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Reactions of di-μ-carbonyl-*cis*-μ-(1-5-η:1′-5′-η-dicyclopentadienyl-dimethylsilane) bis(carbonyliron) with aryllithium reagents. Crystal structures of $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OC_2H_5)C_6H_5\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ and $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OC_2H_5)C_6H_4OCH_3\text{-}p\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$

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Abstract

The reactions of di-μ-carbonyl-*cis*-μ-(1-5-η:1′-5′-η-dicyclopentadienyl-dimethyl silane)bis(carbonyliron), $[Fe_2(\mu\text{-}CO)_2(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**1**), with aryllithium reagents, ArLi (Ar = C_6H_5, *o*-, *m*-, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-ClC_6H_4, *p*-$CF_3C_6H_4$), in ether at low temperature afforded acylmetalate intermediates, followed by alkylation with Et_3OBF_4 in aqueous solution at 0°C or in CH_2Cl_2 at −30°C gave the (dicyclopentadienyldimethylsilane)diiron bridging alkoxycarbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**2**, Ar = C_6H_5; **3**, Ar = *o*-$CH_3C_6H_4$; **4**, Ar = *m*-$CH_3C_6H_4$; **5**, Ar = *p*-$CH_3C_6H_4$; **6**, Ar = *p*-$CH_3OC_6H_4$; **7**, Ar = *p*-ClC_6H_4; **8**, Ar = *p*-$CF_3C_6H_4$), among which the structures of **2** and **6** have been established by X-ray diffraction studies. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Reactions; Diiron; Aryllithium reagents; Bridging carbene complexes; Crystal structures

1. Introduction

The increasing interest in the synthesis, structure and chemistry of a variety of metal–metal bonded cluster complexes stems largely from the fact that many such complexes are well-known to have important roles in many catalytic reactions [1–3]. Since many metal complexes that contain bridging carbene and carbyne ligands are themselves metal clusters or are the precursors of metal cluster complexes, the chemistry of transition metal bridging carbene and carbyne complexes is an area of current interest. In this regards, we are interested in developing the methodologies of the synthesis of transition metal bridging carbene and carbyne complexes. Metal complexes that contain bridging carbene and carbyne ligands have been examined extensively by Stone and co-workers. A wide variety of dimetal bridging carbene and carbyne complexes have been synthesized by Stone and co-workers by reactions [4–6] of carbene and carbyne complexes with low-valent metal species or by reactions [7] of neutral and anionic carbyne complexes with metal hydrides and cationic metal compounds. In our laboratory, one of the methods for preparation of the bridging carbene and carbyne complexes is to conduct the reactions of the highly electrophilic cationic carbyne complexes of manganese and rhenium, $[\eta^5\text{-}C_5H_5\text{-}(CO)_2M\equiv CPh]BBr_4$ (M = Mn or Re), with carbonylmetal anion compounds. We found that both cationic carbyne complexes reacted not only with carbonylmetal monoanionic compounds such as $[NMe_4][FeH(CO)_4]$, $Li[Co(CO)_4]$, $Na[\eta^5\text{-}C_5H_5\text{–}M(CO)_3]$ (M = Mo, W), and $Na[Co(CO)_3PPh_3]$ but also with carbonylmetal dianionic compounds such as $Na_2[Fe(CO)_4]$, $[NEt_4]_2[Fe_2(CO)_8]$, $Na_2[Fe_3(CO)_{11}]$, and $Na_2[W(CO)_5]$, and mixed-dimetal carbonyl anion compounds such as $[N(Ph_3P)_2][FeCo(CO)_8]$ and $[N(Ph_3P)_2][WCo(CO)_9]$ to form the heteronuclear

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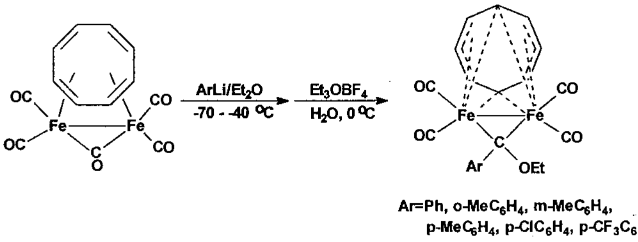
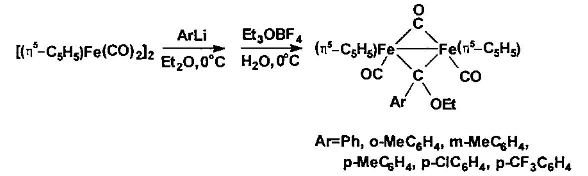
dimetal bridging carbene and/or bridging carbyne complexes [8–10]. Recently, we found another new method for preparation of the dimetal bridging carbene and carbyne complexes: the reactions of olefin-ligated dimetal carbonyl compounds with nucleophilic aryllithium reagents, followed by alkylation with alkylating reagent. For instance, the reactions of pentacarbonyl-(cyclooctatetraene)diiron and bis(η^5-cyclo-pentadienyl)diiron tetracarbonyl with aryllithium reagents followed by alkylation with Et_3OBF_4 gave the olefin-coordinated dimetal bridging alkoxycarbene complexes $[Fe_2\{\mu\text{-}C(OEt)Ar\}(CO)_4(C_8H_8)]$ [11] (Scheme 1) and $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OEt)Ar\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ [12] (Scheme 2), respectively. This offers a new and useful method for preparation and structural modification of the dimetal bridging carbene complexes.

In order to examine the scope of this new synthetic method for dimetal bridging of carbene complexes and the structural modification of the dimetal bridging carbene complexes, and to explore the effect of different olefin ligands on the reaction products, we synthesized di-μ-carbonyl-*cis*-μ-(1-5-η:1′-5′-η-dicyclopentadienyldimethylsilane)bis(carbonyliron), $[Fe_2(\mu\text{-}CO)_2(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**1**), as starting material for use in reactions with aryllithium reagents. These reactions produced a series of (dicyclopentadienyldimethylsilane)diiron bridging alkoxycarbene complexes. In this work we describe these unusual reactions and the structural characterizations of the resulting products.



Scheme 1.



Scheme 2.

