

# Syntheses, structures and reactivities of diindenyl-coordinated diiron bridging carbene complexes

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## Abstract

Compound  $[\text{Fe}_2(\mu\text{-CO})_2(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)_2]$  (**1**) reacts with aryllithium reagents,  $\text{ArLi}$  ( $\text{Ar} = \text{C}_6\text{H}_5$ ,  $p\text{-CH}_3\text{C}_6\text{H}_4$ ,  $p\text{-CF}_3\text{C}_6\text{H}_4$ ) followed by alkylation with  $\text{Et}_3\text{OBF}_4$  to give the diindenyl-coordinated diiron bridging alkoxycarbene complexes  $[\text{Fe}_2\{\mu\text{-C}(\text{OC}_2\text{H}_5)\text{Ar}\}(\mu\text{-CO})(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)_2]$  (**2**,  $\text{Ar} = \text{C}_6\text{H}_5$ ; **3**,  $\text{Ar} = p\text{-CH}_3\text{C}_6\text{H}_4$ ; **4**,  $\text{Ar} = p\text{-CF}_3\text{C}_6\text{H}_4$ ). Complex **4** reacts with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  at low temperature to yield cationic bridging carbyne complex  $[\text{Fe}_2(\mu\text{-CC}_6\text{H}_4\text{CF}_3\text{-}p)(\mu\text{-CO})(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)_2]\text{BF}_4$  (**5**). Cationic **5** reacts with  $\text{NaBH}_4$  in THF at low temperature to afford diiron bridging arylcarbene complex  $[\text{Fe}_2\{\mu\text{-C}(\text{H})\text{C}_6\text{H}_4\text{CF}_3\text{-}p\}(\mu\text{-CO})(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)_2]$  (**6**). The reaction of **5** with  $\text{NaSC}_6\text{H}_4\text{CH}_3\text{-}p$  under the similar conditions gave the bridging arylthiocarbene complex  $[\text{Fe}_2\{\mu\text{-C}(\text{C}_6\text{H}_4\text{CF}_3\text{-}p)\text{SC}_6\text{H}_4\text{CH}_3\text{-}p\}(\mu\text{-CO})(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)_2]$  (**7**). Complex **5** can also react with carbonylmetal anionic compounds  $\text{Na}[\text{M}(\text{CO})_5(\text{CN})]$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) to produce the diiron bridging aryl(penta-carbonylcyanometal)carbene complexes  $[\text{Fe}_2\{\mu\text{-C}(\text{C}_6\text{H}_4\text{CF}_3\text{-}p)\text{NCM}(\text{CO})_5\}(\mu\text{-CO})(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)_2]$  (**8**,  $\text{M} = \text{Cr}$ ; **9**,  $\text{M} = \text{Mo}$ ; **10**,  $\text{M} = \text{W}$ ). The structures of complexes **4**, **6**, **7**, and **10** have been established by X-ray diffraction studies. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Diindenyl; Bridging carbene complexes; Syntheses; Structures; Reactivities

## 1. Introduction

The chemistry of di- and polynuclear metal bridging carbene and bridging carbyne complexes has been receiving considerable current attention in our laboratory, largely because of the interesting chemical properties exhibited by such complexes. A number of dimetal complexes containing bridging carbene and carbyne ligands have been synthesized by Stone and co-workers [1–4] by reactions of carbene or carbyne complexes with low-valent metal species or by reactions of neutral or anionic carbyne complexes with metal hydrides or cationic metal compounds. In our laboratory, one method for preparation of the di- and polynuclear

bridging carbene and bridging carbyne complexes is to conduct the reactions of the highly electrophilic cationic carbyne complexes of manganese and rhenium,  $[\eta^5\text{-C}_5\text{H}_5\text{-}(\text{CO})_2\text{M}\equiv\text{CPh}]\text{BBr}_4$  ( $\text{M} = \text{Mn}, \text{Re}$ ), with carbonylmetal anions [5]. In light of the common method to synthesize the mononuclear metal Fischer-type carbene complexes, we have previously developed a facile way to prepare diiron bridging alkoxycarbene complexes: carbonyl-bridged diiron complexes, such as  $[\text{Fe}_2(\mu\text{-CO})(\text{CO})_4(\eta^8\text{-C}_8\text{H}_8)]$ ,  $[\text{Fe}_2(\mu\text{-CO})_2(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]$  and  $[\text{Fe}_2(\mu\text{-CO})_2(\text{CO})_2\{\text{SiMe}_2(\eta^5\text{-C}_5\text{H}_5)_2\}]$ , reacted with aryllithium reagents followed by alkylation with alkylating agent  $\text{Et}_3\text{OBF}_4$  in aqueous solution at 0 °C to give diiron bridging alkoxycarbene complexes  $[\text{Fe}_2\{\mu\text{-C}(\text{OEt})\text{Ar}\}(\text{CO})_4(\text{C}_8\text{H}_8)]$  [6],  $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{OEt})\text{-Ar}\}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]$  [7], and  $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{OC}_2\text{H}_5)\text{-Ar}\}(\text{CO})_2\{(\eta^5\text{-C}_5\text{H}_4)_2\text{Si}(\text{CH}_3)_2\}]$  [8], respectively. Recently, we have shown a new and convenient method for the preparation of dimetal bridging carbene and/or carbyne

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complexes that is the reactions of diiron cationic bridging carbyne complexes,  $[\text{Fe}_2(\mu\text{-CO})(\mu\text{-C}_6\text{H}_5)(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]\text{BBr}_4$  [9],  $[\text{Fe}_2(\mu\text{-CO})(\mu\text{-C}_6\text{H}_5)(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]\text{Si}(\text{CH}_3)_2\text{BBr}_4$  [10], and  $[\text{Fe}_2(\mu\text{-C}_6\text{H}_5)(\text{CO})_4(\eta^8\text{-C}_8\text{H}_8)]\text{BF}_4$  [11] obtained by treating above corresponding bridging alkoxy-carbene complexes with Lewis acid  $\text{BBr}_3$  or  $\text{HBF}_4$ , with nucleophiles. This offers a useful method for the preparation and structural modification of dimetal bridging carbene complexes.

On the other hand, it was found that the different olefin ligand involving the different cyclopentadienyl ligand in the dimetal cationic bridging carbyne complexes exhibit a great influence on the reactivity of the cationic bridging carbyne complexes toward nucleophiles and the resulting products. For instance, dicyclopentadienyl-coordinated diiron cationic carbyne complexes  $[\text{Fe}_2(\mu\text{-CO})(\mu\text{-C}_6\text{H}_5)(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]\text{BBr}_4$  reacts with  $\text{NaN}(\text{SiMe}_3)_2$  and  $\text{Na}[\text{M}(\text{CO})_5\text{CN}]$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) to give bridging carbene complex  $[\text{Fe}_2(\mu\text{-CO})\{(\mu\text{-C}(\text{N}(\text{SiMe}_3)_2)\text{C}_6\text{H}_5)(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_2\}]$  [12] and bridging carbyne complexes  $[\text{Fe}_2(\mu\text{-CO})(\mu\text{-C}_6\text{H}_5)(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]\text{NCM}(\text{CO})_5$  [9], respectively, while the analogous reactions of dimethylsilane-bridged bis-cyclopentadienyl diiron cationic carbyne complexes  $[\text{Fe}_2(\mu\text{-CO})(\mu\text{-C}_6\text{H}_5)(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]\text{Si}(\text{CH}_3)_2\text{BBr}_4$  give benzonitrile-coordinated diiron complex  $[\text{Fe}_2(\mu\text{-CO})_2(\text{CO})\text{-NC-C}_6\text{H}_5\{(\eta^5\text{-C}_5\text{H}_5)_2\text{Si}(\text{CH}_3)_2\}]$  and bridging phenyl (pentacarbonylcyano metal)carbene complexes  $[\text{Fe}_2(\mu\text{-CO})\{\mu\text{-C}(\text{C}_6\text{H}_5)\text{NCM}(\text{CO})_5\}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]\text{Si}(\text{CH}_3)_2$  [10], respectively.

In order to further explore the reactivity of substituted cyclopentadienyl-coordinated diiron cationic bridging carbyne complexes toward nucleophiles and to further examine the scope of the preparation of dimetal bridging carbene and bridging carbyne complexes, we synthesized diindenyl-coordinated diiron bridging alkoxy-carbene complexes  $[\text{Fe}_2\{\mu\text{-C}(\text{OC}_2\text{H}_5)\text{Ar}\}(\mu\text{-CO})(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)_2]$  ( $\text{Ar} = \text{C}_6\text{H}_5, p\text{-CH}_3\text{C}_6\text{H}_4, p\text{-CF}_3\text{C}_6\text{H}_4$ ) by the reactions of diindenyl-coordinated diiron carbonyl compound,  $[\text{Fe}_2(\mu\text{-CO})_2(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)_2]$  (**1**), where the indenyl can be formally regarded as a cyclo-diene-substituted cyclopentadienyl, with aryllithium reagents followed by alkylation with  $\text{Et}_3\text{OBF}_4$ , and carried out the study of the reactivity of the cationic bridging carbyne complex  $[\text{Fe}_2(\mu\text{-C}_6\text{H}_5)(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)_2]\text{BF}_4$  with nucleophiles involving carbonylmetal anions. These reactions produce a series of novel diindenyl-coordinated dimetal bridging carbene complexes. In this paper, we report these unusual reactions and the structural characterization of the resulting products.

