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Studies on olefin-coordinating transition metal carbene complexes XX *. Synthesis of 1,3-cyclohexadiene(dicarbonyl)[ethoxy(aryl)- carbene]iron complexes and their phosphine adducts. Crystal structure of $C_6H_8(CO)_2FeC(OC_2H_5)C_6H_4CH_3-o$

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Abstract

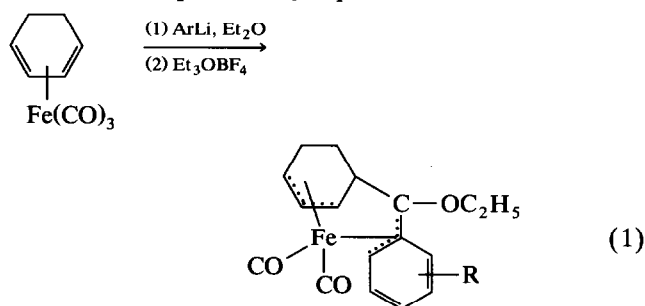
Reaction of 1,3-cyclohexadiene(tricarbonyl)iron (**1**) with *ortho*-substituted aryllithium reagents ArLi (Ar = *o*-CH₃C₆H₄, *o*-CH₃OC₆H₄, *o*-CF₃C₆H₄) in ether at low temperature, and subsequent alkylation of the acylmetalates formed with Et₃OBF₄ in aqueous solution at 0°C or in CH₂Cl₂ at -60°C gave the 1,3-cyclohexadiene(dicarbonyl)[ethoxy(aryl)carbene]iron complexes ($\eta^4-C_6H_8(CO)_2FeC(OC_2H_5)Ar$ (**3**, Ar = *o*-CH₃C₆H₄; **4**, Ar = *o*-CH₃OC₆H₄), and the isomerized product ($\eta^3-C_6H_8(CO)_2FeC(OC_2H_5)C_6H_4CF_3-o$ (**5**), respectively, among which the structure of **3** has been established by an X-ray diffraction study. Complex **3** is monoclinic, space group *P*2₁ with *a* = 8.118(4), *b* = 7.367(4), *c* = 14.002(6) Å, β = 104.09(3)°, *V* = 812.2(6) Å³, *Z* = 2, *D*_c = 1.39 g cm⁻³, *R* = 0.056, and *R*_w = 0.062 for 976 observed reflections. Complexes **3** and **5** were converted into the chelated allyliron phosphine adducts ($\eta^3-C_6H_8(CO)_2(PR^1)_3FeC(OC_2H_5)Ar$ (**6**, Ar = *o*-CH₃C₆H₄, R¹ = Ph; **7**, Ar = *o*-CH₃C₆H₄, R¹ = OPh; **9**, Ar = *o*-CF₃C₆H₄, R¹ = Ph), by reaction with phosphines in petroleum ether at low temperatures.

1. Introduction

Alkene-metal carbene complexes are important intermediates in various reactions of metal carbene complexes with alkenes [1–3]. In recent years, the olefin-coordinated transition metal carbene complexes and/or their isomerized products have been examined extensively in our laboratory [4–13]. Several novel isomerizations of olefin ligands have been observed and a series of isomerized carbene complexes with novel structure have been obtained. However, only a few olefin-coordinated metal carbene complexes were isolated [8,11,12], in which the olefin ligand and carbene ligand coexist stably.

We previously reported the reaction of 1,3-cyclohexadiene(tricarbonyl)iron (**1**) with aryllithium reagents at low temperature to produce the acylmetalates which was dissolved in water at 0°C and then Et₃OBF₄ was

added to the alkylation to give novel isomerized products of cyclohexadiene(dicarbonyl)[ethoxy(aryl)carbene]iron complexes [15] (eqn. (1)).



(R = H, *m*-, *p*-CH₃, *p*-CH₃O, *p*-CF₃)

However, when *o*-CH₃C₆H₄Li was used for the reaction with **1** followed by the alkylation of the acylmetalate intermediate formed with Et₃OBF₄ under the same conditions gave no analogous product owing to the extreme lability of the acylmetalate intermediate. In previous papers [5,6], we showed that the resulting

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products formed depend on the nature of the substituents of the aryl nucleophiles and on the alkylation conditions. An attempt was made to react **1** with *ortho*-substituted aryllithium reagents such as *o*-CH₃C₆H₄Li, *o*-CH₃OC₆H₄Li, and *o*-CF₃C₆H₄Li in order to investigate further the effects of different aryl substituents and different alkylation conditions on the reaction products.

Thus, the 1,3-cyclohexadiene(dicarbonyl)[ethoxy(aryl)carbene]iron complexes and the isomerized carbene complex in which the aryl is an *ortho*-substituted phenyl group, respectively, were obtained by the reaction of **1** with *ortho*-substituted aryllithium reagents in a manner similar to that previously described [15] but under different alkylation conditions. Here we report the synthesis and crystal structure of these cyclohexadiene-coordinated carbene complexes, and their addition reaction with phosphines giving phosphine adducts.

2. Experimental details

All manipulations were carried out under a pre-purified dinitrogen atmosphere in reagent grade solvents and using standard Schlenk techniques. All solvents employed were distilled under a dinitrogen atmosphere from appropriate drying agents: diethyl ether from sodium benzophenone ketyl, petroleum ether (30–60°C) from CaH₂, and CH₂Cl₂ from P₂O₅. The solvents were stored over 4 Å molecular sieves under dinitrogen prior to use. The neutral alumina (Al₂O₃) used for chromatography was deoxygenated at room temperature in a high vacuum for 16 h, deactivated with 5% w/w dinitrogen-saturated water, and stored under dinitrogen. Cyclohexadiene(tricarbonyl)iron (**1**) was purchased from Strem Chemicals, Inc., and used directly. C₆H₈(CO)₂Fe(OC₂H₅)C₆H₄CH₃-*m* (**2**) was prepared as previously reported [15]. Et₃OBF₄ [16] and aryllithium reagents [17–20] were prepared by literature methods.

IR, ¹H NMR and mass spectra were recorded on a Zeiss Specord-75 spectrophotometer, a Varian XL-200 spectrometer, and a Finnigan 4021/MS/DS spectrometer, respectively. The melting points were determined in sealed, dinitrogen-filled capillaries and are not corrected.

2.1. Preparation of C₆H₈(CO)₂FeC(OC₂H₅)C₆H₄CH₃-*o* (**3**)

2.1.1. Alkylation in H₂O

To a solution of 1.0 g (4.55 mmol) of **1** in 50 ml of ether was added dropwise 4.55 mmol of *o*-CH₃C₆H₄Li [17] at –60°C within 15 min with strong stirring. The colour of the mixture turned gradually from light yellow to orange. The reaction mixture was allowed to warm to –50°C and stirred at –50 to –45°C for 3 h.

The resulting orange solution was evaporated to dryness in a high vacuum at –40°C. To the dark-orange solid residue was added Et₃OBF₄ (*ca.* 5 g). This solid mixture was dissolved in 50 ml of dinitrogen-saturated water at 0°C with vigorous stirring and the mixture covered with petroleum ether (30–60°C). Immediately afterwards, Et₃OBF₄ (*ca.* 10 g) was added to the aqueous solution portionwise, with strong stirring, until it became acidic. The aqueous solution was extracted with petroleum ether. The combined extract was dried over anhydrous Na₂SO₄. After removal of the solvent under vacuum, the residue was chromatographed on an alumina (neutral, 100–200 mesh) column (1.6 × 15 cm) at –25°C with petroleum ether as the eluant. The yellow band was eluted and collected. The solvent was removed *in vacuo* and the residue of red oil was recrystallized from petroleum ether at –80°C to give orange crystals of **3**; m.p. 30°C (decomp.), yield 0.742 g (48%, based on **1**). Anal. Found: C, 63.59; H, 5.99; Fe, 16.83. C₁₈H₂₀O₃Fe (340.21) calc.: C, 63.55; H, 5.93; Fe, 16.42%. IR (CH₂Cl₂): ν(CO) 1988vs, 1927vs cm^{–1}; (hexane): 1995sh, 1989vs, 1947sh, 1940vs cm^{–1}. MS: *m/z* 340 (M⁺), 312 (M⁺ – CO), 284 (M⁺ – 2CO).

