Novel dimetal bridging carbene complexes derived from a terminal carbonyl dimetal compound. Syntheses, structures and reactivities of 7*H*-indene-coordinated diiron bridging carbene complexes

Lei Zhang,[a] Jie Sun,[a] Huping Zhu,[a] Qiang Xu,*[b] Nobuko Tsumori*[c] and Jiabi Chen*[a]

Received 23rd May 2006, Accepted 27th June 2006
First published as an Advance Article on the web 12th July 2006
DOI: 10.1039/b607283f

Pentacarbonyl-7*H*-indenediiron, $[Fe_2(CO)_5(\eta^3,\eta^5\text{-}C_9H_8)]$ (**1**), reacts with aryllithium, ArLi (Ar = C_6H_5, $p\text{-}C_6H_5C_6H_4$), followed by alkylation with Et_3OBF_4 to give novel 7*H*-indene-coordinated diiron bridging alkoxycarbene complexes $[Fe_2\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (**2**, Ar = C_6H_5; **3**, Ar = $p\text{-}C_6H_5C_6H_4$). Complexes **2** and **3** react with $HBF_4\cdot Et_2O$ at low temperature to yield cationic bridging carbyne complexes $[Fe_2(\mu\text{-}CAr)(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]BF_4$ (**4**, Ar = C_6H_5; **5**, Ar = $p\text{-}C_6H_5C_6H_4$). Cationic **4** and **5** react with $NaBH_4$ in THF at low temperature to afford diiron bridging arylcarbene complexes $[Fe_2\{\mu\text{-}C(H)Ar\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (**6**, Ar = C_6H_5; **7**, Ar = $p\text{-}C_6H_5C_6H_4$). The similar reactions of **4** and **5** with $NaSC_6H_4CH_3\text{-}p$ produce the bridging arylthiocarbene complexes $[Fe_2\{\mu\text{-}C(Ar)SC_6H_4CH_3\text{-}p\}\text{-}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (**8**, Ar = C_6H_5; **9**, Ar = $p\text{-}C_6H_5C_6H_4$). Cationic **4** and **5** can also react with anionic carbonylmetal compounds $Na[M(CO)_5(CN)]$ (M = Cr, Mo, W) to give the diiron bridging aryl(pentacarbonylcyanometal)carbene complexes $[Fe_2\{\mu\text{-}C(Ar)NCM(CO)_5\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (**10**, Ar = C_6H_5, M = Cr; **11**, Ar = $p\text{-}C_6H_5C_6H_4$, M = Cr; **12**, Ar = C_6H_5, M = Mo; **13**, Ar = $p\text{-}C_6H_5C_6H_4$, M = Mo; **14**, Ar = C_6H_5, M = W; **15**, Ar = $p\text{-}C_6H_5C_6H_4$, M = W). Interestingly, in CH_2Cl_2 solution at room temperature complexes **10–15** were transformed into the isomerized 7*H*-indene-coordinated monoiron complexes $[Fe(CO)_2(\eta^5\text{-}C_9H_8)C(Ar)NCM(CO)_5]$ (**16**, Ar = C_6H_5, M = Cr; **17**, Ar = $p\text{-}C_6H_5C_6H_4$, M = Cr; **18**, Ar = C_6H_5, M = Mo; **19**, Ar = $p\text{-}C_6H_5C_6H_4$, M = Mo; **20**, Ar = C_6H_5, M = W; **21**, Ar = $p\text{-}C_6H_5C_6H_4$, M = W), while complex **3** was converted into a novel ring addition product $[Fe_2\{C(OC_2H_5)C_6H_4C_6H_5\text{-}p\text{-}(\eta^2,\eta^5\text{-}C_9H_8)\}(CO)_5]$ (**22**) under the same conditions. The structures of complexes **2**, **6**, **8**, **14**, **18** and **22** have been established by X-ray diffraction studies.

Introduction

The chemistry of di- and polynuclear metal bridging carbene and bridging carbyne complexes has been receiving considerable current attention, largely because of the interesting chemical properties exhibited by such complexes. A number of di- and polymetal complexes containing bridging carbene and carbyne ligands have been synthesized by Stone *et al.*[1,2] and a series of diiron bridging carbene and carbyne complexes have also been reported.[3–6] In continuation of our interest in developing the methodologies of the synthesis of olefin-coordinated metal carbene and carbyne complexes, we have found a facile method for preparation of the dimetal bridging carbene and bridging carbyne complexes that is to conduct the reactions of olefin-ligated dimetal carbonyl compounds bearing a bridging CO ligand, such as $[Fe_2(\mu\text{-}CO)(CO)_4(\eta^8\text{-}C_8H_8)]$, $[Fe_2(\mu\text{-}CO)_2(CO)_2(\eta^5\text{-}C_5H_5)_2]$ and $[Fe_2(\mu\text{-}CO)_2(CO)_2\{SiMe_2(\eta^5\text{-}C_5H_5)_2\}]$, with aryllithium reagents followed by alkylation with Et_3BF_4 to give diiron bridging alkoxycarbene complexes $[Fe_2\{\mu\text{-}C(OEt)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)]$,[7] $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OEt)Ar\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$,[8] and $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$,[9] respectively. However, only one example of olefin-coordinated dimetal bridging carbyne complex which was synthesized from a terminal carbonyl-ligated dimetal compound (bearing no bridging CO ligand) is known[10] and no example of dimetal bridging carbene complex synthesized in this way has been reported up to now. Recently, we have shown a new and convenient method for the preparation of di- and polymetal bridging carbene and/or bridging carbyne complexes: the reactions of diiron cationic bridging carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$,[11] $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]\text{-}BBr_4$,[12] and $[Fe_2(\mu\text{-}CAr)(CO)_4(\eta^8\text{-}C_8H_8)]BF_4$[13] obtained by treating above corresponding diiron bridging alkoxycarbene complexes with Lewis acid BBr_3 or HBF_4, with nucleophiles involving carbonylmetal anions. This offers an useful method for the preparation and structural modification of dimetal bridging carbene complexes.