## 2. Experimental

All procedures were performed under a dry, oxygen-free  $\text{N}_2$  atmosphere by 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  $\text{N}_2$  atmosphere. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone

ketyl, while petroleum ether (30–60 °C) and  $\text{CH}_2\text{Cl}_2$  were distilled from  $\text{CaH}_2$ . The neutral alumina ( $\text{Al}_2\text{O}_3$ , 100–200 mesh) used for chromatography was deoxygenated at room temperature under high vacuum for 16 h, deactivated with 5% w/w  $\text{N}_2$ -saturated water, and stored under  $\text{N}_2$  atmosphere. Compounds  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  and  $\text{NaBH}_4$ , and  $n\text{-C}_4\text{H}_9\text{Li}$  were purchased from Aldrich Chemical Co. Compound  $[\text{Fe}_2(\mu\text{-CO})_2(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)_2]$  (**1**) [13],  $\text{NaSC}_6\text{H}_4\text{-CH}_3\text{-}p$  [14],  $\text{Na}[\text{Cr}(\text{CO})_5(\text{CN})]$  [15],  $\text{Na}[\text{Mo}(\text{CO})_5(\text{CN})]$  [15], and  $\text{Na}[\text{W}(\text{CO})_5(\text{CN})]$  [15], aryllithium reagents [16–18], and  $\text{Et}_3\text{OBF}_4$  [19] were prepared by the literature methods.

The IR spectra were measured on a Nicolet AV-360 spectrophotometer using NaCl cells with 0.1 mm spacers. All  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at ambient temperature in acetone- $d_6$  solution with TMS or deuterated solvents as the internal reference using a Varian Mercury 300 spectrometer. The  $^{13}\text{C}$  NMR data for complexes **5** and **7–10** were not obtained due to their lability in the solution. 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. Reaction of $[\text{Fe}_2(\mu\text{-CO})_2(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)_2]$ (**1**) with $\text{C}_6\text{H}_5\text{Li}$ to give $[\text{Fe}_2\{\mu\text{-C}(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5\}(\mu\text{-CO})\text{-}(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)_2]$ (**2**)

To a suspension of 0.250 g (0.55 mmol) of **1** in 50 mL of ether at  $-40$  °C was added 0.66 mmol of the freshly prepared  $\text{C}_6\text{H}_5\text{Li}$  [16] ether solution with stirring. The reaction mixture was stirred at  $-40$  to  $-20$  °C for 3 h, during which time the green suspension gradually turned blackish solution. The resulting solution then evaporated under high vacuum at  $-20$  °C to dryness. To the blackish solid residue obtained was added  $\text{Et}_3\text{OBF}_4$  [19] (ca. 5 g). This solid mixture was dissolved in 50 mL of  $\text{N}_2$ -saturated water at 0 °C with vigorous stirring and the mixture covered with petroleum ether (30–60 °C). Immediately afterwards,  $\text{Et}_3\text{OBF}_4$  (ca. 15 g) was added portion wise to the aqueous solution, with strong stirring, until it became acidic. The aqueous solution was extracted with petroleum ether/ $\text{CH}_2\text{Cl}_2$  (5:1). 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 petroleum ether/ $\text{CH}_2\text{Cl}_2$  (3:1) as the eluant. The solvent was removed in vacuo and the residue was recrystallized from petroleum ether/ $\text{CH}_2\text{Cl}_2$  (10:1) at  $-80$  °C to give 0.236 g (76%, based on **1**) of blackish crystals of **2**; m.p. 94–96 °C (dec.); IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  1970 (vs), 1932 (m), 1783 (m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  7.69–7.45 (m, 5H,  $\text{C}_6\text{H}_5$ ), 7.43–7.26 (m, 8H,  $2\text{C}_9\text{H}_7$ ), 6.18–6.17 (dd, 2H,  $2\text{C}_9\text{H}_7$ ), 5.63 (m, 1H,  $\text{CH}_2\text{Cl}_2$ ), 5.27 (t, 2H,  $2\text{C}_9\text{H}_7$ ), 4.90 (m, 2H,  $2\text{C}_9\text{H}_7$ ), 3.61 (q, 2H,  $\text{OCH}_2\text{CH}_3$ ), 1.41 (t, 3H,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  267.2 ( $\mu\text{-C}$ ), 244.5, 213.2 (CO), 158.5, 130.5, 128.7, 127.0, 126.4, 114.0 ( $\text{C}_6\text{H}_5$ ), 101.6, 99.8, 79.8, 79.4, 67.0 ( $\text{OCH}_2\text{CH}_3$ ), 15.1 ( $\text{OCH}_2\text{CH}_3$ ); MS *m/e*

447 ( $M^+ - 3CO - C_2H_5$ ), 342 [ $M^+ - 3CO - C(C_2H_5)C_6H_5$ ], 115 ( $C_9H_7^+$ ), 84 ( $CH_2Cl_2^+$ ). Anal. Calc. for  $C_{30}H_{24}O_4Fe_2 \cdot 0.5CH_2Cl_2$ : C, 60.80; H, 4.18. Found: C, 60.95; H, 4.15%.

2.2. Reaction of **1** with  $p\text{-}CH_3C_6H_4Li$  to give [ $Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_4CH_3\text{-}p\}\text{-}(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_9H_7)_2$ ] (**3**)

Similar to the procedures described above for the reaction of **1** with  $C_6H_5Li$ , compound **1** (0.200 g, 0.44 mmol) was reacted with 0.66 mmol of  $p\text{-}CH_3C_6H_4Li$  [17] at  $-40$  to  $-20$  °C for 3 h. The subsequent alkylation and further treatment in a similar manner as described for the preparation of **2** afforded 0.176 g (70%, based on **1**) of **3** as blackish crystals; m.p. 108–110 °C (dec.); IR ( $CH_2Cl_2$ ):  $\nu(CO)$  1970 (vs), 1952 (w), 1782 (s)  $cm^{-1}$ ;  $^1H$  NMR ( $CD_3COCD_3$ ):  $\delta$  7.51–7.38 (m, 4H,  $p\text{-}CH_3C_6H_4$ ), 7.46–7.23 (m, 8H,  $2C_9H_7$ ), 6.15 (dd, 2H,  $2C_9H_7$ ), 5.62 (m, 2H,  $CH_2Cl_2$ ), 5.25 (t, 2H,  $2C_9H_7$ ), 4.89 (s, 2H,  $2C_9H_7$ ), 3.60 (q, 2H,  $OCH_2CH_3$ ), 2.23 (s, 3H,  $p\text{-}CH_3C_6H_4$ ), 1.40 (t, 3H,  $OCH_2CH_3$ );  $^{13}C$  NMR ( $CD_3COCD_3$ ):  $\delta$  257.0 ( $\mu\text{-}C$ ), 239.8, 218.7 (CO), 161.1, 131.2, 130.0, 128.2, 126.6, 126.5, 125.7, 122.3, 99.56, 79.4, 66.0 ( $OCH_2CH_3$ ), 18.4 ( $OCH_2CH_3$ ), MS  $m/e$  454 [ $M^+ - C_2H_5 - C_6H_4CH_3\text{-}p$ ], 370 [ $M^+ - 2CO - C(OC_2H_5) - C_6H_4CH_3\text{-}p$ ], 342 [ $M^+ - 3CO - C(OC_2H_5)C_6H_4CH_3\text{-}p$ ], 286 [ $M^+ - 3CO - C(OC_2H_5)C_6H_4CF_3\text{-}p - Fe$ ], 115 ( $C_9H_7^+$ ), 84 ( $CH_2Cl_2^+$ ). Anal. Calc. for  $C_{31}H_{26}O_4Fe_2 \cdot CH_2Cl_2$ : C, 58.31; H, 4.28. Found: C, 59.09; H, 4.00%.

