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Novel thermolytic products and their structures derived from thermolysis of isomerized products of spiro[4.4]nona-1,3-diene(dicarbonyl)[ethoxy(aryl)carbene]iron phosphine adducts [(η^3-C_9H_{12})Fe{C(OC_2H_5)Ar}$(CO)_2PPh_3$]

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This paper is dedicated to Professor Robert J. Angelici, Department of Chemistry, Iowa State University, on the occasion of his retirement and 70th birthday and recognition of his brilliant contribution to organometallic chemistry.

Abstract

Heating a benzene solution of the isomerized product of spiro[4.4]nona-1,3-diene(dicarbonyl)[ethoxy(aryl)carbene]iron phosphine adduct [(η^3-C_9H_{12})Fe{C(OC_2H_5)($C_6H_4CH_3$-*o*)}$(CO)_2PPh_3$] (**1**) in a sealed quartz tube at 85–90 °C for 72 h gave the ring-opened η^4 olefin-coordinated dicarbonyliron phosphine complex [Fe{η^4-$C_5H_7CH{=}CHCH_2CH{=}C(OC_2H_5)C_6H_4CH_3$-*o*}$(CO)_2PPh_3$] (**3**) and cyclobutane derivative [$C_{24}H_{22}O_7$] (**4**). The thermal decomposition of analogous isomerized product [(η^3-C_9H_{12})Fe{C(OC_2H_5)($C_6H_4CH_3$-*p*)}-$(CO)_2PPh_3$] (**2**) afforded the corresponding η^4 olefin-coordinated dicarbonyliron phosphine complex [Fe{η^4-$C_5H_7CH{=}CHCH_2CH{=}C(OC_2H_5)C_6H_4CH_3$-*p*}$(CO)_2PPh_3$] (**6**) and compound **4**. The structures of products **3** and **4** have been established by X-ray diffraction studies.

Keywords: Thermolytic product; Crystal structure; Isomerized product; Thermolysis

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1. Introduction

The considerable interest in the synthesis, structure, and chemistry of alkene-coordinated transition-metal carbene complexes stems largely from the possible involvement of these species in many reactions catalyzed by organometallic compounds [1,2]. Especially, the alkene–metal carbene complexes are important intermediates in various reactions of metal carbene complexes with alkenes [3–5]. In recent years, olefin-coordinated transition-metal carbene complexes and/or their isomerized products have been examined widely; a great number of olefin-coordinated metal carbene complexes and/or isomerized products were synthesized, and a series of novel isomerizations of olefin ligands have been observed by the reactions of olefin-ligated metal carbonyls with aryllithium reagents followed by alkylation with alkylating agents in our laboratory [6–12]. However, only very little is known [6a,13] about the reactivity of these olefin-coordinated metal carbene complexes and their isomerized products.

It is well known that the thermal decomposition of carbene complexes usually results in dimerization of the carbene ligand to produce alkene derivatives [14] and that heating a Fischer-type carbene complex with an olefin generally results in addition of the double bond of the olefin to