2.1.2. Alkylation in CH₂Cl₂

Compound **1** (1.0 g, 4.55 mmol) was treated with 4.55 mmol of *o*-CH₃C₆H₄Li, as described above in Section 2.1.1, in ether at –50 to –45°C for 3 h. After removal of the solvent under vacuum at –40°C, the residue was dissolved in 20 ml of CH₂Cl₂ at –60°C. To this solution, 0.90 g of Et₃OBF₄ dissolved in 10 ml of CH₂Cl₂ was added dropwise with stirring within 15 min. The reaction mixture turned from dark red to orange yellow. After being stirred at –40°C for 0.5 h, the solvent was removed *in vacuo* at –40°C. Further treatment as described above gave 0.70 g (45%, based on **1**) of orange crystalline **3** which was identified by its melting point, IR, ¹H NMR and mass spectra.

2.2. Preparation of C₆H₈(CO)₂FeC(OC₂H₅)C₆H₄OC-H₃-*o* (**4**)

2.2.1. Alkylation in H₂O

n-C₄H₉Li [18] (6.47 mmol) was mixed with a solution of *o*-CH₃OC₆H₄Br (1.21 g, 6.47 mmol) in 20 ml of ether at 0°C. The mixture was stirred at room temperature (20–22°C) for 1 h. The resulting ether solution of *o*-CH₃OC₆H₄Li [19] reacted in a manner similar to that described for the preparation of **3**, with 1.0 g (4.55 mmol) of **1** in 50 ml of ether at –25°C for 3.5 h. Subsequent alkylation and further treatment in a similar manner as described for the preparation given in Section 2.1.1 afforded 0.82 g (51%, based on **1**) of light yellow oil. Anal. Found: C, 60.41; H, 5.78.

$C_{18}H_{20}O_4Fe$ (356.21) calc.: C, 60.69; H, 5.66%. IR (CH_2Cl_2): $\nu(CO)$ 1971vs, 1921vs cm^{-1} ; (hexane): 2000sh, 1990vs, 1950sh, 1942vs cm^{-1} . MS: m/z 356 (M^+), 328 ($M^+ - CO$), 300 ($M^+ - 2CO$).

2.2.2. Alkylation in CH_2Cl_2

Compound **1** (1.0 g, 4.55 mmol) was treated as described in Section 2.1. with fresh o - $CH_3OC_6H_4Li$ prepared by the reaction of o - $CH_3OC_6H_4Br$ (1.21 g, 6.47 mmol) with 6.47 mmol of n - C_4H_9Li , in ether at $-25^\circ C$ for 3.5 h. After evaporating the solvent *in vacuo*, the subsequent treatment of the residue as described for the preparation in Section 2.1.2 gave 0.74 g (46%, based on **1**) of light yellow oil of **4** which was identified by its IR, 1H NMR, and mass spectra.

2.3. Preparation of $C_6H_8(CO)_2FeC(OC_2H_5)C_6H_4CF_3$ -*o* (**5**)

2.3.1. Alkylation of H_2O

To a solution of n - C_4H_9Li (11.0 mmol) in 20 ml of ether was added 1.43 g (9.80 mmol) of benzotrifluoride. The mixture was refluxed for 6 h. The resulting ether solution of o - CF_3 - C_6H_4Li [20] was treated in a manner similar to that described in Section 2.1 with 1.0 g (4.55 mmol) of **1** in 50 ml of ether at -50 to $-45^\circ C$ for 3 h. Subsequent alkylation and further treatment similar to procedures described in Section 2.1.1 gave 0.75 g (42%, based on **1**) of orange-red crystals of **5**; m.p. 32 – $34^\circ C$ (decomp.). Anal. Found: C, 55.15; H, 4.56. $C_{18}H_{17}O_3F_3Fe$ (394.18) calc.: C, 54.85; H, 4.35%. IR (CH_2Cl_2): $\nu(CO)$ 1985vs, 1931vs cm^{-1} ; (hexane): 1994vs, 1982sh, 1955vs cm^{-1} . MS: m/z 394 (M^+), 366 ($M^+ - CO$), 338 ($M^+ - 2CO$).

2.3.2. Alkylation in CH_2Cl_2

Compound **1** (1.0 g, 4.55 mmol) was treated in a manner similar to that described above in Section 2.1 with fresh o - $CF_3C_6H_4Li$ ether solution prepared by the reaction of $CF_3C_6H_5$ (1.43 g, 9.80 mmol) with n - C_4H_9Li (11.0 mmol) in ether at -50 to $-45^\circ C$ for 3 h. After vacuum removal of the solvent, the subsequent alkylation and further treatment of the residue as described in Section 2.1.2 afforded 0.58 g (32%, based on **1**) of orange-red crystalline **5** which was identified by its melting point, and IR, 1H NMR and mass spectra.

2.4. Reaction of $C_6H_8(CO)_2FeC(OC_2H_5)C_6H_4CH_3$ -*o* (**3**) with PPh_3 to give $C_6H_8(CO)_2(PPh_3)FeC(OC_2H_5)-C_6H_4CH_3$ -*o* (**6**)

Compound **3** (0.10 g, 0.29 mmol) was dissolved in 30 ml of petroleum ether (30 – $60^\circ C$) at $-60^\circ C$. To this solution was added dropwise PPh_3 (0.15 g, 0.57 mmol) in 10 ml of petroleum ether. The reaction mixture was

stirred at $-60^\circ C$ for 3 h and the orange-red solution gradually turned bright yellow. The resulting mixture was evaporated to dryness under vacuum. The residue was chromatographed on Al_2O_3 (neutral) at $-20^\circ C$ with petroleum ether as the eluant, and the yellow band was collected. After vacuum removal of the solvent, the crude yellow powder product was recrystallized from petroleum ether at $-80^\circ C$ to give 0.15 g (85%, based on **3**) of yellow needles of **6**; m.p. 116 – $117^\circ C$ (decomp.). Anal. Found: C, 71.52; H, 5.90; P, 5.44; Fe, 8.65. $C_{36}H_{35}O_3PFe$ (602.50) calc.: C, 71.77; H, 5.86; P, 5.14; Fe, 9.27%. IR (CH_2Cl_2): $\nu(CO)$ 1970vs, 1910vs cm^{-1} ; (hexane): 1975vs, 1920 cm^{-1} . MS: m/z 602 (M^+), 340 ($M^+ - PPh_3$), 312 ($M^+ - PPh_3 - CO$), 294 ($M^+ - PPh_3 - 2CO$).

2.5. Reaction of **3** with $P(OPh)_3$ to give $C_6H_8(CO)_2-[P(OPh)_3]FeC(OC_2H_5)C_6H_4CH_3$ -*o* (**7**)

To a solution of **3** (0.20 g, 0.58 mmol) in 30 ml of petroleum ether was added dropwise $P(OPh)_3$ (0.35 g, 1.13 mmol) at $-60^\circ C$ with stirring. The reaction solution was stirred at this temperature for 3 h and the orange-red solution gradually turned yellow. Further treatment of the resulting solution was similar to that described in the reaction of **3** with PPh_3 to afford 0.21 g (55%, based on **3**) of light yellow crystals of **7**; m.p. 84 – $85^\circ C$ (decomp.). Anal. Found: C, 66.82; H, 5.50; P, 4.88; Fe, 8.23. $C_{36}H_{35}O_6PFe$ (650.50) calc.: C, 66.47; H, 5.42; P, 4.76; Fe, 8.59%. IR (CH_2Cl_2): $\nu(CO)$ 1995vs, 1938vs cm^{-1} ; (hexane): 2000vs, 1940vs cm^{-1} . MS: m/z 650 (M^+), 622 ($M^+ - CO$), 594 ($M^+ - 2CO$), 284 ($M^+ - 2CO - P(OPh)_3$).