2.3. Reaction of **1** with  $p\text{-}CF_3C_6H_4Li$  to give [ $Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_4CF_3\text{-}p\}\text{-}(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_9H_7)_2$ ] (**4**)

A solution of 0.124 g (0.55 mmol) of  $p\text{-}CF_3C_6H_4Br$  in 20 mL of ether was mixed with 0.55 mmol of  $n\text{-}C_4H_9Li$ . After 40 min stirring at room temperature, the resulting ether solution of  $p\text{-}CF_3C_6H_4Li$  [18] was reacted, as described in the reaction of **1** with  $C_6H_5Li$ , with 0.200 g (0.44 mmol) of **1** at  $-40$  to  $-20$  °C for 3 h, followed by alkylation; further treatment as described that in the preparation gave 0.226 g (81%, based on **1**) of blackish crystals of **4**, m.p. 116–118 °C (dec.). IR ( $CH_2Cl_2$ ):  $\nu(CO)$  1973 (vs), 1935 (w), 1784 (m)  $cm^{-1}$ ;  $^1H$  NMR ( $CD_3COCD_3$ ):  $\delta$  7.65–7.42 (m, 4H,  $p\text{-}CF_3C_6H_4$ ), 7.32–7.26 (m, 8H,  $2C_9H_7$ ), 6.19–6.18 (dd, 2H,  $2C_9H_7$ ), 5.30 (t, 2H,  $2C_9H_7$ ), 4.98 (m, 2H,  $2C_9H_7$ ), 3.62 (q, 2H,  $OCH_2CH_3$ ), 1.43 (t, 3H,  $OCH_2CH_3$ );  $^{13}C$  NMR ( $CD_3COCD_3$ ):  $\delta$  266.0 ( $\mu\text{-}C$ ), 241.0, 213.4 (CO), 161.8, 131.2, 129.2, 127.5, 126.4, 123.6, 123.0, 114.2, 102.2, 100.0, 80.2, 79.8, 67.8 ( $OCH_2CH_3$ ), 15.4 ( $OCH_2CH_3$ ); MS  $m/e$  342 [ $M^+ - 3CO - C(OC_2H_5) - C_6H_4CF_3\text{-}p$ ], 286 [ $M^+ - 3CO - C(OC_2H_5)C_6H_4CF_3\text{-}p - Fe$ ], 115 ( $C_9H_7^+$ ). Anal. Calc. for  $C_{31}H_{23}O_4F_3Fe_2$ : C, 59.27; H, 3.69. Found: C, 59.48; H, 3.70%.

2.4. Reaction of [ $Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_4CF_3\text{-}p\}\text{-}(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_9H_7)_2$ ] (**4**) with  $HBf_4 \cdot Et_2O$  to give [ $Fe_2(\mu\text{-}CC_6H_4CF_3\text{-}p)(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_9H_7)_2$ ]BF<sub>4</sub> (**5**)

To a stirred, blackish red solution of **4** (0.250 g, 0.40 mmol) in 40 mL of ether at  $-60$  °C was added

0.100 mL (0.67 mmol) of  $HBf_4 \cdot Et_2O$ . Immediately, a blackish red precipitate was formed. After stirring at  $-60$  to  $-30$  °C for 1 h, the resulting mixture was filtered, and the solid was washed with ether ( $2 \times 20$  mL) at  $-60$  °C and then dried under high vacuum at  $-30$  °C to give 0.226 g (85%, based on **4**) of **5** as a blackish red solid: IR ( $CH_2Cl_2$ ):  $\nu(CO)$  1992 (vs), 1950 (s), 1782 (s)  $cm^{-1}$ ;  $^1H$  NMR ( $CD_3COCD_3$ ):  $\delta$  8.49–8.01 (m, 4H,  $p\text{-}CF_3C_6H_4$ ), 7.87–7.75 (m, 8H,  $2C_9H_7$ ), 7.40 (m, 2H,  $2C_9H_7$ ), 5.81 (s, 2H,  $2C_9H_7$ ), 5.48 (m, 2H,  $2C_9H_7$ ).

2.5. Reaction of **5** with  $NaBH_4$  to give [ $Fe_2\{\mu\text{-}C(H)C_6H_4CF_3\text{-}p\}\text{-}(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_9H_7)_2$ ] (**6**)

To a solution of **5**, freshly prepared (in situ) by the reaction of **4** (0.200 g, 0.32 mmol) with  $HBf_4 \cdot Et_2O$  (0.080 mL, 0.53 mmol), in 50 mL of THF at  $-80$  °C was added 0.020 g (0.53 mmol) of  $NaBH_4$ . The reaction mixture was stirred at  $-80$  to  $-40$  °C for 3 h, during which time the blackish solution gradually turned brown-red. The resulting solution was evaporated under high vacuum at  $-40$  °C to dryness and the brown-red residue was chromatographed on an  $Al_2O_3$  column at  $-20$  °C with petroleum ether/ $CH_2Cl_2$  (2:1) as the eluant. A brown-red band was eluted and collected. After vacuum removal of the solvent, the residue was recrystallized from petroleum ether/ $CH_2Cl_2$  solution at  $-80$  °C to give 0.148 g (80%, based on **4**) of red crystals of **6**: m.p. 140–142 °C (dec.); IR ( $CH_2Cl_2$ ):  $\nu(CO)$  1991 (vs), 1951 (m), 1782 (s)  $cm^{-1}$ ;  $^1H$  NMR ( $CD_3COCD_3$ ):  $\delta$  10.36 (s, 1H,  $\mu\text{-}CH$ ), 7.44–7.29 (m, 4H,  $C_6H_4CF_3$ ), 7.24–7.19 (m, 8H,  $2C_9H_7$ ), 7.03 (dd, 2H,  $2C_9H_7$ ), 5.64 (s, 2H,  $2C_9H_7$ ), 5.35 (s, 2H,  $2C_9H_7$ );  $^{13}C$  NMR ( $CD_3COCD_3$ ):  $\delta$  256.7 ( $\mu\text{-}C$ ), 226.0, 215.6 (CO), 187.7, 128.7, 128.5, 128.2, 125.0, 123.9 ( $C_6H_5$ ), 106.8, 95.1, 81.8, 79.7; MS  $m/e$  444 ( $M^+ - 3CO - Fe$ ), 354 ( $M^+ - 3CO - H - p\text{-}CF_3C_6H_4$ ), 342 [ $M^+ - 3CO - C(H)C_6H_4CF_3\text{-}p$ ], 115 ( $C_9H_7^+$ ). Anal. Calc. for  $C_{29}H_{19}O_3F_3Fe_2$ : C, 59.63; H, 3.28. Found: C, 58.09; H, 3.42%.

2.6. Reaction of **5** with  $NaSC_6H_4CH_3\text{-}p$  to give [ $Fe_2\{\mu\text{-}C(C_6H_4CF_3\text{-}p)SC_6H_4CH_3\text{-}p\}\text{-}(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_9H_7)_2$ ] (**7**)

To a solution of **5**, freshly prepared (in situ) from the reaction of **4** (0.120 g, 0.19 mmol) with  $HBf_4 \cdot Et_2O$  (0.050 mL, 0.33 mmol), dissolved in 50 mL of THF at  $-80$  °C was added 0.030 g (0.21 mmol) of  $NaSC_6H_4CH_3\text{-}p$ . The reaction mixture was stirred at  $-80$  to  $-40$  °C for 3 h, during this time the reaction solution turned from blackish to dark red gradually. The solvent was removed under vacuum at  $-40$  °C, and the dark red residue was chromatographed on an  $Al_2O_3$  column at  $-25$  °C with petroleum ether/ $CH_2Cl_2$  (2:1) as the eluant. A brown-red band was eluted and collected. After vacuum removal of the solvent, the residue was recrystallized from petroleum ether/ $CH_2Cl_2$  solution at  $-80$  °C to afford 0.080 g (59%, based on **4**) of brown-red crystalline **7**: m.p. 120–122 °C (dec.); IR ( $CH_2Cl_2$ ):  $\nu(CO)$

1980 (vs), 1943 (m), 1793 (s, br)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  7.63–7.33 (m, 8H, *p*- $\text{CF}_3\text{C}_6\text{H}_4$  + *p*- $\text{CH}_3\text{C}_6\text{H}_4$ ), 7.13–6.93 (m, 8H,  $2\text{C}_9\text{H}_7$ ), 6.49 (s, 2H,  $2\text{C}_9\text{H}_7$ ), 5.62 (m, 2H,  $\text{CH}_2\text{Cl}_2$ ), 5.46 (s, 2H,  $2\text{C}_9\text{H}_7$ ), 5.30 (s, 2H,  $2\text{C}_9\text{H}_7$ ), 2.23 (s, 3H, *p*- $\text{CH}_3\text{C}_6\text{H}_4$ ); MS *m/e* 566 [ $\text{M}^+ - 3\text{CO} - \text{Fe}$ ], 342 [ $\text{M}^+ - 3\text{CO} - \text{C}(\text{C}_6\text{H}_4\text{CH}_3\text{-}p)\text{C}_6\text{H}_4\text{CF}_3\text{-}p$ ], 115 ( $\text{C}_9\text{H}_7^+$ ), 84 ( $\text{CH}_2\text{Cl}_2^+$ ). Anal. Calc. for  $\text{C}_{36}\text{H}_{25}\text{O}_3\text{F}_3\text{S} \cdot \text{Fe}_2 \cdot \text{CH}_2\text{Cl}_2$ : C, 56.16; H, 3.44. Found: C, 56.92; H, 3.49%.

