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# Novel ring-coupled reactions of bis(cycloheptatriene)-tris(tricarbonyliron) with aryllithium reagents†

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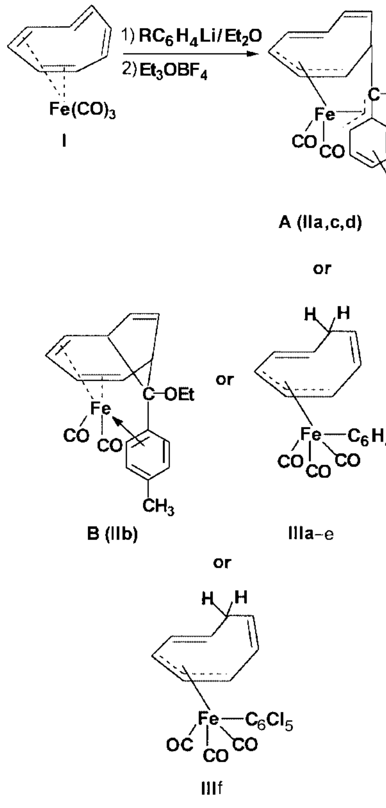
The reactions of the bis(cycloheptatriene)tris(tricarbonyliron), $[(C_7H_8)_2\{Fe(CO)_3\}_3]$ **1**, with aryllithium reagents $RC_6H_4Li$ (R = H, *o*-, *m*-, *p*-$CH_3$, *p*-$OCH_3$), in diethyl ether at low temperature gave acylmetalate intermediates which following alkylation with $Et_3OBF_4$ in aqueous solution at 0 °C led to coupling of the two cycloheptatriene ligands to afford five novel isomerized (bicycloheptatriene)bis(tricarbonyliron)dicarbonyl[ethoxy(aryl)carbene]iron complexes $[\{(CO)_3Fe(C_7H_7)\}_2(CO)_2FeC(OC_2H_5)C_6H_4R]$ (**2**, R = H; **3**, R = *o*-$CH_3$; **4**, R = *m*-$CH_3$; **5**, R = *p*-$CH_3$; **6**, R = *p*-$OCH_3$), of which the structure of **2** has been established by a single-crystal X-ray diffraction study. The reaction of complexes **2** or **5** with $PPh_3$ gave the chelated $\eta^3$-allyliron phosphine adducts $[\{(CO)_3Fe(C_7H_7)\}_2(CO)_2(PPh_3)FeC(OC_2H_5)C_6H_4R]$ (**7**, R = H; **8**, R = *p*-$CH_3$).

## Introduction

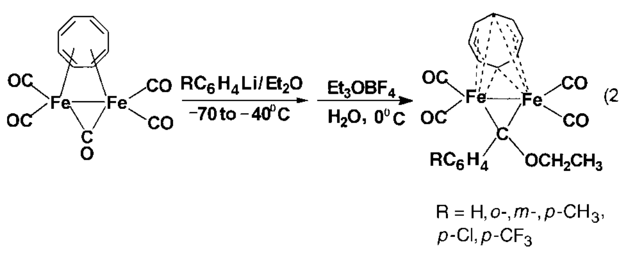
The synthesis, structure, and chemistry of alkene–metal carbene complexes are one area of current interest. Over the past 15 years, olefin-coordinated transition metal carbene and carbyne complexes and/or their isomerized products, as part of a broader investigation of transition metal carbene and carbyne complexes, have been examined extensively in our laboratory.[1] In previous studies, we have shown[1] that a considerable number of the novel olefin-coordinated transition metal carbene complexes and/or their isomerized products were isolated, and a number of novel isomerizations of olefin ligands have been observed, in the reactions of olefin-ligated metal carbonyls with aryllithium reagents followed by alkylation with $Et_3OBF_4$. We have also shown that the isomerizations of the olefin ligands and resulting products depend not only on the olefin ligands but also on the central metals.[1b,2] For instance, the reaction of (cyclooctatetraene)tricarbonyliron, $C_8H_8Fe(CO)_3$, with aryllithium reagents and subsequent alkylation with $Et_3OBF_4$ results in the formation of novel isomerized carbene complexes with two types of structures, **A** and **B**, or (8,8-dihydro-3,4,5-η-cyclooctatrienyl)tricarbonyliron complexes depending on the alkylation conditions, eqn. (1).[1b] Pentacarbonyl(cyclooctatetraene)diiron $[C_8H_8Fe_2(CO)_5]$, where the two iron atoms are directly bonded to each other, reacted with aryllithium reagents under analogous conditions to give the dimetal bridging carbene complexes, eqn. (2).[1d]

In addition, the reaction of (cycloheptatriene)tricarbonyliron $[C_7H_8Fe(CO)_3]$ with aryllithium, followed by alkylation with $Et_3OBF_4$ led to dearomatisation of the cycloheptatriene ring to yield the novel compound $[(Cl_3C\text{-cyclo-}C_7H_8)(CO)_2Fe(COC_6H_4Me\text{-}o)]$ or to ring-opening to give $[(CO)_2Fe\{C(OEt)(C_6H_4Me\text{-}o)C_7H_8\}]$ depending on the alkylation conditions, eqn. (3).[1c] The cycloheptatriene-coordinated carbonyldiiron compound $[C_7H_8Fe_2(CO)_6]$, where the two iron atoms are directly bonded to each other, reacted with aryllithium reagents under analogous conditions to give the novel bridging carbyne complexes, eqn. (4) ($C_6Cl_5$ derivates, rather than $C_6H_4R$, can also be obtained).[1f]



(1)

R = H **a**, *p*-$CH_3$ **b**, *o*-$CH_3$ **c**, *m*-$CH_3$ **d**, *p*-$CF_3$ **e**



(2)

R = H, *o*-, *m*-, *p*-$CH_3$, *p*-Cl, *p*-$CF_3$

In an extension of our research on olefin-coordinating metal carbene complexes, we have now studied the reactions of olefin-ligated trimetal carbonyls with nucleophiles in order to investigate the effect of trinuclear central metals on the isomerization of the olefin ligands and the reaction products. Herein