2.6. Reaction of $C_6H_8(CO)_2FeC(OC_2H_5)C_6H_4CH_3$ -*m* (**2**) with PPh_3 to give $C_6H_8(CO)_2(PPh_3)FeC(OC_2H_5)-C_6H_4CH_3$ -*m* (**8**)

Similar to the procedure described for the reaction of **3** with PPh_3 , Compound **2** (0.10 g, 0.29 mmol) was treated with PPh_3 (0.15 g, 0.57 mmol) at -50 to $-40^\circ C$ for 3 h. Subsequent treatment of the resulting yellow mixture as described above for **6** gave 0.16 g (89%, based on **2**) of yellow crystals of **8**; m.p. 107 – $108^\circ C$ (decomp.). Anal. Found: C, 71.85; H, 5.97; Fe, 8.80. $C_{36}H_{35}O_3PFe$ (602.50) calc.: C, 71.77; H, 5.86; Fe, 9.27%. IR (CH_2Cl_2): $\nu(CO)$ 1985vs, 1925vs cm^{-1} ; (hexane): 1991vs, 1930vs cm^{-1} . MS: m/z 602 (M^+), 340 ($M^+ - PPh_3$), 312 ($M^+ - PPh_3 - CO$), 284 ($M^+ - PPh_3 - 2CO$).

2.7. Reaction of $C_6H_8(CO)_2FeC(OC_2H_5)C_6H_4CF_3$ -*o* (**5**) with PPh_3 to give $C_6H_8(CO)_2(PPh_3)FeC(OC_2H_5)-C_6H_4CF_3$ -*o* (**9**)

The reaction of 0.05 g (0.13 mmol) of **5** in 50 ml of petroleum ether with 0.070 g (0.27 mmol) of PPh_3 at

–50 to –40°C for 3 h, in a similar manner as described for **6**, gave 0.072 g (87%, based on **5**) of yellow crystals of **9**; m.p. 96–98°C (decomp.). Anal. Found: C, 66.07; H, 4.76. $C_{36}H_{32}O_3F_3PFe$ (656.47) calc.: C, 65.87; H, 4.91%. IR (CH_2Cl_2): $\nu(CO)$ 1980vs, 1925vs cm^{-1} ; (hexane): 1988vs, br, 1938vs cm^{-1} . MS: m/z 656 (M^+), 628 ($M^+ - CO$), 600 ($M^+ - 2CO$), 338 ($M^+ - 2CO - PPh_3$).

2.8. Crystal structure determination of **3**

Crystals of $C_6H_8(CO)_2FeC(OC_2H_5)C_6H_4CH_3$ -o (**3**) suitable for X-ray diffraction study were obtained by recrystallization from pentane at –80°C. A single crystal of approximate dimensions $0.28 \times 0.35 \times 0.55$ mm³ was sealed in a capillary under a dinitrogen atmosphere. The X-ray diffraction intensity data of 1923 independent reflections, of which 976 with $I > 3\sigma(I)$ were observable, were collected with a Nicolet R 3M/E four-circle diffractometer at –80°C using Mo $K\alpha$ radiation with a ω – 2θ scan mode within $3^\circ \leq 2\theta \leq 54^\circ$. The data were corrected for Lorentz and polarization effects. The crystals of **3** belong to the monoclinic system. The space group is $P2_1$ with cell dimensions $a = 8.118(4)$, $b = 7.367(4)$, $c = 14.002(6)$ Å, $\beta = 104.09(3)^\circ$, $V = 812.2(6)$ Å³, $Z = 2$, $D_c = 1.39$ g cm^{–3}, and $\mu = 9.35$ cm^{–1} (Mo $K\alpha$).

The position of the Fe atom was determined by using the Patterson function method. The Fe atom was

found to be located in a special position, leading to ambiguous determination of other non-hydrogen atoms. All the non-hydrogen atoms were determined unambiguously by Fourier synthesis using different test models. The structure parameters were refined by a block-diagonal-matrix least-squares method. After refining the atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms, the final discrepancy indices were $R = 0.056$ and $R_w = 0.062$ with 976 reflections.

The atomic coordinates and isotropic thermal parameters of nonhydrogen atoms of **3** are given in Table 2. The bond lengths and angles are listed in Table 3.

3. Results and discussion

3.1. Preparation of complexes 3–5

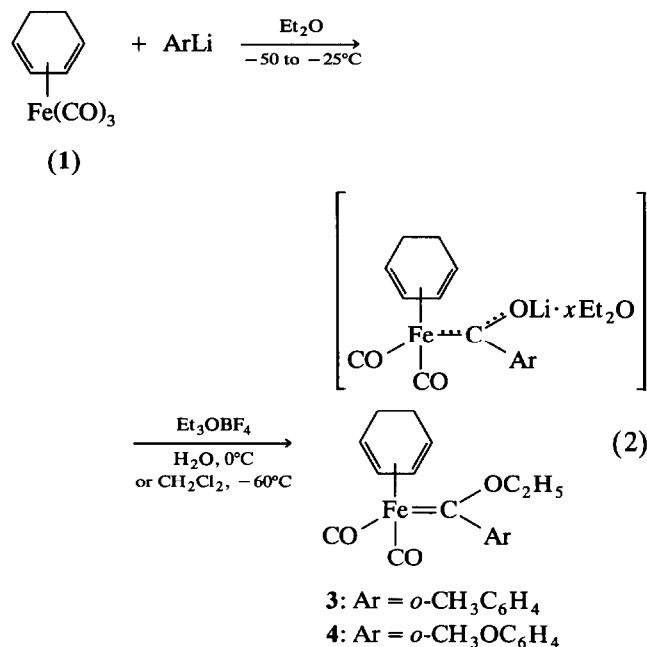
By analogy with the preparation of the isomerized cyclohexadiene(dicarbonyl)[ethoxy(aryl)carbene]iron complexes [15], equimolar quantities of **1** and *ortho*-substituted aryllithium reagents ArLi (Ar = *o*- $CH_3C_6H_4$, *o*- $CH_3OC_6H_4$) were used for the reaction in ether at low temperature. The acylmetalates obtained were subsequently alkylated with Et_3OBF_4 either in aqueous solution at 0°C or in CH_2Cl_2 at –60°C. The reaction products were chromatographed on an alumina column at low temperature and recrystallized from petroleum ether at –80°C to give orange

TABLE 1. ¹H NMR spectra of complexes **3–9** in acetone-*d*₆ at 20°C (δ ppm, TMS as internal reference)

