Studies on Reactivities of Isomerized Cyclohexadiene(dicarbonyl)[ethoxy(aryl)carbene]iron Complexes. Crystal Structures of [$C_6H_8(CO)_3FeC(OC_2H_5)C_6H_5$], [$C_6H_8(CO)_2\{P(OMe)_3\}FeC(OC_2H_5)C_6H_4CF_3$-*p*], and [$C_6H_8(CO)_3FeC(OC_2H_5)C_6H_4CH_3$-*p*]†

Beihan Wang, Ronghua Li, Jie Sun, and Jiabi Chen*

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

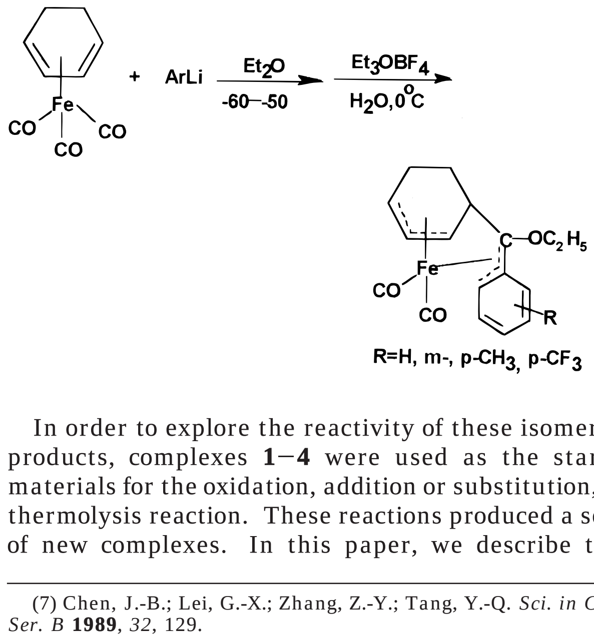
Received March 30, 1998

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on July 22, 1998 on http://pubs.acs.org | doi: 10.1021/om980238k

The reactions of the isomerized cyclohexadiene(dicarbonyl)[ethoxy(aryl)carbene]iron complexes [2-4-η-$C_6H_8(CO)_2FeC(OC_2H_5)Ar$] (**1**, Ar = C_6H_5; **2**, Ar = *m*-$CH_3C_6H_4$; **3**, Ar = *p*-$CH_3C_6H_4$; **4**, Ar = *p*-$CF_3C_6H_4$) with [$(NH_4)_2Ce(NO_3)_6$] in EtOH solution at low temperature give η^3-cyclohexadienyltricarbonyliron complexes [2-4-η-$C_6H_8(CO)_3FeC(OC_2H_5)Ar$] (**5**, Ar = C_6H_5; **6**, Ar = *m*-$CH_3C_6H_4$; **7**, Ar = *p*-$CH_3C_6H_4$; **8**, Ar = *p*-$CF_3C_6H_4$). Compelxes **1**−**4** reacted with CO gas under similar conditions to afford the same products **5**−**8** in high yields. The reaction between compound **4** and Lewis bases P(n-Bu)$_3$, P(OMe)$_3$, P(OPh)$_3$, PPh$_3$, and AsPh$_3$ gave the chelated allyliron adducts [2-4-η-$C_6H_8(CO)_2(L)FeC(OC_2H_5)C_6H_4CF_3$-*p*] (**9**, L = P(n-Bu)$_3$; **10**, L = P(OMe)$_3$; **11**, L = P(OPh)$_3$; **12**, L = PPh$_3$; **13**, L = AsPh$_3$). The thermal decomposition of complexes **3** and **7** yielded the η^3-cyclohexadienyltricarbonyliron complex [3-5-η-$C_6H_8(CO)_3FeC(OC_2H_5)C_6H_4CH_3$-*p*] (**14**). The structures of complexes **5**, **10**, and **14** have been established by X-ray diffraction studies.

Introduction

In recent years, olefin-coordinated transition-metal carbene and carbyne complexes and/or their isomerized products, as part of a broader investigation of transition-metal carbene and carbyne complexes, have been examined widely in our laboratory. In previous studies,[1−6] we have shown that a considerable number of the novel olefin-coordinated metal carbene complexes and/or their isomerized products were isolated and several novel isomerizations of olefin ligands observed by reaction of olefin-ligated metal carbonyls with aryllithium reagents followed by alkylation with Et_3OBF_4. However, the reactivity of these novel olefin-coordinated carbene complexes and their isomerized products has not been fully explored. We are now interested in examining the reactivity of these isomerized carbene complexes. Several years ago, we reported the reactions of 1,3-cyclohexadiene(tricarbonyl)iron with aryllithium reagents followed by alkylation with Et_3OBF_4 to yield the η^3-cyclohexadienyldicarbonyliron complexes [2-4-η-$C_6H_8(CO)_2FeC(OC_2H_5)Ar$] (**1**, Ar = C_6H_5; **2**, Ar = *m*-$CH_3C_6H_4$; **3**, Ar = *p*-$CH_3C_6H_4$; **4**, Ar = *p*-$CF_3C_6H_4$) (eq 1),[7] which we call the isomerized cyclohexadiene(dicarbonyl)[ethoxy(aryl)carbene]iron complexes or the isomerized products of cyclohexadiene(dicarbonyl)[ethoxy(aryl)carbene]iron complexes.[8]



(1)

In order to explore the reactivity of these isomerized products, complexes **1**−**4** were used as the starting materials for the oxidation, addition or substitution, and thermolysis reaction. These reactions produced a series of new complexes. In this paper, we describe these

---

† Dedicated to Prof. Ernst Otto Fischer on the occasion of his 80th birthday and in recognition of his brilliant contributions to organometallic chemistry.