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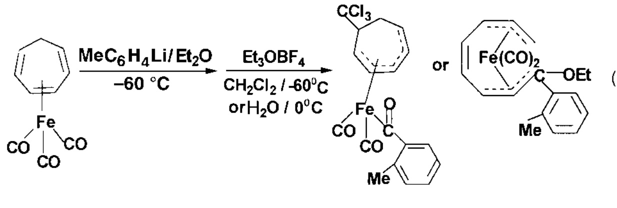
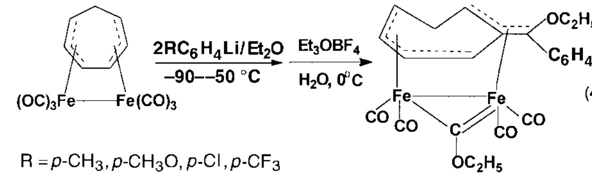
† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4277/



(3)



(4)

we report an unusual reaction of bis(cycloheptatriene)tris(tricarbonyliron), $[(C_7H_8)_2\{Fe(CO)_3\}_3]$ **1**, where the two cycloheptatriene ligands are independently $\eta^4$ bonded to two $Fe(CO)_3$ units and are each $\eta^2$ bonded to the third $Fe(CO)_3$ unit, with aryllithium reagents at low temperature followed by alkylation with $Et_3OBF_4$, as previously described,[1d,2c] to form the novel isomerized (bicycloheptatriene)bis(tricarbonyliron)dicarbonyl[ethoxy(aryl)carbene]iron complexes and their structural characterization.

## Experimental

All procedures were performed under a dry, oxygen-free $N_2$ atmosphere 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. Diethyl ether ($Et_2O$) was distilled from sodium benzophenone ketyl, while light petroleum (bp 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 $N_2$. $PPh_3$ was purchased from Aldrich Chemical Co. Bis(cycloheptatriene)tris(tricarbonyliron), $[(C_7H_8)_2\{Fe(CO)_3\}_3]$ **1**,[3] $Et_3OBF_4$,[4] and aryllithium reagents[5–8] were prepared by literature methods.

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 $SiMe_4$ 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.

### Preparations

**$[\{(CO)_3Fe(C_7H_7)\}_2(CO)_2FeC(OC_2H_5)C_6H_5]$ 2.** To a solution of 0.20 g (0.33 mmol) of **1** dissolved in 40 mL of ether at −78 °C was added 0.66 mmol of $C_6H_5Li$[5] with stirring. The reaction mixture was stirred at −70 to −60 °C for 0.5 h and then at −50 to −40 °C for 4 h, during which time the yellow solution gradually turned orange-red. The resulting solution was evaporated to dryness under high vacuum at −40 °C. To the red residue was added $Et_3OBF_4$[4] (*ca.* 2–3 g). This solid mixture was dissolved in 25 mL of $N_2$-saturated water at 0 °C with vigorous stirring and the mixture covered with light petroleum (30–60 °C). $Et_3OBF_4$ was immediately added to the aqueous solution portionwise, with strong stirring, until it became acidic. The aqueous solution was extracted with light petroleum. The combined extracts were evaporated under vacuum to remove most of the solvent and then chromatographed on an alumina column (1.6 × 15–20 cm) at −20 to −25 °C with light petroleum followed by light petroleum/$CH_2Cl_2$/$Et_2O$ (10 : 1 : 1) as the eluent. The orange-yellow band was eluted and collected. The solvent was removed under vacuum, and the residue was recrystallized from light petroleum/$CH_2Cl_2$ solution at −80 °C to give 0.084 g (36%, based on **1**) of orange-yellow crystals of **2**: mp 102–104 °C decomp.; IR (hexane) $\nu$(CO) 2003 (s), 1997 (vs), 1990 (vs), 1980 (vs), 1965 (s), 1955 (m), 1947 (sh) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.88 (m, 1H, $C_6H_5$), 7.50 (m, 2H, $C_6H_5$), 7.34 (m, 2H, $C_6H_5$), 6.24 (m, 1H, $C_7H_7$), 5.26 (m, 1H, $(C_7H_7)_2$), 5.06 (m, 1H, $(C_7H_7)_2$), 4.44 (m, 1H, $(C_7H_7)_2$), 4.28 (m, 1H, $C_7H_7$), 3.98 (m, 1H, $(C_7H_7)_2$), 3.52 (m, 1H, $(C_7H_7)_2$), 3.32 (m, 1H, $(C_7H_7)_2$), 3.22 (m, 1H, $(C_7H_7)_2$), 3.12 (q, 2H, $OCH_2CH_3$), 2.69 (m, 1H, $(C_7H_7)_2$), 2.50 (m, 1H, $(C_7H_7)_2$), 1.74 (m, 1H, $(C_7H_7)_2$), 1.40 (m, 1H, $(C_7H_7)_2$), 1.28 (t, 3H, $OCH_2CH_3$), 0.90 (m, 1H, $(C_7H_7)_2$); MS *m/z* 540 ($M^+ - CO - Fe(CO)_3$), 512 ($M^+ - 2CO - Fe(CO)_3$), 484 ($M^+ - 3CO - Fe(CO)_3$), 428 ($M^+ - 2Fe(CO)_3$), 434 $[(C_7H_7)_2Fe_2(CO)_5]^+$, 378 $[(C_7H_7)_2Fe_2(CO)_3]^+$, 372 ($M^+ - 2CO - 2Fe(CO)_3$), 322 $[(C_7H_7)_2Fe_2(CO)]^+$, 294 $[(C_7H_7)_2Fe(CO)_2]^+$. Anal. Calc. for $C_{31}H_{24}O_9Fe_3$: C, 52.59; H, 3.42. Found: C, 52.82; H, 3.33%.