Complex	δ (cycloolefin-proton)	δ (aryl-proton)	δ (OCH ₂ CH ₃)
1 ^a	5.48 (m, 2H); 3.30 (m, 2H); 1.80–1.54 (m, 4H)		
2 [15]	5.20 (t, 1H); 4.08 (t, 1H); 3.36 (t, 1H); 2.92 (m, 1H); 2.40–2.22 (m, 2H); 1.64 (m, 2H)	7.56 (m, 2H); 7.12 (m, 1H) 6.90 (m, 1H); 2.48 (s, 3H, <i>m</i> - $CH_3C_6H_4$)	3.68 (q, 2H); 1.30 (t, 3H)
3	5.10 (m, 2H); 2.70 (m, 2H); 1.76–1.50 (m, 4H)	7.08 (m, 3H); 6.74 (m, 1H); 2.10 (s, 3H, <i>o</i> - $CH_3C_6H_4$)	4.70 (q, 2H); 1.49 (t, 3H)
4	5.50 (m, 2H); 2.94 (m, 2H); 1.90–1.74 (m, 4H)	7.28 (m, 2H); 6.94 (m, 2H); 3.80 (s, 3H, <i>o</i> - $CH_3OC_6H_4$)	4.02 (q, 2H); 1.68 (t, 3H)
5	5.35 (t, 1H); 4.27 (t, 1H); 3.50 (t, 1H); 3.00 (m, 1H); 2.44–2.20 (m, 2H); 1.65 (m, 2H)	8.06 (m, 1H); 7.66 (m, 1H); 7.40 (m, 2H)	3.74 (q, 2H); 1.35 (t, 3H)
6	4.54 (m, 1H); 3.80 (m, 1H); 3.14 (m, 1H); 3.00 (m, 1H); 2.58–2.40 (m, 2H); 1.42 (m, 2H)	7.58–7.12 (m, 19H); 2.84 (s, 3H, <i>o</i> - $CH_3C_6H_4$)	4.26 (q, 2H); 0.94 (t, 3H)
7	4.84 (m, 1H); 3.78 (t, 1H); 3.66 (m, 1H); 3.56 (m, 1H); 2.50–2.34 (m, 2H); 1.40 (m, 2H)	7.48–7.06 (m, 19H); 2.44 (s, 3H, <i>o</i> - $CH_3C_6H_4$)	4.32 (q, 2H); 0.88 (t, 3H)
8	5.08 (m, 1H); 4.55 (m, 1H); 3.54 (m, 1H); 3.10 (m, 1H); 2.48–2.24 (m, 2H); 1.30 (m, 2H)	7.62–7.20 (m, 19H); 2.40 (s, 3H, <i>m</i> - $CH_3C_6H_4$)	4.20 (q, 2H); 0.90 (t, 3H)
9	5.02 (m, 1H); 4.62 (m, 1H); 3.58 (m, 1H); 3.13 (m, 1H); 2.52–2.38 (m, 2H); 1.32 (m, 2H)	7.60–7.20 (m, 19H)	4.25 (q, 2H); 1.04 (t, 3H)

^a Purchased from Strem Chemicals, Inc.

or yellow 1,3-cyclohexadiene-coordinated carbene complexes ($\eta^4\text{-C}_6\text{H}_8$) $(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{Ar}$ (**3**, $\text{Ar} = o\text{-CH}_3\text{C}_6\text{H}_4$; **4**, $\text{Ar} = o\text{-CH}_3\text{OC}_6\text{H}_4$) in 45–51% isolated yields (eqn. (2)).



The alkylation conditions are very important for the formation of complexes **3** and **4**. Since the acylmetalates formed by the reaction of **1** with $o\text{-CH}_3\text{C}_6\text{H}_4\text{Li}$

TABLE 3. Bond lengths (Å) and angles (°) for **3**

Fe–C(1)	1.75(1)	C(7)–C(8)	1.45(3)
Fe–C(2)	1.77(2)	C(8)–C(9)	1.39(3)
Fe–C(3)	1.89(2)	C(9)–C(10)	1.38(4)
Fe–C(13)	2.16(2)	C(10)–C(11)	1.40(3)
Fe–C(14)	1.98(2)	C(11)–C(12)	1.51(4)
Fe–C(15)	2.00(3)	O(3)–C(4)	1.47(2)
Fe–C(16)	2.16(3)	C(4)–C(5)	1.46(4)
C(1)–O(1)	1.17(2)	C(13)–C(14)	1.53(5)
C(2)–O(2)	1.18(3)	C(13)–C(18)	1.46(3)
C(3)–O(3)	1.34(2)	C(14)–C(15)	1.37(3)
C(3)–C(6)	1.49(2)	C(15)–C(16)	1.40(4)
C(6)–C(7)	1.38(3)	C(16)–C(17)	1.45(3)
C(6)–C(11)	1.38(3)	C(17)–C(18)	1.51(3)
C(1)–Fe–C(2)	100.6(8)	Fe–C(2)–O(2)	172(2)
C(1)–Fe–C(3)	91.9(7)	Fe–C(3)–O(3)	134(1)
C(1)–Fe–C(13)	170.3(14)	Fe–C(3)–C(6)	123(1)
C(1)–Fe–C(14)	127.1(9)	O(3)–C(3)–C(6)	103(1)
C(1)–Fe–C(15)	100.1(9)	C(3)–O(3)–C(4)	120(2)
C(1)–Fe–C(16)	100.1(8)	O(3)–C(4)–C(5)	106(2)
C(2)–Fe–C(3)	97.5(8)	C(3)–C(6)–C(7)	119(2)
C(2)–Fe–C(13)	88.2(12)	C(3)–C(6)–C(11)	124(2)
C(2)–Fe–C(14)	128.3(9)	C(7)–C(6)–C(11)	117(2)
C(2)–Fe–C(15)	122.3(11)	C(6)–C(7)–C(8)	127(2)
C(2)–Fe–C(16)	84.4(9)	C(7)–C(8)–C(9)	113(2)
C(3)–Fe–C(13)	90.7(8)	C(8)–C(9)–C(10)	120(2)
C(3)–Fe–C(14)	99.1(8)	C(9)–C(10)–C(11)	125(2)
C(3)–Fe–C(15)	134.6(8)	C(10)–C(11)–C(6)	117(2)
C(3)–Fe–C(16)	167.3(6)	C(10)–C(11)–C(12)	122(2)
C(13)–Fe–C(14)	43.2(14)	C(6)–C(11)–C(12)	120(2)
C(13)–Fe–C(15)	71.5(14)	C(18)–C(13)–C(14)	104(3)
C(13)–Fe–C(16)	76.7(9)	C(13)–C(14)–C(15)	114(2)
C(14)–Fe–C(15)	40.2(9)	C(14)–C(15)–C(16)	119(2)
C(14)–Fe–C(16)	70.3(9)	C(15)–C(16)–C(17)	118(2)
C(15)–Fe–C(16)	39.1(10)	C(16)–C(17)–C(18)	108(2)
Fe–C(1)–O(1)	117(2)	C(17)–C(18)–C(13)	117(2)

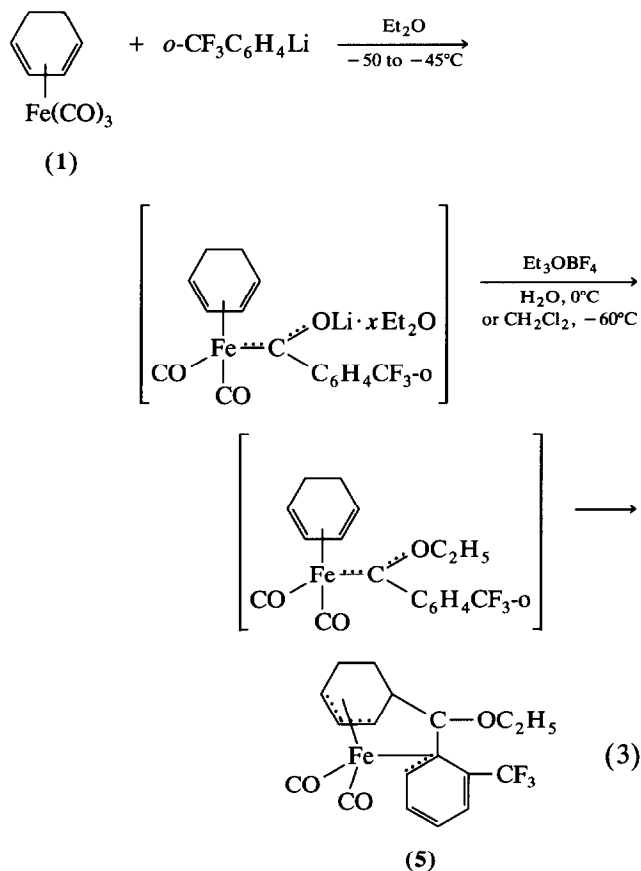
TABLE 2. Atomic coordinates ($\times 10^4$ for Fe and $\times 10^3$ for others) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$)