2. Experimental

All procedures were performed under a dry, oxygen-free N_2 atmosphere using standard Schlenk techniques. Solvents 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 petroleum ether (30–60°C) and CH_2Cl_2 were distilled from CaH_2. The neutral alumina (Al_2O_3, 200–300 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. Compound $[Fe_2(\mu\text{-}CO)_2(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**1**) [13], Et_3BF_4 [14], and aryllithium reagents [15–20] were prepared by literature methods.

The IR spectra were measured on a Perkin–Elmer 983G spectrophotometer. All ^1H-NMR spectra were recorded at ambient temperature in acetone-d_6 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 nitrogen-filled capillaries are uncorrected.

2.1. Preparation of $[Fe_2(\mu\text{-}CO)_2(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (1)

We provide full details of this preparation since neither its synthesis nor experimental procedure were referred to in the Ref. [13]. A Schlenk flask was charged with dicyclopentadienyldimethylsilane (4.00 g, 21.50 mmol), *n*-octane (75 ml), and $Fe(CO)_5$ (5.50 ml (7.85 g, 40.10 mmol)). The mixture was heated at 135°C to reflux under a N_2 atmosphere for 20 h, during which time the orange solution turned dark brown-red. The resulting mixture was cooled to room temperature and then evaporated under vacuum to dryness. The residue was chromatographed on Al_2O_3 with petroleum ether as the eluant. The brown-red band was eluted and collected. After vacuum removal of the solvent, the crude product was recrystallized from petroleum ether or petroleum ether–CH_2Cl_2 at -30°C to give purple-red crystals of complex **1** (7.80 g (47%, based on $Fe(CO)_5$)), m.p. 150°C (dec.); IR (CH_2Cl_2) ν(CO) 1995 (vs, br), 1955 (vs), 1767 (vs, br) cm^{-1}. ^1H-NMR (CD_3COCD_3): δ 5.60 (t, 4H, C_5H_4), 5.20 (t, 4H, C_5H_4), 0.43 (s, 6H, $Si(CH_3)_2$). MS: m/e 410 (M^+), 382 ($M^+ - CO$), 354 ($M^+ - 2CO$), 326 ($M^+ - 3CO$), 298 ($M^+ - 4CO$), 242 $[(C_5H_4)_2Si(CH_3)_2Fe^+]$. Anal. Calc. for $C_{16}H_{14}Fe_2SiO_4$: C, 46.86; H, 3.44. Found: C, 46.66; H, 3.70%.

2.2. Reaction of 1 with C_6H_5Li to give $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OC_2H_5)C_6H_5\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (2)

2.2.1. Alkylation in H_2O

C_6H_5Li (1.34 mmol) was added dropwise with stirring within 15 min to a solution of complex **1** (0.410 g, 1.00 mmol) dissolved in ether (80 ml) at -20°C [15]. The reaction mixture was stirred at -20 to -10°C for

2 h, during which time the orange–red solution gradually turned blackish red. The resulting solution then evaporated under high vacuum at − 20°C to dryness. To the blackish solid residue obtained was added Et_3OBF_4 [14] (ca. 5 g). This solid mixture was dissolved in N_2-saturated water (50 ml) at 0°C with vigorous stirring and the mixture covered with petroleum ether (30–60°C). Immediately afterwards, Et_3OBF_4 (ca. 10 g) was added portionwise to the aqueous solution, with strong stirring, until it became acidic. The aqueous solution was extracted with petroleum ether. After removal of the solvent under vacuum, the dark brown residue was chromatographed on an alumina (neutral) column (1.6 × 15–20 cm) at − 25°C with 15:1 petroleum ether–CH_2Cl_2 as the eluant. The solvent was removed in vacuo and the residue was recrystallized from 10:1 petroleum ether–CH_2Cl_2 at − 80°C to give purple-red crystals of complex **2** (0.43 g (83%, based on **1**)); m.p. 130–132°C (dec.); IR (CH_2Cl_2) ν(CO) 1995 (w), 1972 (vs, br), 1750 (s, br) cm^{-1}. ^{1}H-NMR (CD_3COCD_3): δ 7.66 (d, 2H, C_6H_5), 7.16 (t, 2H, C_6H_5), 7.04 (t, 1H, C_6H_5), 6.05 (m, 2H, C_5H_4), 5.41 (m, 2H, C_5H_4), 5.15 (m, 2H, C_5H_4), 4.84 (m, 2H, C_5H_4), 3.53 (q, 2H, OCH_2CH_3), 1.25 (t, 3H, OCH_2CH_3), 0.50 (s, 3H, $Si(CH_3)_2$), 0.43 (s, 3H, $Si(CH_3)_2$). MS: *m/e* 516 (M^+), 488 ($M^+ - CO$), 460 ($M^+ - 2CO$), 432 ($M^+ - 3CO$), 375 ($M^+ - 3CO–COC_2H_5$), 298 ($M^+ - 3CO–COC_2H_5–C_6H_5$), 242 [$(C_5H_4)_2Si(CH_3)_2Fe^+$]. Anal. Calc. for $C_{24}H_{24}Fe_2SiO_4$: C, 55.84; H, 4.69. Found: C, 55.75; H, 4.54%.

2.2.2. Alkylation in CH_2Cl_2

Complex **1** (0.410 g, 1.00 mmol) was treated with C_6H_5Li (1.34 mmol), as described above in Section 2.2.1, in ether at − 20 to − 10°C for 2 h. After removal of the solvent under vacuum at − 20°C, the residue was dissolved in CH_2Cl_2 (30 ml) at − 60°C. To this solution of Et_3OBF_4 (0.250 g, 1.31 mmol) dissolved in CH_2Cl_2 (10 ml) was added dropwise with stirring within 15 min. The reaction mixture turned from dark brown to brown-red. After being stirred at − 40 to − 30°C for 1 h, the solvent was removed in vacuo at − 30°C. Further treatment of the resulting mixture as described above gave the purple-red crystalline complex **2** (0.44 g (85%, based on **1**)) which was identified by its melting point, IR, ^{1}H-NMR and mass spectra.