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

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

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

(4) Chen, J.-B.; Li, D.-S.; Yu, Y.; Jin, Z.-S.; Zhou, Q.-L.; Wei, G.-C. *Organometallics* **1993**, *12*, 3885.

(5) Yu, Y.; Chen, J.-B.; Chen, J.; Zheng, P.-J. *Organometallics* **1993**, *12*, 4731.

(6) Yu, Y.; Sun, J.; Chen, J.-B. *J. Organomet. Chem.* **1997**, *533*, 13.

(7) Chen, J.-B.; Lei, G.-X.; Zhang, Z.-Y.; Tang, Y.-Q. *Sci. in China, Ser. B* **1989**, *32*, 129.

(8) Chen, J.-B.; Lei, G.-X.; Xu, W.-H.; Jin, X.-L.; Shao, M.-C.; Tang, Y.-Q. *J. Organomet. Chem.* **1985**, *286*, 55.

S0276-7333(98)00238-6 CCC: $15.00 © 1998 American Chemical Society
Publication on Web 07/22/1998

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on July 22, 1998 on http://pubs.acs.org | doi: 10.1021/om980238k

unusual reactions and the structural characterizations of the reaction products.

Experimental Section

All reactions 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 the appropriate drying agents and stored over 4 Å molecular sieves under a N_2 atmosphere. The ethyl alcohol (EtOH) was distilled from $Mg(OEt)_2$, diethyl ether (Et_2O) from sodium benzophenone ketyl, and benzene from sodium metal, while petroleum ether (30−60 °C) was distilled from CaH_2 and CH_2Cl_2 from P_2O_5. The neutral alumina (Al_2O_3) 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. $[(NH_4)_2Ce(NO_3)_6]$, $P(n\text{-}Bu)_3$, PPh_3, $P(OMe)_3$, $P(OPh)_3$, and $AsPh_3$ were purchased from either Strem Chemical Co. or Aldrich Chemical Co. The compounds $[C_6H_8(CO)_2FeC(OC_2H_5)Ar]$ (**1**, Ar = C_6H_5; **2**, Ar = m-$CH_3C_6H_4$; **3**, Ar = p-$CH_3C_6H_4$; **4**, Ar = p-$CF_3C_6H_4$) were prepared as previously described.[7]

The IR spectra were measured on a Shimadzu-IR-440 spectrophotometer. All ^1H NMR spectra were recorded at ambient temperature in acetone-d_6 solution with TMS as the internal reference, using a Bruker AM-300 spectrometer. Electron ionization mass spectra (EIMS) were run on a Hewlett Packard 5989A spectrometer. Melting points obtained on samples in sealed capillaries are uncorrected.

Reaction of $[2\text{-}4\text{-}\eta\text{-}C_6H_8(CO)_2FeC(OC_2H_5)C_6H_5]$ (1) with $(NH_4)_2Ce(NO_3)_6$ To Give $[2\text{-}4\text{-}\eta\text{-}C_6H_8(CO)_3FeC(OC_2H_5)C_6H_5]$ (5). To a solution of **1** (0.50 g, 1.53 mmol) in 60 mL of EtOH was added dropwise 0.84 g (1.53 mmol) of $(NH_4)_2Ce(NO_3)_6$ in 20 mL of EtOH at −35 °C within 20 min. The red solution turned brown-yellow. After it was stirred at −35 to −30 °C for 30 min, the solution was evaporated under vacuum to dryness. The red oil residue was dissolved in 30 mL of N_2-saturated water. The aqueous solution was extracted with ether. The extract was washed with 50 mL of water and then dried over anhydrous Na_2SO_4. After removal of the solvent in vacuo, the residue was chromatographed on an alumina column (1.6 × 10−15 cm) at −10 °C with petroleum ether/Et_2O (15:1) as the eluant. The yellow band was collected. Removal of solvent in vacuo and recrystallization of the crude product from petroleum ether solution at −80 °C gave 0.17 g (30%, based on **1**) of yellow crystals of **5**: mp 52−54 °C (dec); IR (νCO) (n-hexane) 2020 (w), 2000 (s), 1992 (vs) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.58−7.32 (m, 4H, C_6H_5), 7.01 (t, 1H, C_6H_5), 5.00 (m, 1H, C_6H_8), 4.76 (m, 1H, C_6H_8), 4.43 (t, 1H, C_6H_8), 3.53 (m, 1H, C_6H_8), 3.34 (m, 1H, $OC\mathit{H}_2CH_3$), 2.63 (m, 1H, $OC\mathit{H}_2CH_3$), 2.51 (m, 1H, C_6H_8), 2.24 (m, 1H, C_6H_8), 1.55 (m, 2H, C_6H_8), 1.00 (t, 3H, $OCH_2C\mathit{H}_3$); MS *m/e* 326 (M^+ − CO), 298 (M^+ − 2CO), 270 (M^+ − 3CO), 225 (M^+ − 3CO − OC_2H_5), 214 (M^+ − $Fe(CO)_3$), 190 (M^+ − 3CO − C_6H_8). Anal. Calcd for $C_{18}H_{18}O_4Fe$: C, 61.04; H, 5.12. Found: C, 61.20; H, 5.17.

