (trimethylsiloxy)carbene iron complex $[(\text{CO})_2\text{Fe}\{\eta^6\text{-p-C}_6\text{H}_5\text{C}_6\text{H}_4\text{C}(\text{OSiMe}_3)\text{C}_8\text{H}_{12}\}]$ (**11**) yields 9-aryl-9-(trimethylsiloxy)bicyclo[4.2.1]non-2-ene, $[\text{p-C}_6\text{H}_5\text{C}_6\text{H}_4\text{C}\{\text{OSi}(\text{CH}_3)_3\}\text{C}_8\text{H}_{12}]$ (**25**). The thermolyses of the isomerized products of the (cyclooctatetraene)(ethoxycarbene)iron complexes $[\eta^3\text{-C}_8\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{Ar}]$ (**12**, Ar = *o*-CH₃C₆H₄; **13**, Ar = C₆H₅) and $[\eta^4\text{-C}_8\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-p}]$ (**14**) produced the head-bridged cyclooctatriene derivatives $[\text{C}_8\text{H}_8\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}]$ (**26**) and $[\text{C}_8\text{H}_7(\text{OC}_2\text{H}_5)\text{C}(\text{H})\text{Ar}]$ (**27**, Ar = C₆H₅; **28**, Ar = *p*-CH₃C₆H₄), respectively, via C–C bond formation or ethoxy migration. The structures of compounds **15–17**, **20**, **23**, **25**, **26**, and **28** were established by X-ray diffraction studies.

Introduction

The considerable interest in the synthesis, structure, and chemistry of alkene-coordinated transition-metal carbene complexes stems largely from the fact that they are important intermediates in various reactions of transition-metal carbene complexes with alkenes.^{1–3} In recent years, olefin-coordinated transition-metal carbene and carbyne complexes and/or their isomerized products have been examined widely; a great number

of the olefin-coordinated transition-metal carbene complexes and/or their isomerized products were synthesized, and a series of novel isomerizations of olefin ligands have been observed by the reactions of olefin-ligated transition-metal carbonyls with aryllithium reagents followed by alkylation with alkylating reagents in our laboratory.^{4–10} However, only very little is known^{4b,11} about the reactivity of these novel olefin-

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(1) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3754.

(2) Parlier, A.; Rudler, H.; Platzer, N.; Fontanniller, M. Soum, A. *J. Organomet. Chem.* **1985**, *287*, C8.

(3) Harrison, J.-L.; Chauvin, Y. *Makromol. Chem.* **1971**, *141*, 161.

(4) (a) Chen, J.-B.; Lei, G.-X.; Xu, W.-H. *J. Organomet. Chem.* **1985**, *286*, 55. (b) Wang, T.-L.; Chen, J.-B.; Wang, Q.-W. *Acta Chim. Sin. (Chin. Ed.)* **1991**, *49*, 265.

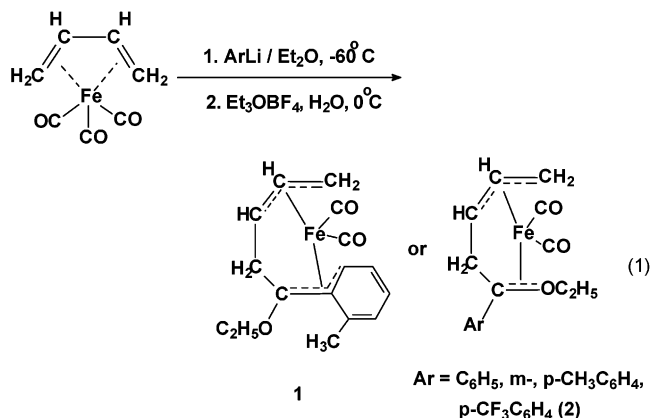
(5) Chen, J.-B.; Lei, G.-X.; Pan, Z.-H.; Zhang, S.-W.; Tang, Y.-Q. *J. Chem. Soc., Chem. Commun.* **1987**, 1273.

(6) Chen, J.-B.; Lei, G.-X.; Shao, M.-C.; Xu, X.-J.; Zhang, Z.-Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1296.

(7) Chen, J.-B.; Lei, G.-X.; Jin, Z.-S.; Hu, L.-H.; Wei, G.-C. *J. Chem. Soc., Chem. Commun.* **1988**, 731. (b) Chen, J.-B.; Lei, G.-X.; Jin, Z.-S.; Hu, L.-H.; Wei, G.-C. *Organometallics* **1988**, *7*, 1652.

coordinated metal carbene and carbyne complexes and their isomerized products. We are now interested in examining the reactivity of these isomerized metal carbene complexes.

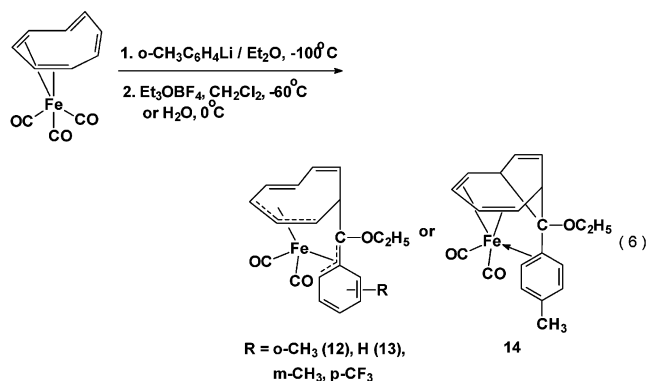
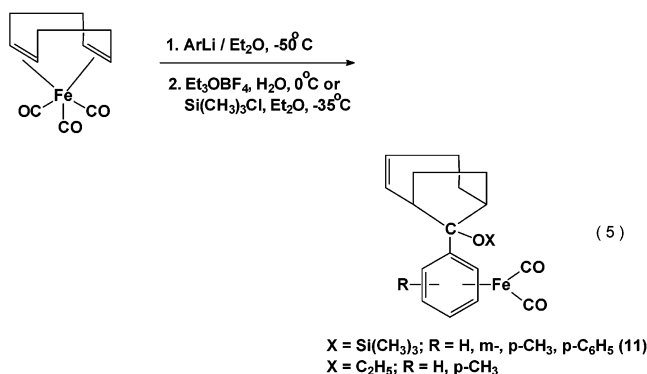
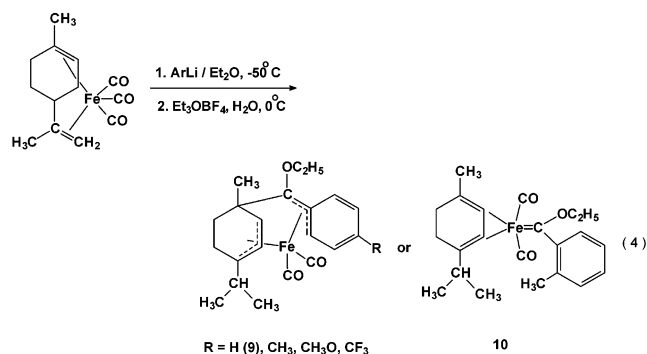
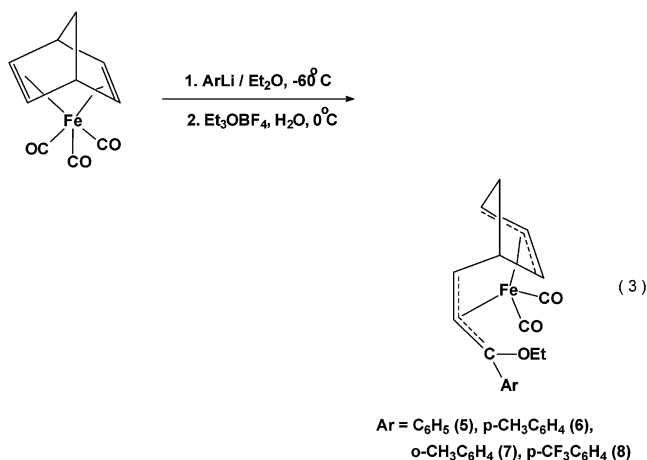
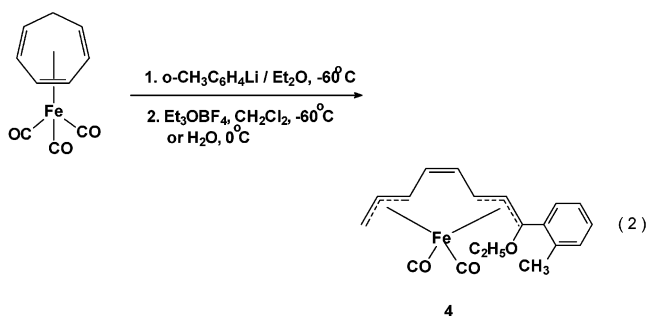
We previously reported that the reactions of (1,3-butadiene)tricarbonyliron with aryllithium reagents followed by alkylation with Et_3OBF_4 in aqueous solution yielded the $(\eta^3\text{-butadienyl})\text{dicarbonyliron}$ complexes $[\text{C}_4\text{H}_6(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{Ar}]$ (eq 1), which we call the



isomerized (butadiene)dicarbonyl[ethoxy(aryl)carbene]iron complexes or the isomerized products of (butadiene)dicarbonyl[ethoxy(aryl)carbene]iron complexes.^{4a}

The reactions of cyclopolyolefin-coordinated transition-metal carbonyl compounds such as (cycloheptatriene)tricarbonyliron, (norbornadiene)tricarbonyliron, (limonene)tricarbonyliron, (spiro[4.4]nona-1,3-diene)tricarbonyliron, and (1,5-cyclooctadiene)tricarbonyliron and (cyclooctatetraene)tricarbonyliron with aryllithium reagent under similar conditions give the novel isomerized products of olefin-coordinated (alkoxycarbene)iron complexes $[\text{C}_7\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}]$ (eq 2),⁵ $[\text{C}_7\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{Ar}]$ (eq 3),⁶ $[(\eta^3\text{-C}_{10}\text{H}_{16})(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{Ar}]$ and $[(\eta^4\text{-C}_{10}\text{H}_{16})(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}]$ (eq 4),⁷ $[(\text{CO})_2\text{Fe}\{\eta^6\text{-RC}_6\text{H}_4\text{C}(\text{OX})\text{C}_8\text{H}_{12}\}]$ ($\text{X} = \text{SiMe}_3$, C_2H_5 ; $\text{R} = \text{H}$, *m*-, *p*- CH_3 , *p*- C_6H_5) (eq 5),⁸ and $[\text{C}_8\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{Ar}]$ ($\text{Ar} = \text{C}_6\text{H}_5$, *o*-, *m*-, *p*- $\text{CH}_3\text{C}_6\text{H}_4$, *p*- $\text{CF}_3\text{C}_6\text{H}_4$) (eq 6),⁹ respectively.

To explore the reactivity of the isomerized products of these olefin-coordinated alkoxycarbene iron complexes and their application in organometallic and organic synthesis, we chose the isomerized (butadiene)(ethoxycarbene)iron complexes $[\text{C}_4\text{H}_6(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{Ar}]$ (**1**, $\text{Ar} = o\text{-CH}_3\text{C}_6\text{H}_4$; **2**, $\text{Ar} = p\text{-CF}_3\text{C}_6\text{H}_4$) and its $\text{P}(\text{OPh})_3$ adduct $[\text{C}_4\text{H}_6(\text{CO})_2\{\text{P}(\text{OPh})_3\}\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CF}_3\text{-p}]$ (**3**) and the ring-opened (cycloheptatriene)(ethoxycarbene)iron complex $[\text{C}_7\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}]$ (**4**), the ring-opened (norbornadiene)(ethoxycarbene)iron com-



(8) Chen, J.-B.; Yin, J.-G.; Fan, Z.-C.; Xu, W.-H. *J. Chem. Soc., Dalton Trans.* **1988**, 2803.

(9) Chen, J.-B.; Lei, G.-X.; Xu, W.-H.; Pan, Z.-H.; Zhang, S.-W.; Zhang, Y.-Y.; Jin, X.-L.; Shao, M.-C.; Tang, Y.-Q. *Organometallics* **1987**, 6, 2461.