**$[\{(CO)_3Fe(C_7H_7)\}_2(CO)_2FeC(OC_2H_5)C_6H_4CH_3\text{-}o]$ 3.** Similar to the preparation of **2**, the reaction of 0.20 g (0.33 mmol) of **1** with 0.68 mmol of *o*-$CH_3C_6H_4Li$[6] at −50 to −40 °C for 4 h, followed by alkylation and further treatment afforded 0.82 g (34%, based on **1**) of orange crystalline **3**: mp 98–100 °C decomp.; IR (hexane) $\nu$(CO) 2007 (sh), 2003 (s), 1955 (vs), 1987 (sh), 1975 (sh), 1967 (vs), 1960 (s) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.40–7.18 (m, 4H, $C_6H_4CH_3$), 6.22 (m, 1H, $(C_7H_7)_2$), 5.60 (m, 1H, $(C_7H_7)_2$), 5.32 (m, 1H, $(C_7H_7)_2$), 5.04 (m, 1H, $(C_7H_7)_2$), 4.74 (m, 1H, $(C_7H_7)_2$), 4.40 (m, 1H, $(C_7H_7)_2$), 4.02 (m, 1H, $(C_7H_7)_2$), 3.56 (m, 1H, $(C_7H_7)_2$), 3.31 (m, 1H, $(C_7H_7)_2$), 3.18 (m, 1H, $(C_7H_7)_2$), 3.12 (q, 2H, $OCH_2CH_3$), 2.68 (m, 1H, $(C_7H_7)_2C_7H_7$), 2.13 (s, 3H, $C_6H_4CH_3$), 1.90 (m, 1H, $(C_7H_7)_2$), 1.52 (m, 1H, $(C_7H_7)_2$), 1.30 (t, 3H, $OCH_2CH_3$), 0.88 (m, 1H, $(C_7H_7)_2$); MS *m/z* 554 ($M^+ - CO - Fe(CO)_3$), 526 ($M^+ - 2CO - Fe(CO)_3$), 498 ($M^+ - 3CO - Fe(CO)_3$), 442 ($M^+ - 2Fe(CO)_3$), 434 $[(C_7H_7)_2Fe_2(CO)_5]^+$, 378 $[(C_7H_7)_2Fe_2(CO)_3]^+$, 386 ($M^+ - 2CO - 2Fe(CO)_3$), 322 $[(C_7H_7)_2Fe_2(CO)]^+$, 294 $[(C_7H_7)_2Fe(CO)_2]^+$. Anal. Calc. for $C_{32}H_{26}O_9Fe_3$: C, 53.23; H, 3.63. Found: C, 53.15; H, 3.96%.

**$[\{(CO)_3Fe(C_7H_7)\}_2(CO)_2FeC(OC_2H_5)C_6H_4CH_3\text{-}m]$ 4.** The reaction of 0.20 g (0.33 mmol) of **1** with 0.66 mmol of *m*-$CH_3C_6H_4Li$[6] was as described in the reaction of **1** with $C_6H_5Li$ at −55 to −40 °C for 4 h. Subsequent alkylation with $Et_3OBF_4$ and further treatment as described above for the preparation of **2** gave 0.105 g (44%, based on **1**) of **4** as orange crystals: mp 146–149 °C decomp.; IR (hexane) $\nu$(CO) 2003 (s), 2000 (sh), 1990 (vs), 1980 (s), 1965 (s), 1955 (s), 1942 (sh) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.60–7.00 (m, 4H, $C_6H_4CH_3$), 6.29 (m, 1H, $(C_7H_7)_2$), 5.78 (m, 1H, $(C_7H_7)_2$), 5.60 (m, 1H, $(C_7H_7)_2$), 5.42 (m, 1H, $(C_7H_7)_2$), 5.00 (m, 1H, $(C_7H_7)_2$), 4.32 (m, 1H, $(C_7H_7)_2$), 4.00 (m, 1H, $(C_7H_7)_2$), 3.62 (m, 1H, $(C_7H_7)_2$), 4.00 (m, 1H, $(C_7H_7)_2$), 3.06 (q, 2H, $OCH_2CH_3$), 2.70 (m, 1H, $(C_7H_7)_2$), 2.52 (s, 3H, $C_6H_4CH_3$), 2.42 (m, 1H, $(C_7H_7)_2$), 1.88 (m, 1H, $(C_7H_7)_2$), 1.77 (m, 1H, $(C_7H_7)_2$), 1.38 (t, 3H, $OCH_2CH_3$), 0.88 (m, 1H, $(C_7H_7)_2$); MS *m/z* 554 ($M^+ - CO - Fe(CO)_3$), 526 ($M^+ - 2CO - Fe(CO)_3$), 498 ($M^+ - 3CO - Fe(CO)_3$), 442 ($M^+ - 2Fe(CO)_3$), 434 $[(C_7H_7)_2Fe_2(CO)_5]^+$, 378 $[(C_7H_7)_2Fe_2(CO)_3]^+$, 386 ($M^+ - 2CO - 2Fe(CO)_3$), 322 $[(C_7H_7)_2Fe_2(CO)]^+$, 294 $[(C_7H_7)_2Fe(CO)_2]^+$. Anal. Calc. for $C_{32}H_{26}O_9Fe_3$: C, 53.23; H, 3.63. Found: C, 53.57; H, 3.95%.

**$[\{(CO)_3Fe(C_7H_7)\}_2(CO)_2FeC(OC_2H_5)C_6H_4CH_3\text{-}p]$ 5.** Compound **1** (0.20 g, 0.33 mmol) was treated, in a manner similar to that described for the reaction of **1** with $C_6H_5Li$, with 0.66 mmol of *p*-$CH_3C_6H_4Li$[6] at −50 to −40 °C for 5 h. Subsequent alkylation and further treatment as described above for the preparation of **2** yielded 0.095 g (40%, based on **1**) of orange crystals of **5**: mp 88–90 °C decomp.; IR (hexane) $\nu$(CO) 2005 (sh), 2003 (s), 1995 (sh), 1990 (vs), 1979 (m), 1965 (s), 1950 (s) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.83 (m, 1H, $C_6H_4CH_3$), 7.48