The following complexes were prepared by similar reactions. **$[2\text{-}4\text{-}\eta\text{-}C_6H_8(CO)_3FeC(OC_2H_5)C_6H_4CH_3\text{-}m]$ (6):** orange-yellow viscous oil (26% yield); IR (νCO) (n-hexane) 2040 (m), 1995 (s), 1983 (vs) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.41−6.83 (m, 4H, $C_6\mathit{H}_4CH_3$), 2.34 (s, 3H, $C_6H_4C\mathit{H}_3$), 4.98 (t, 1H, C_6H_8), 4.76 (t, 1H, C_6H_8), 4.42 (t, 1H, C_6H_8), 3.54 (m, 1H, C_6H_8), 3.36 (m, 1H, $OC\mathit{H}_2CH_3$), 2.65 (m, 1H, $OC\mathit{H}_2CH_3$), 2.53 (m, 1H, C_6H_8), 2.19 (m, 1H, C_6H_8), 1.54 (m, 2H, C_6H_8), 0.96 (t, 3H, $OCH_2C\mathit{H}_3$); MS *m/e* 340 (M^+ − CO), 312 (M^+ − 2CO), 284 (M^+ − 3CO), 239 (M^+ − 3CO − OC_2H_5), 228 (M^+ − $Fe(CO)_3$). Anal. Calcd for $C_{19}H_{20}O_4Fe$: C, 61.97; H, 5.47. Found: C, 62.41; H, 5.77. **$[2\text{-}4\text{-}\eta\text{-}C_6H_8(CO)_3FeC(OC_2H_5)C_6H_4CH_3\text{-}p]$ (7):** orange oil (31% yield); IR (νCO) (n-hexane) 2050 (m), 2000 (s), 1990 (vs) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.48−7.14 (m, 4H, $C_6\mathit{H}_4CH_3$), 2.27 (s, 3H, $C_6H_4C\mathit{H}_3$), 4.97 (t, 1H, C_6H_8), 4.73 (t, 1H, C_6H_8), 4.42 (t, 1H, C_6H_8), 3.52 (m, 1H, C_6H_8), 3.35 (m, 1H, $OC\mathit{H}_2CH_3$), 2.61 (m, 1H, $OC\mathit{H}_2CH_3$), 2.49 (m, 1H, C_6H_8), 2.20 (m, 1H, C_6H_8), 1.54 (m, 2H, C_6H_8), 1.01 (t, 3H, $OCH_2C\mathit{H}_3$); MS *m/e* 340 (M^+ − CO), 312 (M^+ − 2CO), 284 (M^+ − 3CO), 239 (M^+ − 3CO − OC_2H_5), 228 (M^+ − $Fe(CO)_3$). Anal. Calcd for $C_{19}H_{20}O_4Fe$: C, 61.97; H, 5.47. Found: C, 62.15; H, 5.49. **$[2\text{-}4\text{-}\eta\text{-}C_6H_8(CO)_3FeC(OC_2H_5)C_6H_4CF_3\text{-}p]$ (8):** yellow crystals (40% yield); mp 76−78 °C (dec); IR (νCO) (n-hexane) 2060 (s), 1998 (vs), 1988 (vs) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.67 (d, 4H, $C_6H_4CF_3$), 5.05 (t, 1H, C_6H_8), 4.86 (t, 1H, C_6H_8), 4.53 (t, 1H, C_6H_8), 3.57 (m, 1H, C_6H_8), 3.36 (m, 1H, $OC\mathit{H}_2CH_3$), 2.73 (m, 1H, $OC\mathit{H}_2CH_3$), 2.56 (m, 1H, C_6H_8), 2.27 (m, 1H, C_6H_8), 1.58 (m, 2H, C_6H_8), 1.04 (t, 3H, $OCH_2C\mathit{H}_3$); MS *m/e* 394 (M^+ − CO), 366 (M^+ − 2CO), 338 (M^+ − 3CO), 282 (M^+ − $Fe(CO)_3$), 258 (M^+ − 3CO − C_6H_8). Anal. Calcd for $C_{19}H_{17}O_4F_3Fe$: C, 54.05; H, 4.06. Found: C, 54.26; H, 4.26.

Reaction of 1 with CO To Give 5. Carbon monoxide gas was bubbled though a solution of 0.10 g (0.31 mmol) of **1** in 30 mL of EtOH at −35 to −30 °C over a period of 0.5 h, during which time the orange-red solution gradually turned light yellow. After removal of the solvent at −20 °C in vacuo, the residue was chromatographed on Al_2O_3 (neutral) at −10 °C with petroleum ether as the eluant. The yellow band was eluted and collected. Further treatment, as described in the reaction of **1** with $(NH_4)_2Ce(NO_3)_6$, gave 0.10 g (90%, based on **1**) of yellow crystalline **5**, which was idetified by its mp and IR and ^1H NMR spectra.

Similar reactions gave the following complexes: **6** (80% yield), **7** (75% yield), and **8** (95% yield), which were identified by their mp and IR and ^1H NMR spectra.