**2.7. Reaction of 5 with  $\text{Na}[\text{Cr}(\text{CO})_5(\text{CN})]$  to give  $[\text{Fe}_2\text{-}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{CF}_3\text{-}p)\text{NCCr}(\text{CO})_5\}(\mu\text{-CO})(\text{CO})_2\text{-}(\eta^5\text{-C}_9\text{H}_7)_2]$  (8)**

To a suspension of **5**, freshly prepared (in situ) by the reaction of **4** (0.250 g, 0.40 mmol) with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (0.100 mL, 0.67 mmol), in 50 mL of THF at  $-80^\circ\text{C}$  was added 0.100 g (0.41 mmol) of  $[\text{NaCr}(\text{CO})_5(\text{CN})]$ . The reaction mixture was stirred at  $-80$  to  $-40^\circ\text{C}$  for 3 h, during which time the blackish suspension turned dark red solution. The resulting solution was evaporated under high vacuum at  $-40^\circ\text{C}$  to dryness and the blackish residue was chromatographed on an alumina column at  $-25^\circ\text{C}$  with petroleum ether/ $\text{CH}_2\text{Cl}_2$  (3:1) as the eluant. The brown band was eluted and collected. After vacuum removal of the solvent, the residue was recrystallized from petroleum ether/ $\text{CH}_2\text{Cl}_2$  solution at  $-80^\circ\text{C}$  to give 0.138 g (58%, based on **1**) of brown-red crystals of **8**: m.p.  $94\text{--}96^\circ\text{C}$  (dec.); IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2045 (m), 1993 (s), 1949 (vs), 1818 (w)  $\text{cm}^{-1}$ ;  $\nu(\text{CN})$  2109 (w)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  7.79–7.53 (m, 4H, *p*- $\text{CF}_3\text{C}_6\text{H}_4$ ), 7.50–7.44 (m, 8H,  $2\text{C}_9\text{H}_7$ ), 6.56 (m, 2H,  $2\text{C}_9\text{H}_7$ ), 5.41 (t, 2H,  $2\text{C}_9\text{H}_7$ ), 5.00 (m, 2H,  $2\text{C}_9\text{H}_7$ ); MS *m/e* 386 [ $\text{M}^+ - 2\text{CO} - \text{Cr}(\text{CO})_5\text{CN} - \text{CF}_3\text{C}_6\text{H}_4$ ], 318 [ $\text{M}^+ - 2\text{CO} - \text{Cr}(\text{CO})_5\text{CN} - \text{Fe} - \text{C}_6\text{H}_4\text{CF}_3\text{-}p$ ], 290 [ $\text{M}^+ - 3\text{CO} - \text{Cr}(\text{CO})_5\text{CN} - \text{Fe} - \text{C}_6\text{H}_4\text{CF}_3\text{-}p$ ], 278 [ $\text{M}^+ - 3\text{CO} - \text{Cr}(\text{CO})_5\text{CN} - \text{Fe} - \text{CC}_6\text{H}_4\text{CF}_3\text{-}p$ ], 115 ( $\text{C}_9\text{H}_7^+$ ). Anal. Calc. for  $\text{C}_{35}\text{H}_{18}\text{O}_8\text{F}_3\text{NFe}_2\text{Cr} \cdot \text{CH}_2\text{Cl}_2$ : C, 48.79; H, 2.28; N, 1.58. Found: C, 48.45; H, 2.50; N, 1.48%.

**2.8. Reaction of 5 with  $\text{Na}[\text{Mo}(\text{CO})_5(\text{CN})]$  to give  $[\text{Fe}_2\text{-}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{CF}_3\text{-}p)\text{NCMo}(\text{CO})_5\}(\mu\text{-CO})(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)_2]$  (9)**

Using the same procedure above, freshly prepared (in situ) **5** by the reaction of **4** (0.150 g, 0.24 mmol) with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (0.060 mL, 0.40 mmol), suspended in 50 mL of THF at  $-80^\circ\text{C}$  was reacted with 0.080 g (0.28 mmol) of  $[\text{NaMo}(\text{CO})_5(\text{CN})]$ . The reaction mixture was stirred at  $-80$  to  $-40^\circ\text{C}$  for 3 h, during which time the blackish suspension turned dark red solution. Further treatment of the resulting solution as described in the preparation of **8** gave 0.125 g (62%, based on **5**) of brown-red crystalline **9**: m.p.  $82\text{--}84^\circ\text{C}$  (dec.); IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2048 (m), 1994 (s), 1950 (vs), 1810 (m)  $\text{cm}^{-1}$ ;  $\nu(\text{CN})$  2108 (w)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  7.78–7.57 (m, 4H, *p*- $\text{CF}_3\text{C}_6\text{H}_4$ ), 7.53–7.44 (m, 8H,  $2\text{C}_9\text{H}_7$ ), 6.56 (dd, 2H,  $2\text{C}_9\text{H}_7$ ), 5.63 (m, 2H,  $\text{CH}_2\text{Cl}_2$ ), 5.41 (t, 2H,  $2\text{C}_9\text{H}_7$ ), 5.00 (m, 2H,  $2\text{C}_9\text{H}_7$ ); MS *m/e* 384 [ $\text{M}^+ - 3\text{CO} - \text{Mo}(\text{CO})_5\text{-}$

$\text{CN} - \text{C}_9\text{H}_7$ ], 239 [ $\text{M}^+ - 3\text{CO} - \text{C}_9\text{H}_7 - \text{Mo}(\text{CO})_5\text{CN} - \text{CF}_3\text{C}_6\text{H}_4$ ], 227 [ $\text{M}^+ - 3\text{CO} - \text{C}_9\text{H}_7 - \text{C}(\text{CF}_3\text{C}_6\text{H}_4)\text{NCMo}(\text{CO})_5$ ], 115 ( $\text{C}_9\text{H}_7^+$ ), 84 ( $\text{CH}_2\text{Cl}_2^+$ ). Anal. Calc. for  $\text{C}_{35}\text{H}_{18}\text{O}_8\text{F}_3\text{NFe}_2 \cdot \text{Mo} \cdot \text{CH}_2\text{Cl}_2$ : C, 46.48; H, 2.16; N, 1.51. Found: C, 46.22; H, 2.28, N, 1.49%.

**2.9. Reaction of 5 with  $\text{Na}[\text{W}(\text{CO})_5(\text{CN})]$  to give  $[\text{Fe}_2\text{-}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{CF}_3\text{-}p)\text{NCW}(\text{CO})_5\}(\mu\text{-CO})(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)_2]$  (10)**

As described for the reaction of **5** with  $[\text{NaCr}(\text{CO})_5(\text{CN})]$ , freshly prepared (in situ) **5** by the reaction of **4** (0.150 g, 0.24 mmol) with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (0.060 mL, 0.40 mmol), suspended in 50 mL of THF at  $-80^\circ\text{C}$  was reacted with  $[\text{NaW}(\text{CO})_5(\text{CN})]$  (0.100 g, 0.29 mmol) at  $-80$  to  $-40^\circ\text{C}$  for 3 h. The resulting mixture was worked up as described for the preparation of **8** to give 0.160 g (72%, based on **5**) of brown-red crystalline **10**: m.p.  $84\text{--}86^\circ\text{C}$  (dec.); IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2045 (m), 1993 (s), 1944 (vs), 1810 (w)  $\text{cm}^{-1}$ ;  $\nu(\text{CN})$  2112 (w)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  8.02–7.60 (m, 4H, *p*- $\text{CF}_3\text{C}_6\text{H}_4$ ), 7.58–7.30 (m, 8H,  $2\text{C}_9\text{H}_7$ ), 6.56 (dd, 2H,  $2\text{C}_9\text{H}_7$ ), 5.43 (t, 2H,  $2\text{C}_9\text{H}_7$ ), 5.03 (m, 2H,  $2\text{C}_9\text{H}_7$ ); MS *m/e* 412 [ $\text{M}^+ - 2\text{CO} - \text{W}(\text{CO})_5\text{CN} - \text{C}_9\text{H}_7$ ], 356 [ $\text{M}^+ - 2\text{CO} - \text{W}(\text{CO})_5\text{CN} - \text{Fe} - \text{C}_9\text{H}_7$ ], 267 [ $\text{M}^+ - 2\text{CO} - \text{W}(\text{CO})_5\text{CN} - \text{C}_9\text{H}_7 - \text{CF}_3\text{C}_6\text{H}_4$ ], 115 ( $\text{C}_9\text{H}_7^+$ ). Anal. Calc. for  $\text{C}_{35}\text{H}_{18}\text{O}_8\text{F}_3\text{NFe}_2\text{W}$ : C, 45.50; H, 1.95; N, 1.50. Found: C, 45.87; H, 2.04; N, 1.98%.

**2.10. X-ray crystal structure determinations of complexes 4, 6, 7, and 10**

The single crystals of **4**, **6**, **7**, and **10** suitable for X-ray diffraction studies were obtained by recrystallization from petroleum ether/ $\text{CH}_2\text{Cl}_2$  solution at  $-80^\circ\text{C}$ . Single crystals were mounted on a glass fibre and sealed with epoxy glue. The X-ray diffraction intensity data for **4**, **7**, **8**, and **10** were collected with a Bruker Smart diffractometer at  $20^\circ\text{C}$  using  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with a  $2\theta$  scan mode.

The structures of **4**, **6**, **7**, and **10** were solved by the direct methods and expanded using Fourier techniques. For complexes **2**, **6**, and **10**, the some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically, and the hydrogen atoms were included but not refined. For complex **7**, the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included but not refined. For the four complexes, the absorption corrections were applied using SADABS. The final cycle of full-matrix least-squares refinement was based on the observed reflections and the variable parameters and converged with unweighted and weighted agreement to give the agreement factors of *R* and *R<sub>w</sub>*, which are listed in Table 1.