On the other hand, it was found that the olefin ligands in dimetal carbonyl compounds exhibit a great influence on their reactivity towards aryllithium reagents and resulting products,[7–10,14] and that the different olefin ligands in the dimetal cationic bridging carbyne

---

[a] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai, 200032, China*
[b] *National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka, 563-8577, Japan*
[c] *Toyama National College of Technology, 13 Hongo-machi, Toyama-shi, 939-8630, Japan*

complexes also exhibit a great influence on their reactivities towards nucleophiles and the resulting products.[11,12,15]

To develop the new synthetic method for the preparation of di- and polymetallic bridging carbene and bridging carbyne complexes and to further explore the reactivity of the diiron cationic bridging carbyne complexes containing different cycloolefin ligands towards nucleophiles, we investigated the reaction of pentacarbonyl-7*H*-indenediiron, $[Fe_2(CO)_5(\eta^3,\eta^5\text{-}C_9H_8)]$ (**1**), a dimetal compound bearing only terminal CO ligands, with aryllithium reagents, which gave a new type of 7*H*-indene-coordinated diiron bridging alkoxycarbene complexes $[Fe_2\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (Ar = C_6H_5, *p*-$C_6H_5C_6H_4$) and carried out the study of the reactivities of their cationic bridging carbyne complexes towards nucleophiles involving carbonylmetal anions. These reactions produce a series of novel dimetal bridging carbene complexes. In this paper, we report these unusual reactions and the structural characterizations of the resulting products.

Experimental

All procedures were performed under a dry, oxygen-free N_2 atmosphere by using standard Schlenk techniques. All solvents employed were reagent grade and dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under N_2 atmosphere. THF and Et_2O were distilled from sodium benzophenone ketyl, while petroleum ether (bp 30–60 °C) and CH_2Cl_2 were distilled from CaH_2. The neutral alumina (Al_2O_3, 100–200 mesh) used for chromatography was deoxygenated at room temperature under high vacuum for 16 h, deactivated with 5% w/w N_2-saturated water and stored under N_2 atmosphere. Compounds $HBF_4{\cdot}Et_2O$, *p*-$C_6H_5C_6H_4Br$ and $NaBH_4$ were purchased from Aldrich Chemical Co. Compounds $[Fe_2(CO)_5(\eta^3,\eta^5\text{-}C_9H_8)]$ (**1**),[16] $NaSC_6H_4CH_3$-*p*,[17] $Na[M(CO)_5(CN)]$ (M = Cr, Mo, W),[18] aryllithium reagents,[19,20] and Et_3OBF_4[21] were prepared by literature methods.

The IR spectra were measured on a Nicolet AV-360 spectrophotometer using NaCl cells with 0.1 mm spacers. The ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature in acetone-d_6 solution with TMS as the internal reference using a Varian Mercury 300 spectrometer running at 300 MHz. The ^1H and ^{13}C NMR data for compounds **2**, **3**, **8** and **9** can not be obtained or assigned due to their easy transformation (for **3**) or other unknown reason. The ^{13}C NMR data for compounds **10–15** were not obtained since they were easily transformed into monoiron complexes **16–21**. 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.

Reaction of $[Fe_2(CO)_5(\eta^3,\eta^5\text{-}C_9H_8)]$ (1) with C_6H_5Li to give $[Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_5\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (2)

To a solution of 1.0 g (2.71 mmol) of **1** dissolved in 50 mL of ether at −60 °C was added 3.23 mmol of the freshly prepared C_6H_5Li[19] ether solution with stirring. The reaction mixture was stirred at −60 to −30 °C for 3 h, during which time the clear red solution gradually turned turbid solution. The resulting solution then evaporated under high vacuum at −30 °C to dryness. To the red solid residue obtained was added Et_3OBF_4[21] (*ca.* 5 g). This solid mixture was dissolved in 50 mL of N_2-saturated water at 0 °C with vigorous stirring and the mixture covered with petroleum ether (bp 30–60 °C). Immediately afterwards, Et_3OBF_4 (*ca.* 15 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 petroleum ether–CH_2Cl_2 (15 : 1) as the eluent. The red band was eluted and collected. After removal of the solvent, the residue was recrystallized from petroleum ether at −80 °C to give 1.12 g (86%, based on **1**) of red crystals of **2**; mp 84–86 °C (decomp.); IR (CH_2Cl_2) *v*(CO) 2019 (m), 1972 (vs), 1951 (w), 1911 (s) cm^{-1}; MS: *m*/*z* 446 (M^+ − CO), 418 (M^+ − 2CO), 390 (M^+ − 3CO), 362 (M^+ − 4CO), 86 ($C_6H_{14}^+$). Anal. Calc. for $C_{22}H_{18}O_5Fe_2{\cdot}0.5C_6H_{14}$ (hexane): C, 58.06; H, 4.87. Found: C, 57.59; H, 4.70%.

Reaction of 1 with *p*-$C_6H_5C_6H_4Li$ to give $[Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_4C_6H_5\text{-}p\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (3)

A solution of 0.280 g (1.20 mmol) of *p*-$C_6H_5C_6H_4Br$ in 20 mL of ether was mixed with 1.30 mmol of *n*-C_4H_9Li. After 1–2 h stirring at room temperature, the resulting ether solution of *p*-$C_6H_5C_6H_4Li$[20] was reacted, as described for the reaction of **1** with C_6H_5Li, with 0.370 g (1.00 mmol) of **1** at −60 to −30 °C for 3 h. Further treatment of the resulting mixture as described for the preparation of **2** yielded 0.432 g (79%, based on **1**) red crystalline **3**: mp 74–76 °C (decomp.); IR (CH_2Cl_2) *v*(CO) 2019 (m), 1973 (vs), 1951 (w), 1911 (s) cm^{-1}; MS *m*/*z* 382 (M^+ − 4CO − Fe), 337 (M^+ − 4CO − Fe − OC_2H_5), 116 ($C_9H_8^+$). Anal. Calc. for $C_{28}H_{22}O_5Fe_2$: C, 61.13; H, 4.23. Found: C, 61.62; H, 4.54%.