Reaction of 4 with $P(n\text{-}Bu)_3$ To Give $[2\text{-}4\text{-}\eta\text{-}C_6H_8(CO)_2\{P(n\text{-}Bu)_3\}FeC(OC_2H_5)C_6H_4CF_3\text{-}p]$ (9). Compound **4** (0.080 g, 0.20 mmol) was dissolved in 50 mL of petroleum ether (30−60 °C) at −60 °C. To this solution was added dropwise 0.26 mmol of $P(n\text{-}Bu)_3$ in 20 mL of petroleum ether. The reaction mixture was stirred at −50 to −30 °C for 3 h. The resulting yellow mixture was evaporated at −20 °C in vacuo to dryness. The residue was chromatographed on Al_2O_3 at −15 °C with petroleum ether as the eluant. The yellow band was collected. After removal of the solvent, the crude product was recrystallized from petroleum ether/CH_2Cl_2 at −80 °C to give 0.11 g (78%, based on **4**) of yellow crystals of **9**: mp 22−23 °C (dec); IR (νCO) (n-hexane) 1992 (vs), 1940 (vs) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.58 (d, 4H, $C_6H_4CF_3$), 4.32 (m, 1H, C_6H_8), 4.21 (t, 1H, C_6H_8), 3.99 (q, 1H, C_6H_8), 3.47 (m, 1H, C_6H_8), 3.32 (m, 1H, $OC\mathit{H}_2CH_3$), 2.62 (m, 1H, $OC\mathit{H}_2CH_3$), 2.28 (m, 1H, C_6H_8), 2.13 (m, 1H, C_6H_8), 1.48−1.40 (m, 2H, C_6H_8), 1.37 (m, 18H, $[CH_3(C\mathit{H}_2)_3]_3$), 1.00 (t, 3H, $OCH_2C\mathit{H}_3$), 0.88 (m, 9H, $[C\mathit{H}_3(CH_2)_3]_3$); MS *m/e* 596 ($M^+$), 568 ($M^+$ − CO), 540 (M^+ − 2CO), 366 (M^+ − CO − $P(n\text{-}Bu)_3$). Anal. Calcd for $C_{30}H_{44}O_3F_3PFe$: C, 60.41; H, 7.43. Found: C, 60.19; H, 7.58.

The following complexes were prepared by similar reactions. **$[2\text{-}4\text{-}\eta\text{-}C_6H_8(CO)_2\{P(OMe)_3\}FeC(OC_2H_5)C_6H_4CF_3\text{-}p]$ (10):** yellow crystals (85% yield); mp 82 °C (dec); IR (νCO) (n-hexane) 2015 (vs), 1960 (vs) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.61 (d, 3H, $C_6H_4CF_3$), 7.36 (s, 1H, $C_6H_4CF_3$), 4.59 (m, 1H, C_6H_8), 4.38 (m, 1H, C_6H_8), 4.19 (q, 1H, C_6H_8), 3.53 (m, 1H, C_6H_8), 3.46−3.41 (s, s, 9H, $P(OCH_3)_3$), 3.33 (m, 1H, $OC\mathit{H}_2CH_3$), 2.67 (m, 1H, $OC\mathit{H}_2CH_3$), 2.59 (m, 1H, C_6H_8), 2.16 (m, 1H, C_6H_8), 1.54−1.40 (m, 2H, C_6H_8), 1.02 (t, 3H, $OCH_2C\mathit{H}_3$); MS *m/e* 490 (M^+ − CO), 462 (M^+ − 2CO), 366 (M^+ − CO − $P(OMe)_3$). Anal. Calcd for $C_{21}H_{26}O_6F_3PFe$: C, 48.67; H, 5.06. Found: C, 49.01; H, 5.19. **$[2\text{-}4\text{-}\eta\text{-}C_6H_8(CO)_2\{P(OPh)_3\}FeC(OC_2H_5)C_6H_4CF_3\text{-}p]$ (11):** yellow crystals (80% yield); mp 68−70 °C (dec); IR (νCO)(n-hexane) 2040 (m), 1972 (vs) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.58−7.38 (m, 10H, C_6H_5 + $C_6H_4CF_3$), 7.23−7.12 (m, 9H, C_6H_5 + $C_6H_4CF_3$), 4.81 (q, 1H, C_6H_8), 4.30 (q, 1H, C_6H_8), 3.88 (t, 1H, C_6H_8), 3.49 (m, 1H, C_6H_8), 3.31 (m, 1H, $OC\mathit{H}_2CH_3$), 2.64 (m, 1H, $OC\mathit{H}_2CH_3$), 2.49 (m, 1H, C_6H_8), 1.50 (m, 1H, C_6H_8), 1.40−1.20 (m, 2H, C_6H_8), 0.97 (t, 3H, $OCH_2C\mathit{H}_3$); MS *m/e* 648 (M^+ − 2CO), 366 (M^+ − CO − $P(OPh)_3$). Anal. Calcd for

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on July 22, 1998 on http://pubs.acs.org | doi: 10.1021/om980238k

$C_{36}H_{32}O_6F_3PFe$: C, 61.38; H, 4.54. Found: C, 61.12; H, 4.65. **[2-4-η-C_6H_8(CO)$_2$(PPh$_3$)FeC(OC$_2$H$_5$)C$_6$H$_4$CF$_3$-*p*] (12):** yellow powder (90% yield); mp 92−94 °C (dec); IR (νCO) (n-hexane) 1998 (m), 1948 (vs) cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$) δ 7.61 (d, 3H, C$_6$H$_4$CF$_3$), 7.46 (m, 10H, C$_6$H$_5$ + C$_6$H$_4$CF$_3$), 7.29 (m, 6H, C$_6$H$_5$ + C$_6$H$_4$CF$_3$), 4.59 (t, 1H, C$_6$H$_8$), 4.16 (q, 1H, C$_6$H$_8$), 3.54 (m, 1H, C$_6$H$_8$), 3.16 (q, 1H, C$_6$H$_8$), 3.32 (m, 1H, OCH_2CH$_3$), 2.66 (m, 1H, OCH_2CH$_3$), 2.50 (m, 1H, C$_6$H$_8$), 1.86 (m, 1H, C$_6$H$_8$), 1.55−1.25 (m, 2H, C$_6$H$_8$), 0.98 (t, 3H, OCH$_2$CH_3); MS *m*/*e* 600 (M$^+$ − 2CO), 338 (M$^+$ − 2CO − PPh$_3$). Anal. Calcd for $C_{36}H_{32}O_3F_3PFe$: C, 65.87; H, 4.91. Found: C, 65.66; H, 5.19. **[2-4-η-C_6H_8(CO)$_2$(AsPh$_3$)FeC(OC$_2$H$_5$)C$_6$H$_4$CF$_3$-*p*] (13):** yellow powder (80% yield); mp 108−109 °C (dec); IR (νCO)(n-hexane) 1990 (vs), 1938 (vs) cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$) δ 7.62 (d, 3H, C$_6$H$_4$CF$_3$), 7.46 (m, 7H, C$_6$H$_5$ + C$_6$H$_4$CF$_3$), 7.28 (m, 9H, C$_6$H$_5$ + C$_6$H$_4$CF$_3$), 4.78 (q, 1H, C$_6$H$_8$), 4.37 (t, 1H, C$_6$H$_8$), 3.52−3.32 (m, 2H, C$_6$H$_8$), 3.34 (m, 1H, OCH_2CH$_3$), 2.66 (m, 1H, OCH_2CH$_3$), 2.52 (m, 1H, C$_6$H$_8$), 1.95 (m, 1H, C$_6$H$_8$), 1.59−1.40 (m, 2H, C$_6$H$_8$), 0.98 (t, 3H, OCH$_2$CH_3); MS *m*/*e* 644 (M$^+$ − 2CO), 338 (M$^+$ − 2CO − AsPh$_3$). Anal. Calcd for $C_{36}H_{32}O_3F_3AsFe$: C, 61.69; H, 4.61. Found: C, 61.31; H, 4.68.