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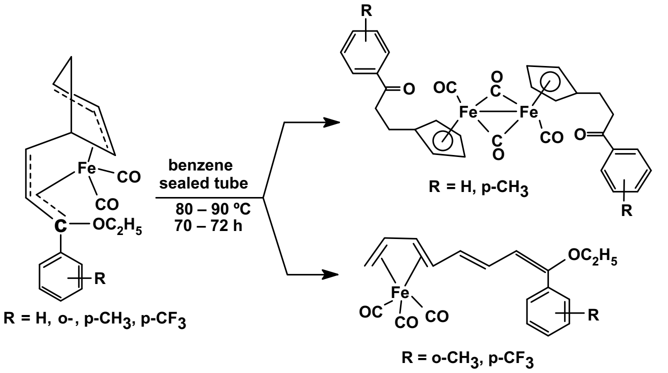
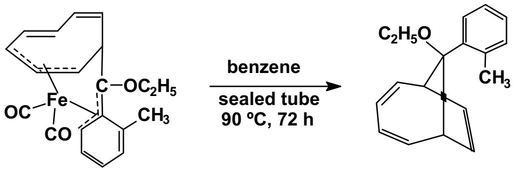
the carbene ligand to form cyclopropane products [15,16]. Recently, we have shown a number of thermolysis reactions of the olefin-coordinated monoiron alkoxycarbene complexes or their isomerized products and the COT-coordinated diiron Fischer-type carbene complexes which produced a series of novel thermolytic products [13b,17,18]. For example, the thermolysis of ring-opened norbornadiene alkoxycarbene complexes $[\eta^3\text{-}C_7H_8(CO)_2FeC(OC_2H_5)\text{-}Ar]$ ($Ar = C_6H_5$, $p\text{-}CH_3C_6H_4$) afforded novel diiron dimers $[\{Fe_2(\mu\text{-}CO)(CO)\{\eta^5\text{-}C_5H_4CH_2CH_2COAr\}_2]$ (Eq. (1)) [17], and the thermolysis of isomerized (limonene)(alkoxycarbene)iron complex $[(\eta^3\text{-}C_{10}H_{16})(CO)_2FeC(OC_2H_5)Ar]$ ($Ar = o\text{-}CH_3C_6H_4$, $p\text{-}CF_3C_6H_4$) produced the η^4 cycloolefin-coordinated tricarbonyl iron complexes $[\{\eta^4\text{-}C_{10}H_{15}\text{-}CH(OC_2H_5)C_6H_5\}Fe(CO)_3]$ (Eq. (1)) [17]. While the thermal decomposition of isomerized products of the (cyclooctatetraene)(ethoxycarbene)iron complexes $[\eta^3\text{-}C_8H_8(CO)_2Fe\text{-}C(OC_2H_5)C_6H_4CH_3\text{-}o]$ and $[\eta^4\text{-}C_8H_8(CO)_2FeC(OC_2H_5)\text{-}C_6H_4CH_3\text{-}p]$ produced the head-bridged cyclooctatriene derivatives $[C_8H_8C(OC_2H_5)C_6H_4CH_3\text{-}o]$ (Eq. (2)) and $[C_8H_7(OC_2H_5)C(H)C_6H_4CH_3\text{-}p]$ (Eq. (3)), respectively, via C–C bond formation or ethoxy migration [17]. We are now interested in further examining the thermolysis reactivity of such isomerized products of the cycloolefin-coordinated metal alkoxycarbene complexes.



(1)



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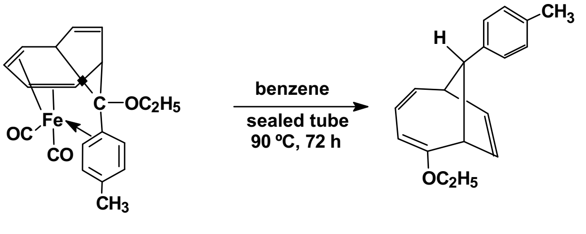
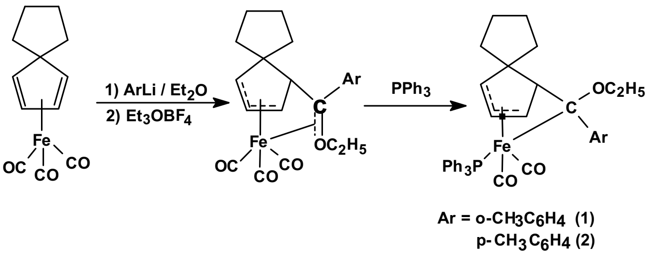


(3)

We previously reported that the reactions of spiro[4.4]-nona-1,3-diene(tricarbonyl)iron with aryllithium reagents ArLi ($Ar = o\text{-}CH_3C_6H_4$, $p\text{-}CH_3C_6H_4$) followed by the alkylation with Et_3OBF_4 and subsequent transformation with PPh_3 yielded the η^3 cycloolefin-coordinated dicarbonyliron phosphine adducts $[(\eta^3\text{-}C_9H_{12})Fe\{C(OC_2H_5)Ar\}\text{-}(CO)_2PPh_3]$ ($Ar = o\text{-}CH_3C_6H_4$, $p\text{-}CH_3C_6H_4$) (Eq. (4)) [19], which we call the isomerized products of spiro[4.4]-nona-1,3-diene(dicarbonyl)[ethoxy(aryl)carbene]iron phosphine adducts or the isomerized spiro[4.4]nona-1, 3-diene(dicarbonyl)[ethoxy(aryl)carbene]iron phosphine adducts. The structures of these phosphine adducts have been confirmed by the X-ray crystallographic studies.