(10) (a) Chen, J.-B.; Lei, G.-X.; Zhang, Z.-Y.; Tang, Y.-Q. *Sci. Chin., Ser. B* **1989**, 32, 129. (b) Yu, Y.; Chen, J.-B. *Organometallics* **1993**, 12, 4731. (c) Chen, J.-B.; Li, D.-S.; Yu, Y.; Chen, C.-G. *Organometallics* **1994**, 13, 3581. (d) Chen, J.-B.; Yu, Y.; Sun, J. *Organometallics* **1997**, 16, 3608. (e) Wang, B.-H.; Li, R.-H.; Sun, J.; Chen, J.-B. *Chem. Commun.* **1998**, 631. (f) Xiao, N.; Zhang, S.; Qiu, Z.-L.; Li, R.-H.; Wang, B.-H.; Xu, Q.; Sun, J.; Chen, J.-B. *Organometallics* **2002**, 21, 3709.

(11) (a) Chen, J.-B.; Yu, Y.; Hu, L.-H.; Jin, Z.-S. *J. Organomet. Chem.* **1993**, 447, 113. (b) Wang, B.-H.; Li, R.-H.; Sun, J.; Chen, J.-B. *Organometallics* **1998**, 17, 3723.

plexes [η^3 -C₇H₈(CO)₂FeC(OC₂H₅)Ar] (**5**, Ar = C₆H₅; **6**, Ar = *p*-CH₃C₆H₄; **7**, Ar = *o*-CH₃C₆H₄; **8**, Ar = *p*-CF₃C₆H₄), the isomerized (limonene)(ethoxycarbene)iron complex [(η^3 -C₁₀H₁₆)(CO)₂FeC(OC₂H₅)C₆H₅] (**9**) and (limonene)-(ethoxycarbene)iron complex [(η^4 -C₁₀H₁₆)(CO)₂FeC(OC₂H₅)C₆H₄CH₃-*o*] (**10**), the isomerized ((1,5-cyclooctadiene)(trimethylsiloxy)carbene)iron complex [(CO)[Fe(CO)₂](η^6 -*p*-C₆H₅C₆H₄C(OSiMe₃)(C₈H₁₂))] (**11**), and the isomerized products of (cyclooctatetraene)(ethoxycarbene)iron complexes [{ η^3 -C₈H₈C(OC₂H₅)Ar}Fe(CO)₂] (**12**, Ar = *o*-CH₃C₆H₄; **13**, Ar = C₆H₅) and [{ η^4 -C₈H₈C(OC₂H₅)C₆H₄CH₃-*p*}Fe(CO)₂] (**14**) as starting materials for the thermolysis reactions, which produced a series of novel thermal decomposition products. In this paper we describe these unusual thermolysis reactions and the structures of the novel thermolytic products.

Experimental Section

All reactions were performed under a dry, oxygen-free N₂ atmosphere using standard Schlenk techniques. All solvents employed were of reagent grade and dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under N₂. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl, while petroleum ether (30–60 °C) and CH₂Cl₂ were distilled from CaH₂. Neutral alumina (Al₂O₃) was deoxygenated under high vacuum for 16 h, deactivated with 5% w/w N₂-saturated water, and stored under N₂. The compounds [C₄H₆(CO)₂FeC(OC₂H₅)C₆H₄CH₃-*o*] (**1**),^{4a} [C₄H₆(CO)₂FeC(OC₂H₅)C₆H₄CF₃-*p*] (**2**),^{4a} [C₄H₆(CO)₂{P(OPh)₃}FeC(OC₂H₅)C₆H₄CF₃-*p*] (**3**; its preparation is similar to that of the PPh₃ adduct^{4b}), [C₇H₈(CO)₂FeC(OC₂H₅)C₆H₄CH₃-*o*] (**4**),⁵ [η^3 -C₇H₈(CO)₂FeC(OC₂H₅)Ar] (**5**, Ar = C₆H₅; **6**, Ar = *p*-CH₃C₆H₄; **7**, Ar = *o*-CH₃C₆H₄; **8**, Ar = *p*-CF₃C₆H₄),⁶ [(η^3 -C₁₀H₁₆)(CO)₂FeC(OC₂H₅)C₆H₅] (**9**),⁷ [(η^4 -C₁₀H₁₆)(CO)₂FeC(OC₂H₅)C₆H₄CH₃-*o*] (**10**),⁷ [(CO)₂Fe{(η^6 -*p*-C₆H₅C₆H₄C(OSiMe₃)(C₈H₁₂))}] (**11**),⁸ [η^3 -C₈H₈(CO)₂FeC(OC₂H₅)Ar] (**12**, Ar = *o*-CH₃C₆H₄; **13**, Ar = C₆H₅),⁹ and [η^4 -C₈H₈(CO)₂FeC(OC₂H₅)C₆H₄CH₃-*p*] (**14**)⁹ were prepared as previously described.

The IR spectra were measured on a Shimadzu IR-440 or a Bio-Rad FTS-185 spectrophotometer in CH₂Cl₂ solvent with a KBr cell. All ¹H NMR and ¹³C NMR spectra were recorded at ambient temperature in acetone-*d*₆ with TMS as the internal reference using a Bruker AM-300 or a Varian Mercury 300 spectrometer. Electron ionization mass spectra (EIMS) were run on a Hewlett-Packard 5989A spectrometer. Melting points obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

Thermolysis of [C₄H₆(CO)₂FeC(OC₂H₅)C₆H₄CH₃-*o*] (1**) To Give [(1-4- η)-C₄H₅CH(OC₂H₅)C₆H₄CH₃-*o*]Fe(CO)₃ (**15**).** Compound **1** (0.43 g, 1.37 mmol) was dissolved in 30 mL of benzene in a 50 mL quartz tube. The orange-red benzene solution was cooled to -80 °C to freeze it, and the tube was sealed under vacuum. The sealed tube was heated to 75–80 °C with stirring for 72 h. After it was cooled to room temperature, the resulting dark solution was transferred to a Schlenk flask and evaporated in vacuo to dryness. The dark residue was chromatographed on Al₂O₃ with petroleum ether/CH₂Cl₂ (10:1) as the eluant. The yellow band was eluted and collected. After vacuum removal of the solvent, the crude product was recrystallized from petroleum ether at -80 °C to give 0.257 g (58%) of orange-yellow crystals of **15**: mp 46–47 °C dec; IR (hexane) ν (CO) 2030 (s), 1992 (s), 1975 (m) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.39–7.13 (m, 4H, CH₃C₆H₄), 5.65 (m, 1H, C₄H₆), 5.40–5.33 (m, 1H, C₄H₆), 4.46 (d, 1H, C₄H₆), 3.25 (q, 2H, OCH₂CH₃), 2.38 (s, 3H, CH₃C₆H₄), 1.73 (m, 1H, C₄H₆), 1.36 (m, 1H, C₄H₆), 1.15 (t, 3H, OCH₂CH₃), 0.42 (dd, 1H, C₄H₆); MS *m/z* 314 [M⁺ - CO], 286 [M⁺ - 2CO], 258 [M⁺ - 3CO]. Anal. Calcd for C₁₇H₁₈O₄Fe: C, 59.67; H, 5.30. Found: C, 59.60; H, 5.33.

Thermolysis of [C₄H₆(CO)₂FeC(OC₂H₅)C₆H₄CF₃-*p*] (2**) To Give [(2-5- η)-CH₃C₄H₃C(OC₂H₅)C₆H₄CF₃-*p*]Fe(CO)₃ (**16**).** Similar to the procedures above for the thermolysis of **1**, compound **2** (0.50 g, 1.36 mmol) in benzene in a quartz tube was heated to 75–80 °C for 72 h. Further treatment of the resulting solution in a manner similar to that described in the thermolysis of **1** gave 0.334 g (62%) of orange-yellow crystals of **16**: mp 50–52 °C dec; IR (hexane) ν (CO) 2048 (m), 1997 (s), 1982 (s) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.72–7.62 (dd, 4H, CF₃C₆H₄), 5.98 (d, 1H, *J* = 5.2 Hz, CHC(OC₂H₅)C₆H₄CF₃), 5.71 (dd, 1H, *J*₁ = 5.2 Hz, *J*₂ = 9.3 Hz, C₄H₆), 3.58 (m, 1H, CHCH₃), 3.28 (q, 2H, *J* = 7.0 Hz, OCH₂CH₃), 1.57 (d, 3H, *J* = 6.5 Hz, CHCH₃), 1.02 (t, 3H, *J* = 7.0 Hz, OCH₂CH₃); MS *m/z* 368 [M⁺ - CO], 340 [M⁺ - 2CO], 312 [M⁺ - 3CO]. Anal. Calcd for C₁₇H₁₅O₄F₃Fe: C, 51.54; H, 3.82. Found: C, 51.48; H, 4.05.

Thermolysis of [C₄H₆(CO)₂{P(OPh)₃}FeC(OC₂H₅)C₆H₄CF₃-*p*] (3**) To Give [(2-5- η)-CH₃C₄H₃(OC₂H₅)C₆H₄CF₃-*p*]Fe(CO)₂{P(OPh)₃} (**17**).** Using the same procedures as for the thermolysis of **1**, 0.35 g (0.51 mmol) of **3** in benzene in a quartz tube was heated to 75–80 °C for 72 h. The resulting solution was worked up as described for the thermolysis of **1** to give 0.192 g (55%) of yellow crystals of **17**: mp 60–62 °C dec; IR (hexane) ν (CO) 2051 (m), 1993 (s), 1978 (s) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.78–7.71 (dd, 4H, CF₃C₆H₄), 7.52–7.12 (m, 15H, C₆H₅), 5.65 (m, 1H, C₄H₆), 5.40 (m, 1H, C₄H₆), 3.75 (m, 1H, C₄H₆), 3.30 (q, 2H, OCH₂CH₃), 1.30 (d, 3H, CHCH₃), 1.05 (t, 3H, OCH₂CH₃); MS *m/z* 678 (M⁺), 368 [M⁺ - P(OPh)₃]. Anal. Calcd for C₃₄H₃₀O₆F₃PFe: C, 60.19; H, 4.46. Found: C, 59.86; H, 4.17.

Thermolysis of [C₇H₈(CO)₂FeC(OC₂H₅)C₆H₄CH₃-*o*] (4**) To Give [(1-2- η):-(7-8- η)-C₇H₈C(OC₂H₅)C₆H₄CH₃-*o*]Fe(CO)₃ (**18**).** As in the thermolysis of **1** above, a solution of compound **4** (0.130 g, 0.37 mmol) in 30 mL of benzene in a quartz tube was heated to 80–90 °C for 70–72 h. Further treatment of the resulting solution as described above for the thermolysis of **1** gave 0.088 g (63%) of yellow crystals of **18**: mp 72–74 °C dec; IR (CH₂Cl₂) ν (CO) 2039 (m), 1971 (s), 1965 (vs) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.27–7.19 (m, 4H, CH₃C₆H₄), 6.19 (d, 1H, *J* = 11.1 Hz, C₇H₈), 5.56 (m, 3H, C₇H₈), 5.23 (t, 1H, *J* = 10.8 Hz, C₇H₈), 4.03 (q, 2H, OCH₂CH₃), 2.65 (t, 1H, *J* = 9.6 Hz, C₇H₈), 2.25 (s, 3H, CH₃C₆H₄), 1.89 (d, 1H, *J* = 7.2 Hz, C₇H₈), 1.32 (t, 3H, *J* = 7.2 Hz, OCH₂CH₃), 0.94 (d, 1H, *J* = 7.5 Hz, C₇H₈); ¹³C NMR δ 213.5 (CO), 160.6 (C(OC₂H₅)), 137.7, 136.5, 131.1, 130.9, 129.7, 127.5 (C₆H₄CH₃-*o*), 127.1, 126.4, 110.1, 87.6, 82.9, 61.4, 40.3 (C₇H₈), 64.3 (OCH₂CH₃), 19.7 (C₆H₄CH₃-*o*), 15.0 (OCH₂CH₃); MS *m/z* 380 (M⁺), 352 [M⁺ - CO], 324 [M⁺ - 2CO], 296 [M⁺ - 3CO]. Anal. Calcd for C₂₀H₂₀O₄Fe: C, 63.18; H, 5.30. Found: C, 62.65; H, 5.27.