2.3. Reaction of **1** with o-$CH_3C_6H_4Li$ to give [$Fe_2(\mu$-CO){μ-C(OC_2H_5)$C_6H_4CH_3$-o}-$(CO)_2$-{(η^5-$C_5H_4)_2Si(CH_3)_2$}] (**3**)

Similar to the procedures described above for the reaction in Section 2.2.1, complex **1** (0.410 g, 1.00 mmol) with *o*-$CH_3C_6H_4Li$ (1.34 mmol) [16] at − 20 to − 10°C for 2 h. The subsequent alkylation and further treatment in a similar manner as described for the reaction in Section 2.2.1 afforded complex **3** (0.48 g (91%, based on **1**)) as purple-red crystals; m.p. 150–152°C (dec.); IR (CH_2Cl_2) ν(CO) 1984 (m), 1961 (vs, br), 1748 (vs, br) cm^{-1}. ^{1}H-NMR (CD_3COCD_3):δ 7.30–6.96 (m, 4H, $C_6H_4CH_3$), 5.48 (m, 2H, C_5H_4), 5.06 (m, 4H, C_5H_4), 4.67 (m, 2H, C_5H_4), 3.42 (q, 2H, OCH_2CH_3), 2.18 (s, 3H, $C_6H_4CH_3$), 0.86 (t, 3H, OCH_2CH_3), 0.33 (s, 6H, $Si(CH_3)_2$). MS: *m/e* 530 (M^+), 502 ($M^+ - CO$), 474 ($M^+ - 2CO$), 446 ($M^+ - 3CO$), 389 ($M^+ - 3CO–COC_2H_5$), 312 ($M^+ - 3CO–COC_2H_5–C_6H_5$), 242 [$(C_5H_4)_2Si(CH_3)_2Fe^+$]. Anal. Calc. for $C_{25}H_{26}Fe_2SiO_4$: C, 56.63; H, 4.94. Found: C, 56.38; H, 5.06%.

2.4. Reaction of **1** with m-$CH_3C_6H_4Li$ to give [$Fe_2(\mu$-CO){μ-C(OC_2H_5)$C_6H_4CH_3$-m}$(CO)_2$-{(η^5-$C_5H_4)_2Si(CH_3)_2$}] (**4**)

2.4.1. Alkylation in H_2O

The reaction of complex **1** (0.410 g, 1.00 mmol) with *m*-$CH_3C_6H_4Li$ (1.34 mmol) [16] was prepared as described above in Section 2.2.1 at − 20 to − 10°C for 2 h. After evaporation of the solvent in vacuo, subsequent alkylation and further treatment of the resulting residue in a manner similar to that described in Section 2.2.1 deep purple-red crystals of complex **4** (0.436 g (82%, based on **1**)) were yielded, m.p. 134–135°C (dec.). IR (CH_2Cl_2)ν(CO) 1972 (vs, br), 1939 (w), 1748 (vs, br) cm^{-1}. ^{1}H-NMR (CD_3COCD_3): δ 7.45 (t, 2H, $C_6H_4CH_3$), 7.05 (t, 1H, $C_6H_4CH_3$), 6.85 (m, 1H, $C_6H_4CH_3$), 6.04 (m, 2H, C_5H_4), 5.61 (m, 1H, CH_2Cl_2), 5.41 (m, 2H, C_5H_4), 5.15 (m, 2H, C_5H_4), 4.83 (m, 2H, C_5H_4), 3.54 (q, 2H, OCH_2CH_3), 2.28 (s, 3H, $C_6H_4CH_3$), 1.26 (t, 3H, OCH_2CH_3), 0.49 (s, 3H, $Si(CH_3)_2$), 0.43 (s, 3H, $Si(CH_3)_2$). MS: *m/e* 530 (M^+), 502 ($M^+ - CO$), 474 ($M^+ - 2CO$), 446 ($M^+ - 3CO$), 389 ($M^+ - 3CO–COC_2H_5$), 312 ($M^+ - 3CO–COC_2H_5–C_6H_5$), 242 [$(C_5H_4)_2Si(CH_3)_2Fe^+$], 84 [$CH_2Cl_2^+$]. Anal. Calc. for $C_{25}H_{26}Fe_2SiO_4$1/2CH_2Cl_2: C, 53.48; H, 4.75. Found: C, 53.45; H, 4.61%.

2.4.2. Alkylation in CH_2Cl_2

Complex **1** (0.410 g, 1.00 mmol) was treated as described in Section 2.2.1 with *m*-$CH_3C_6H_4Li$ (1.34 mmol) in ether at − 20 to − 10°C for 2 h. Further treatment of the resulting mixture in a manner similar to that described in Section 2.2.2 yielded complex **4** (0.43 g (81%, based on **1**)) as deep purple-red crystals which was identified by its m.p., IR, ^{1}H-NMR and mass spectra.

2.5. Reaction of **1** with p-$CH_3C_6H_4Li$ to give $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OC_2H_5)C_6H_4CH_3\text{-}p\}\text{-}(CO)_2\text{-}\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**5**)

Similarly, complex **1** (0.410 g, 1.00 mmol) dissolved in ether (60 ml) was treated with *p*-$CH_3C_6H_4Li$ (1.34 mmol) [16] at −20 to −10°C for 2 h, followed by alkylation; further treatment as described above for the reaction in Section 2.2.1 produced deep purple-red crystals of complex **5** (0.46 g (87%, based on **1**)), m.p. 119–121°C (dec.). IR (CH_2Cl_2) ν(CO) 1972 (vs, br), 1748 (vs, br) cm^{-1}. ^1H-NMR (CD_3COCD_3): δ 7.52 (d, 2H, $C_6H_4CH_3$), 6.97 (d, 2H, $C_6H_4CH_3$), 6.04 (m, 2H, C_5H_4), 5.40 (m, 2H, C_5H_4), 5.15 (m, 2H, C_5H_4), 4.82 (m, 2H, C_5H_4), 3.52 (q, 2H, OCH_2CH_3), 2.24 (s, 3H, $C_6H_4CH_3$), 1.23 (t, 3H, OCH_2CH_3), 0.49 (s, 3H, $Si(CH_3)_2$), 0.42 (s, 3H, $Si(CH_3)_2$). MS: *m*/*e* 530 (M^+), 502 ($M^+ - CO$), 474 ($M^+ - 2CO$), 446 ($M^+ - 3CO$), 389 ($M^+ - 3CO–COC_2H_5$), 312 ($M^+ - 3CO–COC_2H_5–C_6H_5$), 242 [$(C_5H_4)_2Si(CH_3)_2Fe^+$]. Anal. Calc. for $C_{25}H_{26}Fe_2SiO_4$: C, 56.63; H, 4.94. Found: C, 56.16; H, 4.73%.

