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Novel Reaction of (Cycloheptatriene)diiron Hexacarbonyl with Aryllithium Reagents. A New Route to Diiron Carbonyl Complexes with a Bridging Carbyne Ligand

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Summary: The reaction of (cycloheptatriene)diiron hexacarbonyl (1) with aryllithium reagents, ArLi (Ar = p*-*$CH_3C_6H_4$*,* p*-*$CH_3OC_6H_4$*,* p*-*ClC_6H_4*,* p*-*$CF_3C_6H_4$*,* C_6Cl_5*), in diethyl ether at low temperature afforded acylmetalate intermediates, whose alkylation with* Et_3OBF_4 *in aqueous solution at 0 °C gave five new olefin-coordinated dimetal bridging carbyne complexes,* $Fe_2(CO)_4\{\mu\text{-}\eta^4{:}\eta^3\text{-}C_7H_7C(OC_2H_5)Ar[\mu\text{-}C(OC_2H_5)]\}$ *(2, Ar =* p*-*$CH_3C_6H_4$*; 3, Ar =* p*-*$CH_3OC_6H_4$*; 4, Ar =* p*-*ClC_6H_4*; 5, Ar =* p*-*$CF_3C_6H_4$*; 6, Ar =* C_6Cl_5*). The structure of 5 was established by single-crystal X-ray diffraction. Complex 5 crystallizes in the monoclinic system, space group C2/c, with* $a = 24.725(8)$ *Å,* $b = 14.544(2)$ *Å,* $c = 13.950(1)$ *Å,* $\beta = 103.10(6)°$*,* $V = 4886.2(2)$ *Å*^{3}*,* $Z = 8$*,* $D_{calcd} = 1.561$ *g/cm*^{3}*,* $R = 0.045$*, and* $R_w = 0.047$ *for 2094 reflections with* $I > 3\sigma(I)$*.*

Alkene–metal carbene complexes are important intermediates in various reactions of metal carbene complexes with alkenes.[1-3] In recent years, olefin-coordinated transition-metal carbene complexes and/or their isomerized products have been examined extensively in our laboratory.[4-11] We have observed previously several novel isomerizations of olefin ligands, and a series of isomerized carbene complexes with novel structure were isolated by reaction of olefin-ligated monometal carbonyls with nucleophiles. For example, the novel reaction of (cycloheptatriene)tricarbonyliron with aryllithium reagents and subsequent alkylation with Et_3OBF_4 led to addition to and cleavage of the cycloheptatriene ring to give the novel compound $(Cl_3C\text{-cyclo-}C_7H_8)(CO)_2Fe(COC_6H_4Me\text{-}o)$ or ring-opened $(CO)_2Fe\{C(OEt)(C_6H_4Me\text{-}o)C_7H_8\}$ depending on the alkylation conditions.[12] As an extension of our research on olefin-coordinated carbene complexes, we have studied the reaction of (cycloheptatriene)diiron hexacarbonyl (1)[13] with aryllithium reagents in order to investigate the effect of a binuclear central metal unit on the isomerization of an olefin ligand.

(Cycloheptatriene)diiron hexacarbonyl (1) was treated with 2 molar equiv of aryllithium, ArLi (Ar = p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-ClC_6H_4, p-$CF_3C_6H_4$, C_6Cl_5), in diethyl ether at −75 to −50 °C for 4–6 h. The resulting mixture was treated with Et_3OBF_4 in aqueous solution at 0 °C to afford orange crystalline complexes (2–6) with compositions $Fe_2(CO)_4\ \{\mu\text{-}\eta^4{:}\eta^3\text{-}C_7H_7C(OC_2H_5)Ar[\mu\text{-}C(OC_2H_5)]\}$ (Scheme I) in 40–46% yields.[14] Complexes 2–6 are formulated as cycloolefin-coordinated bridging-carbyne-isomerized carbene complexes on the basis of their elemental analyses and spectroscopic studies[15] and a single-crystal X-ray diffraction study for 5.[16]

Complexes 2–6 are soluble in both polar and nonpolar organic solvents and highly sensitive to air and temperature. Their IR spectra showed four CO absorption bands in the ν_{CO} region which indicated an $Fe_2(CO)_4$ moiety in these compounds. In the ^1H NMR spectra of 2–6, two sets of proton signals attributable to ethoxy groups (OC_2H_5) and one set of proton signal attributable to the aryl group were observed, which suggests the presence of two different ethoxy groups but of only one aryl group. The number, chemical shift, multiplicity, and integral