(m, 1H, $C_6H_4CH_3$), 7.22 (m, 2H, $C_6H_4CH_3$), 6.35 (m, 1H, $(C_7H_7)_2$), 5.63 (m, 1H, $(C_7H_7)_2$), 5.44 (m, 1H, $(C_7H_7)_2$), 4.74 (m, 1H, $(C_7H_7)_2$), 4.25 (m, 1H, $(C_7H_7)_2$), 3.98 (m, 1H, $(C_7H_7)_2$), 3.76 (m, 1H, $(C_7H_7)_2$), 3.58 (m, 1H, $(C_7H_7)_2$), 3.23 (m, 1H, $(C_7H_7)_2$), 3.04 (q, 2H, $OCH_2CH_3$), 2.71 (m, 1H, $(C_7H_7)_2$), 2.47 (m, 1H, $(C_7H_7)_2$), 2.26 (s, 3H, $C_6H_4CH_3$), 1.89 (m, 1H, $(C_7H_7)_2$), 1.76 (m, 1H, $(C_7H_7)_2$), 1.36 (t, 3H, $OCH_2CH_3$), 0.89 (m, 1H, $(C_7H_7)_2$); MS *m/z* 574 $[(C_7H_7)_2Fe_3(CO)_8]^+$, 554 ($M^+ - CO - Fe(CO)_3$), 526 ($M^+ - 2CO - Fe(CO)_3$), 498 ($M^+ - 3CO - Fe(CO)_3$), 442 ($M^+ - 2Fe(CO)_3$), 434 $[(C_7H_7)_2Fe_2(CO)_5]^+$, 378 $[(C_7H_7)_2Fe_2(CO)_3]^+$, 386 ($M^+ - 2CO - 2Fe(CO)_3$), 322 $[(C_7H_7)_2Fe_2(CO)]^+$, 294 $[(C_7H_7)_2Fe(CO)_2]^+$. Anal. Calc. for $C_{32}H_{26}O_9Fe_3$: C, 53.23; H, 3.63. Found: C, 53.00; H, 3.98%.

**$[\{(CO)_3Fe(C_7H_7)\}_2(CO)_2FeC(OC_2H_5)C_6H_4OCH_3\text{-}p]$ 6.** A solution of 0.14 g (0.74 mmol) of $p\text{-}CH_3OC_6H_4Br$ in 20 mL of ether was mixed with 0.74 mmol of $n\text{-}C_4H_9Li$.[7] After 30 min stirring at room temperature, the resulting ether solution of $p\text{-}CH_3OC_6H_4Li$[8] was reacted, as described in the reaction of **1** with $C_6H_5Li$, with 0.20 g (0.33 mmol) of **1** at −50 to −40 °C for 4.5 h, followed by alkylation and further treatment as described for the preparation of **2** gave 0.086 g (35%, based on **1**) of **6** as orange crystals: mp 86–88 °C decomp.; IR (hexane) *v* (CO) 2008 (sh), 2005 (s), 2000 (sh), 1995 (vs), 1981(m), 1969 (s), 1952 (s) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.90 (m, 2H, $C_6H_4OCH_3$), 7.55 (m, 1H, $C_6H_4OCH_3$), 7.06 (m, 1H, $C_6H_4OCH_3$), 6.72 (m, 1H, $(C_7H_7)_2$), 5.65 (m, 1H, $(C_7H_7)_2$), 5.45 (m, 1H, $(C_7H_7)_2$), 4.85 (m, 1H, $(C_7H_7)_2$), 4.20 (m, 1H, $(C_7H_7)_2$), 4.04 (m, 1H, $(C_7H_7)_2$), 3.85 (s, 3H, $C_6H_4OCH_3$), 3.65 (m, 1H, $(C_7H_7)_2$), 3.24 (m, 1H, $(C_7H_7)_2$), 3.05 (q, 2H, $OCH_2CH_3$), 2.74 (m, 1H, $(C_7H_7)_2$), 2.46 (m, 1H, $(C_7H_7)_2$), 2.24 (m, 1H, $(C_7H_7)_2$), 1.90 (m, 1H, $(C_7H_7)_2$), 1.78 (m, 1H, $(C_7H_7)_2$), 1.32 (t, 3H, $OCH_2CH_3$), 0.90 (m, 1H, $(C_7H_7)_2$); MS *m/z* 574 $[(C_7H_7)_2Fe_3(CO)_8]^+$, 542 ($M^+ - 2CO - Fe(CO)_3$), 514 ($M^+ - 3CO - Fe(CO)_3$), 458 ($M^+ - 2Fe(CO)_3$), 434 $[(C_7H_7)_2Fe_2(CO)_5]^+$, 378 $[(C_7H_7)_2Fe_2(CO)_3]^+$, 402 ($M^+ - 2CO - 2Fe(CO)_3$), 322 $[(C_7H_7)_2Fe_2(CO)]^+$, 294 $[(C_7H_7)_2Fe(CO)_2]^+$. Anal. Calc. for $C_{32}H_{26}O_{10}Fe_3$: C, 52.07; H, 3.55. Found: C, 52.11; H, 3.60%.

### Reactions

**Of 2 with $PPh_3$ to give $[\{(CO)_3Fe(C_7H_7)\}_2(CO)_2(PPh_3)FeC(OC_2H_5)C_6H_5]$ 7.** Compound **2** (0.025 g, 0.035 mmol) was dissolved in 30 mL of hexane at −30 °C. To this suspension was added dropwise 0.013 g (0.050 mmol) of $PPh_3$ in 10 mL of light petroleum. The reaction mixture was stirred at −15 to −10 °C for 12 h, during which time the orange suspension gradually became a clear yellow solution. The resulting mixture was evaporated to dryness at −15 °C *in vacuo*, and the residue was chromatographed on $Al_2O_3$ at −15 to −20 °C with light petroleum followed by light petroleum/$Et_2O$ (15 : 1) as the eluant. A yellow band was eluted. After vacuum removal of the solvent, the crude product was recrystallized from light petroleum/$CH_2Cl_2$ at −80 °C to give 0.024 g (71%, based on **2**) of yellow crystals of **7**: mp 100–102 °C decomp.; IR (hexane) *v* (CO) 2005 (sh), 2002 (m), 1995 (sh), 1988 (s), 1970 (s), 1955 (vs), 1938 (sh) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.85–7.29 (m, 20H, $C_6H_5$), 6.29 (d, 1H, $C_7H_7$), 5.24 (m, 1H, $(C_7H_7)_2$), 5.00 (t, 1H, $(C_7H_7)_2$), 4.52 (t, 1H, $(C_7H_7)_2$), 4.38 (m, 1H, $C_7H_7$), 4.08 (m, 1H, $(C_7H_7)_2$), 3.66 (m, 1H, $(C_7H_7)_2$), 3.51 (m, 1H, $(C_7H_7)_2$), 3.42 (m, 1H, $(C_7H_7)_2$), 3.14 (q, 2H, $OCH_2CH_3$), 2.63 (m, 1H, $(C_7H_7)_2$), 2.44 (m, 1H, $(C_7H_7)_2$), 1.79 (m, 1H, $(C_7H_7)_2$), 1.46 (m, 1H, $(C_7H_7)_2$), 1.31 (t, 3H, $OCH_2CH_3$), 0.85 (m, 1H, $(C_7H_7)_2$); MS *m/z* 428 ($M^+ - PPh_3 - 2Fe(CO)_3$), 372 ($M^+ - PPh_3 - 2CO - 2Fe(CO)_3$), 344 ($M^+ - PPh_3 - 3CO - 2Fe(CO)_3$), 318 ($FePPh_3^+$), 262 ($PPh_3^+$). Anal. Calc. for $C_{49}H_{35}O_9PFe_3$: C, 60.65; H, 3.64. Found: C, 60.99; H, 3.78%.