2.6. Reaction of **1** with p-$CH_3OC_6H_4Li$ to give $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OC_2H_5)\text{-}C_6H_4OCH_3\text{-}p\}(CO)_2\text{-}\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**6**)

A solution of *p*-$CH_3OC_6H_4Br$ (0.283 g, 1.50 mmol) in ether (20 ml) was mixed with *n*-C_4H_9Li (1.50 mmol) [17]. After 30 min stirring at room temperature, the resulting ether solution of *p*-$CH_3OC_6H_4Li$ [18] was reacted, as described in Section 2.2.1, with complex **1** (0.410 g (1.00 mmol)) at −20 to −5°C for 2 h. After vacuum removal of the solvent at −30°C, the residue was dissolved in CH_2Cl_2 (30 ml) at −70°C. To this solution was added dropwise Et_3OBF_4 (0.250 g, 1.32 mmol) dissolved in CH_2Cl_2 (10 ml) with stirring within 15 min. After being stirred at −40 to −30°C for 1 h, the solvent was removed under vacuum. Further treatment of the residue as described for the preparation of **2** gave the deep brown-red crystalline complex **6** (0.46 g (84%, based on **1**)), m.p. 118–119°C (dec.). IR (CH_2Cl_2) ν(CO) 1994 (w), 1971 (vs, br), 1748 (vs, br) cm^{-1}. ^1H-NMR (CD_3COCD_3) δ 7.56 (dd, 2H, $C_6H_4OCH_3$), 6.71 (dd, 2H, $C_6H_4OCH_3$), 6.05 (m, 2H, C_5H_4), 5.40 (m, 2H, C_5H_4), 5.14 (m, 2H, C_5H_4), 4.82 (m, 2H, C_5H_4), 3.74 (s, 3H, $C_6H_4OCH_3$), 3.53 (q, 2H, OCH_2CH_3), 1.26 (t, 3H, OCH_2CH_3), 0.49 (s, 3H, $Si(CH_3)_2$), 0.42 (s, 3H, $Si(CH_3)_2$). MS: *m*/*e* 546 (M^+), 518 ($M^+ - CO$), 490 ($M^+ - 2CO$), 462 ($M^+ - 3CO$), 405 ($M^+ - 3CO–COC_2H_5$), 328 ($M^+ - 3CO–COC_2H_5$-C_6H_5), 242 [$(C_5H_4)_2Si(CH_3)_2Fe^+$]. Anal. Calc. for $C_{25}H_{26}Fe_2SiO_5$: C, 54.97; H, 4.80. Found: C, 54.78; H, 4.79%.

2.7. Reaction of **1** with p-ClC_6H_4Li to give $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OC_2H_5)C_6H_4Cl\text{-}p\}\text{-}(CO)_2\text{-}\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**7**)

n-C_4H_9Li (1.87 mmol) was added to a solution of *p*-ClC_6H_4Br (0.237 g, 1.25 mmol) in ether (20 ml) at −20°C. After stirring at room temperature for 30 min, the resulting solution of *p*-ClC_6H_4Li [19] was reacted, in a manner similar to that for the reaction of complex **1** with C_6H_5Li, with complex **1** (0.410 g, 1.00 mmol) in ether (60 ml) at −40 to −10°C for 4 h. Subsequent alkylation and further treatment similar to that used in Section 2.2.2 yielded the purple-red crystalline **7** (0.47 g (85%, based on **1**)), m.p. 137–138°C (dec.). IR (CH_2Cl_2) ν(CO) 1993 (v), 1973 (vs, br),1765 (s, br) cm^{-1}. ^1H-NMR (CD_3COCD_3):δ 7.67 (d, 2H, C_6H_4Cl), 7.17 (d, 2H, C_6H_4Cl), 6.05 (m, 2H, C_5H_4), 5.60 (m, 2H, C_5H_4), 5.16 (m, 2H, C_5H_4), 4.85 (m, 2H, C_5H_4), 3.57 (q, 2H, OCH_2CH_3), 1.28 (t, 3H, OCH_2CH_3), 0.50 (s, 3H, $Si(CH_3)_2$), 0.43 (s, 3H, $Si(CH_3)_2$). MS: *m*/*e* 550 (M^+), 522 ($M^+ - CO$), 494 ($M^+ - 2CO$), 466 ($M^+ - 3CO$), 409 ($M^+ - 3CO–COC_2H_5$), 242 [$(C_5H_4)_2Si(CH_3)_2Fe^+$]. Anal. Calc. for $C_{24}H_{23}ClFe_2SiO_4$: C, 52.35; H, 4.21. Found: C, 51.95; H, 4.22%.

2.8. Reaction of **1** with p-$CF_3C_6H_4Li$ to give $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OC_2H_5)C_6H_4CF_3\text{-}p\}\text{-}(CO)_2\text{-}\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**8**)