Thermolysis of [η^3 -C₇H₈(CO)₂FeC(OC₂H₅)C₆H₅] (5**) To Give [(Fe(μ -CO)(CO)(η^5 -C₅H₄CH₂CH₂COC₆H₅))₂] (**19**).** Compound **5** (0.064 g, 0.19 mmol) was dissolved in 30 mL of benzene in a 50 mL quartz tube. The orange-red benzene solution was cooled to -80 °C to freeze it, and the tube was sealed under vacuum. The sealed tube was heated to 80–90 °C with stirring for 70–72 h. After it was cooled to room temperature, the resulting dark solution was transferred to a Schlenk flask and evaporated in vacuo to dryness. The dark residue was chromatographed on Al₂O₃ with petroleum ether/CH₂Cl₂ (10:1) followed by petroleum ether/CH₂Cl₂/Et₂O (5:5:1) as the eluant. The brown-yellow band was eluted and collected. After vacuum removal of the solvent, the crude product was recrystallized from petroleum ether/CH₂Cl₂ (10:1) at -80 °C to give 0.035 g (60%) of brown-red crystals of **19**: mp 140–142 °C dec; IR (CH₂Cl₂) ν (CO) 1991 (vs), 1949 (s), 1769 (vs) cm⁻¹, ν (C=O) 1687 (s) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 8.06 (m, 4H, C₆H₅), 7.63 (m, 2H, C₆H₅), 7.54 (m, 4H, C₆H₅), 4.95 (m, 4H, C₅H₄), 4.71 (m, 4H, C₅H₄), 3.49 (t, 4H, *J* = 7.3 Hz, CH₂COC₆H₅), 2.92 (t, 4H, *J* = 7.3 Hz, C₅H₄CH₂-); MS *m/z* 590 [M⁺ - CO], 253 [FeC₅H₄(CH₂)₂COC₆H₅⁺], 197 [C₅H₄(CH₂)₂COC₆H₅⁺]. Anal. Calcd for C₃₂H₂₆O₆Fe₂: C, 62.17; H, 4.24. Found: C, 61.71; H, 4.55.

Thermolysis of $[\eta^3\text{-C}_7\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-p}]$ (6) To Give $[\{\text{Fe}(\mu\text{-CO})(\text{CO})(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{COC}_6\text{H}_4\text{CH}_3\text{-p})\}_2]$ (20). Similar to the thermolysis of **5**, a solution of **6** (0.062 g, 0.018 mmol) in benzene in a quartz tube was heated to 75–80 °C for 72 h. After the solvent was evaporated, further treatment of the residue in a manner similar to that described for the thermolysis of **5** gave 0.036 g (64%) of **20** as brown-red crystals: mp 136 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 1991 (vs), 1949 (s), 1768 (vs) cm^{-1} , $\nu(\text{C}=\text{O})$ 1682 (m) cm^{-1} ; ^1H NMR ($\text{CD}_3\text{-COCD}_3$) δ 7.95 (d, 4H, J = 8.3 Hz, $\text{CH}_3\text{C}_6\text{H}_4$), 7.33 (d, 4H, J = 8.3 Hz, $\text{CH}_3\text{C}_6\text{H}_4$), 4.94 (s, 4H, C_5H_4), 4.70 (s, 4H, C_5H_4), 3.44 (t, 4H, J = 7.3 Hz, $-\text{CH}_2\text{COC}_6\text{H}_5$), 2.91 (t, 4H, J = 7.3 Hz, $\text{C}_5\text{H}_4\text{CH}_2-$), 2.40 (s, 6H, $\text{CH}_3\text{C}_6\text{H}_4$); MS m/z 478 [$\text{M}^+ - 4\text{CO} - \text{Fe}$], 267 [$\text{FeC}_5\text{H}_4(\text{CH}_2)_2\text{COC}_6\text{H}_4\text{CH}_3^+$], 211 [$\text{C}_5\text{H}_4(\text{CH}_2)_2\text{COC}_6\text{H}_4\text{CH}_3^+$]. Anal. Calcd for $\text{C}_{34}\text{H}_{30}\text{O}_6\text{Fe}_2$: C, 63.19; H, 4.68. Found: C, 62.98; H, 4.88.

Thermolysis of $[\eta^3\text{-C}_7\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}]$ (7) To Give $[\{\eta^4\text{-C}_7\text{H}_8\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}\}\text{Fe}(\text{CO})_3]$ (21). As described above for the thermolysis of **5**, compound **7** (0.280 g, 0.79 mmol) in benzene in a quartz tube was heated to 80–90 °C for 70–72 h. The resulting solution was worked up as described for the thermolysis of **5** to afford 0.180 g (59%) of orange-red crystals of **21**: mp 86–88 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 2041 (m), 1972 (vs, br) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 7.31–7.16 (m, 4H, $\text{CH}_3\text{C}_6\text{H}_4$), 5.95 (dd, 1H, J = 14.8 Hz, J = 10.9 Hz, C_7H_8), 5.65 (dd, 2H, J = 16.0 Hz, J = 11.1 Hz, C_7H_8), 5.51 (dd, 1H, J = 8.9 Hz, J = 4.9 Hz, C_7H_8), 5.34 (ddd, 1H, C_7H_8), 3.93 (q, 2H, J = 7.0 Hz, OCH_2CH_3), 2.25 (s, 3H, $\text{CH}_3\text{C}_6\text{H}_4$), 2.23 (m, 1H, C_7H_8), 1.78 (dd, 1H, J = 8.2 Hz, J = 1.3 Hz, C_7H_8), 1.30 (t, 3H, J = 7.1 Hz, OCH_2CH_3), 0.75 (dd, 1H, J = 9.4 Hz, J = 1.6 Hz, C_7H_8); ^{13}C NMR δ 215.4 (CO) 168.3 ($\text{C}(\text{OC}_2\text{H}_5)$), 137.5, 136.4, 130.9, 130.7, 130.0, 129.4 ($\text{C}_6\text{H}_4\text{CH}_3\text{-o}$), 126.2, 126.0, 110.5, 86.0, 81.8, 67.8, 39.9 (C_7H_8), 63.6 (OCH_2CH_3), 19.5 ($\text{C}_6\text{H}_4\text{CH}_3\text{-o}$), 15.5 (OCH_2CH_3); MS m/z 380 (M^+), 352 [$\text{M}^+ - \text{CO}$], 324 [$\text{M}^+ - 2\text{CO}$], 296 [$\text{M}^+ - 3\text{CO}$]. Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_4\text{Fe}$: C, 63.18; H, 5.30. Found: C, 62.99; H, 5.37.

Thermolysis of $[\eta^3\text{-C}_7\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CF}_3\text{-p}]$ (8) To Give $[\{\eta^4\text{-C}_7\text{H}_8\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CF}_3\text{-p}\}\text{Fe}(\text{CO})_3]$ (22). As described for the thermolysis of **5**, compound **8** (0.200 g, 0.49 mmol) in benzene in a quartz tube was heated to 80–90 °C for 75 h. Subsequent treatment as described for the thermolysis of **5** gave 0.138 g (64%) of orange-red crystals of **22**: mp 91–92 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 2046 (vs), 1975 (vs, br) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 7.76–7.66 (m, 4H, $\text{CF}_3\text{C}_6\text{H}_4$), 6.46 (m, 1H, C_7H_8), 5.80 (m, 1H, C_7H_8), 5.60 (m, 2H, C_7H_8), 5.40 (m, 1H, C_7H_8), 3.98 (q, 2H, OCH_2CH_3), 2.94 (m, 1H, C_7H_8), 2.32 (t, 1H, C_7H_8), 1.83 (m, 1H, C_7H_8), 1.35 (t, 3H, OCH_2CH_3), 0.82 (d, 1H, C_7H_8); MS m/z 434 (M^+), 406 [$\text{M}^+ - \text{CO}$], 378 [$\text{M}^+ - 2\text{CO}$], 350 [$\text{M}^+ - 3\text{CO}$]. Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{O}_4\text{F}_3\text{Fe}$: C, 55.34; H, 3.95. Found: C, 55.18; H, 4.12.

Thermolysis of $[\eta^3\text{-C}_{10}\text{H}_{16}(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5]$ (9) To Give $[\{\eta^4\text{-C}_{10}\text{H}_{15}\text{CH}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5\}\text{Fe}(\text{CO})_3]$ (23). Compound **9** (0.23 g, 0.60 mmol) in benzene in a quartz tube was heated, in a manner similar to that described for the thermolysis of **5**, for 72–75 h. After vacuum removal of the solvent, the residue was worked up as described for the thermolysis of **5** to give 0.128 g (52%) of yellow crystals of **23**: mp 79–80 °C dec; IR (CH_2Cl_2) $\nu(\text{CO})$ 2038 (vs), 1961 (vs, br) cm^{-1} ; ^1H NMR ($\text{CD}_3\text{-COCD}_3$) δ 7.39–7.31 (m, 5H, C_6H_5), 5.22 (d, 1H, J = 6.3 Hz, $\text{C}_{10}\text{H}_{15}$), 4.20 (s, 1H, $\text{CH}(\text{OC}_2\text{H}_5)$), 3.35 (m, 1H, $\text{C}_{10}\text{H}_{15}$), 3.28 (m, 2H, OCH_2CH_3), 2.41 (d, 1H, J = 6.3 Hz, $\text{C}_{10}\text{H}_{15}$), 2.30 (m, 1H, CHMe_2), 2.06 (AB, 1H, J = 15.6 Hz, $\text{C}_{10}\text{H}_{15}$), 1.72 (AB, 1H, J = 15.6 Hz, $\text{C}_{10}\text{H}_{15}$), 1.32 (d, 3H, J = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$), 1.23 (d, 3H, J = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$), 1.12 (t, 3H, J = 6.7 Hz, OCH_2CH_3), 0.86 (s, 3H, $\text{C}_{10}\text{H}_{15}$); ^{13}C NMR δ 213.6 (CO), 139.9, 129.0, 128.9, 128.6, 128.3 (C_6H_5), 115.8, 89.1, 68.5, 64.2, 43.4, 42.9 ($\text{C}_{10}\text{H}_{15}$), 78.9 ($\text{CH}(\text{OC}_2\text{H}_5)$), 65.1 (OCH_2CH_3), 34.0 ($\text{CH}(\text{CH}_3)_2$), 27.3, 25.6 ($\text{CH}(\text{CH}_3)_2$), 19.5 (OCH_2CH_3), 15.4 (CH_3); MS m/z 410 (M^+), 382 [$\text{M}^+ - \text{CO}$], 354 [$\text{M}^+ - 2\text{CO}$], 326 [$\text{M}^+ - 3\text{CO}$]. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_4\text{Fe}$: C, 64.40; H, 6.39. Found: C, 64.33; H, 6.42.