**Table 1** Selected bond lengths (Å) and angles (°) for complex **2** with e.s.d.s. in parentheses

| | | | |
|---|---|---|---|
| Fe(3)–C(23) | 2.05(1) | C(17)–C(18) | 1.52(1) |
| Fe(3)–C(24) | 2.14(1) | C(18)–C(19) | 1.53(1) |
| Fe(3)–C(25) | 2.31(1) | C(19)–C(20) | 1.39(1) |
| Fe(3)–C(19) | 2.21(1) | C(20)–C(21) | 1.41(1) |
| Fe(3)–C(20) | 2.08(1) | C(21)–C(22) | 1.47(1) |
| Fe(3)–C(21) | 2.15(1) | C(16)–C(22) | 1.41(1) |
| C(9)–C(10) | 1.46(1) | C(18)–C(23) | 1.54(1) |
| C(10)–C(11) | 1.40(2) | C(23)–C(24) | 1.42(1) |
| C(11)–C(12) | 1.40(2) | C(24)–C(25) | 1.42(1) |
| C(12)–C(13) | 1.49(1) | C(25)–C(26) | 1.42(2) |
| C(13)–C(14) | 1.51(1) | C(26)–C(27) | 1.35(2) |
| C(14)–C(15) | 1.42(1) | C(27)–C(28) | 1.39(2) |
| C(9)–C(15) | 1.49(1) | C(28)–C(29) | 1.39(2) |
| C(14)–C(16) | 1.43(1) | C(24)–C(29) | 1.43(1) |
| C(16)–C(17) | 1.53(1) | C(23)–O(9) | 1.39(1) |
| Fe(3)–C(23)–C(24) | 73.5(6) | C(13)–C(14)–C(15) | 122.8(10) |
| Fe(3)–C(24)–C(25) | 77.9(7) | C(13)–C(14)–C(16) | 121.5(9) |
| Fe(3)–C(24)–C(23) | 66.9(6) | C(14)–C(15)–C(9) | 124.4(10) |
| Fe(3)–C(25)–C(24) | 65.0(6) | C(15)–C(14)–C(16) | 115.7(9) |
| C(18)–C(23)–C(24) | 121.7(9) | C(14)–C(16)–C(22) | 117.9(9) |
| C(18)–C(23)–O(9) | 116.7(8) | C(16)–C(17)–C(18) | 116.6(9) |
| C(24)–C(23)–O(9) | 115.9(9) | C(17)–C(18)–C(19) | 112.0(9) |
| Fe(3)–C(23)–O(9) | 123.7(7) | C(18)–C(19)–C(20) | 123.4(10) |
| Fe(3)–C(23)–C(18) | 96.5(6) | C(19)–C(20)–C(21) | 122.3(10) |
| C(23)–C(24)–C(25) | 121.1(10) | C(20)–C(21)–C(22) | 125.3(10) |
| C(23)–O(9)–C(30) | 113.5(8) | C(21)–C(22)–C(16) | 127.2(10) |
| C(9)–C(10)–C(11) | 118(1) | C(22)–C(16)–C(17) | 124.5(9) |
| C(10)–C(11)–C(12) | 118(1) | C(14)–C(16)–C(17) | 117.6(9) |
| C(11)–C(12)–C(13) | 129(1) | C(23)–C(24)–C(29) | 120(1) |
| C(12)–C(13)–C(14) | 120.1(9) | C(25)–C(24)–C(29) | 117(1) |

**Of 5 with $PPh_3$ to give $[\{(CO)_3Fe(C_7H_7)\}_2(CO)_2(PPh_3)FeC(OC_2H_5)C_6H_4CH_3\text{-}p]$ 8.** A 0.025 g (0.035 mmol) portion of **5** and 0.013 g (0.050 mmol) portion of $PPh_3$ were reacted in a manner similar to that described in the reaction of **2** with $PPh_3$ for 10 h. The color of the reaction mixture changed from orange to yellow. Further treatment of the resulting solution as described in the reaction of **2** with $PPh_3$ yielded 0.026 (76%, based on **5**) of yellow crystalline **8**: mp 102–104 °C decomp.; IR (hexane) *v* (CO) 2004 (sh), 2002 (s), 1994 (sh), 1988 (vs), 1982 (sh), 1963 (s), 1948 (s) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.82–7.16 (m, 19H, $C_6H_5 + C_6H_4CH_3$), 6.38 (d, 1H, $(C_7H_7)_2$), 5.58 (m, 1H, $(C_7H_7)_2$), 5.35 (m, 1H, $(C_7H_7)_2$), 4.90 (t, 1H, $(C_7H_7)_2$), 4.43 (t, 1H, $(C_7H_7)_2$), 4.18 (t, 1H, $(C_7H_7)_2$), 3.90 (m, 1H, $(C_7H_7)_2$), 3.85 (m, 1H, $(C_7H_7)_2$), 3.50 (m, 1H, $(C_7H_7)_2$), 3.17 (q, 2H, $OCH_2CH_3$), 2.75 (m, 1H, $(C_7H_7)_2$), 2.35 (m, 1H, $(C_7H_7)_2$), 2.30 (s, 3H, $C_6H_4CH_3$), 1.80 (m, 1H, $(C_7H_7)_2$), 1.60 (m, 1H, $(C_7H_7)_2$), 1.34 (t, 3H, $OCH_2CH_3$), 0.86 (m, 1H, $(C_7H_7)_2$); MS *m/z* 722 ($M^+ - PPh_3$), 666 ($M^+ - PPh_3 - 2CO$), 638 ($M^+ - PPh_3 - 3CO$), 610 ($M^+ - PPh_3 - 4CO$), 582 ($M^+ - PPh_3 - 5CO$), 318 ($FePPh_3^+$), 262 ($PPh_3^+$). Anal. Calc. for $C_{50}H_{41}O_9PFe_3$: C, 61.01; H, 4.20. Found: C, 60.88; H, 4.41%.