A solution of *p*-$CF_3C_6H_4Br$ (0.338 g, 1.50 mmol) in ether (20 ml) was mixed with *n*-C_4H_9Li (1.50 mmol). After 40 min stirring at room temperature, the resulting ether solution of *p*-$CF_3C_6H_4Li$ [20] was reacted, as described in Section 2.2.1, with **1** (0.410 g, 1.00 mmol) at −20 to 0°C for 3 h, followed by alkylation; further treatment as described in Section 2.2.2 gave bright purple-red crystals of complex **8** (0.52 g (89%, based on **1**)), m.p. 145–146°C (dec.). IR (CH_2Cl_2) ν(CO) 1974 (vs, br), 1939 (w), 1763 (s, br) cm^{-1}. ^1H-NMR (CD_3COCD_3):δ 7.86 (d, 2H,$C_6H_4CF_3$), 7.50 (d, 2H, $C_6H_4CF_3$), 6.09 (m, 2H, C_5H_4), 5.48 (m, 2H, C_5H_4), 5.20 (m, 2H, C_5H_4), 4.88 (m, 2H, C_5H_4), 3.50 (q, 2H, OCH_2CH_3), 1.29 (t, 3H, OCH_2CH_3), 0.51 (s, 3H, $Si(CH_3)_2$), 0.45 (s, 3H, $Si(CH_3)_2$). MS: *m*/*e* 584 (M^+), 556 ($M^+ - CO$), 528 ($M^+ - 2CO$), 500 ($M^+ - 3CO$), 443 ($M^+ - 3CO–COC_2H_5$), 242 [$(C_5H_4)_2Si–(CH_3)_2Fe^+$]. Anal. Calc. for $C_{25}H_{23}Fe_2F_3SiO_4$: C, 52.84; H, 3.97. Found: C, 52.55; H, 3.99%.

2.9. X-ray crystal structure determinations of complexes **2** and **6**

The single crystals of **2** and **6** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether–CH_2Cl_2 solution at −80°C. Single crystals were mounted on a glass fibre and sealed with epoxy glue. The X-ray diffraction intensity data

Table 1
Crystal data and experimental details for complexes **2** and **6**

	2	**6**
Formula	$C_{24}H_{24}O_4SiFe_2$	$C_{25}H_{26}O_5SiFe_2$
Formula weight	516.23	546.26
Space group	$P2_1/n$ (no.14)	$P2_1/c$ (no.14)
a (Å)	10.160(1)	16.486(9)
b (Å)	18.180(4)	9.021(6)
c (Å)	12.563(2)	16.834(9)
β (°)	96.86(1)	98.86(4)
V (Å^3)	2304.0(7)	2473(2)
Z	4	4
D_{calc} (g cm^{-3})	1.488	1.467
F (000)	1064.00	1128.00
μ (Mo–K_α) (cm^{-1})	13.37	12.53
Radiation (monochromated in incident beam)	Mo–K_α ($\lambda = 0.71069$ Å)	Mo–K_α ($\lambda = 0.71069$ Å)
Diffractometer	Rigaku AFC7R	Rigaku AFC7R
Temperature (°C)	20	20
Orientation reflections: no.; range (2θ), (°)	25; 18.6−24.7	16; 10.4−19.6
Scan method	ω–2θ	ω–2θ
Data collection range, 2θ (°)	5–50	5–45
No.of unique data, total	3872	2684
No.of unique data with $I > 2.00\sigma(I)$	2280	974
No.of parameters refined	281	273
Correction factors, max./min.	0.8699–1.0000	0.8683–1.1290
R [a]	0.042	0.074
R_w [b]	0.043	0.065
Quality-of-fit indicator [c]	1.14	1.91
Largest shift /esd. final cycle	0.00	0.00
Largest peak, e$^-$ Å^{-3}	0.28	0.50
Minimum peak, e$^-$ Å^{-3}	−0.29	−0.47

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

[b] $R_w = [\Sigma w\,(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$

[c] Quality-of-fit $= [\Sigma w\,(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$

for 3872 and 2684 independent reflections, of which 2280 and 974 with $I > 2.00\sigma(I)$ for **2** and **6** were observable, were collected with a Rigaku AFC7R diffractometer at 20°C using Mo–K_α radiation with an ω–2θ scan mode within the ranges $5° \leq 2\theta \leq 50°$ for **2**, and $5° \leq 2\theta \leq 45°$ for **6**, respectively.

The structures of **2** and **6** were solved by direct methods and expanded using Fourier techniques. For **2**, the non-hydrogen atoms were refined anisotropically. For **6**, some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. For both complexes, the hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was respectively based on 2280 and 974 observed reflections and 281, and 273 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.042$ and $R_W = 0.043$ for **2** and $R = 0.074$ and $R_W = 0.065$ for **6**, respectively. All the calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

The details of the crystallographic data and the procedures used for data collection and reduction information for **2** and **6** 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 **2** and **6** are given in the Supporting Information. The molecular structures of **2** and **6** are given in Figs. 1 and 2, respectively.

3. Results and discussion

Similar to the reactions of (cyclooctatetraene)diiron hexacarbonyl and bis(μ-cyclopentadienyl)diiron tetracarbonyl with aryllithium reagents [11,12], di-μ-carbonyl-*cis*-μ-(1-5-η:1′-5′-η-dicyclopentadienyldimethylsilane)bis(carbonyliron), $[Fe_2(\mu\text{-}CO)_2(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**1**), was treated with a 30–35% molar excess of aryllithium reagents, ArLi (Ar = C_6H_5, *o*-, *m*-, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-ClC_6H_4, *p*-$CF_3C_6H_4$), in ether at low temperature afforded acylmetalate intermediates, followed by alkylation with Et_3OBF_4 in aqueous solution at 0°C or in CH_2Cl_2 at −30°C. After removal of the solvents under vacuum at low temperature, the residues were chromatographed on an alumina column at −20 to −25°C, and the crude products were recrystallized from petroleum ether–CH_2Cl_2 solution at −80°C to give purple-red crystalline complexes **2**–**8** with the compositions $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (Scheme 3) in 81–91% isolated yields.

Complexes **2**–**8** are formulated as the (dicyclopentadienyldimethylsilane)diiron bridging alkoxy(aryl)carbene complexes on the basis of their elemental analyses, spectroscopic studies, and the single-crystal X-ray diffraction studies of complexes **2** and **6**. Complexes **2**–**8** are the first examples of silyl-bridged dicyclopentadienyl dimetal complexes with a bridging carbene ligand, in which the dicyclopentadienyl–dimethylsilane ligand coordinates the two iron atoms through its two cyclopenta-dienyl ring in η^5-bonding.

There are two bridging CO ligands which have the same chemical environment in the starting material **1**. Therefore it was expected that di-bridging alkoxy(aryl)carbene diiron complexes should exist in the resulting products when treating complex **1** with aryllithium reagents. However, no expected di-bridging alkoxy(aryl)carbene diiron complexes or their derivatives were obtained from the reactions even though more than two molar equivalents of aryllithium reagent were used for the reactions.