The details of the crystallographic data and the procedures used for data collection and reduction information for **4**, **6**, **7**, and **10** are given in Table 1. The selected bond lengths and angles are listed in Table 2. The atomic coordinates and *B<sub>iso</sub>*/*B<sub>eq</sub>*, anisotropic displacement parameters, complete bond lengths and angles, least-squares planes

Table 1  
Crystal data and experimental details for complexes **4**, **7**, **8**, and **10**

Compound	<b>4</b>	<b>6</b>	<b>7</b> · CH <sub>2</sub> Cl <sub>2</sub>	<b>10</b> · CH <sub>2</sub> Cl <sub>2</sub>
Formula	C <sub>31</sub> H <sub>23</sub> O <sub>4</sub> F <sub>3</sub> Fe <sub>2</sub>	C <sub>29</sub> H <sub>19</sub> O <sub>3</sub> F <sub>3</sub> Fe <sub>2</sub>	C <sub>37</sub> H <sub>27</sub> O <sub>3</sub> Cl <sub>2</sub> F <sub>3</sub> SFe <sub>2</sub>	C <sub>36</sub> H <sub>20</sub> O <sub>8</sub> Cl <sub>2</sub> F <sub>3</sub> NFe <sub>2</sub> W
Formula weight	628.19	584.14	791.25	1017.98
Space group	<i>P2<sub>1</sub>/c</i> (No. 14)	<i>Pnma</i> (No.53)	<i>P2<sub>1</sub>/n</i> (No. 14)	<i>P2<sub>1</sub>/c</i> (No. 14)
<i>a</i> (Å)	16.7771(13)	11.3883(9)	15.054(5)	13.0139(8)
<i>b</i> (Å)	9.6117(7)	14.6661(11)	12.185(4)	9.6277(6)
<i>c</i> (Å)	17.8962(14)	14.5225(10)	19.219(7)	29.7705(19)
$\alpha$ (°)		90		
$\beta$ (°)	111.526(2)	90	107.131(6)	99.0320(10)
$\gamma$ (°)		90		
<i>V</i> (Å <sup>3</sup> )	2684.6(4)	2425.6(3)	3369.2(19)	3683.8(4)
<i>Z</i>	4	4	4	4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.554	1.660	1.560	1.835
<i>F</i> (000)	1280	1184	1608	463
Crystal size (mm)	0.198 × 0.167 × 0.097	0.175 × 0.157 × 0.078	0.375 × 0.309 × 0.021	0.168 × 0.127 × 0.062
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	11.38	12.50	11.35	41.04
Orientation reflections: number; range (2 $\theta$ ) (°)	2510; 4.894–43.444	1098; 5.326–47.100	1553; 4.518–39.440	2921; 4.525–39.418
Collected data range, 2 $\theta$ (°)	4.62–54.00	3.94–56.52	3.04–52.00	3.16–52.00
Number of unique data, total with [ <i>I</i> > 2.00 $\sigma$ ( <i>I</i> )]	5848, 2825	3019, 1479	6582, 2853	7190, 4478
Number of parameters refined	416	180	434	463
Correction factors, maximum–minimum	0.8622–1.0000	0.83023–1.00000	0.75514–1.00000	0.84931–1.00000
<i>R</i> <sup>a</sup>	0.0534	0.0697	0.0721	0.0595
<i>R</i> <sub>w</sub> <sup>b</sup>	0.1089	0.1376	0.1314	0.1283
Quality of fit in dicator <sup>c</sup>	1.079	0.946	0.889	0.944
Maximum shift/estimated standard deviations final cycle	0.094	0.001	0.001	0.098
Largest peak (e/Å <sup>3</sup> )	1.228	0.430	0.442	2.223
Minimum peak (e/Å <sup>3</sup> )	-0.740	-0.516	-0.430	-1.087

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ ;  $w = 1/\sum^2(|F_o|)$ .

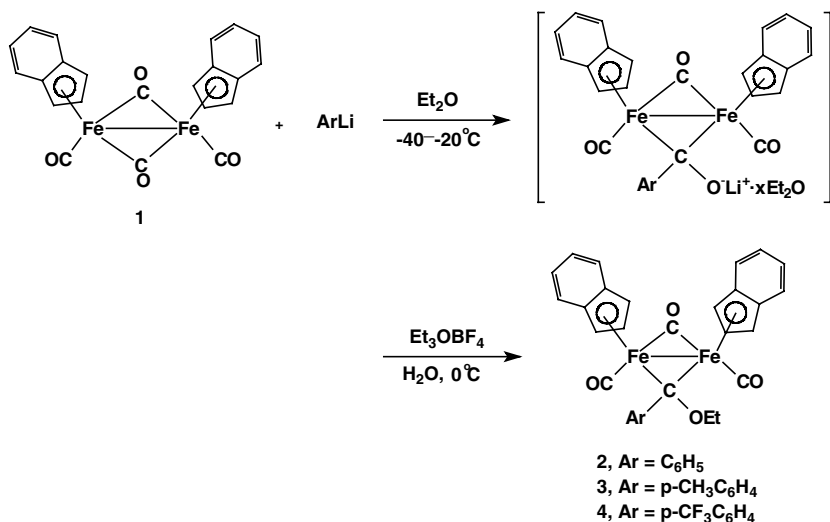
<sup>c</sup> Quality-of-fit =  $[\sum w(|F_o|^2 - |F_c|^2)|^2 / (N_{\text{observed}} - N_{\text{parameters}})]^{1/2}$ .

for **4**, **6**, **7**, and **10** are deposited in the Cambridge Crystallographic Data Center, CCDC. The molecular structures of **4**, **6**, **7**, and **10** are given in Figs. 1–4, respectively.

### 3. Results and discussion

Compound [Fe<sub>2</sub>( $\mu$ -CO)<sub>2</sub>(CO)<sub>2</sub>( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>] (**1**) reacts with about 20–30% molar excess of the aryllithium reagents, ArLi (R = C<sub>6</sub>H<sub>5</sub>, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), in ether at low tem-

perature (–40 to –20 °C) for 3–4 h, followed by alkylation with Et<sub>3</sub>OBF<sub>4</sub>. After removal of the solvent under high vacuum at low temperature, the residue was chromatographed on an alumina column at low temperature, and the crude product was recrystallized from petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> solution at –80 °C to afford the diindenyl-coordinated diiron bridging alkoxy carbene complexes [Fe<sub>2</sub>{ $\mu$ -C(OC<sub>2</sub>H<sub>5</sub>)-Ar}( $\mu$ -CO)(CO)<sub>2</sub>( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>] (**2**, Ar = C<sub>6</sub>H<sub>5</sub>; **3**, Ar = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; **4**, Ar = *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) (Eq. (1)) in 70–81% yields.



(1)

Table 2  
Selected bond lengths (Å)<sup>a</sup> and angles (°)<sup>a</sup> for complexes **4**, **6**, **7**, and **10**

Complex	<b>4</b>	<b>6</b> (Fe(1) = Fe, Fe(2) = FeA)	<b>7</b>	<b>10</b>
Fe(1)–Fe(2)	2.5392(9)	2.5393(15)	2.5647(16)	2.5551(19)
Fe(1)–C(3)	2.007(4)	1.960(6)	2.025(6)	1.992(9)
Fe(2)–C(3)	2.023(4)	1.960(6)	2.017(6)	1.984(9)
Fe(1)–C(4)	1.909(5)	1.919(6)	1.936(7)	1.952(9)
Fe(2)–C(4)	1.898(5)	1.919(6)	1.915(7)	1.936(10)
Fe(1)–C(1)	1.731(5)	1.739(6)	1.728(9)	1.761(12)
Fe(2)–C(2)	1.748(5)		1.753(8)	1.763(11)
C(3)–O(3)	1.413(4)			
C(3)–S(1)			1.860(7)	
C(3)–N(1)				1.454(11)
C(3)–C(5)	1.503(5)	1.445(10)	1.486(8)	1.508(12)
C(4)–O(4)	1.170(4)	1.170(8)	1.152(7)	1.131(10)
S(1)–C(31)			1.778(7)	
N(1)–C(11)				1.134(10)
C(11)–W(1)				2.135(10)
Fe(1)–C(Cp) (av)	2.158	2.152	2.160	2.154
Fe(2)–C(Cp) (av)	2.140		2.144	2.155
Fe(1)–Fe(2)–C(3)	50.68(12)		50.76(18)	50.2(3)
Fe(1)–C(3)–Fe(2)	78.10(15)	80.7(3)	78.8(2)	80.0(3)
Fe(2)–Fe(1)–C(3)	51.22(11)	49.63(14)	50.49(19)	49.9(3)
Fe(1)–Fe(2)–C(4)	48.35(14)		48.6(2)	49.2(3)
Fe(1)–C(4)–Fe(2)	83.7(2)	82.9(3)	83.5(3)	82.2(4)
Fe(2)–Fe(1)–C(4)	47.98(15)	48.57(15)	50.49(19)	48.7(3)
C(3)–Fe(1)–C(4)	98.05(19)	97.2(2)	97.1(3)	97.1(4)
C(3)–Fe(2)–C(4)	97.88(19)		98.1(3)	97.9(4)
Fe(1)–C(1)–O(1)	177.6(4)	176.9(6)	174.2(7)	177.2(12)
Fe(1)–C(3)–C(5)	119.0(3)	127.9(3)	124.9(5)	124.5(7)
Fe(2)–C(3)–C(5)	120.4(3)	127.9(3)	118.4(5)	121.7(6)
Fe(1)–C(3)–S(1)			108.7(3)	
Fe(1)–C(3)–N(1)				112.8(6)
Fe(2)–C(2)–O(2)	173.4(4)		175.9(7)	175.0(10)
Fe(2)–C(3)–S(1)			117.6(3)	
Fe(2)–C(3)–N(1)				114.6(6)
C(5)–C(3)–S(1)			106.8(4)	
C(5)–C(3)–N(1)				102.9(7)
C(3)–S(1)–C(31)			113.1(3)	
C(3)–N(1)–C(11)				178.9(9)
N(1)–C(11)–W(1)				178.9(9)

<sup>a</sup> Estimated standard deviations in the least significant figure are given in parentheses.