### Crystal structure determination of complex 2

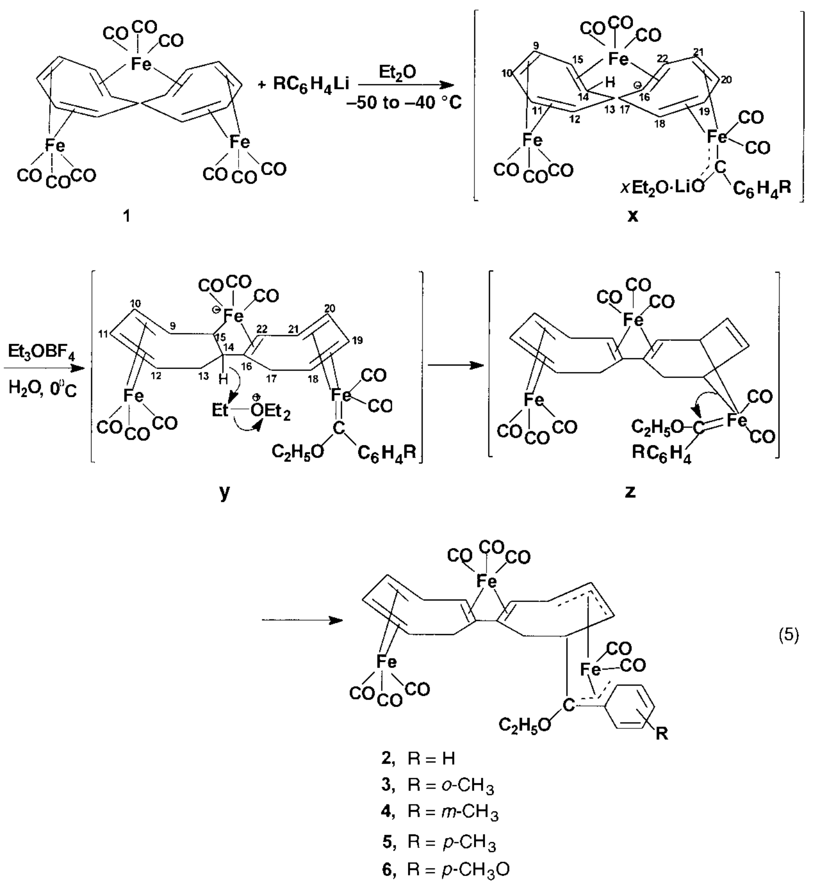
The single crystals of **2** suitable for an X-ray diffraction study were obtained by recrystallization from light petroleum/$CH_2Cl_2$ solution at −80 °C. A single crystal of **2** was mounted on a glass fibre and sealed with epoxy glue. Crystal data: $C_{31}H_{24}O_9Fe_3$, $M = 708.07$, monoclinic, space group $P2_1/n$, $a = 11.073(5)$, $b = 22.020(5)$, $c = 13.144(6)$ Å, $\beta = 111.25(3)°$, $V = 2986(2)$ Å$^3$, $Z = 4$, $D_c = 1.574$ g $cm^{-3}$, $\mu = 14.90$ $cm^{-1}$ (Mo-Kα).

A total of 4408 unique reflections were collected within 5–50° in the conventional $\omega$–$2\theta$ scan mode with a Rigaku AFC7R diffractometer at 20 °C using Mo-Kα radiation, of which 2043 observed reflections $[I > 1.50\sigma(I)]$ were used in the structure solution (direct methods) and refinement (full-matrix least-squares method) to give final $R = 0.060$ and $Rw = 0.055$.

Selected bond lengths and angles are given in Table 1.

CCDC reference number 186/1679.

See http://www.rsc.org/suppdata/dt/1999/4277/ for crystallographic files in .cif format.



(5)

2, R = H
3, R = *o*-CH$_3$
4, R = *m*-CH$_3$
5, R = *p*-CH$_3$
6, R = *p*-CH$_3$O

## Results and discussion

The bis(cycloheptatriene)tris(tricarbonyliron), [(C$_7$H$_8$)$_2$-{Fe(CO)$_3$}$_3$] **1**, was treated with two molar equivalents of aryllithium reagents, ArLi (Ar = C$_6$H$_5$, *o*-, *m*-, *p*-CH$_3$C$_6$H$_4$, *p*-CH$_3$OC$_6$H$_4$)), in ether at −50 to −40 °C for 4 to 5 h. The acylmetalate intermediates formed were subsequently alkylated with Et$_3$OBF$_4$ in aqueous solution at 0 °C. After removal of the solvent under vacuum at low temperature, the solid residue was chromatographed on an alumina column at −20 to −25 °C, and the crude products were recrystallized from light petroleum at −80 °C to afford orange crystalline complexes **2**–**6** with composition [{(CO)$_3$Fe(C$_7$H$_7$)}$_2$(CO)$_2$FeC(OC$_2$H$_5$)C$_6$H$_4$R], eqn. (5), in reasonable yields.

When three molar equivalents, instead of two, of aryllithium reagent were used for the reaction under the same conditions, the same products (**2**–**6**) were obtained in small amounts. However, when more than 3 molar equivalents of the aryllithium reagent were used, a decomposition reaction occurred not giving the expected products (**2**–**6**). This might be caused by either (a) decomposition of the acylmetalate intermediate by an excess of aryllithium or (b) an excess of aryllithium reagent attacked further CO ligands of the Fe(CO)$_3$ units to form an extremely labile di- or tri-acylmetalate intermediate, which was rapidly decomposed on alkylation with Et$_3$OBF$_4$ in aqueous solution.