Reaction of 2 with $HBF_4{\cdot}Et_2O$ to give $[Fe_2(\mu\text{-}CC_6H_5)(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]BF_4$ (4)

To a stirred, red solution of **2** (0.120 g, 0.25 mmol) in 30 mL of ether at −60 °C was added 0.045 mL (0.30 mmol) of $HBF_4{\cdot}Et_2O$. Immediately, a brick red precipitate was formed. The mixture was stirred at −60 to −30 °C for 1 h. The resulting mixture was filtered and the solids were washed with ether (2 × 20 mL) at −60 °C and then dried under high vacuum at −30 °C to give 0.120 g (90%, based on **2**) of **4** as a brick red solid: IR (CH_2Cl_2) *v*(CO) 2074 (s), 2047 (vs), 2025 (m), 2005 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.79–7.66 (m, 5H, C_6H_5), 7.17 (d, 1H, C_9H_8, J = 2.7), 6.67 (s, 2H, C_9H_8,), 5.86 (s, 1H, C_9H_8), 5.64 (s, 1H, C_9H_8), 4.23 (s, 1H, C_9H_8), 1.89 (d, 1H, C_9H_8, J = 9.6), 1.02 (dd, 1H, C_9H_8, J = 7.5, 9.3).

Preparation of $[Fe_2(\mu\text{-}CC_6H_5C_6H_4\text{-}p)(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]BF_4$ (5)

This complex was prepared in a manner similar to that for **4** using **3** (0.100 g, 0.18 mmol) and $HBF_4{\cdot}Et_2O$ (0.040 mL, 0.27 mmol). A brick red solid product of **5** was obtained in a yield of 0.100 g (95%, based on **3**): IR (CH_2Cl_2) *v*(CO) 2073 (s), 2046 (vs), 2024 (m), 2003 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 8.01–7.49 (m, 9H, $C_6H_5C_6H_4$), 7.17 (d, 1H, C_9H_8, J = 2.4), 6.68 (dd, 2H, C_9H_8, J = 1.2, 5.2), 5.88 (d, 1H, C_9H_8, J = 0.9), 5.66 (dd, 1H, C_9H_8, J = 0.9, 2.1), 4.23 (s, 1H, C_9H_8), 1.92 (d, 1H, C_9H_8, J = 9.9), 1.11 (d, 1H, C_9H_8, J = 6.9).

Reaction of 4 with $NaBH_4$ to give $[Fe_2\{\mu\text{-}C(H)C_6H_5\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (6)

To a suspension of **4**, freshly prepared (*in situ*) **4** by reaction of **2** (0.200 g, 0.42 mmol) with $HBF_4 \cdot Et_2O$ (0.045 mL, 0.30 mmol), in 50 mL of THF at −80 °C was added 0.020 g (0.53 mmol) of $NaBH_4$. The solution turned from a brick turbid solution to a deep red gradually. After stirring at −80 to −40 °C for 2–3 h, the resulting solution was evaporated *in vacuo* at −40 °C to dryness and residue was chromatographed on an Al_2O_3 column at −25 °C with petroleum ether–CH_2Cl_2 (5 : 2) as the eluent. 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 0.132 g (73%, based on **2**) of brown–red crystals of **6**: mp 152–154 °C (decomp.); IR (CH_2Cl_2) *ν*(CO) 2017 (s), 1976 (vs), 1957 (m), 1912 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) *δ* 7.66–7.06 (m, 5H, C_6H_5), 7.08 (s, 1H, μ-CH), 5.97 (t, 1H, C_9H_8, *J* = 2.4), 5.31 (dd, 1H, C_9H_8, *J* = 0.6, 6.0), 4.93 (s, 1H, C_9H_8), 3.87 (m, 1H, C_9H_8), 3.68 (d, 1H, C_9H_8, *J* = 2.7), 3.23 (d, 1H, C_9H_8, *J* = 9.0), 3.05 (t, 1H, C_9H_8, *J* = 1.8), 2.63 (dd, 1H, C_9H_8, *J* = 6.9, 10.5); ^{13}C NMR (CD_3COCD_3) *δ* 222.6, 218.3, 216.8 (CO), 159.2 (μ-C), 143.7, 128.5, 127.9, 125.8 (C_6H_5), 97.7, 94.8, 90.7, 84.9, 78.9, 68.9, 64.4 (C_9H_8), 48.8; MS *m*/*z* 402 (M^+ − CO), 374 (M^+ − 2CO), 318 (M^+ − 4CO), 317 (M^+ − 4CO − H), 240 (M^+ − 4CO − H − C_6H_5). Anal. Calc. for $C_{20}H_{14}O_4Fe_2$: C, 55.86; H, 3.28. Found: C, 55.39; H, 3.62%.

Reaction of 5 with $NaBH_4$ to give $[Fe_2\{\mu\text{-}C(H)C_6H_4C_6H_5\text{-}p\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (7)