Atom	x	y	z	U_{eq}
Fe	2460(3)	5000	1772(1)	15(1)
C(1)	58(2)	454(2)	89(1)	17(5)
O(1)	–72(2)	426(2)	33(1)	32(4)
C(2)	315(2)	697(2)	127(1)	25(6)
O(2)	366(2)	815(2)	84(1)	48(6)
C(3)	127(2)	617(2)	260(1)	12(4)
O(3)	6(2)	744(2)	246(1)	30(5)
C(4)	–57(4)	824(4)	148(1)	57(10)
C(5)	–146(3)	990(4)	164(1)	45(7)
C(6)	158(2)	576(3)	367(1)	20(5)
C(7)	103(3)	412(3)	396(1)	31(6)
C(8)	131(2)	341(4)	496(1)	30(6)
C(9)	215(2)	464(3)	566(1)	30(7)
C(10)	265(3)	630(4)	538(1)	46(8)
C(11)	245(3)	689(3)	441(1)	34(6)
C(12)	300(3)	876(3)	416(2)	38(7)
C(13)	478(2)	508(6)	292(1)	33(5)
C(14)	383(3)	327(4)	273(1)	36(7)
C(15)	364(4)	261(4)	180(1)	50(9)
C(16)	426(3)	363(4)	112(1)	44(8)
C(17)	595(3)	439(4)	144(1)	51(9)
C(18)	627(2)	479(4)	253(1)	32(7)

and $o\text{-CH}_3\text{OC}_6\text{H}_4\text{Li}$ are extremely labile, the decomposition occurred immediately when the acylmetalates were dissolved in water at 0°C during the alkylation with Et_3OBF_4 in aqueous solution to give no expected carbene complexes or their isomerized products as mentioned in the Introduction. Thus, in the present work, the alkylation of the acylmetalates were performed as follows: to the acylmetalate obtained was added first a part of Et_3OBF_4 and then water at 0°C to avoid decomposition of the acylmetalate before alkylation, and then immediately afterwards Et_3OBF_4 was added portionwise to the aqueous solution until it became acidic, or the acylmetalate was dissolved in CH_2Cl_2 at -60°C , to which was added dropwise Et_3OBF_4 , resulting in the isolation of the expected cyclohexadiene-coordinated carbene complex.

Interestingly, when $o\text{-CF}_3\text{C}_6\text{H}_4\text{Li}$ was used for the reaction with **1**, followed by the alkylation of acylmetalate formed with Et_3OBF_4 in aqueous solution or in

CH_2Cl_2 under the same conditions, no expected carbene complex but the isomerized cyclohexadiene(dicarbonyl)[ethoxy-(*o*-trifluoromethylphenyl)carbene]iron complex, $(\eta^3\text{-C}_6\text{H}_8)(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CF}_3\text{-}o$ (**5**) was obtained in 42% yield (eqn. (3)).

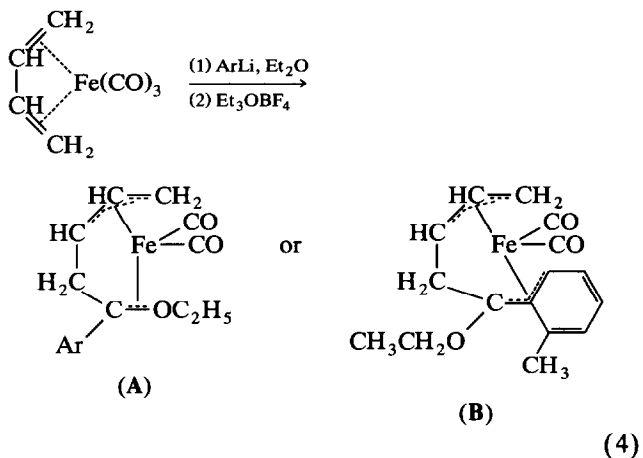


Complexes **3** and **5** are orange crystals of low melting point, and **4** is a light yellow oil at room temperature. Complexes **3**–**5** are soluble both in polar and non-polar organic solvents and very sensitive to air and temperature; oxidative decomposition occurred on exposure to air at room temperature for a few minutes. The formulations of complexes **3**, **4**, and **5** were supported by elemental analyses, IR, ^1H NMR, and mass spectra. Complex **3** was established by an X-ray crystallographic study (below). Until now, only one example of cyclohexadiene-coordinated iron carbene complex, $(\eta^4\text{-C}_{10}\text{H}_{16})(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}o$, has been isolated [11].

The IR spectra (see Experimental section) of complexes **3**–**5** showed two strong CO absorption bands in the $\nu(\text{CO})$ region which signified a $\text{Fe}(\text{CO})_2$ moiety in these complexes. In the ^1H NMR spectra (Table 1), the chemical shift, multiplicity and integral intensity of the proton signals attributed to the cyclohexadiene ligand in complexes **3** and **4** are similar to those in starting

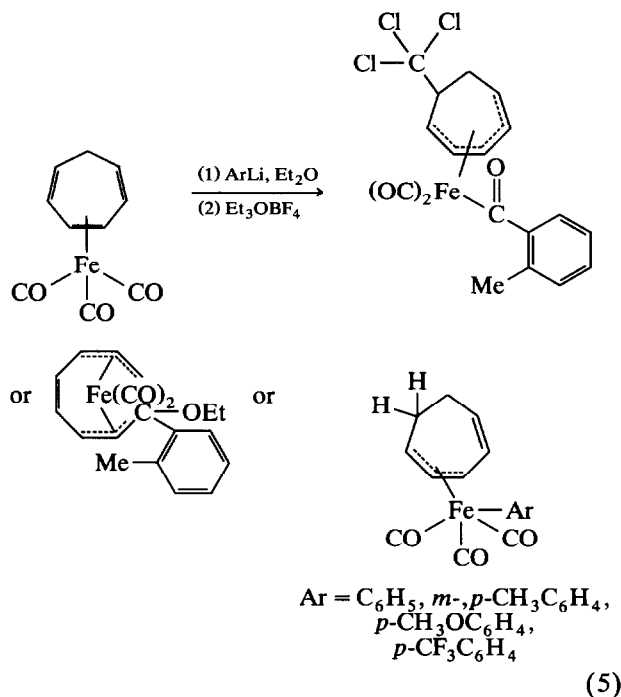
material **1** (see Table 1), which suggested that no isomerization of the cyclohexadiene ligand occurred in both complexes, and the added ethoxy and aryl substituents exerted no significant influence on the proton signals of the cyclohexadiene ligand. Besides the IR and mass spectra, the ^1H NMR spectrum of complex **5** is also very similar to that found in analogous isomerized products $\text{C}_6\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}m$ (**2**) (shown in Table 1) and $\text{C}_6\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5$ [15]; the structure of the latter has been established by an X-ray diffraction study [15]. Therefore, it could be considered that the structure of **5** is the same as $\text{C}_6\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5$ and **2**.

Surprisingly, we found that the reaction processes and resulting products in the reactions of alkene-ligated iron carbonyls with *ortho*-substituted aryllithium such as *o*- $\text{CH}_3\text{C}_6\text{H}_4\text{Li}$ are different from that with *meta*- and *para*-substituted aryllithium reagents. For example, (butadiene)tricarbonyliron reacted with aryllithium reagents such as $\text{C}_6\text{H}_5\text{Li}$, *m*-, *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{Li}$, *p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{Li}$, *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{Li}$, and *m*-, *p*- $\text{ClC}_6\text{H}_4\text{Li}$, followed by alkylation with Et_3OBF_4 to give type **A** isomerized products, while *o*- $\text{CH}_3\text{C}_6\text{H}_4\text{Li}$ was used for the reaction under the same conditions to afford type **B** isomerized product [4] (eqn. (4)).