Thermolysis of $[\eta^4\text{-C}_{10}\text{H}_{16}(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}]$ (10) To Give $[\{\eta^4\text{-C}_{10}\text{H}_{15}\text{CH}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}\}\text{Fe}(\text{CO})_3]$ (24). Compound **10** (0.090 g, 0.23 mmol) in benzene in a quartz tube was heated, in a manner similar to that described for the thermolysis of **9**, for 72–75 h. After vacuum removal of the solvent, the residue was worked up as described for the thermolysis of **9** to give 0.046 g (46%) of white crystals of **24**: mp 87–88 °C; IR (CH_2Cl_2) $\nu(\text{CO})$ 2038 (vs), 1964 (vs, br) cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 7.37–7.35 (m, 1H, $\text{C}_6\text{H}_4\text{CH}_3\text{-o}$), 7.20–7.18 (m, 3H, $\text{C}_6\text{H}_4\text{CH}_3\text{-o}$), 5.30–5.27 (dd, 1H, J = 6.6 Hz, J = 2.1 Hz, $\text{C}_{10}\text{H}_{15}$), 4.50 (s, 1H, $\text{CH}(\text{OC}_2\text{H}_5)$), 3.33–3.31 (m, 1H, $\text{C}_{10}\text{H}_{15}$), 3.25–3.17 (q, 2H, J = 6.9 Hz, OCH_2CH_3), 2.57 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.41 (d, 1H, J = 6.6 Hz, $\text{C}_{10}\text{H}_{15}$), 2.30–2.25 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 2.24–2.18 (dd, 1H, J = 15.9 Hz, J = 2.7 Hz, $\text{C}_{10}\text{H}_{15}$), 1.83–1.77 (dd, 1H, J = 15.9 Hz, J = 3.3 Hz, $\text{C}_{10}\text{H}_{15}$), 1.31 (d, 3H, J = 6.6 Hz, $\text{CH}(\text{CH}_3)_2$), 1.24 (d, 3H, J = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$), 1.10–1.06 (t, 3H, J = 6.9 Hz, OCH_2CH_3), 0.91 (s, 3H, CH_3); ^{13}C NMR δ 212.9 (CO), 138.1, 137.5, 130.3, 128.7, 127.3, 125.4 ($\text{C}_6\text{H}_4\text{CH}_3\text{-o}$), 115.4, 83.0, 67.9, 65.1, 43.9, 41.4 ($\text{C}_{10}\text{H}_{15}$), 78.9 ($\text{CH}(\text{OC}_2\text{H}_5)$), 64.1 (OCH_2CH_3), 33.4 ($\text{CH}(\text{CH}_3)_2$), 27.8 ($\text{C}_6\text{H}_4\text{CH}_3\text{-o}$), 25.1, 20.4 ($\text{CH}(\text{CH}_3)_2$), 18.9 (OCH_2CH_3), 14.8 (CH_3); MS m/z 424 (M^+), 396 [$\text{M}^+ - \text{CO}$], 340 [$\text{M}^+ - 3\text{CO}$]. Anal. Calcd for $\text{C}_{23}\text{H}_{28}\text{O}_4\text{Fe}$: C, 65.10; H, 6.65. Found: C, 64.99; H, 6.85.

Thermolysis of $[(\text{CO})_2\text{Fe}\{\eta^6\text{-p-C}_6\text{H}_5\text{C}_6\text{H}_4\}\text{C}(\text{OSiMe}_3)\text{-C}_8\text{H}_{12}]$ (11) To Give $[\{p\text{-C}_6\text{H}_5\text{C}_6\text{H}_4\text{C}(\text{OSiMe}_3)\text{C}_8\text{H}_{12}\}]\text{Fe}(\text{CO})_3]$ (25). Compound **11** (0.095 g, 0.20 mmol) in benzene in a quartz tube was heated, in a manner similar to that described for the thermolysis of **5**, at 80–90 °C for 72 h. Further treatment as used for the thermolysis of **5** gave 0.040 g (54%) of yellow crystals of **25**: mp 68–70 °C; ^1H NMR (CD_3COCD_3) δ 7.73–7.35 (m, 9H, $\text{C}_6\text{H}_5\text{C}_6\text{H}_4$), 6.04 (m, 1H, C_8H_{12}), 5.45 (m, 1H, C_8H_{12}), 3.19 (t, 1H, J = 8.7 Hz, C_8H_{12}), 3.01 (t, 1H, J = 6.7 Hz, C_8H_{12}), 2.49–2.26 (m, 3H, C_8H_{12}), 1.91–1.75 (m, 3H, C_8H_{12}), 1.67 (q, 1H, J = 14.7 Hz, $\text{C}_{10}\text{H}_{16}$), 1.50–1.45 (m, 1H, C_8H_{12}), –0.21 (s, 9H, $\text{Si}(\text{CH}_3)_3$); ^{13}C NMR δ 141.5, 141.3, 140.3, 135.7, 131.7, 130.0, 129.7, 129.6, 128.1, 127.6, 127.5, 127.1 ($\text{C}_6\text{H}_5\text{C}_6\text{H}_4$), 91.9, 49.5, 48.2, 48.1, 32.8, 27.7, 27.6, 24.0 (C_8H_{12}), 1.76 ($\text{OSi}(\text{CH}_3)_3$); MS m/z 362 (M^+), 285 [$\text{M}^+ - \text{C}_6\text{H}_5$], 73 [$\text{Si}(\text{CH}_3)_3^+$]. Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{OSi}$: C, 79.50; H, 8.34. Found: C, 79.32; H, 8.15.

Thermolysis of $[\eta^3\text{-C}_8\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}]$ (12) To Give $[\text{C}_8\text{H}_8\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}]\text{Fe}(\text{CO})_3$ (26). As described for the thermolysis of **5**, compound **12** (0.30 g, 0.89 mmol) in benzene in a quartz tube was heated at 90–95 °C for 70–72 h. The resulting solution was worked up as described for the thermolysis of **5** to yield 0.126 g (56%) of light yellow crystals of **26**: mp 80 °C; ^1H NMR (CDCl_3) δ 7.26–7.08 (m, 4H, $\text{CH}_3\text{C}_6\text{H}_4$), 6.21–6.08 (m, 4H, C_8H_8), 5.48 (m, 1H, C_8H_8), 5.03 (m, 1H, C_8H_8), 3.67 (m, 1H, C_8H_8), 3.29 (m, 1H, C_8H_8), 2.88 (q, 2H, OCH_2CH_3), 2.51 (s, 3H, $\text{CH}_3\text{C}_6\text{H}_4$), 1.01 (t, 3H, OCH_2CH_3); MS m/z 252 (M^+), 223 [$\text{M}^+ - \text{C}_2\text{H}_5$], 207 [$\text{M}^+ - \text{OC}_2\text{H}_5$], 116 [$\text{M}^+ - \text{OC}_2\text{H}_5 - \text{CH}_3\text{C}_6\text{H}_4$], 104 [C_8H_8^+]. Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}$: C, 85.67; H, 7.99. Found: C, 85.52; H, 8.10.

Thermolysis of $[\eta^3\text{-C}_8\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5]$ (13) To Give $[\text{C}_8\text{H}_7(\text{OC}_2\text{H}_5)\text{C}(\text{H})\text{C}_6\text{H}_5]\text{Fe}(\text{CO})_3$ (27). Using the same procedures as for the thermolysis of **5**, a solution of **13** (0.22 g, 0.66 mmol) in 30 mL of benzene in a quartz tube was heated to 90–95 °C for 72 h. The resulting solution was worked up as described for the thermolysis of **5** to give 0.07 g (38%) of **27** as white crystals: mp 73–74 °C; ^1H NMR (CD_3COCD_3) δ 7.25–7.16 (m, 5H, C_6H_5), 5.87–5.73 (m, 2H, C_8H_7), 5.33 (dd, 1H, J = 5.4 Hz, J = 2.4 Hz, C_8H_7), 5.25 (dd, 1H, J = 5.3 Hz, J = 2.6 Hz, C_8H_7), 5.12 (d, 1H, J = 7.8 Hz, C_8H_7), 3.79 (q, 2H, J = 7.0 Hz, OCH_2CH_3), 3.16 (s, 1H, CHC_6H_5), 3.01–3.02 (m, 2H, C_8H_7), 1.28 (t, 3H, J = 7.1 Hz, OCH_2CH_3); ^{13}C NMR δ 146.1, 128.9, 128.0, 127.8, 127.4, 126.7 (C_6H_5), 167.2, 122.9, 122.4, 120.3, 95.6, 56.9, 51.3, 46.6 (C_8H_7), 63.8 (OCH_2CH_3), 14.7 (OCH_2CH_3); MS m/z 238 [M^+], 237 [$\text{M}^+ - \text{H}$], 209 [$\text{M}^+ - \text{C}_2\text{H}_5$], 193 [$\text{M}^+ - \text{OC}_2\text{H}_5$]. Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}$: C, 85.68; H, 7.61. Found: C, 85.27; H, 7.68.

Table 1. Crystal Data and Experimental Details for Complexes 15–17, 20, and 23

	15	16	17	20	23
formula	C ₁₇ H ₁₈ O ₄ Fe	C ₁₇ H ₁₅ O ₄ F ₃ Fe	C ₃₄ H ₃₀ O ₆ F ₃ PFe	C ₃₄ H ₃₀ O ₆ Fe ₂	C ₂₂ H ₂₆ O ₄ Fe
formula wt	342.17	396.15	678.42	646.28	410.28
space group	P $\bar{1}$ (No. 2)	P2 ₁ (No. 4)	P $\bar{1}$ (No. 2)	P $\bar{1}$ (No. 2)	P2 ₁ /c (No. 14)
<i>a</i> (Å)	11.043(3)	11.255(6)	12.172(3)	6.2085(13)	15.6971(10)
<i>b</i> (Å)	9.844(2)	8.077(4)	13.874(6)	6.8829(14)	10.3674(7)
<i>c</i> (Å)	7.735(3)	19.699(7)	9.873(2)	17.776(4)	13.0516(8)
α (deg)	87.09(2)		98.95(2)	79.897(4)	
β (deg)	79.70(3)	94.17(4)	91.45(2)	87.619(4)	90.5760(10)
γ (deg)	92.82(2)		77.87(2)	75.751(4)	
<i>V</i> (Å ³)	824.7(4)	1786(1)	1610.1(9)	724.8(3)	2123.9(2)
<i>Z</i>	2	4	2	2	4
<i>D</i> _{calcd} (g/cm ³)	1.378	1.474	1.399	1.481	1.283
<i>F</i> (000)	356.00	808.00	700.00	334	864
μ (Mo K α) (cm ⁻¹)	9.27	8.90	5.78	10.46	7.32
radiation (monochromated in incident beam)	Mo K α (λ = 0.710 69 Å),	Mo K α (λ = 0.710 69 Å),	Mo K α (λ = 0.710 69 Å),	Mo K α (λ = 0.710 73 Å),	Mo K α (λ = 0.710 73 Å),
diffractometer	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R	Brock Smart	Brock Smart
temp (°C)	20	20	20	20	20
orientation rflns: no.; range (2 θ) (deg)	19; 18.3–21.8	9; 13.4–20.7	16; 13.9–21.1	4.66–42.82	4.72–38.36
scan method	ω –2 θ	ω –2 θ	ω –2 θ	ω –2 θ	ω –2 θ
data collec range, 2 θ (deg)	5–50.00	5–45.00	5–45.00	4.66–56.62	4.70–56.64
unique data					
total no.	2692	1901	4200	3172	4963
no. with <i>I</i> > 3.00 σ (<i>I</i>)	2315	713	2261	1836 (<i>I</i> > 2.00 σ (<i>I</i>))	1920 (<i>I</i> > 2.00 σ (<i>I</i>))
no. of params refined	272	226	406	251	337
correcn factors, max–min	0.8361–1.0000	0.8512–1.0000	0.9050–1.0246	0.8442–1.0000	0.8961–1.0000
<i>R</i> ^a	0.037	0.058	0.048	0.0482	0.0417
<i>R</i> _w ^b	0.048	0.063	0.053	0.0898	0.0691
quality-of-fit indicator ^c	1.91	1.83	1.57	0.778	0.722
max shift/esd final cycle	0.00	0.08	0.00	0.027	0.000
max peak, e/Å ³	0.33	0.27	0.40	0.646	0.353
min peak, e/Å ³	–0.47	–0.26	–0.35	–0.526	–0.167

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^c Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{params}})]^{1/2}$.

Thermolysis of [η^4 -C₈H₈(CO)₂FeC(OC₂H₅)C₆H₄CH₃-*p*] (14) To Give [C₈H₇(OC₂H₅)C(H)C₆H₄CH₃-*p*] (28). Using the same procedures as for the thermolysis of **5**, a solution of **13** (0.30 g, 0.89 mmol) in 30 mL of benzene in a quartz tube was heated to 90–95 °C for 72 h. The resulting solution was worked up as described for the thermolysis of **5** to give 0.117 g (52%) of **28** as colorless crystals: mp 86 °C; ¹H NMR (CDCl₃) δ 6.97–6.90 (m, 4H, CH₃C₆H₄), 5.72–5.58 (m, 2H, C₈H₇), 5.18 (m, 1H, C₈H₇), 5.10 (m, 1H, C₈H₇), 4.98 (d, 1H, C₈H₇), 3.61 (q, 2H, OCH₂CH₃), 2.89–2.85 (m, 2H, C₈H₇), 2.13 (s, 3H, CH₃C₆H₄), 1.94 (m, 1H, –CHC₆H₄CH₃), 1.16 (t, 3H, OCH₂CH₃); MS *m/z* 252 (M⁺), 251 [M⁺ – H], 160 [M⁺ – H – CH₃C₆H₄], 115 [M⁺ – H – CH₃C₆H₄ – OC₂H₅]. Anal. Calcd for C₁₈H₂₀O: C, 85.67; H, 7.99. Found: C, 85.82; H, 7.96.