Thermolysis of 3 To Give [3-5-η-C_6H_8)(CO)$_3$FeC(OC$_2$H$_5$)C$_6$H$_4$CH$_3$-*p*] (14). Compound **3** (0.30 g, 0.88 mmol) was dissolved in 30 mL of benzene in a 50 mL quartz tube. The tube was cooled at −80 °C to freeze the benzene solution and sealed under vacuum. The sealed tube was heated at 90 °C with stirring for 72 h. After cooling, the dark solution was evaporated in vacuo to dryness. The dark residue was chromatographed on Al$_2$O$_3$ with petroleum ether/Et$_2$O (20:1) as the eluant. The yellow band was collected. After vacuum removal of the solvent, the crude product was recrystallized from petroleum ether at −80 °C to give 0.093 g (28%) of yellow crystals of **14**: mp 85−86 °C (dec); IR (νCO) (n-hexane) 2060 (vs), 1980 (vs), 1940 (m) cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$) δ 7.10 (m, 4H, C$_6H_4$CH$_3$), 2.30 (s, 3H, C$_6$H$_4$CH_3), 5.13 (t, 1H, C$_6$H$_8$), 5.01 (t, 1H, C$_6$H$_8$), 4.34 (m, 1H, C$_6$H$_8$), 2.80 (m, 1H, OCH_2CH$_3$), 2.58 (m, 1H, OCH_2CH$_3$), 2.34 (m, 2H, C$_6$H$_8$), 2.17−2.08 (m, 2H, C$_6$H$_8$), 0.90 (t, 3H, OCH$_2$CH_3); MS *m*/*e* 340 (M$^+$ − CO), 312 (M$^+$ − 2CO), 284 (M$^+$ − 3CO), 228 (M$^+$ − Fe(CO)$_3$). Anal. Calcd for $C_{19}H_{20}O_4Fe$: C, 61.97; H, 5.47. Found: C, 62.19; H, 5.60.

Thermolysis of 7 To Give 14. Similar to the procedure described for the thermolysis of **3**, a benzene solution of **7** (0.10 g, 0.27 mmol) in a sealed tube was heated at 90 °C for 72 h. Subsequent treatment of the resulting mixture afforded 0.043 g (43%) of **14**, which was identified by its mp and IR, ^{1}H NMR, and mass spectra.

X-ray Crystal Structure Determinations of Complexes 5, 10, and 14. The single crystals of **5**, **10**, and **14** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether or a petroleum ether/CH$_2$Cl$_2$ solution at −80 °C. The single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data were collected with a Rigaku AFC7R diffractometer at 20 °C using Mo Kα radiation with an ω−2θ scan mode.

Table 1. Crystal Data and Experimental Details for Complexes 5, 10, and 14

	5	10	14
formula	$C_{18}H_{18}O_4Fe$	$C_{21}H_{26}O_6F_3PFe$	$C_{19}H_{20}O_4Fe$
fw	354.18	518.25	368.21
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	9.363(2)	10.515(3)	13.147(4)
b (Å)	12.936(2)	12.575(6)	8.302(3)
c (Å)	7.509(2)	9.619(3)	16.030(4)
α (deg)	99.39(2)	94.30(3)	
β (deg)	108.62(2)	101.33(2)	97.02(2)
γ (deg)	98.61(2)	108.17(2)	
V (Å^3)	830.3(3)	1172.3(8)	1736.6(8)
Z	2	2	4
d_{calcd} (g/cm^3)	1.417	1.468	1.408
μ (Mo Kα) (cm^{-1})	9.24	7.68	8.86
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
diffractometer	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R
temperature (°C)	20	20	20
orientation reflns: no.; range (2θ) (deg)	20; 23.4−26.3	17; 18.8−21.3	17; 14.4−21.5
scan method	ω−2θ	ω−2θ	ω−2θ
data coll. range, 2θ (deg)	5−50	5−45	5−45
no. of unique data, total with *I* > 3.00σ(*I*)	2511, 2066	3067, 1877 (*I* > 2.00σ(*I*))	2422, 1629
no. of params refined	280	329	218
corr factors, max−min	0.8803−0.9997	0.8812−1.0000	0.9339−1.0000
R^a	0.030	0.056	0.032
R_w^{b}	0.036	0.067	0.032
quality-of-fit indicator^c	1.40	1.99	1.32
max shift/error in final cycle	0.04	0.16	0.00
max peak, e$^-$/Å^3	0.34	047	0.21
min peak, e$^-$/Å^3	−0.22	−0.34	−0.18