In addition, complex **1** has two forms of coordinated carbonyl ligands, terminal and bridging CO. It was expected that the aryllithium reagents could attack both terminal CO and bridging CO to produce an alkoxy-

Table 2
Selected bond lengths (Å) [a] and angles (°) [a] for complexes **2** and **6**

	2	**6**		**2**	**6**
Fe(1)–Fe(2)	2.513(1)	2.503(6)	C(1)–C(2)	1.522(7)	1.49(3)
Fe(1)–C(1)	2.023(5)	2.04(2)	C(1)–O(4)	1.413(6)	1.44(3)
Fe(2)–C(1)	2.021(5)	2.05(3)	O(4)–C(26)	1.410(7)	1.44(3)
Fe(1)–C(10)	1.897(6)	1.75(3)	C(26)–C(27)	1.469(8)	1.50(4)
Fe(2)–C(10)	1.914(6)	2.02(4)	Si–C(17)	1.863(6)	1.85(3)
C(10)–O(2)	1.178(6)	1.23(4)	Si–C(18)	1.862(6)	1.85(3)
Fe(1)–C(8)	1.746(6)	1.73(3)	Si–C(23)	1.824(7)	1.84(3)
C(8)–O(1)	1.156(6)	1.14(2)	Si–C(24)	1.849(7)	1.84(3)
Fe(2)–C(9)	1.735(6)	1.68(3)	Fe(1)–C(Cp) (avg.)	2.118	2.112
C(9)–O(3)	1.152(6)	1.22(3)	Fe(2)–C(Cp) (avg.)	2.128	2.118
Fe(1)–Fe(2)–C(1)	51.6(1)	52.2(7)	Fe(2)–C(1)–C(2)	123.1(4)	114(1)
Fe(1)–C(1)–Fe(2)	76.9(2)	75.4(9)	Fe(1)–C(10)–O(2)	139.2(5)	160(3)
Fe(2)–Fe(1)–C(1)	51.5(1)	52.4(8)	Fe(2)–C(10)–O(2)	138.3(5)	116(2)
Fe(1)–Fe(2)–C(10)	48.4(2)	43.9(9)	Fe(1)–C(8)–O(1)	174.7(5)	174(2)
Fe(1)–C(10)–Fe(2)	82.5(2)	82(1)	Fe(2)–C(9)–O(3)	173.8(5)	173(2)
Fe(2)–Fe(1)–C(10)	49.0(2)	53(1)	Fe(1)–C(17)–Si	120.4(3)	121(1)
C(1)–Fe(1)–C(10)	97.3(2)	101(1)	Fe(2)–C(18)–Si	119.5(4)	119(1)
C(1)–Fe(2)–C(10)	96.8(2)	93(1)	C(17)–Si–C(18)	106.8(2)	106(1)
Fe(1)–C(1)–O(4)	113.5(3)	111(1)	C(1)–C(2)–C(3)	119.1(5)	120(2)
Fe(1)–C(1)–C(2)	117.6(3)	127(1)	C(1)–C(2)–C(7)	124.1(5)	121(2)
Fe(2)–C(1)–O(4)	113.2(3)	110(1)	O(4)–C(26)–C(27)	110.4(5)	108(2)

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

(aryl)arbene and a bridging alkoxy(aryl)carbene complexes when treating complex **1** with aryllithium reagents. However, only diiron bridging alkoxycarbene complexes were obtained, which could be produced via an attack of nucleophilic aryllithium reagents on a bridging CO of complex **1**. In fact, it is uncertain whether the nucleophilic attack in the initial step occurs actually on the bridging CO or the terminal CO. Brown et al. [21] and Koelle [22] have shown that the nucleophilic attack on the coordinated carbonyls relates to the electron density at CO. In general, the CO having a lower electron density is easily attacked by nucleophiles. Atwood et al. [23], based on the experimental results of the reaction of bis(η-cyclopentadienyl)diiron tetracarbonyl with $LiAlH_4$ and according to the viewpoint of Brown and Koelle et al., presumed that in the initial step of the reaction process, the nucleophilic hydride attack at coordinated carbonyl occurred on the terminal CO having a lower electron density but not on the bridging CO having a higher electron density [24]. Our results of the reactions of **1** with the aryllithium reagents seem to be contrary to the experimental results of Atwood et al. However, we consider that the reaction of a carbonylmetal compound having two forms of coordinating CO groups (terminal and bridging CO) with a nucleophilic reagent is very complicated. The reaction course and resulting product of the carbonylmetal compound with nucleophile depend not only on the structure of the metal carbonyls themselves but also on the nucleophilic ability of the nucleophile and the stability of the acylmetalate intermediate formed by the reaction of carbonylmetal compound with nucleophile, as well as the experimental conditions and others. Under a different experimental system, the reaction pathway could be different. As for the reaction of complex

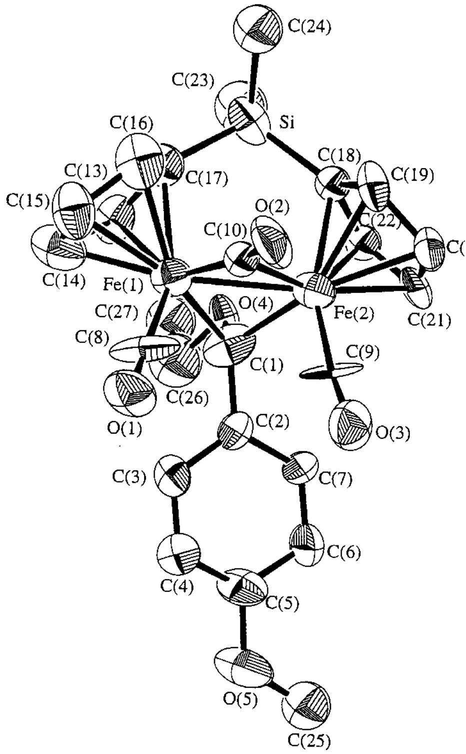


Fig. 1. Molecular structure of **2**, showing the atomic numbering scheme. Thermal ellipsoids are shown at 40% probability.