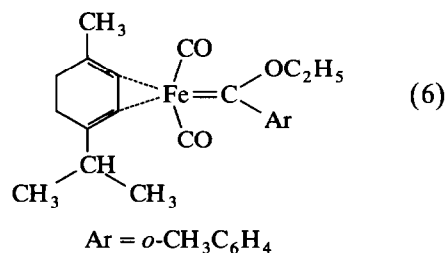
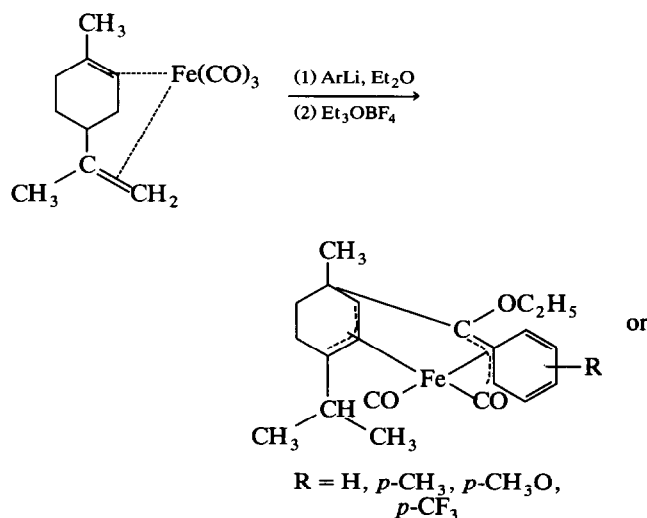


In the case of the isoprene ligand, a similar reaction of (isoprene)tricarbonyliron with most aryllithium reagents produced the isomerized products of isoprene(dicarbonyl)[ethoxy(aryl)carbene]iron complexes with type **A** structure [21] as shown above. However, the reaction between *o*- $\text{CH}_3\text{C}_6\text{H}_4\text{Li}$ and (isoprene)tricarbonyliron under the same conditions gave no analogous product. In contrast, (cycloheptatriene)tricarbonyliron was treated with *o*- $\text{CH}_3\text{C}_6\text{H}_4\text{Li}$ to give the novel compound $(\text{Cl}_3\text{C-cyclo-C}_7\text{H}_8)(\text{CO})_2\text{Fe}(\text{CO-C}_6\text{H}_4\text{Me-}o)$ or ring-opened $(\text{CO})_2\text{Fe}\{\text{C}(\text{OEt})(\text{C}_6\text{H}_4\text{Me-}o)\text{C}_7\text{H}_8\}$ depending on the alkylation conditions [6]. When other aryllithium such as $\text{C}_6\text{H}_5\text{Li}$, *m*-, *p*-

$\text{CH}_3\text{C}_6\text{H}_4\text{Li}$, $p\text{-CH}_3\text{OC}_6\text{H}_4\text{Li}$, and $p\text{-CF}_3\text{C}_6\text{H}_4\text{Li}$ were used for the reaction under the same conditions, no analogous products but $(\eta^3\text{-C}_7\text{H}_9)(\text{CO})_3\text{FeAr}$ complexes [22] were obtained (eqn. (5)).



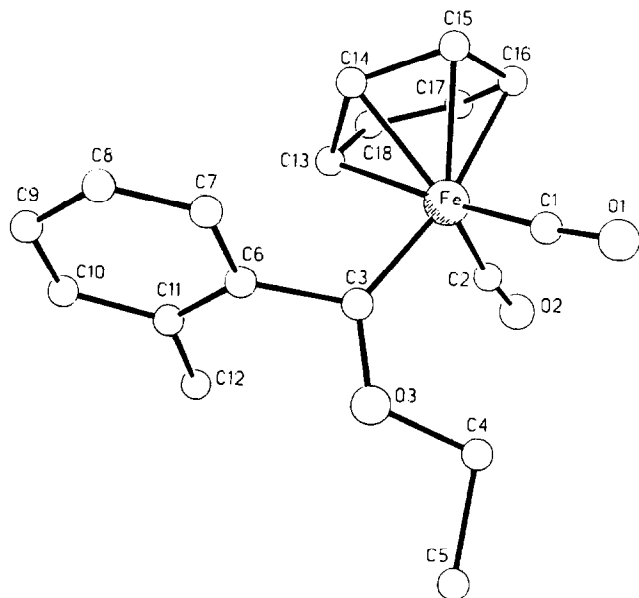
Moreover, reaction of (limonene)tricarbonyliron with aryllithium reagents ArLi ($\text{Ar}=\text{C}_6\text{H}_5$, $p\text{-CH}_3\text{C}_6\text{H}_4$, $p\text{-CH}_3\text{OC}_6\text{H}_4$, $p\text{-CF}_3\text{C}_6\text{H}_4$) and subsequent alkylation with Et_3OBF_4 afforded the isomerized (limonene)dicarbonyl[ethoxy(aryl)carbene] iron complexes, $(\eta^3\text{-C}_{10}\text{H}_{16})(\text{CO})_2\text{Fe}(\text{OC}_2\text{H}_5)\text{Ar}$, while $o\text{-CH}_3\text{C}_6\text{H}_4\text{Li}$ was treated similarly with (limonene)tricarbonyliron to give the limonene-coordinated carbene complex, $(\eta^4\text{-C}_{10}\text{H}_{16})(\text{CO})_2\text{Fe}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}o$ [11] (eqn. (6)).



This special influence of *ortho*-substituted phenyl upon the reaction processes and resulting products in the reactions of alkene-ligated iron carbonyls with aryllithium reagents, which we call the “*ortho*-position effect” of aryl substituents. The action of generating the “*ortho*-position effect” is both the electron effect and the steric factor of the aryl substituent, because of the fact that only $o\text{-CH}_3\text{C}_6\text{H}_4\text{Li}$ and $o\text{-CH}_3\text{OC}_6\text{H}_4\text{Li}$, in which the *ortho*-substituted methyl or methoxy group is an electron-releasing group, were used for the reaction with 1 giving cyclohexadiene-coordinated carbene complexes 3 and 4, respectively. The reaction of $o\text{-CF}_3\text{C}_6\text{H}_4\text{Li}$ in which the trifluoromethyl group is an electron-withdrawing group gave isomerized product 5 instead of the expected cyclohexadiene-coordinated carbene complex. The increase in electropositivity on the carbene carbon atom of the carbene intermediate formed by the reaction of 1 with $o\text{-CF}_3\text{C}_6\text{H}_4\text{Li}$, arising from the strong electron-withdrawing effect of the $o\text{-CF}_3\text{C}_6\text{H}_4$ substituent, caused the carbene carbon atom to bond to the cyclohexene ring accompanied by isomerization of the cyclohexadiene ligand. With regard to the steric factor, the steric hindrance of the $o\text{-CF}_3\text{C}_6\text{H}_4$ group should be larger than that of the two other aryl substituents. Thus the carbene intermediate complex formed, in which the diene ligand and carbene ligand cannot coexist stably owing to the steric hindrance, was unstable and isomerization occurred to afford the more stable isomerized product 5. In accordance with the increase in the steric hindrance of aryl substituents in the order $\text{C}_6\text{H}_5 < p\text{-CH}_3\text{C}_6\text{H}_4 < p\text{-CF}_3\text{C}_6\text{H}_4 \leq p\text{-H}_3\text{OC}_6\text{H}_4 < m\text{-CH}_3\text{C}_6\text{H}_4 < o\text{-CH}_3\text{C}_6\text{H}_4 < o\text{-CH}_3\text{O}_6\text{H}_4 \leq o\text{-CF}_3\text{C}_6\text{H}_4$, the stability of the products decreased.