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

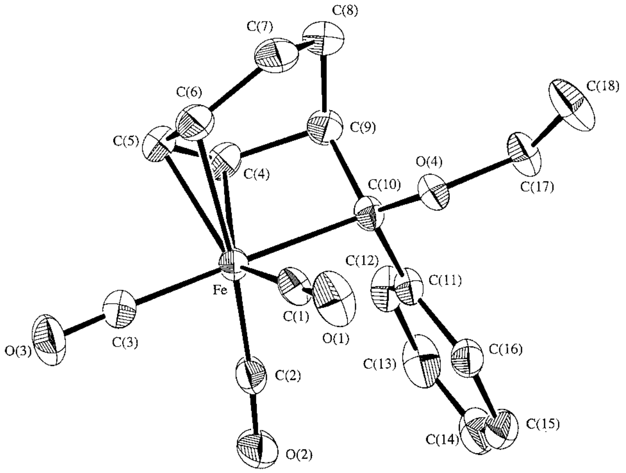


Figure 1. Molecular structure of **5**, showing the atom-numbering scheme.

The structure of **5** was solved by the heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement gave agreement factors of *R* = 0.030 and R_w = 0.036. The structures of **10** and **14** were solved by direct methods and expanded using Fourier techniques. For **10**, most of the non-hydrogen atoms were refined anisotropically but some atoms were disordered and refined in the constrainted program. The populations are 61%, 60%, 57%, and 60% for F(1), F(2), F(3), and C(22), and 39%, 40%, 43%, and 40% for F(1′), F(2′), F(3′), and C(22′), respectively. The hydrogen atoms were included but not refined. For **14**, the non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically. The final cycle of full-matrix least-squares refinement gave agreement factors of *R* = 0.056 and R_w = 0.067 for **10** and *R* = 0.032 and R_w = 0.032 for **14**.

The details of the crystallographic data and the procedures used for data collection and reduction information for **5**, **10**, and **14** are given in Table 1. The selected bond lengths and angles are listed in Table 2. The atomic coordinates and B_{iso}/B_{eq}, anisotropic displacement parameters, complete bond lengths and angles, least-squares planes for **5**, **10**, and **14** and the molecular structures of **10** and **14** are given in the Supporting Information. The molecular structure of **5** is given in Figure 1.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on July 22, 1998 on http://pubs.acs.org | doi: 10.1021/om980238k

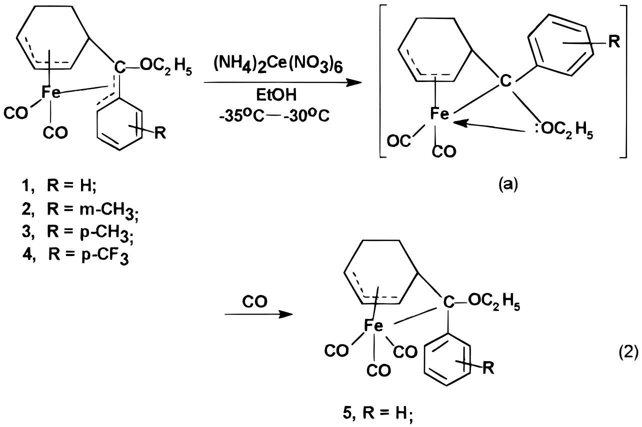
Table 2. Selected Bond Lengths (Å) and Angles (deg)[a] for Complexes 5, 10, and 14

	5	**10**	**14**		**5**	**10**	**14**
Fe−C(1)	1.773(3)	1.749(9)	1.801(5)	C(6)−C(7)	1.500(5)	1.52(1)	1.506(5)
Fe−C(2)	1.797(3)	1.753(8)	1.781(4)	C(7)−C(8)	1.513(5)	1.50(2)	1.512(5)
Fe−C(3)	1.820(3)		1.793(4)	C(8)−C(9)	1.528(5)	1.54(1)	1.531(4)
Fe−C(4)	2.196(3)	2.161(8)	2.148(4)	C(4)−C(9)	1.519(4)	1.531(9)	1.486(5)
Fe−C(5)	2.092(3)	2.085(9)	2.075(4)	C(8)−C(10)			1.523(5)
Fe−C(6)	2.160(3)	2.174(9)	2.214(4)	C(9)−C(10)	1.519(4)	1.51(1)	
Fe−C(10)	2.176(3)	2.138(6)	2.176(3)	C(10)−O(4)	1.426(3)	1.456(7)	1.455(4)
Fe−P		2.196(2)		C(10)−C(11)	1.504(4)	1.486(9)	1.518(4)
C(4)−C(5)	1.383(4)	1.40(1)	1.398(5)	O(4)−C(17)	1.448(3)	1.441(7)	1.429(4)
C(5)−C(6)	1.411(5)	1.44(1)	1.393(5)				
Fe−C(4)−C(9)	92.6(2)	92.5(5)	1.06.9(2)	C(4)−C(5)−C(6)	117.3(3)	116.8(7)	117.5(3)
Fe−C(10)−C(8)			99.3(2)	C(5)−C(6)−C(7)	119.5(3)	118.3(10)	117.8(3)
Fe−C(10)−C(9)	93.4(2)	93.8(4)		C(6)−C(7)−C(8)	111.0(3)	110.7(8)	109.3(3)
Fe−C(10)−C(11)	108.7(2)	110.2(4)	115.6(2)	C(7)−C(8)−C(9)	11.24(3)	112.9(8)	109.0(3)
Fe−C(10)−O(4)	112.1(2)	112.9(4)	105.4(2)	C(4)−C(9)−C(8)	109.0(3)	107.8(6)	109.9(3)
C(3)−Fe−C(10)	176.5(1)		175.0(2)	C(5)−C(4)−C(9)	117.8(3)	117.4(6)	119.3(3)
P−Fe−C(10)		177.5(2)		C(8)−C(9)−C(10)	114.0(3)	113.9(7)	
C(8)−C(10)−O(4)			110.1(3)	C(9)−C(8)−C(10)			108.6(3)
C(9)−C(10)−O(4)	115.1(2)	114.3(6)		C(8)−C(10)−C(11)			117.7(3)
C(10)−O(4)−C(17)	114.2(2)	114.8(5)	115.0(2)	C(9)−C(10)−C(11)	115.1(2)	116.9(6)	