Using the same procedures as in the reaction of **4** with $NaBH_4$, freshly prepared (*in situ*) **5** from the reaction of **3** (0.100 g, 0.18 mmol) with $HBF_4 \cdot Et_2O$ (0.040 mL, 0.27 mmol), was treated with 0.010 g (0.27 mmol) of $NaBH_4$ at −80 to −40 °C for 3 h. Further treatment of the resulting solution as done for the preparation of **6** yielded 0.074 g (85%, based on **3**) of brown–red crystals of **7**: mp 164–165 °C (decomp.); IR (CH_2Cl_2) *ν*(CO) 2016 (s), 1976 (vs), 1957 (s), 1911 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) *δ* 7.72–7.32 (m, 9H, *p*-$C_6H_5C_6H_4$), 7.09 (s, 1H, μ-CH), 6.00 (s, 1H, C_9H_8), 5.33 (s, 1H, C_9H_8), 4.94 (s, 1H, C_9H_8), 3.89 (s, 1H, C_9H_8), 3.71 (s, 1H, C_9H_8), 3.25 (d, 1H, C_9H_8, *J* = 9.0), 3.08 (s, 1H, C_9H_8), 2.64 (d, 1H, C_9H_8, *J* = 8.4); ^{13}C NMR (CD_3COCD_3) *δ* 222.4, 216.5, 215.5, 215.1 (CO), 158.8 (μ-C), 142.1, 137.8, 129.4, 128.4, 127.5, 126.9, 126.6 (C_6H_5), 97.5, 94.7, 90.5, 84.7, 78.7, 68.7, 64.3, 48.6 (C_9H_8); MS *m*/*z* 450 (M^+ − 2CO), 394 (M^+ − 4CO), 338 (M^+ − 4CO − Fe), 185 (M^+ − 4CO − Fe − $C_6H_5C_6H_4$), 116 ($C_9H_8^+$). Anal. Calc. for $C_{26}H_{18}O_4Fe_2$: C, 61.70; H, 3.58. Found: C, 61.04; H, 3.67%.

Reaction of 4 with $NaSC_6H_4CH_3$-*p* to give $[Fe_2\{\mu\text{-}C(C_6H_5)SC_6H_4CH_3\text{-}p\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (8)

To a suspension of **4**, freshly prepared (*in situ*) by the reaction of **2** (0.130 g, 0.27 mmol) with $HBF_4 \cdot Et_2O$ (0.050 mL, 0.37 mmol), in 50 mL of THF at −80 °C was added 0.040 g (0.25 mmol) of $NaSC_6H_4CH_3$-*p*. The mixture turned from brick turbid solution to deep red solution gradually. After stirring at −80 to −40 °C for 3 h. The solvent was removed *in vacuo* at −40 °C and the residue was chromatographed on an Al_2O_3 column at −25 °C with petroleum ether–CH_2Cl_2 (5 : 1) as the eluent. A brown–red band was collected. After vacuum removal of the solvent, the residue was recrystallized from petroleum ether–CH_2Cl_2 solution at −80 °C to afford 0.108 g (71%, based on **2**) of brown–red crystalline **8**: mp 72–74 °C (decomp.); IR (CH_2Cl_2) *ν*(CO) 2017 (m), 1982 (vs), 1960 (m), 1939 (s) cm^{-1}; MS *m*/*z* 317 (M^+ − 4CO − $CH_3C_6H_4S$), 261 (M^+ − 4CO − Fe − $CH_3C_6H_4S$), 172 [M^+ − 4CO − Fe − $C(C_6H_5)SC_6H_4CH_3$], 115 (C_9H_8 − 1)$^+$. Anal. Calc. for $C_{27}H_{20}O_4SFe_2$: C, 58.73; H, 3.65. Found: C, 58.51; H, 3.80%.

Reaction of 5 with $NaSC_6H_4CH_3$-*p* to give $[Fe_2\{\mu\text{-}C(C_6H_4C_6H_5\text{-}p)SC_6H_4CH_3\text{-}p\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (9)

Freshly prepared (*in situ*) **5** by the reaction of **3** (0.100 g, 0.18 mmol) with $HBF_4 \cdot Et_2O$ (0.040 mL, 0.27 mmol) was treated, in a manner similar to that described for the preparation of **4**, with 0.040 g (0.27 mmol) of $NaSC_6H_4CH_3$-*p* at −80 to −40 °C for 3 h. The resulting solution was worked up as described for the preparation of **8** to yield 0.100 g (87%, based on **3**) of **9** as brown–red crystals: mp 124–126 °C; IR (CH_2Cl_2) *ν*(CO) 2018 (s), 1981 (vs), 1961 (m), 1922 (m) cm^{-1}; MS *m*/*z* 475 (M^+ − $C_6H_5C_6H_4$), 391 (M^+ − 3CO − $C_6H_5C_6H_4$), 363 (M^+ − 4CO − $C_6H_5C_6H_4$), 240 (M^+ − 4CO − $C_6H_5C_6H_4$ − $CH_3C_6H_4S$), 115 (C_9H_8 − 1)$^+$. Anal. Calc. for $C_{33}H_{24}O_4SFe_2$: C, 63.08; H, 3.85. Found: C, 63.25; H, 3.86%.

Reaction of 4 with $Na[Cr(CO)_5(CN)]$ to give $[Fe_2\{\mu\text{-}C(C_6H_5)NCCr(CO)_5\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (10)

To a suspension of **4**, freshly prepared (*in situ*) from **2** (0.400 g, 0.84 mmol) and $HBF_4 \cdot Et_2O$ (0.200 mL, 1.50 mmol), in 50 mL of THF at −80 °C was added 0.200 g (0.83 mmol) of $[NaCr(CO)_5(CN)]$. The reaction mixture was stirred at −80 to −40 °C for 2 h, during which time the turbid solution gradually turned deep red solution. The resulting solution was evaporated *in vacuo* at −40 °C to dryness and the residue was chromatographed on Al_2O_3 at −25 °C with petroleum ether–CH_2Cl_2 (5 : 1) as the eluent. The brown 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 0.365 g (67%, based on **2**) of brown–red crystals of **10**: mp 102–103 °C (decomp.); IR (CH_2Cl_2) *ν*(CO) 2053 (m), 2029 (m), 1994 (s), 1974 (m), 1947 (vs, br) cm^{-1}; *ν*(CN) 2115 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) *δ* 7.89–7.24 (m, 5H, C_6H_5), 6.37 (t, 1H, C_9H_8, *J* = 2.4), 5.70 (t, 1H, C_9H_8, *J* = 2.7), 4.98 (dd, 1H, C_9H_8, *J* = 0.6, 2.1), 4.03–3.99 (m, 2H, C_9H_8), 3.38 (d, 1H, C_9H_8, *J* = 9.6), 2.93 (t, 1H, C_9H_8, *J* = 1.8), 2.86 (m, 1H, C_9H_8); MS *m*/*z* 540 (M^+ − CO − C_6H_5), 373 [M^+ − 2CO − $Cr(CO)_5CN$], 345 [M^+ − 3CO − $Cr(CO)_5CN$]. Anal. Calc. for $C_{26}H_{13}O_9NCrFe_2$: C, 48.26; H, 2.03; N, 2.16. Found: C, 48.32, H, 2.28; N, 2.18%.