3.2. Crystal and molecular structure of $\text{C}_6\text{H}_8(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}o$ (3)

The results of the structural analysis of complex 3 showed that the Fe atom is coordinated by seven carbon atoms. Each of the two CO ligands forms a $\sigma\text{-}\pi$ bond with the Fe atom and provides a pair of electrons for the Fe atom. The C(13), C(14), C(15), and C(16) atoms of the cyclohexadiene ligand form a delocalized π molecular orbital and provide four π -electrons to bond to the Fe atom on side-on mode. The carbene carbon C(3) is coordinated to the Fe atom

Fig. 1. Molecular structure of **3**.

using a pair of bonding electrons to satisfy the 18-electron rule. The molecular structure of **3** is shown in Fig. 1. The bond length of Fe–C(3) is 1.89(2) Å which signifies a higher double bond character and is somewhat shorter than that found (1.915(15) Å) in (1-methyl-4-isopropyl)dicarbonyl[ethoxy(*o*-tolyl)carbene]iron, ($\eta^4\text{-C}_{10}\text{H}_{16}$)(CO)₂FeC(OC₂H₅)C₆H₄CH₃-*o* [11]. The sum of the three bond angles around the C(3) atom (O(3)–C(3)–C(6) 103°, Fe–C(3)–C(6) 123°, Fe–C(3)–O(3) 134°) is exactly 360° which shows that these atoms are coplanar. Hence, it is concluded that the C(3) atom forms three σ -bonds with the three atoms around it, using its sp² hybridized orbitals and a coordinating double bond with the Fe atom using its one π electron.

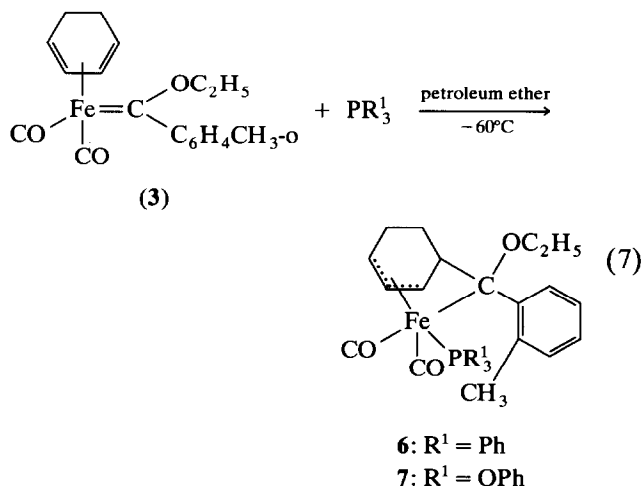
The bond length of C(3)–O(3) of 1.34(2) Å is essentially comparable with that (1.324(17) Å) found in ($\eta^4\text{-C}_{10}\text{H}_{16}$)(CO)₂FeC(OC₂H₅)C₆H₄CH₃-*o* [11]. Compared with the bond length of C(3)–O(3) (1.42(1) Å) found in the isomerized product of cyclohexadiene(dicarbonyl)[ethoxy(phenyl)carbene]iron, C₆H₈(CO)₂FeC(OC₂H₅)C₆H₅ [15] and the bond length of C(1)–O(1) (1.406(4) Å) found in isomerized (limonene)dicarbonyl[ethoxy(*p*-tolyl)carbene]iron complex, ($\eta^3\text{-C}_{10}\text{H}_{16}$)(CO)₂FeC(OC₂H₅)C₆H₄CH₃-*p* [11], the bond length of C(3)–O(3) in **3** is obviously shortened. In the isomerized product C₆H₈(CO)₂FeC(OC₂H₅)C₆H₅, the C(3) atom forms a single bond with the Fe atom using its approximate pure p_z orbital, and the C(3)–O(3) distance (1.42(1) Å) is essentially a normal C–O single bond distance. The shortening of the C(3)–O(3) distance in **3** could be caused by the partial delocalization

of the π -electron on O(3) owing to the effect of the Fe–C(3) π bond.

The perpendicular distance of the Fe atom to the plane composed of C(13), C(14), C(15), and C(16) is 1.64 Å. The C(17) and C(18) atoms are out of this plane by 0.89 and 1.07 Å, respectively, in the opposite direction from the Fe atom. If the C(13) and C(15) atoms are not considered, the remaining five coordinating atoms (C(1), C(2), C(3), C(14) and C(16)) around the Fe atom constructed a twisted triangular bipyramid polyhedron, among which the C(1), C(2) and C(14) atoms form an equatorial plane, and the C(3) and C(16) atoms are the two apices of the triangular bipyramid. This configuration is similar to that of tetracarbonyl[ethoxy(pentachlorophenyl)carbene]iron, (CO)₄FeC(OC₂H₅)C₆Cl₅ [21]. A difference between **3** and (CO)₄FeC(OC₂H₅)C₆Cl₅ is that the coordinated polyhedron in **3** generated a greater distortion arising from the coordination of the cyclohexadiene ligand with the Fe atom in η^4 mode. This distortion could lead to a decrease in the stability of the complex.

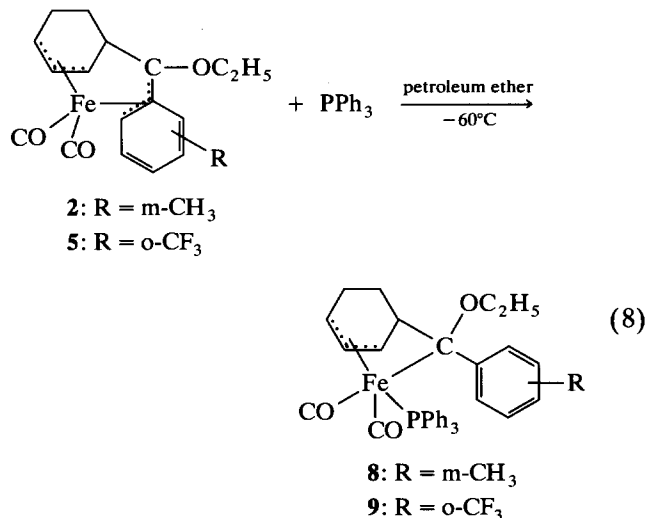
3.3. Reactions of complexes **3–5** and **2** with PPh₃ or P(OPh)₃: preparation of complexes **6–9**

1,3-Cyclohexadiene(dicarbonyl)[ethoxy(*o*-tolyl)carbene]iron (**3**) was treated with an excess of triphenylphosphine, PPh₃, in petroleum ether (30–60°C) at –60°C for 3 h. The reaction mixture was chromatographed on an alumina column at low temperature with petroleum ether as the eluant and the crude product was recrystallized from petroleum ether at –80°C to give a yellow needle of the chelated allyliron phosphine adduct, ($\eta^3\text{-C}_6\text{H}_8$)(CO)₂(PPh₃)FeC(OC₂H₅)C₆H₄CH₃-*o* (**6**) (eqn. (7)) in 85% yield.



Triphenyl phosphite, P(OPh)₃, reacted similarly with **3** to afford the analogous light-yellow phosphite adduct, ($\eta^3\text{-C}_6\text{H}_8$)(CO)₂[P(OPh)₃]FeC(OC₂H₅)C₆H₄CH₃-*o* (**7**) (eqn. (7)) in 55% yield.

The isomerized cyclohexadiene(dicarbonyl)[ethoxy(aryl)carbene] iron complexes, $(\eta^3\text{-C}_6\text{H}_8)(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}m$ (**2**) and $(\eta^3\text{-C}_6\text{H}_8)(\text{CO})_2\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CF}_3\text{-}o$ (**5**) also reacted similarly with PPh_3 to produce the analogous chelated allyliron phosphine adducts $(\eta^3\text{-C}_6\text{H}_8)(\text{CO})_2(\text{PPh}_3)\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CH}_3\text{-}m$ (**8**) and $(\eta^3\text{-C}_6\text{H}_8)(\text{CO})_2(\text{PPh}_3)\text{FeC}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_4\text{CF}_3\text{-}o$ (**9**) (eqn. (8)) in 89% and 87% yields, respectively.