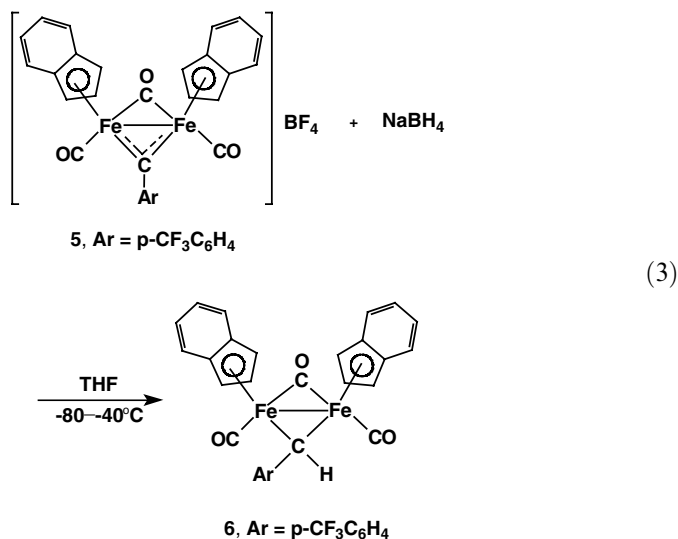
Complexes **2–4** are soluble in polar organic solvents but slightly soluble in nonpolar solvents. They are very sensitive to air and temperature in solution but relatively stable as the solid. The proposed structure for **2–4** was first supported by elemental analyses and spectroscopic data. The IR spectra of complexes **2–4** showed the two CO absorption bands at 1932–1973 cm<sup>-1</sup> in the terminal  $\nu(\text{CO})$  region and one at 1782–1784 cm<sup>-1</sup> in the bridging  $\nu(\text{CO})$  region, evidence an (CO)<sub>2</sub>Fe<sub>2</sub>( $\mu$ -CO) moiety in these complexes and suggested that only one  $\mu$ -CO ligand was converted into a bridging carbene ligand upon the reaction of **1** with nucleophilic aryllithium and subsequent alkylation with Et<sub>3</sub>OBF<sub>4</sub> in four-carbonyl compound **1**. The further characterization for their structures was obtained by X-ray analysis of **4**, which firmly confirmed that products **2–4** are diindenyl-coordinated diiron complexes with a bridging carbene ligand, in which the two indenyl ligands are coordinated the two iron atoms through their cyclopentadienyl ring moiety in  $\eta^5$ -bonding.

There are two bridging CO ligands which have the same chemical environment in the starting **1**. It was expected that the diiron di-bridging alkoxy(aryl)carbene complexes should exist in the resulting products when treating **1** with aryllithium reagents. However, no expected diiron di-bridging alkoxy(aryl)carbene 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, compound **1** has two forms of coordinated carbonyl ligands, terminal and bridging CO. It can be expected that the aryllithium reagent could attack both terminal and bridging CO ligands to produce a terminal alkoxy(aryl)carbene and a bridging alkoxy(aryl)carbene complexes when treating **1** with aryllithium reagent. However, only a diiron bridging alkoxy(aryl)carbene complex was obtained, which could be produced via an attack of nucleophilic aryllithium reagent on a bridging CO of **1** although this attack is



The freshly prepared (in situ) cationic carbyne complex **5** reacts with  $\text{NaBH}_4$  in THF at  $-80$  to  $-40$  °C for 3 h. After workup as described in Section 2, a brown-red bridging arylcarbene complex  $[\text{Fe}_2\{\mu\text{-C}(\text{H})\text{C}_6\text{H}_4\text{CF}_3\text{-}p\}\{\mu\text{-CO}(\text{CO})_2\text{-}(\eta^5\text{-C}_9\text{H}_7)_2\}]$  (**6**) was obtained in 80% yield (Eq. (3)), supported by microanalytic and spectroscopic data and its X-ray diffraction analysis.



The  $^1\text{H}$  NMR spectrum had a resonance at 10.36 ppm, characteristic for a  $\mu\text{-CHR}$  group. However, this resonance has undergone a significant upfield shift, as compared to that of analogous cyclopentadienyl-coordinated bridging arylcarbene complex  $[\text{Fe}_2\{\mu\text{-CO}\}\{\mu\text{-C}(\text{H})\text{C}_6\text{H}_4\text{CH}_3\text{-}p\}\{\text{CO}\}_2\{\eta\text{-C}_5\text{H}_5\}_2]$  ( $\delta$  12.40) [12], which probably is arising from that the H atom is influenced by the ring current of the dindenyl moiety.

The molecular structure of **6** is shown in Fig. 2. Complex **6** has a mirror plane passing through C(5) and C(8) of the benzene ring, the C(11) and F(1) atoms, the C(4) and O(4) atoms, and the bridging carbene carbon (C(3)). The two Fe atoms are coordinated symmetrically (relative to the mirror) by the two indenyl groups, respectively. The Fe–Fe distance in **6** (2.5393(15) Å) is essentially the same as that in the bridging alkoxy-carbene complex **4** (2.5392(9) Å) and close to that of analogous cyclopentadienyl-coordinated complex  $[\text{Fe}_2\{\mu\text{-CO}\}\{\mu\text{-C}(\text{H})\text{C}_6\text{H}_4\text{CH}_3\text{-}p\}\{\text{CO}\}_2\{\eta\text{-C}_5\text{H}_5\}_2]$  (2.523(2) Å) [12], but is significantly shorter than that found in analogous COT-coordinated complex  $[\text{Fe}_2\{\mu\text{-C}(\text{H})\text{C}_6\text{H}_4\text{CF}_3\text{-}p\}\{\text{CO}\}_4\{\eta^8\text{-C}_8\text{H}_8\}]$  (2.7069(11) Å) [11a]. In addition to the molecular configuration, an apparent difference in the structure of **4** and **6** is the shorter C(3)–C(5) bond in **6** (1.445(10) Å), which is intermediate between C–C single and C=C double bond lengths, as compared to **4** (1.503(5) Å).

Cationic bridging carbyne complexes **5** also reacts with  $\text{NaSC}_6\text{H}_4\text{CH}_3\text{-}p$  under the similar conditions to give the diindenyl-coordinated diiron bridging arylthiocarbene complexes  $[\text{Fe}_2\{\mu\text{-C}(\text{C}_6\text{H}_4\text{CF}_3\text{-}p)\text{SC}_6\text{H}_4\text{CH}_3\text{-}p\}\{\mu\text{-CO}(\text{CO})_2\text{-}(\eta^5\text{-C}_9\text{H}_7)_2\}]$  (**7**) (Eq. (4)) in 59% yield.

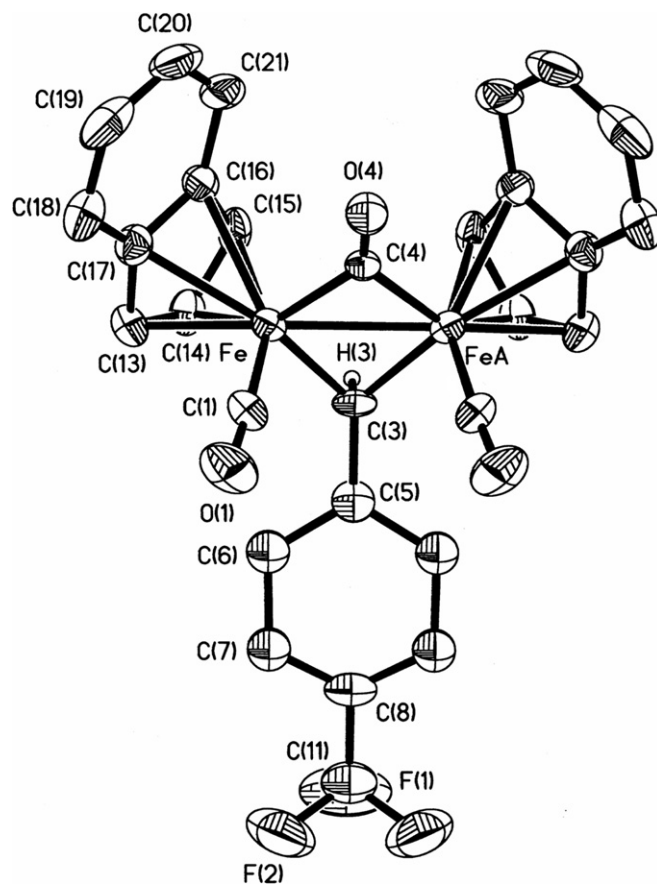
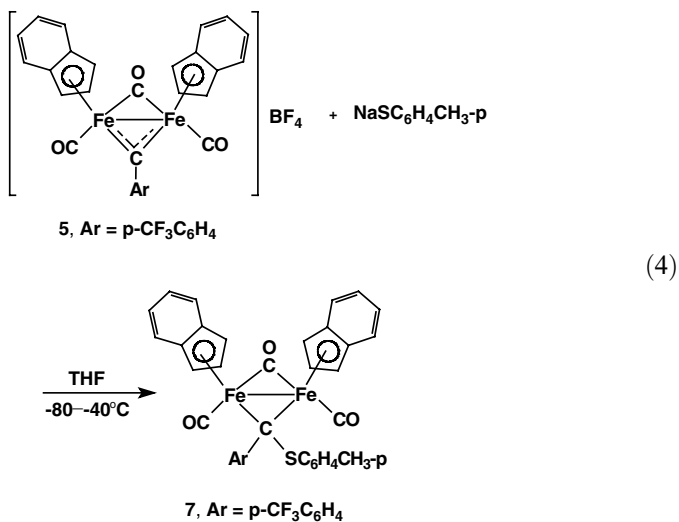