The following complexes were prepared by similar reactions.

$[Fe_2\{\mu\text{-}C(C_6H_4C_6H_5\text{-}p)NCCr(CO)_5\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (11)

Brown–red crystals (70% yield); mp 76–78 °C (decomp.); IR (CH_2Cl_2) *ν*(CO) 2053 (m), 2028 (m), 1994 (s), 1974 (m), 1948 (vs) cm^{-1}; *ν*(CN) 2116 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) *δ* 7.98–7.37 (m, 9H, *p*-$C_6H_5C_6H_4$), 6.38 (t, 1H, C_9H_8, *J* = 3.0), 5.73 (t, 1H, C_9H_8, *J* = 6.3), 4.99 (dd, 1H, C_9H_8, *J* = 0.6, 1.8), 4.06–4.03 (m, 2H, C_9H_8), 3.40 (d, 1H, C_9H_8, *J* = 9.0), 2.96 (t, 1H, C_9H_8, *J* = 1.2), 2.89 (t, 1H, C_9H_8, *J* = 2.1); MS *m*/*z* 393 [M^+ − 4CO − $Cr(CO)_5CN$], 228 [M^+ − 4CO − $C(C_6H_5C_6H_4)NCCr(CO)_5$], 172

$[M^+ - 4CO - Fe - C(C_6H_5C_6H_4)NCCr(CO)_5]$. Anal. Calc. for $C_{32}H_{17}O_9NCrFe_2$: C, 53.15; H, 2.37; N, 1.94. Found: C, 53.09; H, 2.68; N, 1.88%.

$[Fe_2\{\mu\text{-}C(C_6H_5)NCMo(CO)_5\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (12)

Brown–red crystals (71% yield); mp 44–46 °C (decomp.); IR (CH_2Cl_2) ν(CO) 2056 (m), 2029 (m), 1994 (s), 1975 (m), 1950 (vs, br) cm^{-1}; ν(CN) 2114 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.91–7.25 (m, 5H, C_6H_5), 6.38 (t, 1H, C_9H_8, $J = 2.7$), 5.73 (t, 1H, C_9H_8, $J = 5.7$), 4.98 (s, 1H, C_9H_8), 4.04–4.00 (m, 2H, C_9H_8), 3.40 (d, 1H, C_9H_8, $J = 9.6$), 2.94 (t, 1H, C_9H_8, $J = 1.2$), 2.88 (m, 1H, C_9H_8); MS *m/z* 373 $[M^+ - 2CO - Mo(CO)_5CN]$, 317 $[M^+ - 4CO - Mo(CO)_5CN]$, 240 $[M^+ - 4CO - C(C_6H_5)NC - Mo(CO)_5 - C_6H_5]$, 116 ($C_9H_8^+$). Anal. Calc. for $C_{26}H_{13}O_9NMoFe_2$: C, 45.19; H, 1.90; N, 2.03. Found: C, 45.05; H, 2.01; N, 2.06%.

$[Fe_2\{\mu\text{-}C(C_6H_4C_6H_5\text{-}p)NCMo(CO)_5\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (13)

Brown–red crystals (78% yield); mp 82–84 °C (decomp.); IR (CH_2Cl_2) ν(CO) 2056 (m), 2029 (m), 1994 (s), 1975 (m), 1951 (vs, br) cm^{-1}; ν(CN) 2114 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.98–7.37 (m, 9H, $C_6H_5C_6H_4$-*p*), 6.40 (t, 1H, C_9H_8, $J = 3.3$), 5.75 (t, 1H, C_9H_8, $J = 6.9$), 5.00 (d, 1H, C_9H_8, $J = 0.9$), 4.07–4.01 (m, 2H, C_9H_8), 3.40 (d, 1H, C_9H_8, $J = 9.3$), 2.97 (t, 1H, C_9H_8, $J = 1.5$), 2.92 (m, 1H, C_9H_8), 1.16–1.10 (m, 4H, $CH_3(CH_2)_4CH_3$), 0.85 (t, 3H, $CH_3(CH_2)_4CH_3$); MS *m/z* 412 $[M^+ - 3CO - Mo(CO)_5CN]$, 384 $[M^+ - 4CO - Mo(CO)_5CN]$, 231 $[M^+ - 4CO - Mo(CO)_5CN - C_6H_5C_6H_4]$, 219 $[M^+ - 4CO - C(C_6H_5C_6H_4)NCMo(CO)_5]$, 86 ($C_6H_{14}^+$). Anal. Calc. for $C_{32}H_{17}O_9NMoFe_2\cdot 0.5C_6H_{14}$ (hexane): C, 51.53; H, 2.99; N, 1.83. Found: C, 51.75; H, 2.78; N, 1.86%.