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

Results and Discussion

The ammonium ceric nitrate [$(NH_4)_2Ce(NO_3)_6$] is an excellent oxidizing agent in the oxidation of the η^3-allyl-coordinated carbonyliron compound to organic compounds.[9,10] It is interesting to understand how complexes **1**−**4**, as diallyl-like compounds, react with $(NH_4)_2Ce(NO_3)_6$ and what product is formed. Thus, complexes **1**, **2**, **3**, and **4** were treated, respectively, with $(NH_4)_2Ce(NO_3)_6$ in ethanol solution at −35 to −30 °C. After workup, as described in the Experimental Section, the η^3-cyclohexadienyl-coordinated tricarbonyliron complexes [2-4-η-$C_6H_8(CO)_2FeC(OC_2H_5)Ar$] (**5**−**8**) (eq 2) were obtained in 26−40% yields.



1, R = H;
2, R = m-CH_3;
3, R = p-CH_3;
4, R = p-CF_3

5, R = H;
6, R = m-CH_3;
7, R = p-CH_3;
8, R = p-CF_3

A possible reaction pathway (eq 2) to complexes **5**−**8** could proceed via an intermediates a, where the ethoxy group is coordinated to the iron atom through the oxygen atom. This intermediate might be an equilibrium isomer of complexes **1**−**4** in the solution. The analogous ethoxy-coordinated carbonyliron complexes have been isolated in the reaction[8] of (butadiene)tricarbonyliron with aryllithium reagents followed by alkylation with Et_3OBF_4. Then one CO generated by decomposition of complexes **1**−**4** is coordinated to the iron atom to displace the coordination of the ethoxy group in a, giving the Fe atom in an 18-electron configuration.

In order to explore this possibility, we investigated the reaction of carbon monoxide gas with complexes **1**−**4** under the same conditions. These reactions produced the same products **5**−**8** in high yields (75−95%). This result shows that complexes **1**−**4** can indeed convert to complexes **5**−**8** by addition of carbon monoxide but cannot oxidized with $(NH_4)_2Ce(NO_3)_6$ to organic compounds.

Complexes **5**−**8** are air sensitive in solution but relatively stable as a solid. The elemental analysis and IR, ^{1}H NMR, and mass spectra (Experimental Section) are all consistent with the structures shown. An X-ray diffraction study for complex **5** was carried out in order to firmly establish its structure.

The structure of **5** (Figure 1) shows that the Fe atom has three terminal carbonyl groups, as anticipated from the IR spectrum, and bonds to an allyl-type η^3-bond composed of the C(4), C(5), and C(6) atoms and links to the C(10) atom in an η^1-bond to satisfy the 18-electron rule. The bond lengths of the Fe−C(4), Fe−C(5), and Fe−C(6) bonds are 2.196(3), 2.092(3), and 2.160(3) Å, respectively, among which the Fe−C(5) distance is obviously shorter than that of the other two. In contrast with **1**,[7] where the C(3) atom forms three σ-bonds with three adjacent atoms (C(6), C(12), and O(3)) and a π-bond with the Fe atom, the corresponding carbon atom C(10) in **5** forms four σ-bonds with the C(9), C(11), O(4), and Fe atoms. The C(10)−C(11) distance of 1.540(4) Å is markedly longer than the similar bond in **1** (1.45(2) Å).[7] This indicates that the π bond between the C(10) atom and the benzene ring is no longer in existence in **5**. the cyclohexadienyl ring adopts a twisted boat form configuration; the C(5) and C(8) atoms are the heads of the boat.

In view of the reaction of complexes **1**−**4** with CO to give carbonyl adducts **5**−**8**, the Lewis bases such as phosphines and phosphites might also react with com-

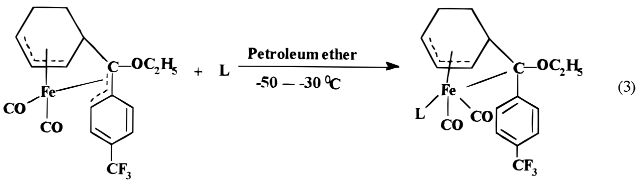
---

(9) Donaldson, W. A.; Ramaswamy, M. *Tetrahedron Lett.* **1989**, *30*, 1343.

(10) Annis, G. D.; Ley, S. V.; Self, C. R.; Sivaramakrishnan, R. *J. Chem. Soc., Perkin Trans.* **1981**, 270.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on July 22, 1998 on http://pubs.acs.org | doi: 10.1021/om980238k

plexes **1**−**4**. Thus, a preliminary study was made of the reactions of compound **4** with P(n-Bu)$_3$, PPh$_3$, P(OMe)$_3$, P(OPh)$_3$, and AsPh$_3$ in petroleum ether at low temperature. These give the chelated η^3-allyliron phosphine or phosphite and arsine adducts, [2-4-η-C$_6$H$_8$(CO)$_2$(L)-FeC(OC$_2$H$_5$)C$_6$H$_4$CF$_3$-*p*] (**9**−**13**) (eq 3) in 78−90% yields.