Fig. 2. Molecular structure of **6**, showing the atom-numbering scheme with 45% thermal ellipsoids.



The elemental analysis and spectroscopic data (Section 2) supported the proposed structure of complex **7** shown in Eq. (4). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data indicated the presence of two indenyl groups and a bridging carbene ligand. The further characterization for its molecular structure was obtained by X-ray structural determination.

The molecular structure of **7** (Fig. 3) resembles that of **6**, except the substituent on the  $\mu\text{-carbene}$  carbon is an  $p\text{-CH}_3\text{C}_6\text{H}_4\text{S}$  group in **7** but a H atom in **6**. The two indenyl



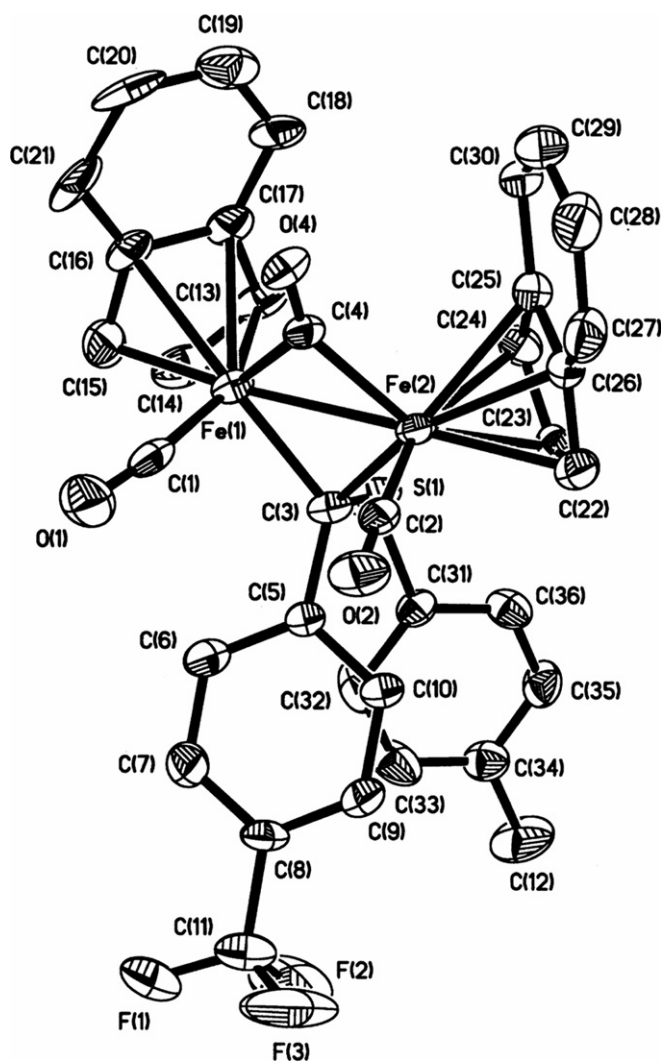
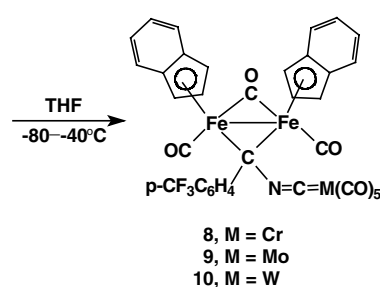
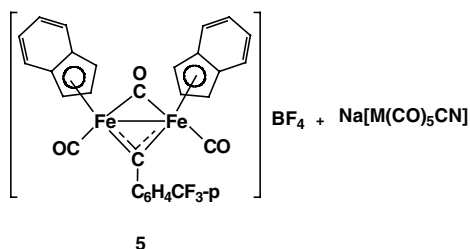


Fig. 3. Molecular structure of **7**, showing the atom-numbering scheme with 45% thermal ellipsoids.

groups are in a *cis*, almost totally eclipsed configuration. The distances between the Fe atoms and the Cp ring planes of the indenyl ligands are nearly 1.78 Å. The least-squares plane calculations show that the carbon atoms in the indene ring are coplanar and the two CO groups coordinated to the same Fe atom are not coplanar arising from the bridge. The distance of the Fe–Fe bond bridged by the  $\mu$ -carbene ligand in **7** is 2.5647(16) Å, which is obviously longer than that in **4** and **6**. The  $\mu$ -carbene carbon almost symmetrically bridges the Fe–Fe bond with C(3)–Fe(1) of 2.025(6) Å and C(3)–Fe(2) of 2.017(6) Å. The C(3)–S bond length of 1.860(7) indicates that it is essentially single bond as comparison with standard C(sp<sup>2</sup>)–S (1.76 Å) [21] single bond and C(sp<sup>3</sup>)–S (1.81 Å) [21] single bond distances. In molecule **7**, the two benzene rings are on the opposite side of the two indene rings. The angles between the two indene ring planes and the benzene ring C(5) through C(10) and the benzene ring C(31) through C(36) planes are 76.91° and 45.49°, respectively. The benzene ring composed by C(5) through C(10) plane and the

benzene ring composed by C(31) through C(36) plane are at angles of 62.05° and 69.27° and of 16.56° and 86.05°, respectively, to the planes of the two indene rings. Thus, compound **7** exists in a *cis* structure to avoid steric repulsion between the six-membered aryl rings and the indene rings.

The highly electrophilic complex **5** also reacts with anionic carbonylmetal compound containing a CN negative substituent, Na[M(CO)<sub>5</sub>CN] (M = Cr, Mo, W), in THF at low temperature to afford diindenyl-coordinated diiron bridging aryl(penta-carbonylcyano)metal carbene complexes [Fe<sub>2</sub>{ $\mu$ -C(C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>-*p*)NCM(CO)<sub>5</sub>}( $\mu$ -CO)(CO)<sub>2</sub>( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>] (**8**, M = Cr; **9**, M = Mo; **10**, M = W) (Eq. (5)) in 58–72% isolated yields, respectively.



(5)

On the basis of elemental analyses and spectroscopic evidence, as well as X-ray crystallography, products **8–10** are formulated as the diindenyl-coordinated diiron bridging carbene complexes with a M(CO)<sub>5</sub>CN (M = Cr, Mo, W) moiety bonded to the  $\mu$ -carbene carbon through the N atom. The IR and <sup>1</sup>H NMR spectra of **8–10** are consistent with their structures shown in Eq. (5). The IR spectra of **8–10** in the  $\nu$ (CO) region show the four absorption bands of the CO groups at ca. 2048–1810 cm<sup>-1</sup>. The characteristic  $\nu$ (CN) stretching vibration occurs at ca. 2108–2112 cm<sup>-1</sup>, similar to those of analogous aryl(pentacarbonylcyano)metal carbene complexes [Fe<sub>2</sub>( $\mu$ -CO){ $\mu$ -C(C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>-*p*)NCM(CO)<sub>5</sub>}(CO)<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (M = Cr, Mo, W) (at ca. 2125 cm<sup>-1</sup>) [9]. The <sup>1</sup>H NMR spectra of **8–10** showed the signals for the indenyl and aryl rings at ca. 8.02–7.30 ppm which are downfield of those in **4**, **6**, and **7** (at 7.63–6.93 ppm) because of the stronger electron-accepting ability of (CO)<sub>5</sub>M(CN) as compared to OC<sub>2</sub>H<sub>5</sub>, H, and *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>S groups. The structures of complexes **8–10** are further confirmed by a single-crystal X-ray diffraction of **10**.

The molecular structure of **10** (Fig. 4) resembles that of **7**, except that the *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>S substituent at the  $\mu$ -carbene carbon in **7** is replaced by the W(CO)<sub>5</sub>CN group in **10**.