$[Fe_2\{\mu\text{-}C(C_6H_5)NCW(CO)_5\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (14)

Brown–red crystals (63% yield); mp 100–102 °C (decomp.); IR (CH_2Cl_2) ν(CO) 2054 (m), 2029 (m), 1994 (s), 1975 (m), 1944 (vs, br) cm^{-1}; ν(CN) 2116 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.90–7.25 (m, 5H, C_6H_5), 6.38 (t, 1H, C_9H_8, $J = 3.0$), 5.73 (t, 1H, C_9H_8, $J = 6.3$), 4.99 (d, 1H, C_9H_8, $J = 1.8$), 4.05–4.00 (m, 2H, C_9H_8), 3.40 (d, 1H, C_9H_8, $J = 6.3$), 2.96 (t, 1H, C_9H_8, $J = 1.8$), 2.91 (m, 1H, C_9H_8); MS *m/z* 562 $(M^+ - 5CO - C_6H_5)$, 354 $[M^+ - CO - W(CO)_5CN]$, 326 $[M^+ - 2CO - W(CO)_5CN]$, 298 $[M^+ - 3CO - W(CO)_5CN]$, 270 $[M^+ - 4CO - W(CO)_5CN]$, 116 ($C_9H_8^+$). Anal. Calc. for $C_{26}H_{13}O_9NWFe_2$: C, 40.09; H, 1.68; N, 1.80. Found: C, 39.82; H, 1.68; N, 1.85%.

$[Fe_2\{\mu\text{-}C(C_6H_4C_6H_5\text{-}p)NCW(CO)_5\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (15)

Brown–red crystals (67% yield); mp 80–82 °C (decomp.); IR (CH_2Cl_2) ν(CO) 2054 (m), 2017 (m), 1994 (m), 1977 (w), 1933 (vs, br) cm^{-1}; ν(CN) 2117 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.97–7.35 (m, 5H, C_6H_5), 6.40 (t, 1H, C_9H_8, $J = 2.7$), 5.75 (t, 1H, C_9H_8, $J = 5.4$), 5.00 (s, 1H, C_9H_8), 4.07–4.02 (m, 2H, C_9H_8), 3.41 (d, 1H, C_9H_8, $J = 9.0$), 2.98 (t, 1H, C_9H_8, $J = 1.8$), 2.91 (t, 1H, C_9H_8, $J = 2.4$), 1.12 (m, 4H, $CH_3(CH_2)_4CH_3$), 0.84 (t, 3H, $CH_3(CH_2)_4CH_3$); MS *m/z* 350 $[M^+ - W(CO)_5CN - C_6H_5C_6H_4]$, 294 $[M^+ - 2CO - W(CO)_5CN - C_6H_5C_6H_4]$, 238 $[M^+ - 4CO - W(CO)_5CN - C_6H_5C_6H_4]$, 86 ($C_6H_{14}^+$). Anal. Calc. for $C_{32}H_{17}O_9NCWFe_2\cdot 0.5C_6H_{14}$ (hexane): C, 46.81; H, 2.69; N, 1.56. Found: C, 46.64; H, 2.52; N, 1.95%.

Transformation of 10 into $[Fe(CO)_2(\eta^5\text{-}C_9H_8)C(C_6H_5)NCCr(CO)_5]$ (16)

A solution of **10** (0.250 g, 0.39 mmol) in 20 mL of $CH_2Cl_2$was stirred at room temperature for 12 h, during this time the red solution gradually turned yellow turbid solution. The solvent was removed *in vacuo* and the residue was chromatographed on Al_2O_3 with petroleum ether–CH_2Cl_2 (10 : 1) as the eluent. The yellow band was collected. After removal of the solvent, the residue was recrystallized from petroleum ether–CH_2Cl_2 at −80 °C to give 0.066 g (32%) of yellow crystalline **16**: mp 114–116 °C (decomp.); IR (CH_2Cl_2) ν(CO) 2060 (m), 2018 (s), 1970 (w), 1946 (vs, br) cm^{-1}; ν(CN) 2138 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.51–7.09 (m, 5H, C_6H_5), 6.80 (dd, 1H, C_9H_8, $J = 2.7, 10.8$), 5.69 (d, 1H, C_9H_8, $J = 1.5$), 5.52 (s, 2H, C_9H_8), 4.60 (dd, 1H, C_9H_8, $J = 1.2, 3.9$), 3.36 (m, 1H, C_9H_8), 2.90 (m, 1H, C_9H_8,), 1.96 (d, 1H, C_9H_8, $J = 6.9$), 1.18–1.11 (m, 4H, $CH_3(CH_2)_4CH_3$), 0.86 (t, 3H, $CH_3(CH_2)_4CH_3$); ^{13}C NMR (CD_3COCD_3) δ 218.6, 216.3, 214.1 (CO), 149.4, 137.1, 129.6, 123.7, 121.6 (C_6H_5), 91.5, 88.2, 85.6, 78.1, 76.9, 63.5, 57.0, 38.3 (C_9H_8); MS *m/z* 367 $[M^+ - 2CO - Fe(CO)_2]$, 317 $[M^+ - Cr(CO)_5CN]$, 289 $[M^+ - CO - Cr(CO)_5CN]$, 261 $[M^+ - 2CO - Cr(CO)_5CN]$, 86 ($C_6H_{14}^+$). Anal. Calc. for $C_{24}H_{13}O_7NCrFe\cdot 0.5C_6H_{14}$ (hexane): C, 56.08; H, 3.48; N, 2.42. Found: C, 56.61; H, 3.11; N, 2.27%.

The following complexes were obtained by similar transformation.

$[Fe(CO)_2(\eta^5\text{-}C_9H_8)C(C_6H_4C_6H_5\text{-}p)NCCr(CO)_5]$ (17)