(3)

4

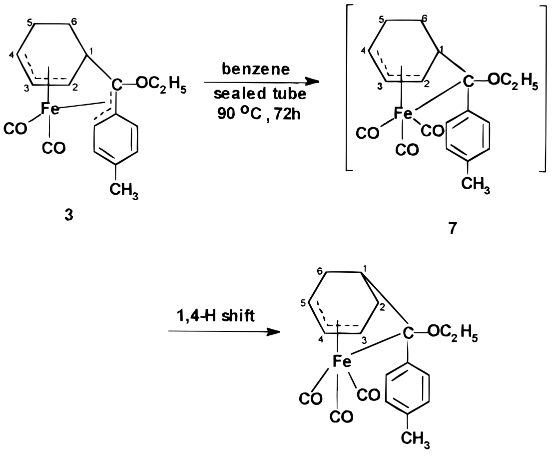
9, L=P(n-Bu)$_3$;
10, L=P(OMe)$_3$;
11, L=P(OPh)$_3$;
12, L=PPh$_3$;
13, L=AsPh$_3$

The formation of chelated allyliron adducts **9**−**13** is expected because these Lewis bases are strong two-electron donors which displace the benzene ring to coordinate to the Fe atom. The analogous coordination displacement of the benzene ring by a Lewis base has been observed in the reaction of [{η^4-C$_6$H$_5$CH=CH)CH-(C$_6$H$_5$)N(C$_6$H$_5$)C(OC$_2$H$_5$)=}Fe(CO)$_2$] with Lewis bases.[11] However, other Lewis bases, such as CH$_3$CN, PhCH$_2$-NH$_2$, SPh$_2$, SMe$_2$, and NEt$_3$, do not react with compound **4** since they are weaker two-electron donors.

Complexes **9**−**13** are stable in the solid state but slowly oxidize in solution in air. Their IR spectra showed two strong CO stretching vibration bands in the νCO region in accordance with the existence of the Fe-(CO)$_2$ moiety. The ^{1}H NMR spectra of **9**−**13** are similar to those of the parent compound **4** and CO adduct **8** except for the complex signals attributed to the protons of the aryl groups. Thus, the principle structural framework of complexes **9**−**13** could be considered to be similar to that of complexes **1**−**4** and **8**. This was further confirmed by an X-ray diffraction study of **10**.

The structure of complex **10** (Supporting Information) resembles that of **5**, except that the ligands on the Fe atom are the two CO groups and one P(OMe)$_3$ group in **10** but the three CO groups in the latter. The Fe−P distance of 2.196(2) Å is close to that in analogous compound [Fe(CO)$_3$P(OMe)$_3$]$_2$ (2.155(1) Å).[12] The Fe−C(4), Fe−C(5), and Fe−C(6) bond lengths, 2.161(8), 2.085(9), and 2.174(9) Å, respectively, are very close to those of **5**.

The thermal decomposition of carbene complexes usually results in dimerization of the carbene ligand to produce alkene derivatives.[13] In order to compare the thermolysis of the isomerized carbeneiron complexes **1**−**4** with that of carbene complexes, we investigated the thermolysis reaction of **3**. Heating a solution of **3** in a sealed tube at 90 °C for 72 h gave a new η^3-cyclohexadienyltricarbonyliron complex [3-5-η-C$_6$H$_8$(CO)$_3$-FeC(OC$_2$H$_5$)C$_6$H$_4$CH$_3$-*p*] (**14**) (eq 4) in 28% yield. The structure of **14** was established by its single-crystal X-ray structure analysis.



3

7

14

(4)

A possible reaction pathway to complex **14** (eq 4) might involve the intermediate **7** formed by addition of one CO generated by thermal decomposition of **3** to the Fe atom. Intermediate **7** underwent a 1,4-hydrogen shift, namely, a hydrogen atom at the C-5 ring position migrates to the C-2 position to form the thermodynamically stable complex **14**. To confirm this presumption, complex **7** was used in the thermal decomposition under the same conditions, resulting in the formation of the same product **14** (eq 5) in higher (43%) yield.

$$\mathbf{7} \xrightarrow[\text{sealed tube, 90 °C, 72 h}]{\text{benzene}} \mathbf{14} \qquad (5)$$

The molecular structure of **14** (Supporting Information) resembles that of **5** and has many common features, except that the six-membered ring comprised of C(4)−C(9) adopts a chair form in **14** but a boat form in **5**. The distances of the Fe atom to the C(4), C(5), and C(6) atoms are 2.148(4), 2.075(4), and 2.214(4) Å, respectively, similar to those of **5** and **10**.

Acknowledgment. Financial support from the National Natural Science Foundation of China and the Science Foundation of the Chinese Academy of Sciences is gratefully acknowledged.

Supporting Information Available: Tables of atomic coordinates and B_{iso}/B_{eq}, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **5**, **10**, and **14** and molecular structural figures for **10** (Figure 2) and **14** (Figure 3) (24 pages). Ordering information is given on any current masthead page.

OM980238K

---

(11) Yin, J.-G.; Chen, J.-B.; Xu, W.-H.; Zhang, Z.-Y.; Tang, Y.-Q. *Organometallics* **1988**, *7*, 21.

(12) Ginderow, P. D. *Acta Crystallogr.* **1974**, *B30*, 2798.

(13) Dötz, K. H. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 587.