X-ray Crystal Structure Determinations of Complexes 15–17, 20, 23, 25, 26, and 28. Single crystals of complexes **15–17**, **20**, **23**, **25**, **26**, and **28** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH₂Cl₂ at –80 °C. Single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data were collected with Rigaku AFC7R and Bruker Smart diffractometers at 20 °C using Mo K α radiation with an ω –2 θ scan mode.

The structures of **15**, **17**, **20**, **23**, **25**, **26**, and **28** were solved by direct methods and expanded using Fourier techniques, while the structure of **16** was solved by heavy-atom Patterson methods and expanded using Fourier techniques. For complexes **15–17**, **20**, **23**, **25**, **26**, and **28**, the non-hydrogen atoms were refined anisotropically. For all eight complexes, the hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement gave agreement factors of *R* = 0.037 and *R*_w = 0.048 for **15**, *R* = 0.058 and *R*_w = 0.063 for **16**, *R* = 0.048 and *R*_w = 0.053 for **17**, *R* = 0.0482 and *R*_w = 0.0898 for **20**, *R* = 0.0417 and *R*_w = 0.0691 for **23**, *R* = 0.0458 and *R*_w = 0.0673 for **25**, *R* = 0.037 and *R*_w = 0.045 for **26**, and *R* = 0.058 and *R*_w = 0.056 for **28**.

The details of the crystallographic data and the procedures for data collection and reduction information for **15–17**, **20**, **23**, **25**, **26**, and **28** are given in Tables 1 and 2, respectively. Selected bond lengths and angles are listed in Tables 3 and 4, respectively. The atomic coordinates and *B*_{iso}/*B*_{eq} values, anisotropic displacement parameters, all bond lengths and angles, and least-squares planes for **15–17**, **20**, **23**, **25**, **26**, and **28** are given in the Supporting Information. The molecular structures of **15–17**, **20**, **23**, **25**, **26**, and **28** are given in Figures 1–8, respectively.

Results and Discussion

It is well-known that the thermal decomposition of carbene complexes usually results in dimerization of the carbene ligand to produce alkene derivatives.¹² What happens when the isomerized (alkoxycarbene)iron complexes are subjected to thermolysis? To compare their thermolysis reactivities, we investigated the thermal decomposition of the isomerized (butadiene)(alkoxycarbene)iron complexes **1** and **2**. An orange-red benzene solution of compound **1** in a sealed tube was heated with stirring to 75–80 °C for 70–72 h. After workup as described in the Experimental section, the new H-migrating (η^4 -butadienyl)tricarbonyliron complex [(1–4- η)-C₄H₅C(H)(OC₂H₅)C₆H₄CH₃-*o*]Fe(CO)₃ (**15**) was obtained in 58% yield (eq 7). However, analogous thermolysis of complex **2** leads to a 1,4-H-migration to occur, giving the (η^4 -isoprenyl)tricarbonyliron complex [(2–5- η)-CH₃C₄H₃(OC₂H₅)C₆H₄CF₃-*p*]Fe(CO)₃ (**16**) (eq 8) in 62% yield.

Products **15** and **16** are orange-yellow crystals; they are soluble in polar and nonpolar organic solvents and

Table 2. Crystal Data and Experimental Details for Complexes 25, 26, and 28

	25	26	28
formula	C ₂₄ H ₃₀ OSi	C ₃₆ H ₄₀ O ₂	C ₁₈ H ₂₀ O
formula wt	362.57	504.71	252.36
space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ (No. 4)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> (Å)	17.722(6)	12.864(2)	13.282(3)
<i>b</i> (Å)	7.263(2)	7.629(3)	6.162(5)
<i>c</i> (Å)	18.688(6)	14.550(5)	17.551(7)
β (deg)	117.818(5)	94.91(2)	96.49(3)
<i>V</i> (Å ³)	2127.3(12)	1422.8(7)	1427(1)
<i>Z</i>	4	2	4
<i>D</i> _{calcd} (g/cm ³)	1.132	1.178	1.174
<i>F</i> (000)	784	544.00	544.00
μ (Mo K α) (cm ⁻¹)	1.20	0.71	0.70
radiation (monochromated in incident beam)	Mo K α (λ = 0.710 73 Å)	Mo K α (λ = 0.710 69 Å)	Mo K α (λ = 0.710 69 Å)
diffractometer	Brock Smart	Rigaku AFC7R	Rigaku AFC7R
temp (°C)	20	20	20
orientation rflns: no.; range (2 θ) (deg)	4.32–25.30	15; 18.3–21.5	8; 14.0–18.7
scan method	ω -2 θ	ω -2 θ	ω -2 θ
data collec range, 2 θ (deg)	2.62–51.00	5–50.00	5–50.00
unique data			
total no.	3960	2714	2654
no. with <i>I</i> > 3.00 σ (<i>I</i>)	864	2131 (<i>I</i> > 3.00 σ (<i>I</i>))	601 (<i>I</i> > 3.00 σ (<i>I</i>))
no. of params refined	254	342	173
correcn factors, max–min	0.7647–1.0000	0.9771–1.0000	0.9143–1.0000
<i>R</i> ^a	0.0458	0.037	0.058
<i>R</i> _w ^b	0.0673	0.045	0.056
quality-of-fit indicator ^c	0.536	1.44	1.61
max shift/esd final cycle	0.080	0.01	0.00
max peak, e/Å ³	0.142	0.12	0.18
min peak, e/Å ³	–0.176	–0.19	–0.22

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^c Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{params}})]^{1/2}$.

Table 3. Selected Bond Lengths (Å)^a and Angles (deg)^a for Complexes 15–17, 20, and 23

	15	16	17	20	23	15	16	17	20	23
Fe–C(4)	2.106(3)	2.14(2)	2.155(7)	2.105(4)	2.092(3)	C(4)–C(11)	1.50(2)	1.476(9)		
Fe–C(5)	2.052(3)	2.05(2)	2.054(7)	2.120(3)	2.029(3)	C(8)–C(9)			1.525(5)	1.541(4)
Fe–C(6)	2.069(3)	2.13(2)	2.074(7)	2.137(3)	2.066(3)	C(9)–C(10)	1.494(6)	1.47(1)	1.501(5)	1.543(4)
Fe–C(7)	2.135(3)	2.19(2)	2.165(7)	2.135(3)	2.091(3)	C(8)–C(11)	1.521(4)			
Fe–C(1)	1.770(4)	1.72(2)	1.776(8)	1.743(4)	1.763(4)	C(10)–C(11)			1.504(5)	1.509(4)
Fe–C(2)	1.788(3)	1.74(2)	1.774(9)	1.911(4)	1.768(3)	C(1)–O(1)	1.147(4)	1.19(2)	1.146(8)	1.155(4)
Fe–C(3)	1.794(3)	1.82(2)		2.077(4)	1.762(4)	C(2)–O(2)	1.140(4)	1.16(2)	1.138(8)	1.186(4)
C(3)–C(4)				1.421(5)		C(3)–O(3)	1.137(4)	1.11(2)		1.153(3)
C(4)–C(5)	1.402(5)	1.42(2)	1.445(9)	1.398(6)	1.410(3)	C(4)–O(4)	1.35(2)	1.410(7)		
C(5)–C(6)	1.403(5)	1.43(2)	1.430(10)	1.399(5)	1.404(3)	C(10)–O(3)			1.202(5)	
C(6)–C(7)	1.412(4)	1.38(2)	1.411(9)	1.414(5)	1.412(4)	C(10)–O(4)				1.427(3)
C(3)–C(7)				1.423(5)		Fe–Fe(A)			2.5303(12)	
C(4)–C(9)					1.516(3)	Fe–P		2.145(2)		
C(7)–C(8)	1.508(4)	1.53(2)	1.49(1)	1.491(5)	1.502(4)					
C(3)–C(4)–C(5)				107.3(4)		C(8)–C(9)–C(10)			113.1(4)	108.3(2)
C(4)–C(5)–C(6)	118.5(3)	120(1)	118.5(6)	108.6(3)	115.1(3)	C(9)–C(10)–C(11)			117.4(4)	115.7(3)
C(5)–C(6)–C(7)	117.5(3)	117(1)	120.9(6)	109.2(4)	112.2(3)	Fe–C(1)–O(1)	177.8(4)	173(1)	175.5(7)	176.9(3)
C(6)–C(7)–C(3)				106.2(3)		Fe–C(2)–O(2)	175.4(3)	178(1)	176.8(8)	138.5(3)
C(6)–C(7)–C(8)	121.6(3)	119(1)	119.0(7)	125.1(4)	122.5(3)	Fe–C(3)–O(3)	179.0(3)	177(2)		179.4(3)
C(4)–C(3)–C(7)				108.7(4)		Fe(A)–C(2)–O(2)			138.6(3)	
C(5)–C(4)–C(9)					118.4(2)	Fe–C(2)–Fe(A)			82.74(15)	
C(4)–C(9)–C(10)					112.9(2)	C(2)–Fe–Fe(A)			48.75(11)	
C(5)–C(4)–C(11)		122(2)	121.0(6)			C(2)–Fe(A)–Fe			48.51(12)	
C(7)–C(8)–C(9)				114.3(3)	110.6(3)					

^a Estimated standard deviations in the least significant figure are given in parentheses.

stable in the solid state but slowly oxidized in solution in air. Their elemental analyses and IR, ¹H NMR, and mass spectra (Experimental Section) are all consistent with the structures shown in eqs 7 and 8. Their IR spectra show three strong CO stretching vibration bands in the ν (CO) region, in accordance with the existence of the Fe(CO)₃ moiety. The ¹H NMR spectra of **15** and **16** showed five (for **15**) or four (for **16**) proton signals for the olefin ligands, which are very different from those of the parent compounds **1** and **2**, suggesting that complete isomerization of the olefin ligand had occurred.

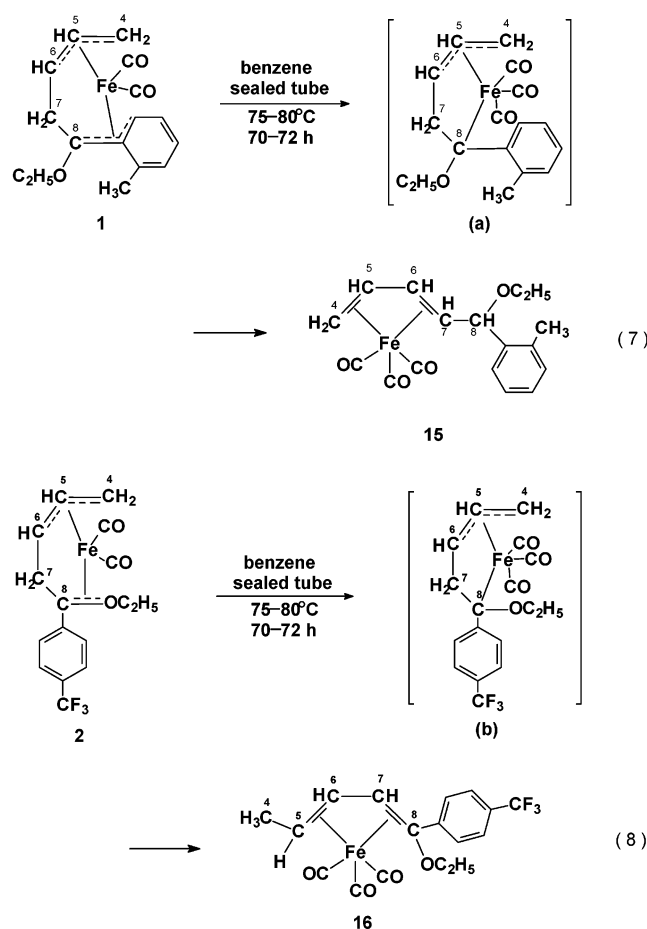
The X-ray diffraction studies for complexes **15** and **16** unequivocally established their structures.