On the basis of the elemental analyses, spectral analyses, and the single-crystal X-ray diffraction study of complex **2**, complexes **2**–**6** are formulated as the isomerized bicycloheptatriene-coordinated bis(tricarbonyliron)dicarbonyl-[ethoxy(aryl)carbene]iron complexes, where the two original cycloheptatriene ligands of **1** are now coupled to give a bicycloolefin ligand with a (CO)$_2$FeC(OC$_2$H$_5$)C$_6$H$_4$R moiety $\sigma$ bonded to the bicycloolefin ligand through the "carbene" carbon (C(23)) and linked to the Fe atom in an allyl-type $\eta^3$-bond. The two remaining Fe(CO)$_3$ units are bonded respectively to the two butadiene-like residues of the resulting bicycloolefin ligand.

There are three olefin-coordinated Fe(CO)$_3$ units in **1**, two of which have the same chemical environment. Therefore it was expected that isomerized bicycloheptatriene-coordinated di- or tri-alkoxy(aryl)carbene iron complexes should exist in the resulting products when treating **1** with aryllithium reagents. However, no isomerized di- or tri-alkoxycarbene complexes or their derivatives were obtained from the reactions even though three molar equivalents of aryllithium reagent were used for the reactions.

It is not yet clear how the two cycloheptatriene ligands couple to become a bicycloolefin ligand. We conjecture that the formation pathway of complexes **2**–**6** could involve an acylmetalate intermediate **x** formed by attack of the aryllithium nucleophile on a CO ligand of the Fe(CO)$_3$ units. At the same time, the basic aryllithium abstracts a proton from the C(16) atom of the cycloheptatriene ligand to form a cycloheptatrienyl anion. Subsequently, the two cycloheptatriene rings were coupled with bonding of C(14) to C(16) and dissociation of the Fe–C(14) bond upon alkylation of intermediate **x** with Et$_3$OBF$_4$ in aqueous solution to give intermediate **y**, an anionic species, where the $^-$Fe(CO)$_3$ anion moiety is bonded to the C(15), C(16) and C(22) atoms. As soon as unstable ethoxycarbene complex **y** was formed, a hydrogen on C(14) was transferred to the triethyloxonium cation and a $\pi$-bond rearrangement of the two double bonds of the butadiene-like residue in the bicycloheptatriene ligand occurred to generate another unstable intermediate, metallacycle **z**, which is eventually converted into the stable isomerized alkoxycarbene complexes **2**–**6**, this pathway is similar to that of the isomerized cyclohexadiene-coordinated complexes[9] and isomerized divinylbenzene-coordinated alkoxycarbene complexes.[10] A possible alternative pathway for coupling of the two cycloheptatriene ligands could proceed *via* an iron hydride and/or dihydrogen intermediate.[11] This would be generated by Fe(2) abstracting a proton from C(14) and C(16) of the two cycloheptatriene ligands to form the two cycloheptatrienyl ions. Then the two ionic species couple to form a new butadiene-like residue bonding to the Fe(CO)$_3$ unit

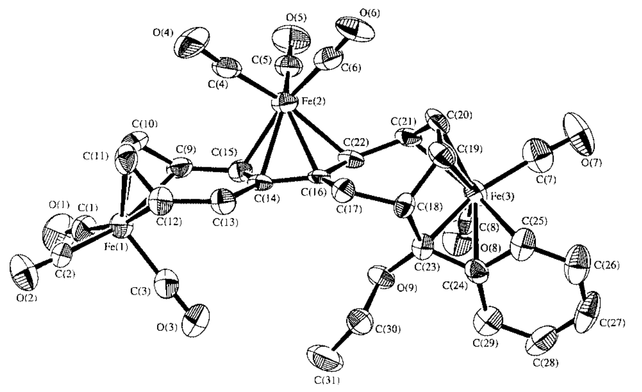


**Fig. 1** Molecular structure of **2**, showing the atom-numbering scheme.

accompanied by dissociation of dihydrogen from Fe(2) during alkylation with $Et_3OBF_4$.

The formation of complexes **2**–**6** is surprising since the two cycloheptatriene rings couple to form a bicycloolefin ligand during the course of the reaction. Such coupling reactions of olefin ligands has been observed for the first time, although a number of novel isomerizations of olefin ligands have been observed by us as mentioned in the Introduction.

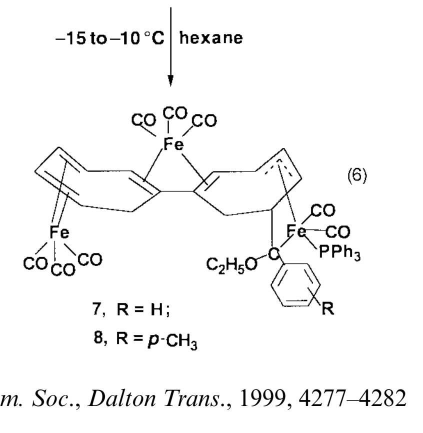
It is interesting that aryllithium reagents with a strong electron withdrawing group, such as *p*-$CF_3C_6H_4Li$, react with **1** under the same conditions to give no analogous complexes but rather decomposed product. This might arise from the extreme lability of intermediate **y** caused by the strong electron withdrawing effect of the *p*-$CF_3C_6H_4$ group.

Complexes **2**–**6** are soluble in polar and non-polar organic solvents. They are very sensitive to air and temperature in solution but stable for short periods on exposure to air at room temperature in the crystalline state. The IR and the solution $^1H$ NMR spectra, as well as the mass spectra are consistent with the proposed structure shown in eqn. (5). The IR spectra of complexes **2**–**6** in the $\nu$ CO region (Experimental section) show seven absorption bands at *ca.* 2008–1942 $cm^{-1}$, which are very different from that of **1** (three absorption bands at 2000, 1982, and 1965 $cm^{-1}$). The $^1H$ NMR spectra of complexes **2**–**6** given in the Experimental section show fourteen sets of proton signals attributed to the cycloolefin ligand arising from the nucleophilic addition to and coupling of the cycloheptatriene rings. As a result, the structure of the olefin ligand is a bicycloolefin ring with a $C(OC_2H_5)C_6H_4R$ moiety bonding to the ring carbon (C(18)). Thus, the $^1H$ NMR spectrum (six sets at $\delta$ 5.65 (m, 2H), 5.40 (m, 2H), 3.56 (m, 4H), 3.32 (m, 2H), 3.21 (m, 2H), 1.56 (d, 2H)) of the original seven-membered ring in **1** has become more complex. In addition, in the $^1H$ NMR spectra of complexes **2**–**6**, a triplet (*ca.* $\delta$ 1.28–1.38) and a quartet (*ca.* $\delta$ 3.04–3.12), and a set of multiplet (*ca.* $\delta$ 7.00–7.90) bands were observed from each of the complexes, which are characteristic for the presence of the ethoxy and aryl groups.