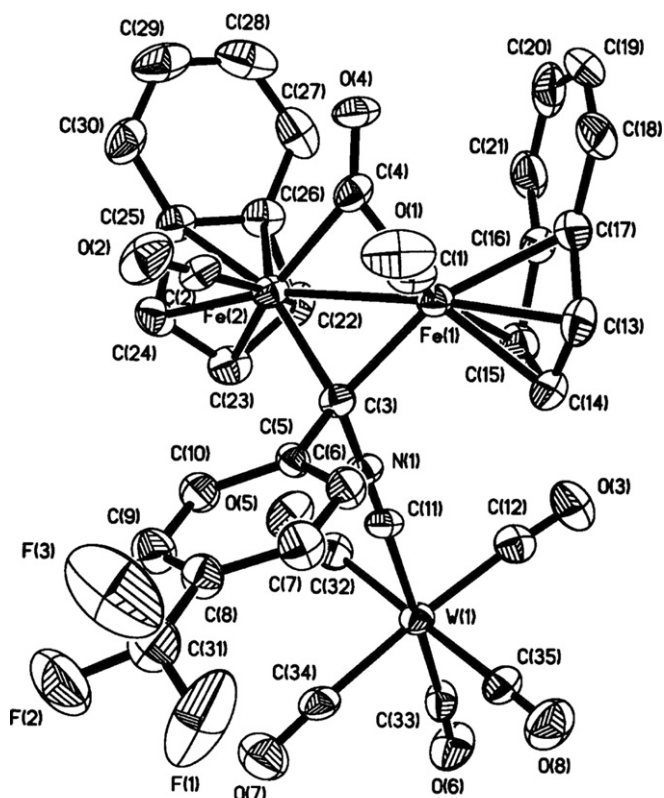


Fig. 4. Molecular structure of **10**, showing the atom-numbering scheme with 45% thermal ellipsoids.

Many structural features of the principal portion of  $[\text{Fe}_2(\mu\text{-CC}_6\text{H}_4\text{CF}_3\text{-}p)(\mu\text{-CO})(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)_2]$  of **10** are essentially the same as those of the same unit in **7**, as illustrated by their parameters (the value for **10** is following by the same parameters for **7**): Fe–Fe (2.5551(19), 2.5647(16) Å), average Fe– $\mu\text{-C}(3)$  (1.988, 2.021 Å), average Fe–C(4) (1.944, 1.925 Å), average Fe–C(Cp) (2.154, 2.152 Å). The two C–N bond lengths of the  $\text{C}(\text{C}_6\text{H}_5)\text{NCW}(\text{CO})_5$  moiety in **10** are very different. C(3)–N(1) has a bond length of 1.454(11) Å, which is between the normal C–N and C=N distances. The other is C(11)–N(1) with the bond length of 1.134(10) Å, indicating high triple-bond character. The shorter W(1)–C(11) distance (2.135(10) Å) in **10** signifies its high double bond character. The C(3), N(1), C(11), and W(1) atoms are colinear with a C(3)–N(1)–C(11) angle of 178.9(9)° and a N(1)–C(11)–W(1) angle of 178.9(9)°, indicating that the C(3)–N(1)–C(11)–W fragment is almost linear.

The reaction pathway to complexes **8–10** could proceed via attack of the  $(\text{CO})_5\text{M}=\text{C}=\text{N}^-$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) anion, a representation of the same electronic structure of the  $^-\text{M}(\text{CO})_5(\text{CN})$  anion, at the  $\mu$ -carbyne carbon of cationic **5**, similar to that of the reactions of  $[\text{Fe}_2(\mu\text{-CO})(\mu\text{-CC}_6\text{H}_4\text{CH}_3\text{-}p)(\text{CO})_2((\eta^5\text{-C}_5\text{H}_5)_2)]$  with  $\text{Na}[\text{M}(\text{CO})_5\text{CN}]$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) [9].

In summary, we have synthesized a new type of the diindenyl-coordinated diiron bridging alkoxy-carbene complexes

**2–4** and discovered the reactions of the cationic bridging carbyne complex **5** of **4** with the nucleophiles involving carbonylmetal anions, which produced a series of novel diindenyl-coordinated diiron bridging carbene complexes. This provides an useful and convenient method for the preparation and structural modification of such dimetal bridging carbene complexes. Further studies on the scope of the reaction and the application in organometallic and organic synthesis are now being carried out in our laboratory.

#### 4. Supplementary material

Crystallographic data for the structural analysis of complexes **4**, **6**, **7**, and **10** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 602212 for **4**, 602213 for **6**, 602214 for **7**, and 602215 for **10**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1233 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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#### References

- [1] F.G.A. Stone, in: U. Schubert (Ed.), *Advances in Metal Carbene Chemistry*, Kluwer Academic Publishers, Dordrecht, 1989, p. 11.
- [2] (a) T.V. Ashworth, J.A.K. Howard, M. Laguna, F.G.A. Stone, *J. Chem. Soc., Dalton Trans.* (1980) 1593; (b) G.A. Carriedo, J.A.K. Howard, F.G.A. Stone, *J. Chem. Soc., Dalton Trans.* (1984) 1555; (c) M.E. Garcia, J.C. Jeffery, P. Sherwood, F.G.A. Stone, *J. Chem. Soc., Dalton Trans.* (1987) 1209; (d) L. Busetto, J.C. Jeffery, R.M. Mills, F.G.A. Stone, M.J. Went, P. Woodward, *J. Chem. Soc., Dalton Trans.* (1983) 101.
- [3] (a) J.A.K. Howard, K.A. Mead, J.R. Moss, R. Navarro, F.G.A. Stone, P. Woodward, *J. Chem. Soc., Dalton Trans.* (1981) 743; (b) D. Hodgson, J.A.K. Howard, F.G.A. Stone, M.J. Went, *J. Chem. Soc., Dalton Trans.* (1985) 331.
- [4] M.U. Pilotti, F.G.A. Stone, L. Topaloglu, *J. Chem. Soc., Dalton Trans.* (1991) 1621.
- [5] (a) J.-B. Chen, R.-T. Wang, *Coord. Chem. Rev.* 231 (2002) 109; (b) N. Xiao, Q. Xu, S. Tsubota, J. Sun, J.-B. Chen, *Organometallics* 21 (2002) 2764; (c) L. Zhang, N. Xiao, Q. Xu, J. Sun, J.-B. Chen, *Organometallics* 24 (2005) 5807.
- [6] J.-B. Chen, D.-S. Li, Y. Yu, Z.-S. Jin, Q.-L. Zhou, G.-C. Wei, *Organometallics* 12 (1993) 3885.
- [7] J.-B. Chen, D.-S. Li, Y. Yu, C.G. Chen, *Organometallics* 13 (1994) 3581.
- [8] R.-T. Wang, J. Sun, J.-B. Chen, *J. Organomet. Chem.* 617–618 (2001) 292.
- [9] Y.-J. Liu, R.-T. Wang, J. Sun, J.-B. Chen, *Organometallics* 19 (2000) 3784.
- [10] (a) R.-T. Wang, Q. Xu, J. Sun, Li-C. Song, J.-B. Chen, *Organometallics* 20 (2001) 4092; (b) R.-T. Wang, J. Sun, J.-B. Chen, Q. Xu, Y. Souma, *J. Organomet. Chem.* 658 (2002) 214.

- [11] (a) S. Zhang, Q. Xu, J. Sun, J.-B. Chen, *Organometallics* 22 (2003) 1816;  
(b) S. Zhang, Q. Xu, J. Sun, J.-B. Chen, *Chem. Eur. J.* 9 (2003) 5111.
- [12] Y.-J. Liu, R.-T. Wang, J. Sun, J.-B. Chen, *Organometallics* 19 (2000) 3498.
- [13] (a) S.G. Davies, K.S. Holland, K.H. Sutton, J.P. McNally, *Isr. J. Chem.* 31 (1991) 25;  
(b) J. Li, A.D. Hunter, R. McDonald, B.D. Santarsiero, S.G. Dott, J.L. Atwood, *Organometallics* 11 (1992) 3050.
- [14] E.E. Reid *Organic Chemistry of Bivalent Sulfur*, vol. 1, Chemical Publishing Co. Inc., New York, NY, 1958.
- [15] R.B. King, *Inorg. Chem.* 6 (1967) 25.
- [16] G. Wittig, *Angew. Chem.* 53 (1940) 243.
- [17] H. Gilman, E.A. Zoellner, W.M. Selby, *J. Am. Chem. Soc.* 55 (1933) 1252.
- [18] E.O. Fischer, J.-B. Chen, U. Schubert, *Z. Naturforsch. B* 37 (1982) 1284.
- [19] H. Meerwein, G. Hinze, P. Hofmann, E. Kroniny, E. Pfeil, *J. Prakt. Chem.* 147 (1937) 257.
- [20] N. Xiao, Q. Xu, J. Sun, J.-B. Chen, *Dalton Trans.* (2005) 3250.
- [21] (a) B. Rozsondai, G. Schultz, I. Hargittai, *J. Mol. Struct.* 70 (1981) 309;  
(b) S. Samdal, H.M. Seip, T. torgrimsen, *J. Mol. Struct.* 57 (1979) 105.