(4)

To further explore the thermolysis reactivity of the isomerized products of the cycloolefin-coordinated alkoxycarbene iron complexes and their application in organometallic and organic synthesis, we investigated the thermolysis reactions of isomerized products of spiro[4.4]nona-1, 3-diene(dicarbonyl)[ethoxy(aryl)carbene]iron phosphine adducts $[(\eta^3\text{-}C_9H_{12})Fe\{C(OC_2H_5)Ar\}(CO)_2PPh_3]$ (**1**, $Ar = o\text{-}CH_3C_6H_4$; **2**, $Ar = p\text{-}CH_3C_6H_4$), which produced the novel thermal decomposition products. Herein we report these unusual thermolysis reactions and the structures of the novel thermolytic products.

2. Experimental

2.1. General procedure and materials

All procedures were performed under a dry, oxygen-free N_2 atmosphere by using standard Schlenk techniques. All solvents employed were reagent grade and dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under N_2 atmosphere. Benzene was distilled from sodium, while petroleum ether (30–60 °C) and CH_2Cl_2 were distilled from CaH_2. The neutral alumina (Al_2O_3, 100–200 mesh) used for chromatography was deoxygenated at room temperature under high vacuum for 16 h, deactivated with 5% w/w N_2-saturated water, and stored under N_2 atmosphere. Compounds **1** and **2** were prepared as previously described [19].

The IR spectra were measured on a Nicolet AV-360 spectrophotometer using NaCl cells with 0.1 mm spacers. The ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature in acetone-d_6 solution with TMS as the internal reference using a Varian Mercury 300 spectrometer running at 300 MHz. Electron ionization mass spectra (EIMS) were run on a Hewlett–Packard 5989A spectrometer. HRMS spectrum was measured on Finnigan

MAT 8430 spectrometer. Melting points obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

2.2. Thermolysis of $[(\eta^3\text{-}C_9H_{12})Fe\{C(OC_2H_5)(C_6H_4CH_3\text{-}o)\}(CO)_2PPh_3]$ (**1**) in benzene to give $[Fe\{\eta^4\text{-}C_5H_7CH{=}CHCH_2CH{=}C(OC_2H_5)C_6H_4CH_3\text{-}o\}(CO)_2PPh_3]$ (**3**), $[C_{24}H_{22}O_7]$ (**4**), and $[Fe(CO)_3(PPh_3)_2]$ (**5**)