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(14) Typical preparation of **2**: To a solution of 0.30 g (0.81 mmol) of **1** in 50 mL of ether was added dropwise to 1.62 mmol of p-$CH_3C_6H_4Li$ at −75 °C with strong stirring. The reaction solution turned gradually from orange to orange-red. The reaction mixture was stirred at −75 to −60 °C for 4 h, during which time the orange-red solution turned dark red gradually. After removal of the solvent under high vacuum at −50 °C, to the dark red solid residue obtained was added ca. 5 g of Et_3OBF_4. The solid mixture was dissolved in 50 mL of N_2-saturated water at 0 °C with vigorous stirring and the resulting solution covered with petroleum ether (30–60 °C). Immediately afterwards Et_3OBF_4 (ca. 10 g) was added in portions, with strong stirring, to the aqueous solution until it became acidic. The aqueous solution was extracted with petroleum ether. The combined extracts were evaporated to dryness 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. A yellow band was eluted and collected. The solvent was evaporated under high vacuum, and the residue was recrystallized from petroleum ether/CH_2Cl_2 solution at −80 °C to afford 0.18 g (43%, based on **1**) of orange crystals of **2**, mp 110–112 °C dec. Anal. Calcd for $C_{24}H_{24}O_6Fe_2$: C, 55.42; H, 4.65. Found: C, 55.20; H, 4.38. IR (hexane; ν_{CO}): 2000 vs, 1990 vs, 1982 m, 1960 vs cm^{-1}. ^1H NMR (CD_3COCD_3; δ): 7.40 (d, 2H), 7.20 (d, 2H), 5.77 (m, 1H), 5.65 (m, 1H), 5.46 (dd, 2H), 4.16 (q, 2H, OCH_2CH_3), 3.60 (q, 2H, OCH_2CH_3), 2.34 (s, 3H, $C_6H_4CH_3$), 2.28 (t, 1H), 1.82 (t, 3H, OCH_2CH_3), 1.68 (m, 1H), 1.34 (m, 1H), 1.17 (t, 3H, OCH_2CH_3). MS: *m/e* 520 (M^+), 492 ($M^+ - CO$), 464 ($M^+ - 2CO$), 436 ($M^+ - 3CO$), 408 ($M^+ - 4CO$).

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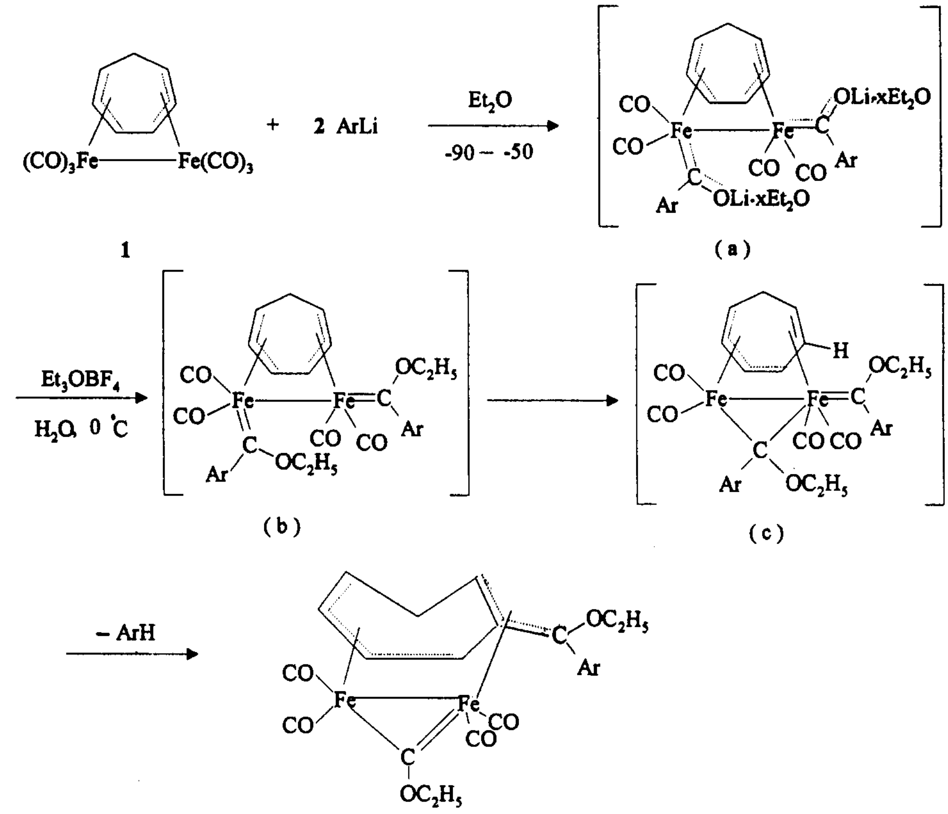
Scheme I