A possible pathway to complex **15** might involve the intermediate [$\{(1-3-\eta)\text{-C}_4\text{H}_6\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}\}\text{Fe}(\text{CO})_3$] (a) formed by dissociation of the coordinating benzene ring and addition of one CO generated by thermal decomposition of **1** to the Fe atom. This intermediate then underwent a 1,2-hydrogen shift aided by the central metal: namely, a hydrogen atom at the C-7 position migrated to the C-8 position with bonding of the Fe atom to the C-7 atom to form the thermody-

Table 4. Selected Bond Lengths (Å)^a and Angles (deg)^a for Complexes 25, 26, and 28

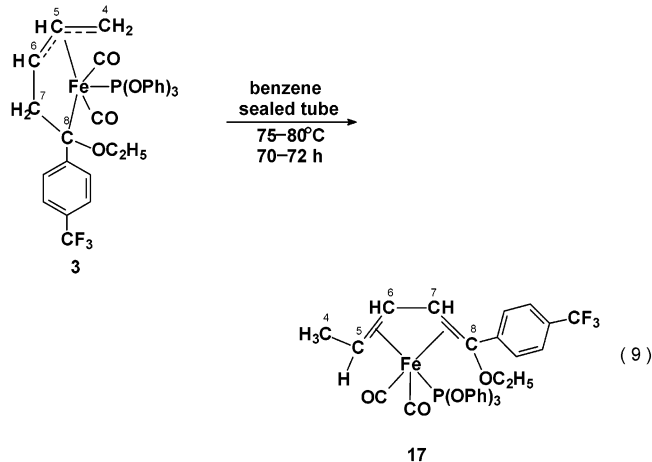
	25	26	28		25	26	28
C(1)–C(2)	1.559(6)	1.562(4)	1.54(1)	C(9)–C(2)	1.545(6)	1.503(4)	1.50(1)
C(2)–C(3)	1.528(6)	1.508(4)	1.51(1)	C(1)–C(5)		1.552(4)	
C(3)–C(4)	1.518(5)	1.312(4)	1.33(1)	C(1)–C(7)	1.517(6)		1.55(1)
C(4)–C(5)	1.471(6)	1.521(4)	1.44(1)	C(1)–C(10)	1.516(5)	1.535(4)	1.52(1)
C(5)–C(6)	1.331(6)	1.498(4)	1.35(1)	C(1)–O(1)	1.452(5)	1.430(3)	
C(6)–C(7)	1.518(6)	1.344(4)	1.52(1)	C(6)–O(1)			1.39(1)
C(7)–C(8)	1.547(5)	1.449(5)	1.51(1)	O(1)–C(17)		1.425(4)	1.42(1)
C(8)–C(9)	1.534(5)	1.336(5)	1.34(1)	O(1)–Si	1.640(3)		
C(1)–C(2)–C(3)	113.9(4)	101.5(2)	111.7(8)	C(9)–C(2)–C(1)	101.3(4)	113.8(2)	102.7(8)
C(2)–C(3)–C(4)	118.5(4)	111.7(2)	125.6(9)	C(9)–C(2)–C(3)	113.7(4)	107.6(3)	106.8(9)
C(3)–C(4)–C(5)	117.0(5)	111.1(3)	133.3(10)	C(2)–C(1)–C(5)		101.8(2)	
C(4)–C(5)–C(6)	128.5(6)	107.1(3)	125.6(10)	C(2)–C(1)–C(7)	102.7(4)		102.6(8)
C(4)–C(5)–C(1)		101.2(2)		C(1)–O(1)–C(17)		114.0(2)	
C(5)–C(6)–C(7)	126.3(6)	126.3(3)	127.9(9)	C(6)–O(1)–C(17)			117.1(8)
C(6)–C(7)–C(8)	111.5(4)	129.4(3)	107.4(9)	C(2)–C(1)–O(1)	102.8(3)	112.0(2)	
C(7)–C(8)–C(9)	106.0(4)	129.2(3)	109.7(10)	C(1)–C(10)–C(11)	122.0(4)	120.6(3)	
C(8)–C(9)–C(2)	106.5(4)	126.8(3)	112.1(10)	C(1)–O(1)–Si	133.8(3)		

^a Estimated standard deviations in the least significant figure are given in parentheses.



namically stable compound **15**, similar to the thermolysis of the isomerized (cyclohexadiene)(alkoxycarbene)iron complex [(2,4- η)-C₆H₈(CO)₂FeC(OC₂H₅)C₆H₄CH₃-o].^{11b} The formation pathway of product **16** could be via the analogous intermediate [{(1-3- η)-C₄H₆C(OC₂H₅)C₆H₄-CF₃-p}Fe(CO)₃] (b), formed by dissociation of the coordinated OC₂H₅ group and addition of one CO generated by thermal decomposition of **2** to the Fe atom. Then intermediate b underwent an 1,4-H shift with an H atom at the C-5 position migrating to the C-8 position accompanied by dissociation of the Fe–C(8) bond and bonding of the Fe atom to the C-5 atom to form the stable complex **16**. To confirm this presumption, the

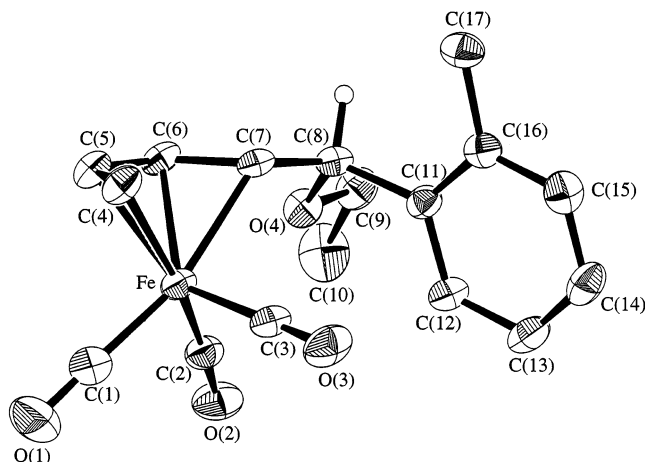
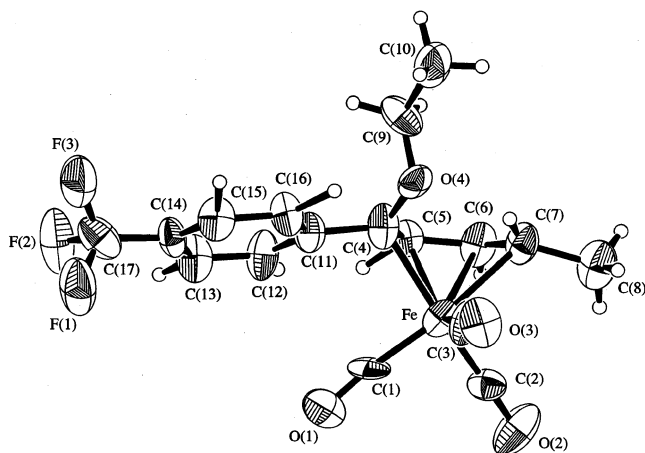
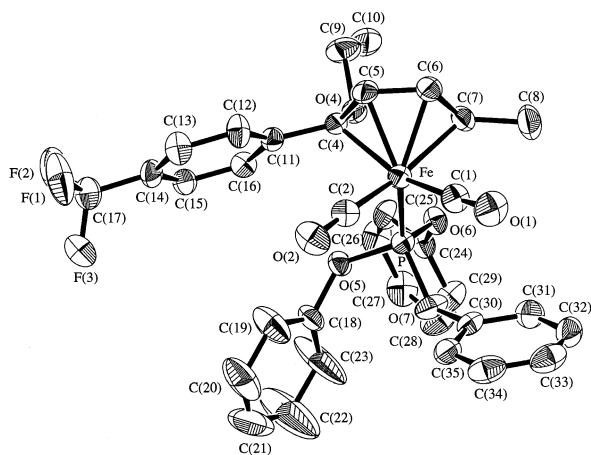
complex [C₄H₆(CO)₂{P(OPh)₃}FeC(OC₂H₅)C₆H₄CF₃-p] (**3**), a P(OPh)₃ adduct of **2**, obtained by the reaction of complex **2** with P(OPh)₃, which can be regarded as an analogue of the intermediate [{(1-3- η)-C₄H₆C(OC₂H₅)C₆H₄CF₃-p}Fe(CO)₃] (b), was used in the thermal decomposition under analogous conditions, resulting in the formation of the analogous thermolytic product [{(2-5- η)-C₅H₆(OC₂H₅)C₆H₄CF₃-p}Fe(CO)₂{P(OPh)₃}] (**17**) in 55% yield (eq 9).



The molecular structure of **15** (Figure 1) resembles that of **16** (Figure 2) and has many common features, except the diene ligand is a CH₂=CHCH=CHCH-(OC₂H₅)C₆H₄CH₃-o chain in **15** but a CH₃CH=CHCH=C(OC₂H₅)C₆H₄CF₃-p chain in **16**. Both complexes have approximately the same steric configuration. The distances of the Fe atom to the C(4), C(5), C(6), and C(7) atoms are respectively 2.106(3), 2.052(3), 2.069(3), and 2.135(3) Å for **15** and 2.14(2), 2.05(2), 2.13(2), and 2.19(2) Å for **16**.

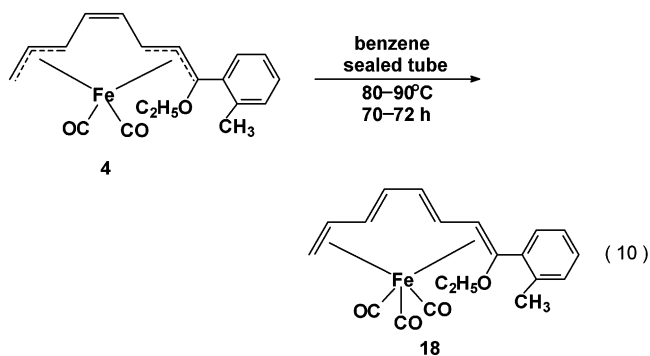
The molecular structure of complex **17** (Figure 3) is very similar to that of **16**, except that the ligand on the Fe atom is a CO group instead of a P(OPh)₃ group. The principal structural features of **17** are essentially the same as those in **16**. The distances of the Fe atom to the C(4), C(5), C(6), and C(7) atoms are 2.155(7), 2.054(7), 2.074(3), and 2.165(7) Å, respectively, very close to those of **16** and **15**.

Interestingly, a similar thermolysis of the ring-opened (cycloheptatriene)(alkoxycarbene)iron complex [C₇H₈-

**Figure 1.** Molecular structure of **15**.**Figure 2.** Molecular structure of **16**.**Figure 3.** Molecular structure of **17**.

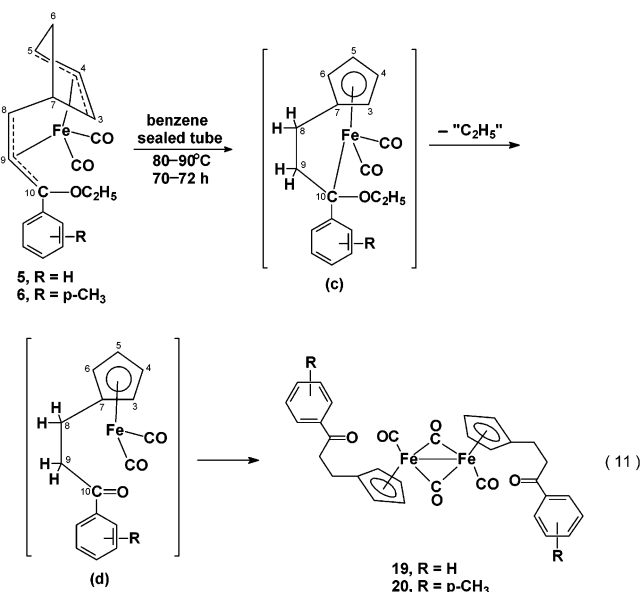
(CO)₂FeC(OC₂H₅)C₆H₄CH₃-o] (**4**) results in the isomerization of the olefin ligand to give a 63% yield of the yellow crystalline conjugated-olefin-coordinated tricarbonyliron compound [(1-2-η):(7-8-η)-C₇H₈C(OC₂H₅)-C₆H₄CH₃-o]Fe(CO)₃] (**18**) (eq 10). Since X-ray-quality crystals of **18** could not be obtained, its tentatively proposed structure is based on elemental analysis and IR, ¹H NMR, and mass spectral data.