Compound **1** (0.130 g, 0.20 mmol) was dissolved in benzene (30 mL) in a quartz tube. The tube was cooled at −80 °C to freeze the benzene solution and sealed under high vacuum. The sealed tube was heated to 90–95 °C for 72 h, during which time the red solution turned dark turbid. After cooling, the dark yellow solution was evaporated in vacuo to dryness. The residue was chromatographed on Al_2O_3 with petroleum ether as the eluant. The orange–yellow band which was eluted first and collected. Then a yellow band was eluted with petroleum ether/CH_2Cl_2 (10:1) and a third light yellow band was eluted with petroleum ether/CH_2Cl_2/Et_2O (10:1:1). After vacuum removal of the solvent from the above three eluates, the residues were recrystallized from petroleum ether/CH_2Cl_2 or petroleum ether/Et_2O at −80 °C. From the first orange fraction, 0.036 g (27%) of golden yellow crystals of **5** [20] was obtained: m.p. 262–266 °C dec (lit. [20a] 264–270 °C); IR (CH_2Cl_2) ν(CO) 1982 (vs) cm^{-1} (lit. [20a] 1883 cm^{-1}); ^1H NMR ($CDCl_3$) δ 7.26 (s, br); MS *m*/*e* 636 ($M^+{-}CO$), 608 ($M^+{-}2CO$), 580 ($M^+{-}3CO$), 262 (PPh_3^+). From the second yellow fraction, 0.052 g (41%) of yellow crystalline **3** was obtained: m.p. 109–111 °C dec.; IR (CH_2Cl_2) ν(CO) 1962 (vs), 1897(s) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.43–7.31 (m, 15H, PPh_3), 7.18–7.10 (m, 4H, *o*-$CH_3C_6H_4$), 5.02 (dd, 1H, $J = 8.7$ Hz, H_4), 4.55 (t, 1H, $J = 7.8$ Hz, H_{11}), 3.64 (q, 2H, $J = 7.8$ Hz, OCH_2CH_3), 2.82 (m, 1H, H_9), 2.54 (m, 1H, H_9), 2.15 (s, 3H,$CH_3C_6H_4$), 1.77 (m, 6H, $H_{10,7,8}$), 1.19 (t, 3H, $J = 7.8$ Hz, OCH_2CH_3), 0.24 (d, 1H, $J = 13.5$ Hz, H_6), −0.95 (m, 1H, H_3); ^{13}C NMR (CD_3COCD_3) δ 215.8 (CO), 154.4, 137.3, 136.8, 136.4, 133.0, 132.9, 132.8, 130.1, 129.8, 129.6, 129.5, 128.5, 128.4, 128.3, 125.4, 112.5, 102.1, 79.6, 68.8, 63.6, 60.4, 41.4, 32.6, 31.6, 31.3, 22.6, 18.9, 14.3; MS *m*/*e* 586 ($M^+{-}2CO$), 324 ($M^+{-}2CO{-}PPh_3$), 268 [$M^+{-}PPh_3{-}Fe(CO)_2$], 262 (PPh_3^+). *Anal.* Calc. for $C_{39}H_{39}O_3PFe \cdot (C_2H_5)_2O$ (ether): C, 72.09; H, 6.89. Found: C,72.61; H, 6.63%. From the third fraction, a cyclobutane derivative of **4** (0.012 g, 13%) as light yellow crystals was obtained: m.p. 131 °C; ^1H NMR ($CDCl_3$) δ 7.77–7.28 (m, 10H, $2C_6H_5$), 3.91 (s, 3H, OCH_3), 3.27 (m, 1H), 2.25 (m, 1H), 1.81 (m, 1H), 1.29 (s, 6H, $2CH_3$); MS *m*/*z* 422 (M^+); HRMS calcd for $C_{24}H_{22}O_7$ [M^+]: 422.1366. Found: 422.1368.

2.3. Thermolysis of **1** in benzene-d_6 (C_6D_6) to give **3**, **4**, and **5**

As described above for the thermolysis of **1** in benzene, 0.130 g (0.20 mmol) of compound **1** dissolved in benzene-d_6 (6 mL) in a quartz tube was heated at 85–90 °C for 72 h. Further treatment as described for the thermolysis of **1** in benzene gave 0.049 g (39%) of **3**, 0.011 g (12%) of **4**, and 0.038 g (29%) of **5**, which were identified by their IR and ^1H NMR spectra.

2.4. Thermolysis of $[(\eta^3\text{-}C_9H_{12})Fe\{C(OC_2H_5)(C_6H_4CH_3\text{-}p)\}(CO)_2PPh_3]$ (**2**) to give $[Fe\{\eta^4\text{-}C_5H_7CH{=}CHCH_2\text{-}CH{=}C(OC_2H_5)C_6H_4CH_3\text{-}p\}(CO)_2PPh_3]$ (**6**), $[C_{24}H_{22}O_7]$ (**4**), and $[Fe(CO)_3(PPh_3)_2]$ (**5**)