2, Ar = p-CH$_3$C$_6$H$_4$

3, Ar = p-CH$_3$OC$_6$H$_4$

4, Ar = p-ClC$_6$H$_4$

5, Ar = p-CF$_3$C$_6$H$_4$

6, Ar = C$_6$Cl$_5$

intensity of the proton signals attributed to the cycloheptatriene ligand are essentially different from those of 1,[13] which showed that an isomerization of the cycloheptatriene ligand had occurred in complexes 2–6.

The molecular structure of 5 (Figure 1) showed that an added ethoxy group and an aryl group are on the "carbene" carbon atom (C(60)) and the other added ethoxy group is on the bridging carbyne carbon atom (C(10)), as anticipated from the ^{1}H NMR spectrum. In the cycloolefin ligand, the C(74)–C(77) atoms in the η^4-bonding mode are bonded side-on to the Fe(1) atom, and C(71) is bonded to C(60) to form a new C–C bond, so as to cause the C(72), C(71), and C(60) atoms to form an η^3 bond to the Fe(2) atom. The Fe(1)–Fe(2) bond distance of 2.6706(7) Å in 5 is much shorter than that (2.866(1) Å) found in 1[13] but somewhat longer than that found (2.533(1) Å) in [Fe$_2$Cp$_2$(CO)$_2$(μ-CO){μ-C(CN)NHPh}].[17] The alkylidyne carbon asymmetrically bridges the Fe–Fe bond (C(10)–Fe(1) = 1.857(4), C(10)–Fe(2) = 1.804(4) Å). This asymmetry is more marked than that in [Fe$_2$Cp$_2$(CO)$_2$(μ-CO){μ-C(CN)NHPh}] (C(4)–Fe(1) = 2.004(2), C(4)–Fe(2) = 2.028(2) Å).[17] The Fe(2)–C(10) distance (1.804(4) Å) is significantly shorter than the Fe═C$_{\text{carbene}}$ bond in C$_{10}$H$_{16}$(CO)$_2$FeC(OC$_2$H$_5$)C$_6$H$_4$CH$_3$-*o* (1.915(15) Å)[9] and C$_6$H$_8$(CO)$_2$FeC(OC$_2$H$_5$)C$_6$H$_4$CH$_3$-*o* (1.89(2) Å).[18] In the di- and trimetal complexes [FeMo{μ-CC$_6$H$_4$Me-4)}(CO)$_2$(η-C$_5$H$_5$)][19a] and

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(15) Satisfactory elemental analyses were obtained for the compounds described. **3**: mp 113–114 °C dec; IR (ν_{CO}; hexane) 2002 vs, 1995 vs, 1960 vs, 1950 m cm^{-1}; ^{1}H NMR (δ, CD$_3$COCD$_3$) 7.42 (d, 2H), 6.92 (d, 2H), 5.73 (m, 1H), 5.62 (m, 1H), 5.46 (dd, 2H), 4.13 (q, 2H, OCH_2CH$_3$), 3.82 (s, 3H, C$_6$H$_4$OCH_3), 3.54 (q, 2H, OCH_2CH$_3$), 2.25 (t, 1H), 1.80 (t, 3H, OCH$_2$$CH_3$), 1.66 (m, 1H), 1.32 (m, 1H), 1.15 (t, 3H, OCH$_2$$CH_3$); MS *m/e* 536 (M$^+$). **4**: mp 117–118 °C dec; IR (ν_{CO}; hexane) 2005 vs, 1997 vs, 1968 vs, 1955 m, br cm^{-1}; ^{1}H NMR (δ; CD$_3$COCD$_3$) 7.52 (d, 2H), 7.40 (d, 2H), 5.78 (m, 1H), 5.58 (m, 1H), 5.48 (dd, 2H), 4.14 (q, 2H, OCH_2CH$_3$), 3.62 (q, 2H, OCH_2CH$_3$), 2.28 (t, 1H), 1.81 (t, 3H, OCH$_2$$CH_3$), 1.68 (m, 1H), 1.35 (m, 1H), 1.17 (t, 3H, OCH$_2$$CH_3$); MS *m/e* 540 (M$^+$). **5**: mp 116–118 °C dec; IR (ν_{CO}; hexane) 1998 sh, 1992 vs, br, 1960 s, 1940 s cm^{-1}; ^{1}H NMR (δ; CD$_3$COCD$_3$) 8.24 (m, 1H), 7.90 (m, 1H), 7.72 (m, 2H), 5.62 (m, 1H), 5.48 (dd, 2H), 4.16 (q, 2H, OCH_2CH$_3$), 3.65 (q, 2H, OCH_2CH$_3$), 2.30 (t, 1H), 1.79 (t, 3H, OCH$_2$$CH_3$), 1.72 (m, 1H), 1.33 (m, 1H), 1.19 (t, 3H, OCH$_2$$CH_3$); MS: *m/e* 574 (M$^+$). **6**: mp 120–121 °C dec; IR (ν_{CO}; hexane) 2001 vs, 1992 vs, 1982 s, 1965 s cm^{-1}; ^{1}H NMR (δ; CD$_3$COCD$_3$) 5.84 (m, 1H), 5.62 (m, 1H), 5.40 (dd, 2H), 4.52 (q, 2H, OCH_2CH$_3$), 3.56 (q, 2H, OCH_2CH$_3$), 2.24 (t, 1H), 1.74 (m, 1H), 1.38 (m, 1H), 1.30 (t, 3H, OCH$_2$$CH_3$), 1.12 (t, 3H, OCH$_2$$CH_3$); MS: *m/e* 676 (M$^+$).