Yellow crystals (36% yield); mp 70–72 °C (decomp.); IR (CH_2Cl_2) ν(CO) 2060 (m), 2018 (s), 1971 (w), 1946 (vs, br) cm^{-1}; ν(CN) 2138 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.40–6.98 (m, 9H, *p*-$C_6H_5C_6H_4$), 6.80 (d, 2H, C_9H_8, $J = 2.7$), 5.69 (dd, 1H, C_9H_8, $J = 0.9, 1.5$), 5.52 (t, 1H, C_9H_8, $J = 0.6$), 4.60 (dd, 1H, C_9H_8, $J = 1.2, 3.0$), 3.36 (m, 1H, C_9H_8), 2.86 (d, 1H, C_9H_8, $J = 1.5$), 1.96 (d, 1H, C_9H_8, $J = 6.9$), 1.20–1.12 (m, 4H, $CH_3(CH_2)_4CH_3$), 0.87 (t, 3H, $CH_3(CH_2)_4CH_3$); ^{13}C NMR (CD_3COCD_3) δ 218.8, 216.2, 215.8, 214.3, 148.9, 137.0, 130.9, 123.0, 128.9, 128.1, 126.8, 123.6, 122.1, 121.6, 91.7, 88.3, 85.8, 84.6, 78.10, 75.4, 63.6, 57.1, 39.2; MS *m/z* 365 $[M^+ - CO - Cr(CO)_5CN]$, 337 $[M^+ - 2CO - Cr(CO)_5CN]$, 281 $[M^+ - Cr(CO)_5CN - Fe(CO)_2]$, 86 ($C_6H_{14}^+$). Anal. Calc. for $C_{30}H_{17}O_7NCrFe\cdot 0.5C_6H_{14}$ (hexane): C, 60.58; H, 3.70; N, 2.14. Found: C, 60.95; H, 3.44; N, 1.81%.

$[Fe(CO)_2(\eta^5\text{-}C_9H_8)C(C_6H_5)NCMo(CO)_5]$ (18)

Yellow crystals (41% yield); mp 114–116 °C (decomp.); IR (CH_2Cl_2) ν(CO) 2064 (m), 2019 (s), 1980 (vs), 1948 (vs) cm^{-1}; ν(CN) 2136 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.40–7.10 (m, 5H, C_6H_5), 6.81 (d, 2H, C_9H_8, $J = 2.4$), 5.69 (s, 1H, C_9H_8), 5.61 (m, 2H, CH_2Cl_2), 5.53 (s, 1H, C_9H_8), 4.60 (t, 1H, C_9H_8, $J = 2.7$), 3.37 (dd, 1H, C_9H_8, $J = 1.5, 2.1$), 2.93 (d, 1H, C_9H_8, $J = 1.8$), 1.96 (d, 1H, C_9H_8, $J = 6.6$); ^{13}C NMR (CD_3COCD_3) δ 215.7, 215.4, 204.3 (CO), 146.6, 131.1, 128.5, 126.5, 123.4, 121.3 (C_6H_5), 94.4, 91.4, 87.9, 86.3, 85.5, 74.9, 66.2, 56.5, 42.3 (C_9H_8); MS *m/z* 317 $[M^+ - Mo(CO)_5CN]$, 289 $[M^+ - CO - Mo(CO)_5CN]$, 261 $[M^+ - 2CO - Mo(CO)_5CN]$, 205 $[M^+ - Fe(CO)_2 - Mo(CO)_5CN]$, 84 ($CH_2Cl_2^+$). Anal. Calc. for $C_{24}H_{13}O_7NMoFe{\cdot}CH_2Cl_2$: C, 45.22; H, 2.28; N, 2.11. Found: C, 45.13; H, 2.05; N, 2.14%.

[Fe(CO)$_2$(η^5-C_9H_8)C($C_6H_4C_6H_5$-*p*)NCMo(CO)$_5$] (19)

Yellow crystals (30% yield); mp 52–54 °C (decomp.); IR (CH_2Cl_2) *ν*(CO) 2064 (m), 2019 (s), 1971 (w), 1948 (vs, br) cm^{-1}; *ν*(CN) 2136 (w) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.69–7.36 (m, 9H, *p*-$C_6H_5C_6H_4$), 6.84 (d, 2H, C_9H_8, J = 2.4), 5.73 (s, 1H, C_9H_8), 5.55 (s, 1H, C_9H_8), 4.61 (t, 1H, C_9H_8, J = 2.4), 3.41 (s, 1H, C_9H_8), 2.89 (d, 1H, C_9H_8, J = 1.5), 1.98 (d, 1H, C_9H_8, J = 6.6); ^{13}C NMR (CD_3COCD_3) δ 215.7, 214.0, 204.2 (CO), 147.5, 140.2, 138.8, 136.6, 129.1, 127.5, 126.8, 123.9, 121.7, 121.4 (*p*-$C_6H_5C_6H_4$), 94.4, 91.5, 88.0, 85.6, 83.0, 77.9, 75.0, 56.6, 47.4 (C_9H_8); MS *m*/*z* 365 [M^+ − CO − $Mo(CO)_5CN$], 337 [M^+ − 2CO − $Mo(CO)_5CN$], 184 [M^+ − 2CO − $Mo(CO)_5CN$ − $C_6H_5C_6H_4$]. Anal. Calc. for $C_{30}H_{17}O_7NMoFe$: C, 54.99; H, 2.62; N, 2.14. Found: C, 55.66; H, 2.98; N, 2.26%.

[Fe(CO)$_2$(η^5-C_9H_8)C(C_6H_5)NCW(CO)$_5$] (20)

Yellow crystals (37% yield); mp 138–140 °C (decomp.); IR (CH_2Cl_2) *ν*(CO) 2062 (m), 2019 (s), 1971 (w), 1942 (vs, br) cm^{-1}; *ν*(CN) 2138 (w) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.39–6.99 (m, 5H, C_6H_5), 6.80 (d, 2H, C_9H_8, J = 2.4), 5.68 (s, 1H, C_9H_8), 5.52 (s, 1H, 6.56, C_9H_8), 4.59 (d, 2H, C_9H_8, J = 0.6), 3.25 (d, 1H, C_9H_8, J = 1.5), 2.88 (m, 1H, C_9H_8), 1.95 (d, 1H, C_9H_8, J = 6.9); ^{13}C NMR (CD_3COCD_3) δ 216.3, 214.4, 195.3 (CO), 148.9, 143.9, 137.2, 130.2, 129.2, 128.4, 126.6, 124.0, 121.8 (C_6H_5), 94.2, 88.6, 86.3, 84.9, 78.4, 75.6, 63.9, 57.1, 39.5 (C_9H_8); MS *m*/*z* 585 (M^+ − 3CO), 501 [M^+ − 2CO − $Fe(CO)_2$], 263 [M^+ − 2CO − $W(CO)_5CN$]. Anal. Calc. for $C_{24}H_{13}O_7NWFe$: C, 43.21; H, 1.96; N, 2.10. Found: C, 42.99; H, 2.11; N, 2.03%.