Using the same procedures described above, compound **2** (0.150 g, 0.23 mmol) in benzene (30 mL) in a quartz tube was heated at 90–95 °C for 72 h. Subsequent treatment of the black resulting solution as described for the thermolysis of **1** afforded 0.058 g (40%) of yellow crystalline **6**, 0.015 g (16%) of **4** and 0.038 g (28%) of **5**. Products **4** and **5** were identified by their IR and ^1H NMR spectra. Product **6**: m.p. 118–120 °C dec.; IR (CH_2Cl_2) ν(CO) 1960 (vs), 1894(s) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.41–7.33 (m, 15H, PPh_3), 7.21–7.15 (m, 4H, *p*-$CH_3C_6H_4$), 5.03 (dd, 1H, $J = 8.6$ Hz, H_4), 4.56 (t, 1H, $J = 7.6$ Hz, H_{11}), 3.62 (q, 2H, $J = 7.7$ Hz, OCH_2CH_3), 2.81 (m, 1H, H_9), 2.52 (m, 1H, H_9), 2.13 (s, 3H, *p*-$CH_3C_6H_4$), 1.75 (m, 6H, $H_{10,7,8}$), 1.18 (t, 3H, $J = 7.8$ Hz, OCH_2CH_3), 0.23 (d, 1H, $J = 13.5$ Hz, H_6), −0.94 (m, 1H, H_3); ^{13}C NMR (CD_3COCD_3) δ 215.6 (CO), 154.1, 137.0, 136.6, 136.2, 132.8, 132.7, 133.1, 130.3, 129.6, 129.4, 129.1, 128.1, 128.3, 128.2, 125.6, 112.7, 101.9, 79.6, 68.7, 63.5, 60.4, 41.3, 32.6, 31.5, 31.2, 22.5, 18.8, 14.2; MS *m*/*e* 586 ($M^+{-}2CO$), 324 ($M^+{-}2CO{-}PPh_3$), 268 [$M^+{-}PPh_3{-}Fe(CO)_2$], 262 (PPh_3^+). *Anal.* Calc. for $C_{39}H_{39}O_3PFe$: C, 72.90; H, 6.12. Found: C, 72.52; H, 6.48%.

2.5. X-ray crystal structure determinations of complexes **3** and **4**

The single crystals of complexes **3** and **4** suitable for X-ray diffraction studies were obtained by recrystallization from petroleum ether/CH_2Cl_2 or petroleum ether/Et_2O at −80 °C. Single crystals were mounted on a glass fibre and sealed with epoxy glue. The X-ray diffraction intensity data for the two complexes were collected with a Bruker Smart diffractometer at 20 °C using Mo Kα radiation with an ω–2θ scan mode.

The structures of **3** and **4** were solved by the direct methods and expanded using Fourier techniques. For both compounds, the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included but not refined. The absorption corrections were applied using SADABS. The final cycle of full-matrix least-squares refinement was based on the observed reflections and the variable parameters converged with the unweighted and weighted agreement to give the agreement factors listed in Table 1.

The details of the crystallographic data and the procedures used for data collection and reduction information for **3** and **4** are given in Table 1. The molecular structures

Table 1
Crystal data and experimental details for complexes **3** and **4**

	3 · Et_2O	**4**
Formula	$C_{43}H_{49}O_4PFe$	$C_{24}H_{22}O_7$
Formula weight	716.64	422.42
Space group	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)
a (Å)	36.861(3)	9.6406(12)
b (Å)	13.7572(12)	13.2005(16)
c (Å)	14.8558(13)	16.860(2)
β (°)	106.069(2)	101.451(2)
V (Å^3)	7239.1(11)	2102.9(4)
Z	8	4
D_{calcd} (g/cm^3)	1.315	1.334
$F(000)$	3040	888
μ (Mo Kα) (cm^{-1})	5.03	0.98
Orientation reflections: number; range (2θ) (°)	2871; 4.477–44.101	2313; 4.930–46.173
Data collection range, 2θ (°)	2.30–56.56	3.94–50.00
Number of unique data, total with $I > 2.00\sigma(I)$	8469	3710
	4493	2215
No. of parameters refined	545	296
Correction factors, maximum–minimum	0.76577–1.00000	0.7236–1.0000
R[a]	0.0519	0.0721
R_w[b]	0.1051	0.1657
Quality of fit in dicator[c]	0.866	0.855
Maximum shift/estimated final cycle	3.022	0.001
Largest peak (e$^-$/Å^3)	0.684	0.319
Minimum peak (e$^-$/Å^3)	−0.363	−0.351

[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 $= [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

of **3** and **4** are shown in Figs. 1 and 2, respectively, and the principal bond lengths and angles for complexes **3** and **4** are also shown in Figs. 1 and 2. The atomic coordinates and B_{iso}/B_{eq}, anisotropic displacement parameters, complete bond lengths and angles, least-squares planes for **3** and **4** are given in the Supporting Information.

3. Results and discussion

As mentioned in the Introduction, in order to further examine the thermolysis behavior of isomerized cycloolefin-coordinated alkoxycarbene iron complexes, we carried out the study of the thermolysis reactions of the isomerized products of spiro[4.4]nona-1,3-diene(dicarbonyl)[ethoxy(aryl)carbene]iron phosphine adducts **1** and **2**.