(16) X-ray crystallographic data for **5**: $C2/c$, a = 24.725(8) Å, b = 14.544(2) Å, c = 13.950(1) Å, β = 103.10(6)°, V = 4886.2(2) Å^3, Z = 8, D_{calcd} = 1.561 g/cm^{-3}, μ(Mo Kα) = 12.477 cm^{-1}, F(000) = 2336, T = 298 K. Of 5618 reflections collected (0° ≤ 2θ ≤ 50°), 2094 with $I > 3\sigma(I)$ were used in the refinement of the structure. The structure solution by direct methods (MULTAN-86) revealed the metal atom coordinates, and the subsequent difference Fourier methods yielded the positions of the remaining non-hydrogen atoms. The unit-weighted anisotropic full-matrix least-squares refinement for all non-hydrogen atoms converged to R = 0.045 and R_w = 0.047 (GOF = 4.26; Δ/ρ = 0.27 e/Å^3).

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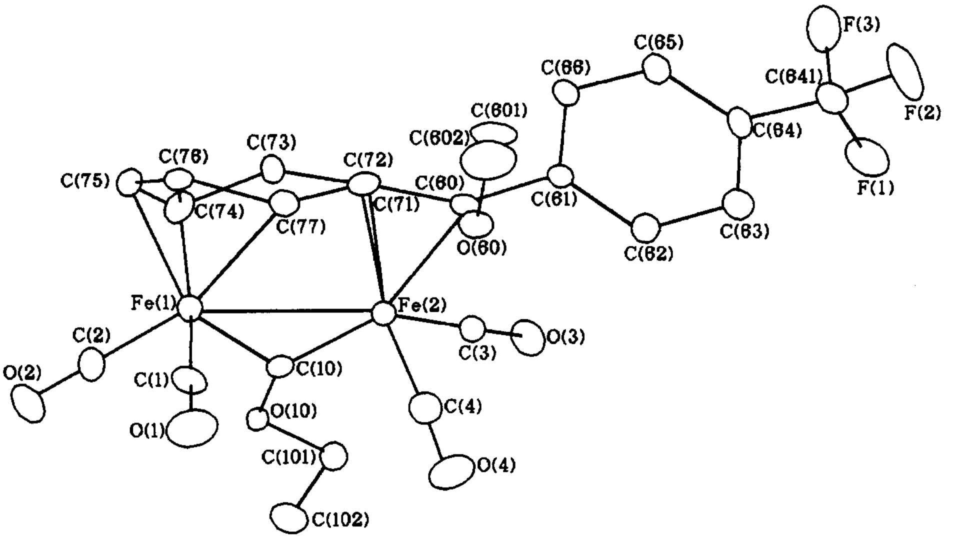