The diamagnetic complexes **6–9** are soluble in both polar and non-polar organic solvents. In the solid state they are stable in air at room temperature for several hours, and in solution they are slowly oxidized in air. The IR and mass spectra for **6–9** are given in the Experimental section. Their IR spectra showed the two strong CO stretching vibration bands in the $\nu(\text{CO})$ region in accordance with the existence of the $\text{Fe}(\text{CO})_2$ moiety in these complexes. The molecular ion peaks and characteristic fragments generated by successive loss of CO or phosphine ligands were shown in the mass spectra of **6–9**. The solution ^1H NMR spectra (Table 1) of complexes **6–9** are consistent with their structure. The ^1H NMR spectra of **6** and **7** showed complex signals attributed to the protons of the cyclohexadiene ligand, which indicated that isomerization of the cyclohexadiene ligand occurred. The signals at δ 4.84–4.54, 3.80–3.78, and 3.66–3.14 ppm could be assigned to the three η^3 -allyl protons, while the other signals at 3.56–3.00, 2.58–2.34 and 1.42–1.40 ppm could be assigned to the protons attached to the saturated carbon atom of the cyclohexene ring, which are very similar to those found in complexes **8** and **9**. The ^1H NMR spectra of **8** and **9** are similar to those of the parent compounds **2** and **5** except the complex signals attributed to the protons of the phenyl groups, arising from the addition of PPh_3 . Thus, it could be consid-

ered that the principal structural framework of complexes **6–9** is similar to that of complexes **2** and **5**.

The formation of chelated allyliron phosphine adducts **8** and **9** is expected for the reaction of **2** and **5** with phosphine because PPh_3 is a strong two-electron donor, which coordinated to the Fe atom to displace the coordination of the benzene ring in complexes **2** and **5**. The analogous reactions were observed in the reaction of $[(\eta^4\text{-C}_6\text{H}_5\text{CH}=\text{CH})\text{CH}(\text{C}_6\text{H}_5)\text{N}(\text{C}_6\text{H}_5)\text{C}(\text{OC}_2\text{H}_5)=]\text{Fe}(\text{CO})_2$ with Lewis bases such as PPh_3 , $\text{P}(\text{OPh})_3$, AsPh_3 and CH_3CN , in which the addition of the Lewis base to and the dissociation of the coordinated benzene ring from the Fe atom led to η^2 -olefin carbene complexes [10]. However, it was unexpected that the reaction of complex **3** with PPh_3 or $\text{P}(\text{OPh})_3$ gave chelated allyliron phosphine adduct **6** or phosphite adduct **7**. Generally, the reaction of carbene complexes such as $(\text{CO})_5\text{M}=\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5$ ($\text{M}=\text{Cr}$, W) with tertiary phosphines in pentane at low temperature produced phosphorus ylide complexes after addition of the phosphines to the carbene carbon atom which precipitated as a pale yellow solid from the reaction solution [23–25]. In contrast, the reaction of cyclohexadiene-coordinated iron carbene complex **3** with PPh_3 gave no expected ylide complex but the chelated allyliron phosphine adduct **6**. The polarizability and solubility of product **6** also showed that it is a neutral carbonyliron phosphine adduct instead of a ylide compound since it is soluble in pentane and petroleum ether and can be purified by chromatography on alumina with petroleum ether as the eluant and by recrystallization from petroleum ether at low temperature.

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References

- 1 C. P. Casey, N. W. Vollendorf and K. J. Haller, *J. Am. Chem. Soc.*, **106** (1984) 3754.
- 2 A. Parlier, H. Rudler, N. Platzler, M. Fontanille and A. Soum, *J. Organomet. Chem.*, **287** (1985) C8.
- 3 J. L. Herrison and Y. Chauvin, *Makromol. Chem.*, **141** (1971) 161.
- 4 J.-B. Chen, G.-X. Lei, W.-H. Xu, X.-L. Jin, M.-C. Shao and Y.-Q. Tang, *J. Organomet. Chem.*, **286** (1985) 55.
- 5 J.-B. Chen, G.-X. Lei, W.-H. Xu, Z.-H. Pan, S.-W. Zhang, Z.-Y. Zhang, X.-L. Jin, M.-C. Shao and Y.-Q. Tang, *Organometallics*, **6** (1987) 2461.
- 6 J.-B. Chen, G.-X. Lei, Z.-H. Pan, Z.-W. Zhang and Y.-Q. Tang, *J. Chem. Soc., Chem. Commun.*, (1987) 1273.
- 7 J.-B. Chen, J.-G. Yin, W.-H. Xu, L.-H. Lai, Z.-Y. Zhang and M.-C. Shao, *Organometallics*, **6** (1987) 2607.

- 8 J.-B. Chen, J.-G. Yin, G.-X. Lei, W.-H. Xu, M.-C. Shao, Z.-Y. Zhang and Y.-Q. Tang, *J. Organomet. Chem.*, 329 (1987) 69.
- 9 J.-B. Chen, G.-X. Lei, M.-C. Shao, X.-J. Xu and Z.-Y. Zhang, *J. Chem. Soc., Chem. Commun.*, (1988) 1296.
- 10 J.-G. Yin, J.-B. Chen, W.-H. Xu, Z.-Y. Zhang and Y.-Q. Tang, *Organometallics*, 7 (1988) 21.
- 11 J.-B. Chen, G.-X. Lei, Z.-S. Jin, L.-H. Hu and G.-C. Wei, *Organometallics*, 7 (1988) 1652.
- 12 J.-B. Chen, J.-G. Yin, Z.-C. Fan and W.-H. Xu, *J. Chem. Soc., Dalton Trans.*, (1988) 2803.
- 13 J.-B. Chen, J.-G. Yin, G.-X. Lei, Y.-Y. Wang and G.-D. Lin, *J. Chem. Soc., Dalton Trans.*, (1989) 635.
- 14 J.-B. Chen and B.-H. Wang, *J. Organomet. Chem.*, 440 (1992) 67.
- 15 J.-B. Chen, G.-X. Lei, Z.-Y. Zhang and Y.-Q. Tang, *Sci. China, B*, 32 (1989) 129.
- 16 H. Meerwein, G. Hinze, P. Hofmann, E. Kroniny and E. Pfeil, *J. Prakt. Chem.*, 147 (1937) 257.
- 17 H. Gilman, E. A. Zoellner and W. H. Selby, *J. Am. Chem. Soc.*, 55 (1933) 1252.
- 18 R. G. Jones and H. Gilman, *Org. React. (NY)*, 6 (1951) 352.
- 19 H. Gilman, W. Langham and F. W. Moore, *J. Am. Chem. Soc.*, 62 (1940) 2327.
- 20 J. D. Roberts and D. Y. Curtin, *J. Am. Chem. Soc.*, 68 (1946) 1658.
- 21 T.-L. Wang, J.-B. Chen, W.-H. Xu, S.-W. Zhang, Z.-H. Pan and Y.-Q. Tang, *Acta Chim. Sinica*, 1 (1987) 85.
- 22 J.-B. Chen and G.-X. Lei, unpublished results.
- 23 F. R. Kreissl, C. G. Kreiter and E. O. Fischer, *Angew. Chem., Int. Ed. Engl.*, 11 (1972) 643.
- 24 F. R. Kreissl, E. O. Fischer, C. G. Kreiter and H. Fischer, *Chem. Ber.*, 106 (1973) 1262.
- 25 H. Fischer, E. O. Fischer, C. G. Kreiter and H. Werner, *Chem. Ber.*, 107 (1974) 2459.