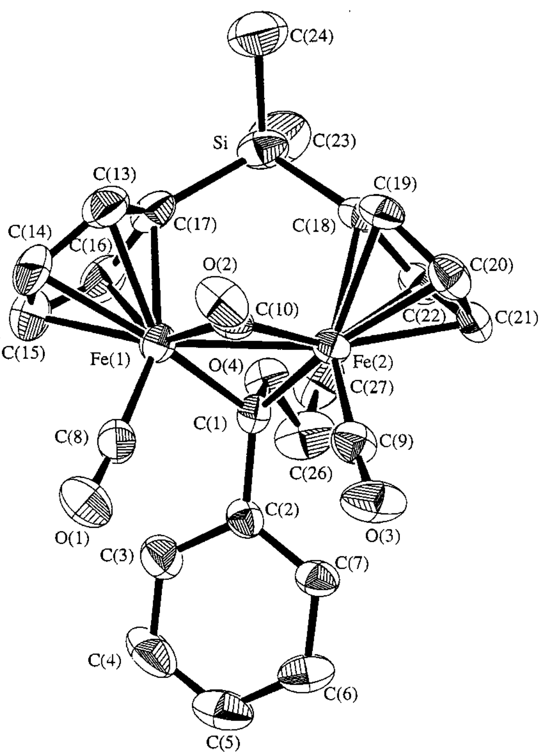
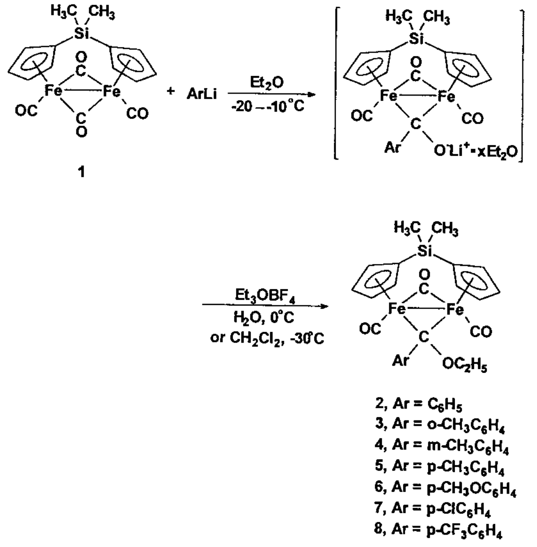


Fig. 2. Molecular structure of **6**, the atomic numbering scheme with 40% thermal ellipsoids.



Scheme 3.

1 with aryllithium reagents under the present conditions, the nucleophilic aryllithium attack in the initial step occurred on the bridging CO that is possible. In the reaction, however, either aryllithium first attacked the bridging CO or the aryllithium first attacked the terminal CO, though of the acylmetalate intermediate which might have isomers (terminal and bridging) that can be converted to each other in the solution, only the more stable acylmetalate intermediate formed can be converted to the products (**2**–**8**) upon the alkylation with alkylating reagents.

Complexes **2**–**8** are soluble in polar organic solvents but only slightly soluble in non-polar solvents. They are sensitive to air and temperature in solution but stable for short periods on exposure to air at room temperature in the solid state. The IR spectra and the solution ^{1}H-NMR spectra, as well as the mass spectra, are consistent with the proposed structure shown in Scheme 3. The IR spectra of complexes **2**–**8** showed one to two strong, broad CO absorption bands at 1939–1994 cm^{-1} and one CO absorption band at 1748–1765 cm^{-1} in the ν(CO) region, which signified a $(CO)_2Fe(\mu\text{-}CO)$ moiety in complexes **2**–**8** and suggested that only one μ-CO ligand converted into a bridging carbene ligand upon the reaction of complex **1** with nucleophilic aryllithium and subsequent alkylation with Et_3OBF_4 in the four-carbonyl complex **1**. The data given in the Section 2 showed that the different aryl substituents exerted certain influence on the absorption bands and the ν(CO) frequency, specifically, on the (μ-CO) frequency in these complexes. For example, complexes **7** and **8** with a electron-withdrawing group (p-ClC_6H_4 or p-$CF_3C_6H_4$) showed the ν(μ-CO) stretching vibration band at 1763–1765 cm^{-1}, shifting to high vibration frequency by 15–17 cm^{-1}, as compared with that (1748 cm^{-1}) in complexes **3**–**6** with a electron-pushing group ($CH_3C_6H_4$ or $CH_3OC_6H_4$). In the ^{1}H-NMR spectra of **2**–**8** given in the Section 2, a triplet (ca.1.29–0.86 ppm) and a quartet (ca. 3.57–3.42 ppm) and a set of multiplet (ca. 7.86–6.71 ppm) bands were observed for each of the complexes, which showed characteristically the presence of the ethoxy and aryl groups. From the ^{1}H-NMR spectra, it also noted that the proton signals attributed to the dicyclopentadienyl protons showed only two resonances at 5.60 and 5.20 ppm in starting complex **1** but four or three resonances at about 6.09–4.67 ppm in the resulting complexes **2**–**8**. This might arise from the conversion of a bridging CO ligand into a μ-carbene ligand, leading to a change in the chemical environment of the cyclopentadienyl ring in **2**–**8**. The mass spectra of complexes **2**–**8**, given in Section 2, showed the expected molecular ion peaks and principal fragments produced by successive loss of CO ligands and the μ-carbene ligand, as well as the featured ions bearing useful structural information from the fragments generated by further cleavage of these principal fragments.