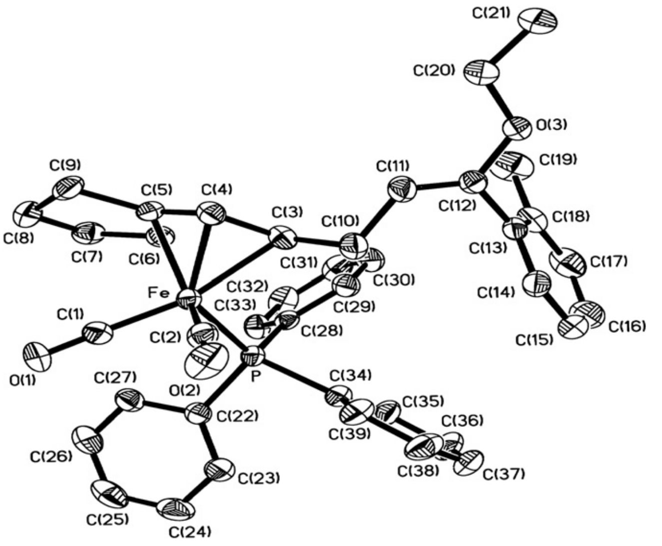
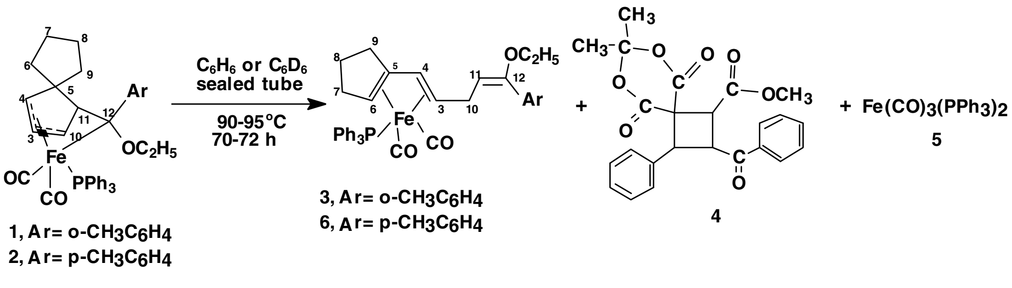


Fig. 1. ORTEP diagram of **3**. Selected bond lengths (Å) and angles (°): Fe–C(3) = 2.123(3), Fe–C(4) = 2.054(3), Fe–C(5) = 2.091(3), Fe–C(6) = 2.158(3), C(3)–C(4) = 1.416(4), C(4)–C(5) = 1.401(4), C(5)–C(6) = 1.408(4), C(5)–C(9) = 1.504(5), C(6)–C(7) = 1.515(5), C(3)–C(10) = 1.508(5), C(10)–C(11) = 1.498(5), C(11)–C(12) = 1.313(4); C(4)–C(5)–C(6) = 120.0(3), C(3)–C(4)–C(5) = 117.7(3), C(4)–C(3)–C(10) = 122.3(3), C(3)–C(10)–C(11) = 113.3(3), C(10)–C(11)–C(12) = 127.5(4), C(3)–C(4)–C(5)–C(6) = −3.8(4), C(10)–C(3)–C(4)–C(5) = 174.8(3).

An orange-red benzene solution of compound **1** in a sealed tube was heated with stirring at 90–95 °C for 72 h. After workup as in the Section 2, the η^4 olefin-coordinated carbonyliron phosphine complex [Fe{η^4-$C_5H_7CH{=}CHCH_2CH{=}C(OC_2H_5)C_6H_4CH_3$-*o*}$(CO)_2PPh_3$] (**3**), cyclobutane derivative **4**, and $Fe(CO)_3(PPh_3)_2$ (**5**) (Eq. (5)) were obtained in 41%, 13%, and 27% yields, respectively. The analogous thermolyses of compound **2** gave the corresponding η^4 olefin-coordinated carbonyliron complex [Fe{η^4-$C_5H_7CH{=}CHCH_2CH{=}C(OC_2H_5)C_6H_4CH_3$-*p*}-$(CO)_2PPh_3$] (**6**) and products **4** and **5** (Eq. (5)). The structures of **3** and **4** have been established by their single-crystal X-ray diffraction studies. Product **5** is a known compound [20], which was identified by its mp, and IR, ^{1}H NMR, and mass spectra. Product **6** was assigned the similar structure of **3** since its spectral data are similar to those of **3** (Section 2).