The molecular structure (Fig. 1) of complex **2** established by X-ray diffraction analysis confirms the assigned structure and has many features in common with the previously determined analogous complex $[(CO)_3Fe(m\text{-}C_{10}H_{10})(CO)_2FeC(OC_2H_5)C_6H_4CH_3\text{-}o]$.[10] The "carbene" carbon atom (C(23)) in **2** is now bonded to a carbon atom (C(18)) of the bicycloolefin ligand as well as bonding to the ethoxy and phenyl groups and therefore becomes four-coordinate. The sum of the bond angles around C(23) is 355°, only deviating slightly from 360°, which means that the "carbene" carbon atom is $\sigma$ bonded to the three adjacent atoms (C(18), C(24), and O(9)) using its $sp^2$-hybridized orbitals and $\pi$-bonded to Fe(3) using its approximately pure $p_z$ orbital. The Fe(3)–C(23) bond length of 2.05(1) Å is much longer than the $Fe–C_{carbene}$ bond in the olefin-coordinated carbene iron complexes $[C_{10}H_{16}(CO)_2FeC(OC_2H_5)C_6H_4CH_3\text{-}o]$ (1.915(15) Å)[1e] and $[C_6H_8(CO)_2FeC(OC_2H_5)C_6H_4CH_3\text{-}o]$ (1.89(2) Å),[12] but is somewhat shorter than that of the corresponding Fe–C bond in the analogous complexes $[C_8H_8(CO)_2FeC(OC_2H_5)C_6H_5]$ (2.127(6) Å)[1b] and $[(CO)_3Fe(m\text{-}C_{10}H_{10})(CO)_2FeC(OC_2H_5)C_6H_4CH_3\text{-}o]$ (2.114(9) Å).[10] It is noteworthy that in order to form an allyl-type $\eta^3$-bond to the Fe atom, the benzene ring has resumed Kekule structural character to a certain extent, this is demonstrated by the alternate change of the bond lengths in the benzene ring. Owing to the variation in the $Fe–C_{carbene}$ bond type in complexes **2**–**6**, caused by bonding of (C(18) of the bicycloolefin ligand to the "carbene" carbon (C(23)), the products **2**–**6** may also be regarded as isomerized bicycloheptatriene carbene complexes as described for the isomerized butadiene alkoxycarbeneiron complexes $[C_4H_6(CO)_2FeC(OC_2H_5)C_6H_4R]$.[1a]

The dihedral angle between the plane defined by C(9), C(10), C(11), and C(12) and the plane comprised of C(13), C(14), and C(15) is 130.52°, and the dihedral angle between the plane defined by C(18) through C(21) and the plane comprised of C(14), C(15), C(16), and C(22) is 43.57°. The angle between the C(14)C(15)C(16)C(22) and C(13)C(14)C(15) planes is 178.91°. From the torsion angle data, it can be seen that the C(9), C(12), C(13), C(14), C(15), C(16), C(17), and C(22) atoms lie approximately in the same plane. The benzene ring plane defined by C(24) through C(29) is, respectively, oriented at 100.77, 106.78, and 85.51° with respect to the C(9)C(10)C(11)C(12) plane, the C(14)C(15)C(16)C(22) plane, and the C(18)C(19)C(20)C(21) plane. The $Fe(1)(CO)_3$ unit is located 1.592 Å below the C(9)C(10)C(11)C(12) plane, while the $Fe(2)(CO)_3$ unit is located 1.650 Å above the C(14)C(15)C(16)C(22) plane. The $(CO)_2FeC(OC_2H_5)C_6H_5$ moiety is located 1.835 Å below the C(18)C(19)C(20)C(21) plane. The average distance of Fe(1) from the atoms C(9), C(10), C(11), and C(12) is 2.09 Å, which is slightly shorter than that of Fe(2) to C(14), C(15), C(16), and C(22) (2.11 Å), but is much shorter than that of Fe(3) to C(19), C(20), and C(21) (2.15 Å).

In view of the reactions of the isomerized cyclohexadiene(dicarbonyl)[ethoxy(aryl)carbene]iron complexes $[C_6H_8(CO)_2FeC(OC_2H_5)C_6H_4R]$[9] with Lewis bases such as phosphines and phosphites to give $\eta^3$-allyliron phosphine or phosphite adducts,[13] the structurally analogous complexes **2**–**6** might also react with Lewis bases, which is indeed the case. The reactions of complexes **2** and **5** with $PPh_3$ in hexane at low temperature afforded the chelated $\eta^3$-allyliron phosphine adducts $[\{(CO)_3Fe(C_7H_7)\}_2(CO)_2(PPh_3)FeC(OC_2H_5)C_6H_5]$ **7** and $[\{(CO)_3Fe(C_7H_7)\}_2(CO)_2(PPh_3)FeC(OC_2H_5)C_6H_4CH_3\text{-}p]$ **8**, eqn. (6), in 71% and 76% yields, respectively.



The formation of the chelated allyliron adducts **7** and **8** is expected because the phosphine is an excellent two-electron donor, which displaces the benzene ring and coordinates to the Fe atom. Analogous coordination displacement of the benzene ring by a Lewis base has also been observed in the reactions of $[\{\eta^4\text{-}C_6H_5CH{=}CH\}CH(C_6H_5)N(C_6H_5)C(OC_2H_5){=}\}Fe(CO)_2]$ with Lewis bases.[14]

Complexes **7** and **8** are soluble in polar and non-polar organic solvents. Their IR spectra showed seven CO stretching vibration bands in the *ν* CO region, similar to those of complexes **2**–**6**. The $^1$H NMR spectra of **7** and **8** are similar to those of the parent compounds **2** and **5** except for complex signals attributed to the protons of the aryl groups. Thus, the principal structural framework of complexes **7** and **8** could be considered to be analogous to that of complexes **2**–**6**.

The ring-coupled reactions further show that different olefin ligands and different central metals exert a great effect on the isomerization of the olefin ligands and their resulting products in the reaction of olefin-ligated carbonylmetal compounds with aryllithium reagents.

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