Products **18** and **21** (vide infra) have the same composition and very similar ¹H NMR, ¹³C NMR, and mass spectra, indicating that compounds **18** and **21** should have the same olefin ligand. The only difference



between them is the coordination site of the Fe(CO)₃ moiety on the olefin ligand. By comparing the ¹H NMR and H-H COSY spectra of compounds **18** and **21**, we prefer the structure shown in eq 10 for **18**. In the ¹H NMR spectra of **18** and **21**, we could find three upfield peaks (2.65, 1.89, and 0.94 ppm for **18** and 2.23, 1.78, and 0.75 ppm for **21**) which could be assigned to the protons on the carbons of the olefin ligand coordinated to the Fe(CO)₃ moiety, as shown in many diene-coordinated organoiron complex molecules.¹³ It should be noted, however, that conjugated polyolefin ligands are known to coordinate to the Fe(CO)₃ moiety in a variety of ways; thus, the structural assignment of **18** in eq 10 must be regarded as tentative.

Of special interest are the thermal decomposition reactions of the ring-opened norbornadiene alkoxy-carbene complexes [η³-C₇H₈(CO)₂FeC(OC₂H₅)Ar] (**5**, Ar = C₆H₅; **6**, Ar = *p*-CH₃C₆H₄; **7**, Ar = *o*-CH₃C₆H₄; **8**, Ar = *p*-CF₃C₆H₄). Heating a solution of complex **5** in benzene in a sealed tube at 80–90 °C for 70–72 h gives the novel diiron dimer [{Fe(μ-CO)(CO)(η⁵-C₅H₄CH₂CH₂COC₆H₅)}₂] (**19**) in 60% yield (eq 11). Like **5**, the thermolysis of



compound **6** under the same conditions also affords the corresponding diiron dimer [{Fe(μ-CO)(CO)(η⁵-C₅H₄CH₂CH₂COC₆H₅)}₂] (**20**) (eq 11) in 64% yield.

However, the thermolyses of complexes **7** and **8** under conditions the same as those for **5** and **6** give no

(13) Marks, T. J. In *The Organic Chemistry of Iron*; von Gustorf Koerner, E. A., Grevels, F.-W., Fischler, I., Eds.; Academic Press: New York, 1978; Vol. 1, p 116.

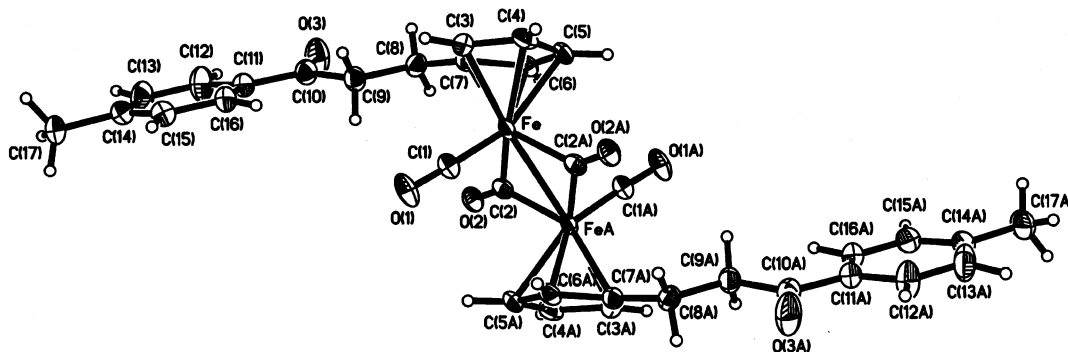
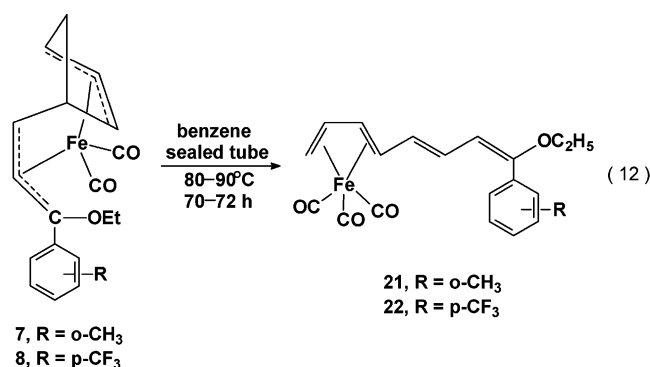


Figure 4. Molecular structure of **20**.

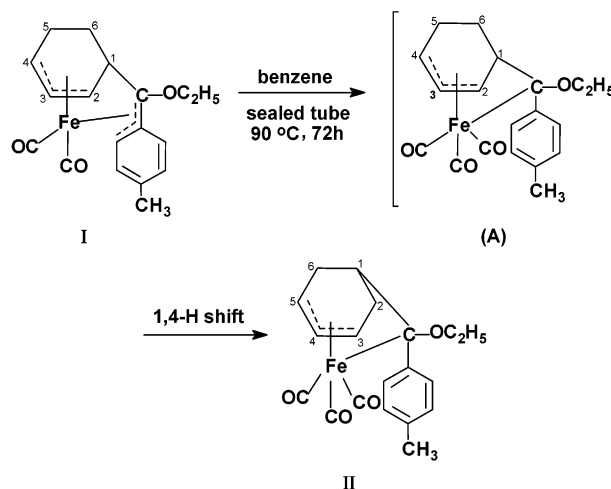
analogous dimers but rather the new acyclic (1,3-diene)-tricarbonyliron complexes [$\{\eta^4\text{-C}_7\text{H}_8\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}o\}\text{Fe}(\text{CO})_3$] (**21**) and [$\{\eta^4\text{-C}_7\text{H}_8\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CF}_3\text{-}p\}\text{Fe}(\text{CO})_3$] (**22**) in 59 and 64% yields, respectively (eq 12),



among which compound **22** is known and whose structure has previously been established previously by a single-crystal X-ray diffraction study.^{7a} It is clear that, on heating of compound **7** or **8**, another five-membered ring of the norbornadiene ligand has been opened with breaking of the C–C σ -bond and the formation of an η^4 π -bond with the Fe atom. To satisfy the 18-electron configuration, one CO generated by thermal decomposition of **7** or **8** is coordinated to the Fe atom.

Products **19** and **20** are air-sensitive, orange-red crystals. Their infrared spectra exhibit two strong bands at ca. 2046–2041 and 1975–1972 cm^{-1} , which indicates the high symmetry of both complexes. The ^1H NMR spectra of complexes **19** and **20** with two single signals for the Cp rings at ca. 4.95–4.94 (4H) and 4.71–4.70 ppm (4H) and two triplet signals at ca. 3.49–3.44 (4H) and 2.92–2.91 ppm (4H) also suggest a high symmetry in both molecules. This has been confirmed by the X-ray diffraction study of complex **20**. The X-ray-determined structure of **20** (Figure 4) shows that it is a new diiron dimer with the two $\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{COAr}$ ligands coordinated respectively to the two Fe atoms through the Cp rings and the two $\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{COAr}$ ligands in a trans configuration to avoid steric hindrance. The distance of the Fe–Fe bond bridged by the two $\mu\text{-CO}$ ligands is 2.5303(12) Å, which is the same within experimental error as that found in the analogous complex [$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$]₂ (2.531(2) Å).¹⁴ The distance between the Fe atom and the Cp ring plane is approximately 1.7405 Å. In **20** there exist two different

Scheme 1

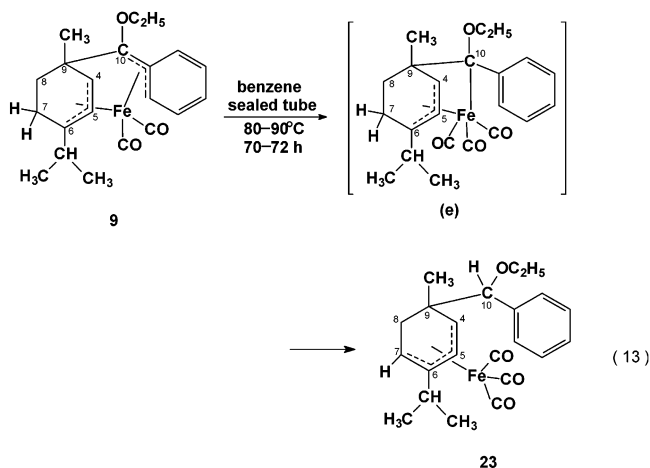


coordinated CO groups, and the bond lengths of Fe–C are also different: Fe–CO(bridged, sp^2) is 1.911(4) Å, while Fe–CO(nonbridged, sp) is 1.743(4) Å.

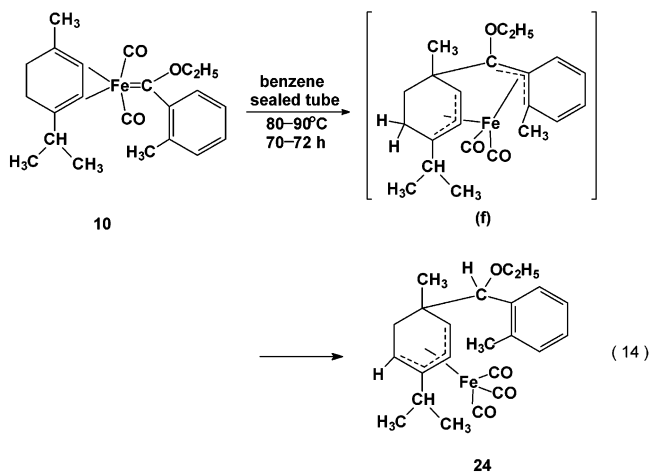
A possible reaction pathway to products **19** and **20** could be via the unstable intermediate c, formed by a 1,2-H shift and a 1,4-H shift or by two 1,3-H shifts: namely, a H atom at the C-7 ring position migrating to the C-8 chain position and another H atom at the C-6 ring position migrating to the C-9 chain position or the both H atoms migrating to the C-9 and C-8 positions, respectively, accompanied by the dissociation of the Fe–C(8) and Fe–C(9) bonds. This intermediate then lost the C_2H_5 group from oxygen with dissociation of the Fe–C(10) bond to form an unsaturated 17-electron species (d). Two d fragments could form the dimer product **19** or **20** by their dimerization.

We have previously shown that the thermal decomposition of the isomerized cyclohexadiene alkoxycarbene complex [$2,4\text{-}\eta\text{-C}_6\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}p$] (**I**) yielded the η^3 -cyclohexadienyl tricarbonyl complex [$2,4\text{-}\eta\text{-C}_6\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}p$] (**II**) (Scheme 1).^{11b} A similar thermolysis should occur for the isomerized (limonene)(alkoxycarbene)iron complex [$\eta^3\text{-C}_{10}\text{H}_{16}\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2$] (**9**), an analogue of **I**, which is actually the case. However, the thermolytic product is different from that of **I**. The thermal decomposition of complex **9** under conditions the same as those for **I** produces a 52% yield of the η^4 cyclic olefin-coordinated tricarbonyliron complex [$\{\eta^4\text{-C}_{10}\text{H}_{15}\text{CH}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5\}\text{Fe}(\text{CO})_3$] (**23**) (eq 13), whose structure has been established by X-ray crystallography.

(14) Bryan, R. F.; Greene, P. T.; Newlands, M. J.; Field, D. S. J. *Chem. Soc. A* **1970**, 3068.



Surprisingly, the thermolysis of the (limonene)-(alkoxycarbene)iron complex $[(\eta^4\text{-C}_{10}\text{H}_{16})(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}]$ (**10**) affords a 46% yield of the analogous cyclic η^4 olefin coordinated tricarbonyliron complex $[(\eta^4\text{-C}_{10}\text{H}_{15}\text{CH}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o})\text{Fe}(\text{CO})_3]$ (**24**) (eq 14), instead of the expected alkene derivative¹² formed by dimerization of the carbene ligand.