1, Ar= o-CH3C6H4
2, Ar= p-CH3C6H4

3, Ar= o-CH3C6H4
6, Ar= p-CH3C6H4

4

5

(5)

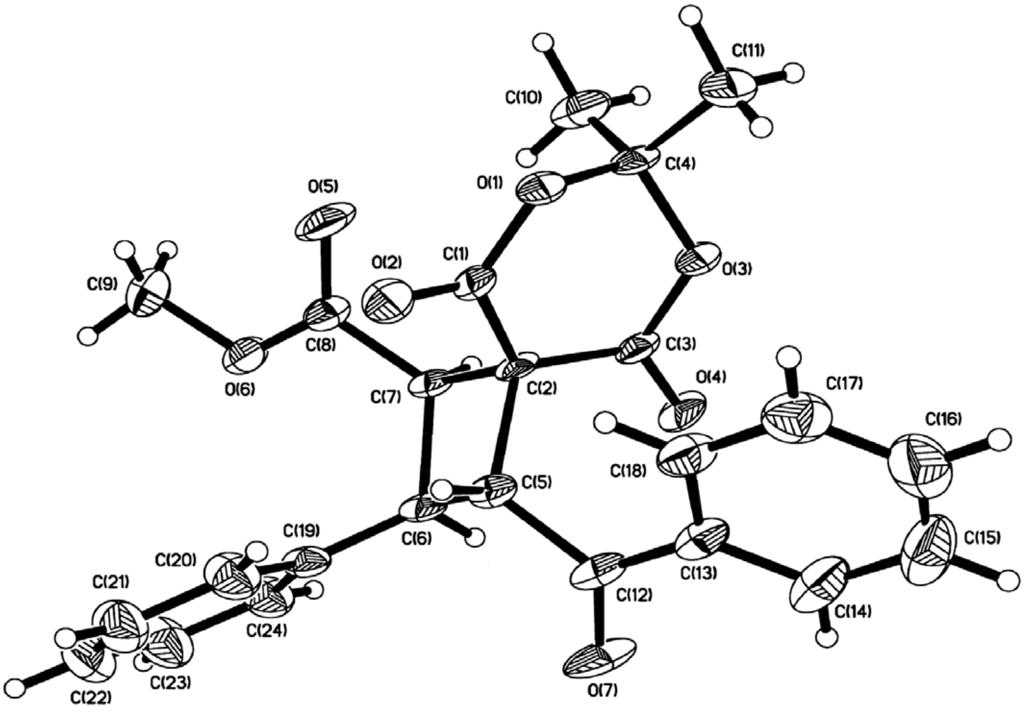


Fig. 2. ORTEP diagram of **4**. Selected bond lengths (Å) and angles (°): C(2)–C(5) = 1.571(3), C(5)–C(6) = 1.539(4), C(6)–C(7) = 1.581(3), C(2)–C(7) = 1.582(4), C(2)–C(1) = 1.532(3), C(2)–C(3) = 1.500(4), C(5)–C(12) = 1.522(4), C(6)–C(19) = 1.505(4), C(7)–C(8) = 1.502(4), C(1)–O(1) = 1.331(3), C(3)–O(3) = 1.337(3), C(4)–O(1) = 1.446(3), C(4)–O(3) = 1.452(3); C(5)–C(2)–C(7) = 87.26(18), C(2)–C(5)–C(6) = 92.64(18), C(5)–C(6)–C(7) = 88.42(19), C(6)–C(7)–C(2) = 90.62(18), C(7)–C(2)–C(5)–C(6) = 7.84(18), C(4)–O(1)–C(1)–C(2) = 9.8(3), O(1)–C(1)–C(2)–C(3) = 13.5(3).