Figure 1. Molecular structure of $Fe_2(CO)_4\{\mu\text{-}\eta^4{:}\eta^3\text{-}C_7H_7C(OC_2H_5)Ar\{\mu\text{-}C(OC_2H_5)\}\}$ (**5**). Selected bond distances (Å) and angles (deg): Fe(1)–Fe(2) = 2.6706(7), Fe(1)–C(10) = 1.857(4), Fe(2)–C(10) = 1.804(4), C(10)–O(10) = 1.320(4), Fe(2)–C(60) = 2.212(3), C(60)–O(60) = 1.404(4), C(60)–C(71) = 1.417(5), Fe(1)–C(74) = 2.133(4), Fe(1)–C(75) = 2.059(5), Fe(1)–C(76) = 2.061(4), Fe(1)–C(77) = 2.2669(6), Fe(2)–C(71) = 2.011(3), Fe(2)–C(72) = 2.084(3), C(71)–C(72) = 1.421(5), C(71)–C(77) = 1.467(3), C(72)–C(73) = 1.490(5), C(73)–C(74) = 1.506(6), C(74)–C(75) = 1.429(6), C(75)–C(76) = 1.367(6), C(76)–C(77) = 1.438(5); Fe(1)–Fe(2)–C(10) = 43.9(1), Fe(1)–C(10)–Fe(2) = 93.7(2), Fe(2)–Fe(1)–C(10) = 42.4(1), Fe(2)–C(60)–O(60) = 113.1(2), Fe(2)–C(60)–C(61) = 115.3(2), Fe(2)–C(60)–C(71) = 62.9(2), Fe(1)–C(10)–O(10) = 125.9(3), Fe(2)–C(10)–O(10) =140.5(3), C(71)–C(60)–O(60) = 118.5(3), C(71)–C(60)–C(61) = 124.2(5).

$[FeReCr\{\mu\text{-}CC_6H_4Me\text{-}4)\}(CO)_{12}]$,[19b] the Fe–μ-C distances, 2.008(5) and 1.872(8) Å, respectively, are longer than those in **5**. These data strongly suggest that in **5** the Fe(2)–μ-C(10) linkage is a double bond, thus giving the Fe(2) atom an 18-electron configuration.

The Fe(2)–C(60) bond length of 2.212(3) Å is much longer than the $Fe{=}C_{carbene}$ bond in $C_{10}H_{16}(CO)_2FeC(OC_2H_5)C_6H_4CH_3\text{-}o$ and $C_6H_8(CO)_2FeC(OC_2H_5)C_6H_4CH_3\text{-}o$ and is comparable with that of the Fe–C(3) bond (2.110(7) Å) in $C_4H_6(CO)_2FeC(OC_2H_5)C_6H_4CH_3\text{-}o$[4] and the Fe–C(7) bond (2.127(6) Å) in $C_8H_8(CO)_2FeC(OC_2H_5)C_6H_5$.[5] Owing to the variation of the bond type of $Fe(2)\text{–}C(60)_{carbene}$ caused by the bonding of C(71) to the carbene carbon (C(60)), the resulting products **2**–**6** may also be regarded as isomerized carbene complexes, as described in the complexes $C_4H_6(CO)_2FeC(OC_2H_5)Ar$.[4]

A possible mechanism for the formation of these complexes (Scheme I) might involve the unstable diethoxycarbene complex b formed by the alkylation of the acylmetalate intermediate a (cf. the reaction[20,21] of $Re_2(CO)_{10}$ with $LiSiPh_3$). The intermediate b then isomerizes to the bridging carbene complex intermediate c owing to its lability (cf. ref 21). There are several known examples of this kind of complex.[22] Further isomerization of c (cf. the reaction of (cyclooctatetraene)tricarbonyliron[5] and (tetrafluorobenzobicyclo[2.2.2]octatriene)tricarbonyliron[6]) affords the final products **2**–**6**, via an elimination of the arene (ArH) which leads to the formation of the Fe(2)–μ-C double bond and the linkage of the carbene carbon C(60) to the cycloheptatriene ring.

A number of dimetal bridging carbyne complexes have been synthesized by Stone et al. by reactions[19] of alkylidyne complexes with low-valent metal species or by reactions[23] of anionic carbyne complexes with cationic metal compounds. Complexes **2**–**6**, as dimetal complexes with a bridging carbyne ligand, were the novel and unexpected products of the reactions of an olefin-ligated metal carbonyl compound with aryllithium reagents followed by alkylation with Et_3OBF_4. Undoubtedly, this is a direct, simple, and convenient method for the preparation of such dimetal bridging carbyne complexes.

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Supplementary Material Available: Text giving synthetic procedures for **3**–**6** and tables of X-ray crystal structure data for **5** (14 pages). Ordering information is given on any current masthead page.

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