The formation of product **23** shown in eq 13 might be via the intermediate **e**, formed by addition of one CO ligand derived from thermal decomposition of **9** to the Fe atom, similar to that of **II**, which was formed presumably via the analogous intermediate **A** (Scheme 1). Intermediate **e** underwent a 1,4-H shift, namely, a H atom at the C-7 ring position migrated to the C-10 position, with dissociation of the Fe-C(10) bond and bonding of the Fe atom to the ring C(7) atom to eventually yield the η^4 cycloolefin coordinated tricarbonyliron complex **23**. The formation of **24** might involve the initial intermediate **f**, an analogue of **9**, formed by its thermal isomerization. Intermediate **f** further underwent thermolysis as for **9** to give the product **24**.

The molecular structure of **23** is shown in Figure 5. The structure of **23** consists of a cyclic $\text{C}_{10}\text{H}_{16}\text{CH}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}$ unit η^4 bonded to the $\text{Fe}(\text{CO})_3$ moiety through the limonene ring. The average distance from the Fe atom to the four coordinated carbon atoms of the limonene ring is 2.070 Å, which is nearly the same as that found in its parent complex **10** (2.098 Å).^{7b} Product **24** is assigned a similar structure, since its spectral data are similar to those of **23** (see Experimental Section).

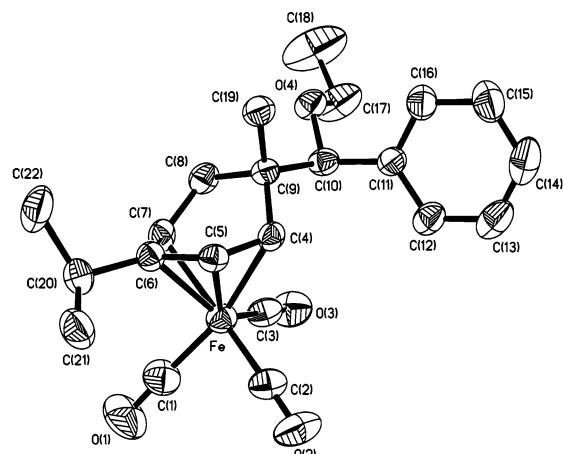


Figure 5. Molecular structure of **23**.

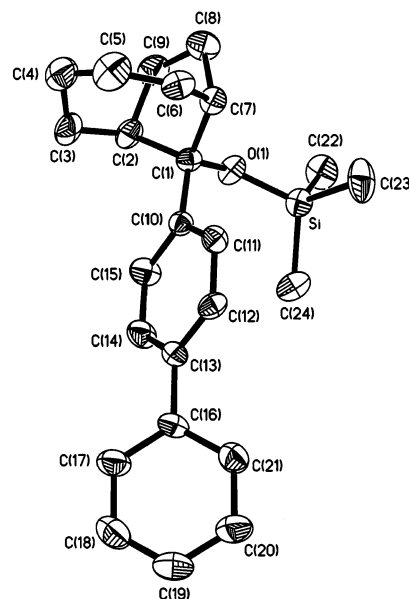
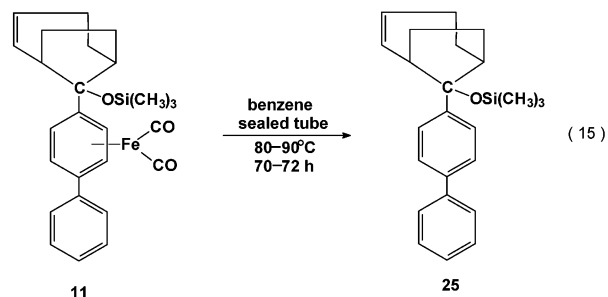


Figure 6. Molecular structure of **25**.

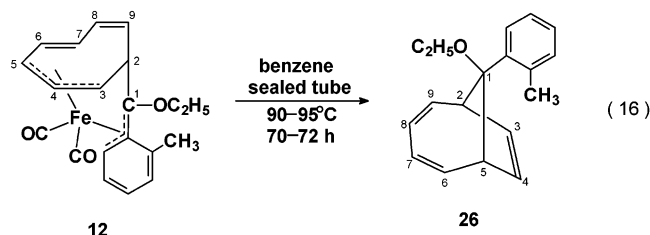
In contrast to the thermolysis of complexes **1–10** to give olefin-coordinated carbonyliron compounds, the thermolysis of the isomerized $(\eta^6\text{-arene})(1,5\text{-cyclooctadiene})(\text{trimethylsiloxy})\text{carbene}$ iron complex $[\text{Fe}(\text{CO})_2\text{-}\{(\eta^6\text{-}p\text{-C}_6\text{H}_5\text{C}_6\text{H}_4\text{C}(\text{OSiMe}_3)(\text{C}_8\text{H}_{12}))\}]$ (**11**) led to the dissociation of the $\text{Fe}(\text{CO})_2$ moiety to afford an organic compound, 9-aryl-9-(trimethylsiloxy)bicyclo[4.2.1]non-2-ene, $[p\text{-C}_6\text{H}_5\text{C}_6\text{H}_4\text{C}(\text{OSiMe}_3)(\text{C}_8\text{H}_{12})]$ (**25**), in moderate (54%) yield (eq 15). The structure of **25** has also been



confirmed by a single-crystal X-ray diffraction study (Figure 6), which shows that the configuration of the cyclooctene ligand was kept.

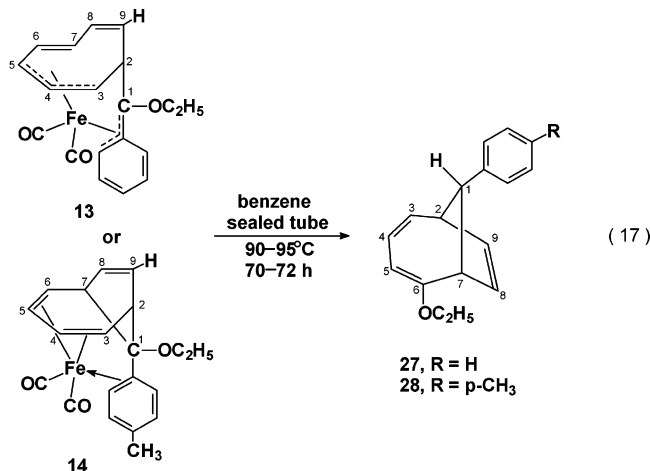
It is likely interesting that the thermolysis of the isomerized product of the (cyclooctatetraene)(ethoxy-

carbene)iron complex $[\eta^3\text{-C}_8\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{-CH}_3\text{-o}]$ (**12**) under analogous conditions yields an organic product, the head-bridged cyclooctatriene derivative $[\text{C}_8\text{H}_8\text{C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-o}]$ (**26**) (eq 16), in 56% yield.



The possible formation mechanism for product **26** might involve a tricarbonyliron intermediate, the analogue of the intermediate **A** shown in Scheme 1, and subsequent C–C reductive elimination that delivers the C(1) atom to the ring C-5 position with retention of C(1) configuration to form the C–C bond. The spontaneous demetalation of the $16e$ (η^2 -alkene)tricarbonyliron species formed could occur to give the product **26**.

However, the analogous thermolysis of the isomerized products $[\eta^3\text{-C}_8\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5]$ (**13**) and $[\eta^4\text{-C}_8\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-p}]$ (**14**) produce the novel ethoxy-migrating head-bridged cyclooctatriene derivatives $[\text{C}_8\text{H}_7(\text{OC}_2\text{H}_5)\text{C}(\text{H})\text{C}_6\text{H}_5]$ (**27**) and $[\text{C}_8\text{H}_7(\text{OC}_2\text{H}_5)\text{C}(\text{H})\text{C}_6\text{H}_4\text{CH}_3\text{-p}]$ (**28**) in 38% and 52% yields, respectively (eq 17), which are quite rare in the reactions of olefin-coordinated transition-metal complexes.



While the mechanism of the thermolytic reaction in eq 17 is not known, it is possible that it proceeds via the migrations of the ethoxy group and hydrogen aided by the center metal: namely, the OC_2H_5 group migrates from the C-1 position to the ring C-6 position, and the H atom at the C-6 ring position migrates to the C-1 position with the dissociation of the $\text{Fe}(\text{CO})_2$ moiety and bonding of the C(1) atom to the C-7 position. The formation of product **27** might be via the intermediate $[\eta^4\text{-C}_8\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5]$, which is the phenyl analogue of complex **14**. Further thermolysis of the intermediate could produce product **27** in the same manner as for compound **14**. The ethoxy group may transfer to another site of the organic ligand with the aid of the center metal iron as previously reported.¹⁵

(15) Buchholz, D.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1990**, 381, 97.

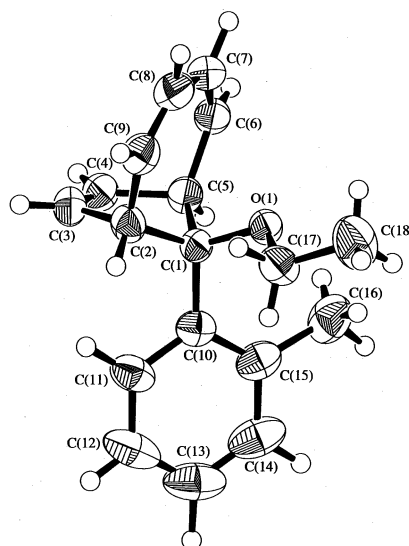


Figure 7. Molecular structure of **26**.

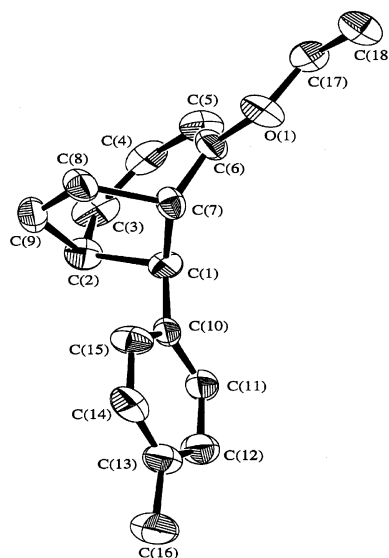


Figure 8. Molecular structure of **28**.

However, in compound **13** the C–C bond formation and the migrations of the ethoxy group and hydrogen can simultaneously happen to form a bridged-ring system, which may be the first example in olefin-coordinated organoiron complexes. The ortho methyl on the *o*-tolyl group in complex **12** could prevent the migration of the ethoxy group to the ring, giving only compound **26**.

To establish the exact positions of the bridging carbons and ethoxy group on the cyclooctatriene ring of products **26–28**, we determined the single-crystal structures of compounds **26** and **28**. The molecular structures of **26** and **28**, shown in Figures 7 and 8, respectively, confirmed the structures shown in eqs 16 and 17, respectively.

In summary, the isomerized products of olefin-coordinated alkoxycarbene iron complexes exhibit a remarkable range of thermolysis reactivity to produce a series of novel thermolytic products. Fortunately, the products of these thermolyses often formed crystals that could be characterized by X-ray diffraction studies. The thermal decomposition of the chain olefin coordinated isomerized alkoxycarbene iron complexes **1–3**, and the cycloolefin coordinated isomerized alkoxycarbene com-

plexes of six-membered rings such as compounds **9** and **10** involving $\text{I}^{11\text{b}}$ and of seven-membered rings such as complexes **4–8** give chain or cyclic conjugated diene coordinated tricarbonyliron compounds or diiron dimers, while the thermolysis of the eight-membered-ring cycloolefin coordinated isomerized alkoxy carbene complexes such as compounds **11–14** produce the novel cycloolefin derivatives. These thermolytic reactions could be used in the syntheses of new olefin-coordinated carbonylmetal compounds and special cycloolefin derivatives, which are difficult to prepare using the usual synthetic methods.

Acknowledgment. Financial support from the National Natural Science Foundation of China and the NEDO of Japan is gratefully acknowledged.

Supporting Information Available: Tables of positional parameters and $B_{\text{iso}}/B_{\text{eq}}$ values, H atom coordinates, anisotropic displacement parameters, all bond lengths and angles, and least-squares planes for **15–17**, **20**, **23**, **25**, **26**, and **28**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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