The X-ray structure of **3** (Fig. 1) shows that a five-membered ring of the spiro ring ligand was opened with breaking of the C–C σ-bond and formation of an η^4 π-bond coordinating to the Fe atom through the two conjugated double bonds, one of which is a cyclic and the other is an acyclic. The distances from the Fe atom to the four coordinated carbon atoms are different: the longest distance is Fe–C(6) = 2.158(3) Å, and the shortest distance is Fe–C(4) = 2.054(3) Å; the distances of Fe–C(3) and Fe-(5) are 2.123(3) and 2.091(3) Å, respectively. This difference could be caused by the steric hindrance of the bulky PPh_3 ligand. The bond lengths between the four-coordinated carbon atoms are almost identical (C(3)–C(4) = 1.416(4) Å, C(4)–C(5) = 1.401(4) Å, C(5)–C(6) = 1.408(4) Å), which are shorter than that of C–C single bonds but longer than that of C=C double bonds. The C(3), C(4), C(5), and C(6) atoms are nearly lie in a plane with a torsion angle of C(3)–C(4)–C(5)–C(6) = 5.7(4)°.

The molecular structure of **4** (Fig. 2) shows that it is a spiro organic compound consisting of a four-membered ring and a six-membered ring. The C(2), C(5), C(6), and C(7) atoms construct a planar square (C(7)–C(2)–C(5)–C(6) = 7.84(18), C(2)–C(5)–C(6) = 92.64(18), C(5)–C(6)–C(7) = 88.42(19), C(6)–C(7)–C(2) = 90.62(18)). The bond lengths of C(2)–C(5), C(5)–C(6), C(6)–C(7), and C(2)–C(7) are 1.571(3), 1.539(4), 1.581(3), and 1.582(4) Å, respectively, which are approximately equal and obviously longer than the normal C–C single bonds.

A possible mechanism for the formation of products **3** and **6** might be via an homolysis of the C–C σ-bond in spiro ring ligand corresponding to C(5)–C(11) with the formations of the cyclic double bond C(5)–C(6) and acyclic double bond C(4)–C(3) and with the coordination of the Fe atom to satisfy the 18-electron configuration. While the formation of compound **4**, a minor product, is unexpected and surprising, and we do not know the chemistry involved. However, it is certain that product **4** was derived from starting **1** or **2** on thermal decomposition by losing the $Fe(CO)_2PPh_3$ moiety, which can be converted into $Fe(CO)_3(PPh_3)_2$ (**5**) by abstracting a CO and a PPh_3 ligands generated from the decomposition of **1** or **2**. Indeed, we have isolated the by-product **5** by column chromatography (Section 2 and Eq. (5)). The phenyl groups in product **4** might come from the solvent benzene or PPh_3 ligand of starting compound **1** or **2**. However, the solvent benzene can be excluded since the thermolysis of compound **1** in deuterated benzene (C_6D_6) under the same conditions as those in benzene also afforded product **4** in similar yield (12%) but no deuterated product **4**-d_{10} (Eq. (5)). Thus, the most possible source of the phenyl groups in compound **4** is the PPh_3. It is not excluded that the phenyl groups in product **4** were derived from the tolyl group of starting **1** or **2**, as mentioned below. As for the origin of the CH_3 groups in molecule **4**, we speculate that it might come from the tolyl substituent or ethoxy group of **1** or **2**. Further cleavage could occur in the $CH_3C_6H_4$ or OC_2H_5 group in

1 or **2** aided by metal iron species under heating to lose the CH_3 group to become a C_6H_5 or OCH_3 group by abstracting a hydrogen from the solvent and provide its CH_3 or C_6H_5 group for the formation of **4**. While the source of the oxygen atom in product **4** is only CO ligands or ethoxy group of starting **1** or **2** because the thermolysis reaction was carried out in a vacuum sealed tube using water- and oxygen-free benzene. Due to no relative reference and lack of further experimental evidence, the mechanism proposed above is a speculation only.

In summary, we have found that the remarkable thermolysis reactions of the isomerized spiro[4.4]nona-1,3-diene(dicarbonyl)[ethoxy(aryl)carbene]iron phosphine adduct, and the novel thermolytic products were obtained. The thermolysis results further indicate that the different cycloolefin ligands exert a great influence on the thermolysis behavior of the isomerized iron alkoxycarbene complexes and the resulting products. Further studies on the scope of these thermolysis reactions and application in organic and organometallic synthesis are being carried out in our laboratory.

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Appendix A. Supplementary material

CCDC 657153 and 657154 contain the supplementary crystallographic data for **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.11.029.

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