The molecular structures of complexes **2** and **6**, established by X-ray diffraction studies, are shown in Figs. 1 and 2, respectively. Complexes **2** and **6** have approximately the same steric configuration. The $\mu\text{-}C(OC_2H_5)C_6H_5$ moiety in **2** and the $\mu\text{-}C(OC_2H_5)\text{-}C_6H_4OCH_3$ moiety in **6** are on opposite sides of dicyclopentadienyl-dimethylsilane ligand, as can be visualized in the ORTEP diagrams of **2** and **6** respectively in Figs. 1 and 2. Both complexes are of the diiron system with Fe–Fe bond distances of 2.513(1) and 2.503(6) Å, respectively; the ethoxy and aryl groups are attached to the one with the bridged CO group. The perpendicular distances from the Fe atom to the Cp ring plane are respectively 1.744(7) and 1.758(4) Å in **2** and 1.76(1) and 1.73(2) Å in **6**. The least-squares plane calculations show that in both complexes the carbon atoms in the two Cp rings are coplanar and the two CO ligands coordinated on the same Fe atom are not coplanar arising from bridging. In complexes **2** and **6**, there exists two different coordinated CO ligands and the bond distances of Fe–C(CO) are also different. For example, in complex **2** Fe–CO (bridged, sp^2) distances are 1.897(6) and 1.914(6) Å, while Fe–CO (nonbridged, sp) are 1.746(6) and 1.735 (6) Å, respectively.

In complex **2**, the distance of the Fe–Fe bond bridged by the μ-carbene ligand is close in value to that found in analogous bridging carbene complex $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OEt)\text{–}C_6H_5\}(CO)_2(\eta\text{-}C_5H_5)_2]$ (2.512(1) Å) [12] but obviously shorter than that found in diiron bridging carbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(SEt)C_6H_5\}(CO)_2(\eta\text{-}C_5H_5)_2]$ (2.527(2) Å) [25], $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(SC_6H_5)\text{-}C_6H_5\}(CO)_2(\eta\text{-}C_5H_5)_2]$ (2.523(2) Å) [25], and $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OEt)C_6H_4CF_3\text{-}p\}(CO)_4(C_8H_8)]$ (2.686(1) Å) [11]. The μ-carbene carbon almost symmetrically bridges the Fe–Fe bond with C(1)–Fe(1) of 2.023(5) and C(1)–Fe(2) of 2.0021(5) Å. The μ-C–Fe distances are somewhat longer than the μ-Fe–CO bond (C(10)–Fe(1) 1.897(6), C(10)–Fe(2) 1.914(6) Å) but approximately equal to those in complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(SEt)C_6H_5\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (C(1)–Fe(1) 2.03(1) and C(1)–Fe(2) 2.00(1) Å) [12], $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(SC_6H_5)\text{-}C_6H_5\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (C(1)–Fe(1) 2.026(8) and C(1)–Fe(2) 2.032(8) Å) [12], $[Fe_2\{\mu\text{-}C(OEt)C_6H_4CF_3\text{-}p\}(CO)_4(C_8H_8)]$ (C–Fe(1) 2.063(3) Å, C–Fe(2) 2.010(3)) [11], and $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(CN)NHPh\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (C(4)–Fe(1) 2.004(2) Å, C(4)–Fe(2) 2.028(2) Å) [26].

In **2**, the benzene ring lies in the *trans* position of the dicyclopentadienyl–dimethylsilane ligand. The Si atom is bridged to the two Cp rings with the identical Si–C bond lengths (Si–C(17) 1.863(6) and Si–C(18) 1.862(6) Å). The C(17)–Si–C(18) bond angle is 106.8(2)°. The Si, Fe(1), Fe(2), C(17) and C(18) atoms lie essentially in the same plane to construct a siliceous dimetal five-membered ring. The dihedral angles between the plane defined by Si, C(17), Fe(1), Fe(2), and C(18) and the plane comprised of Fe(1), Fe(2), and C(10) and the SiC(17)Fe(1)Fe(2)C(18) plane and the Fe(1)Fe(2)C(1) plane are 105.17 and 100.02°, respectively, while the dihedral angle between the Fe(1)Fe(2)C(1) and Fe(1)Fe(2)C(10) planes is 154.81°. The angles between the SiC(17)Fe(1)Fe(2)C(18) and Cp ring C(13)C-(14)C(15)–C(16)C(17) planes and the SiC(17)Fe-(1)Fe(2)C(18) and Cp ring C(18)C(19)C(20)–C(21)C(22) planes, respectively, are 84.39 and 83.41°. The dihedral angle between the Fe(1)Fe(2)C(1) plane and the benzene ring plane comprised of C(2) through C(7) is 130.36°, and the dihedral angle between the Fe(1)Fe(2)C(1) and Fe(1)Fe(2)C(10) planes is 154.81°. The angle between the two cyclopentadienyl ring planes is 83.48°. The benzene ring C(2)C(3)C(4)C(5)C(6)C(7) plane is, respectively, oriented at an angle of 130.36, 74.32, and 32.52° with respect to the Fe(1)Fe(2)C(1) plane, the Fe(1)Fe(2)C(10) plane, and the SiC(17)Fe(1)Fe(2)C(18) plane; while the benzene ring plane is oriented respectively at angles of 100.27 and 113.21° with respect to the Cp ring C(13)C(14)C(15)C(16)C(17) plane and C(18)C(19) C(20)C(21)C(22) plane. Thus, complex **2** exists in a *cis* structure to avoid steric repulsion between the six-membered aryl ring and the dicyclopentadienyldimethylsilane ligand.

The structure of **6** (Fig. 2) is very similar to that of **2**, except that the substituent on the μ-carbene carbon is a *p*-methoxyphenyl group instead of a phenyl group. Many structural features of **6** are essentially the same as those in **2**: the Fe–Fe distance, the two μ-C–Fe distances, and the angle between the ligand planes C(13) through C(17) and C(18) through C(22).

Although a number of dimetal bridging carbene complexes have been synthesized by Stone et al. and by us as mentioned in the Section 1, complexes **2**–**8**, as dimetal complexes with a bridging carbene ligand, were synthesized in high yield by the reactions of a bis(μ-CO)metal compound with nucleophilic aryllithium reagents in one-pot reaction. Analogous reactions were observed only in the case of pentacarbonyl(cyclooctatetraene)diiron and bis(η^5-cyclopentadienyl)diiron tetracarbonyl compounds (Schemes 1 and 2). The title reaction further demonstrates that it is a most direct, simple, and convenient method for the preparation of such dimetal bridging carbene complexes.

4. Supplementary material

Tables of atomic coordinates, thermal parameters, H atom coordinates, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for complexes **2** and **6** are available. Crystallographic data for the structural analysis in this paper have been deposited at the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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