[Fe(CO)$_2$(η^5-C_9H_8)C($C_6H_4C_6H_5$-*p*)NCW(CO)$_5$] (21)

Yellow crystals (29% yield); mp 44–46 °C (decomp.); IR (CH_2Cl_2) *ν*(CO) 2062 (m), 2019 (s), 1972 (w), 1942 (vs, br) cm^{-1}; *ν*(CN) 2138 (w) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.66–7.31 (m, 9H, *p*-$C_6H_5C_6H_4$), 6.84 (d, 2H, C_9H_8, J = 2.4), 5.73 (d, 1H, C_9H_8, J = 1.2), 5.57 (d, 1H, C_9H_8, J = 0.6), 4.62 (t, 1H, C_9H_8, J = 3.0), 3.42 (m, 1H, C_9H_8), 2.90 (dd, 1H, C_9H_8, J = 5.1, 9.0), 1.98 (d, 1H, C_9H_8, J = 6.9), 1.20–1.12 (m, 4H, $CH_3(CH_2)_4CH_3$), 0.86 (t, 3H, $CH_3(CH_2)_4CH_3$); ^{13}C NMR (CD_3COCD_3) δ 213.6, 213.0, 194.7 (CO), 148.1, 146.7, 142.2, 133.9, 129.0, 126.8, 126.7 (*p*-$C_6H_5C_6H_4$), 95.3, 93.9, 90.5, 85.6, 78.5, 74.6, 69.0, 50.9, 45.7 (C_9H_8); MS *m*/*z* 337 [M^+ − 2CO − $W(CO)_5CN$], 281 [M^+ − $W(CO)_5CN$ − $Fe(CO)_2$], 86 ($C_6H_{14}^+$). Anal. Calc. for $C_{30}H_{17}O_7NWFe{\cdot}0.5C_6H_{14}$ (hexane): C, 50.41; H, 3.07; N, 1.78. Found: C, 50.22; H, 2.69; N, 1.77%.

Transformation of 3 into [Fe_2{C(OC_2H_5)$C_6H_4C_6H_5$-*p*(η^2,η^5-C_9H_8)}(CO)$_5$] (22)

A CH_2Cl_2 solution (20 mL) of **3** (0.080 g, 0.15 mmol) in a closed Schlenk flask was stirred at room temperature for 12 h, during which time the deep red solution turned orange. The solvent was removed *in vacuo* and the residue was chromato-graphed on Al_2O_3 with petroleum ether–CH_2Cl_2 (10 : 1) as the eluent. The orange band was eluted and collected. After removal of the solvent, the residue was recrystallized from petroleum/CH_2Cl_2 at −80 °C to give 0.045 g (53%) of red crystals of **22**: mp 92–94 °C (decomp.); IR (CH_2Cl_2) *ν*(CO) 2031 (s), 1987 (vs), 1964 (m), 1938 (w) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.73–7.30 (m, 9H, *p*-$C_6H_5C_6H_4$), 5.63 (m, 2H, C_9H_8 + CH_2Cl_2), 5.14–5.06 (m, 2H, C_9H_8), 4.84 (d, 1H, C_9H_8, J = 3.6), 4.29 (s, 1H, C_9H_8), 3.64 (t, 1H, C_9H_8, J = 6.0), 3.18 (m, 1H, C_9H_8), 2.48 (d, 2H, OCH_2CH_3, J = 3.6, 11.1), 1.62 (d, 1H, C_9H_8, J = 7.8), 1.01 (t, 3H, OCH_2CH_3, J = 7.2); ^{13}C NMR (CD_3COCD_3) δ 220.7, 216.8, 206.4 (CO), 153.9, 141.2, 136.9, 129.4, 127.5, 127.0 ($C_6H_5C_6H_4$-*p*), 91.9, 86.3, 82.3, 78.7, 73.2, 68.2, 61.7, 46.3, 35.1 (C_9H_8), 20.7, 14.7 (OCH_2CH_3); MS *m*/*z* 353 [M^+ − 2CO − C_2H_5 − $Fe(CO)_3$], 337 [M^+ − 2CO − Fe $(CO)_3$ − OC_2H_5], 184 [M^+ − 2CO − $Fe(CO)_3$ − OC_2H_5 − $C_6H_5C_6H_4$], 84 ($CH_2Cl_2^+$). Anal. Calc. for $C_{29}H_{22}O_6Fe_2{\cdot}CH_2Cl_2$: C, 54.34; H, 3.65. Found: C, 54.38; H, 3.82%.

X-Ray crystal structure determinations of complexes 2, 6, 8, 14, 18 and 22

The single crystals of complexes **2**, **6**, **8**, **14**, **18** and **22** suitable for X-ray diffraction studies were obtained by recrystallization from petroleum ether–CH_2Cl_2 at −80 °C. Single crystals were mounted on a glass fibre and sealed with epoxy glue. The X-ray diffraction intensity data for the six complexes were collected with a Bruker Smart diffractometer at 20 °C using Mo-Kα radiation with an ω–2θ scan mode.

The structures of **2**, **6**, **8**, **14**, **18** and **22** were solved by the direct methods and expanded using Fourier techniques. For the six complexes, the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included but not refined. 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 listing in Table 1.

The details of the crystallographic data and the procedures used for data collection and reduction information for **2**, **6**, **8**, **14**, **18** and **22** are given in Table 1. The molecular structures of **2**, **6**, **8**, **14**, **18** and **22** are given in Fig. 1–6, respectively.

CCDC reference numbers 608256–608261.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607283f

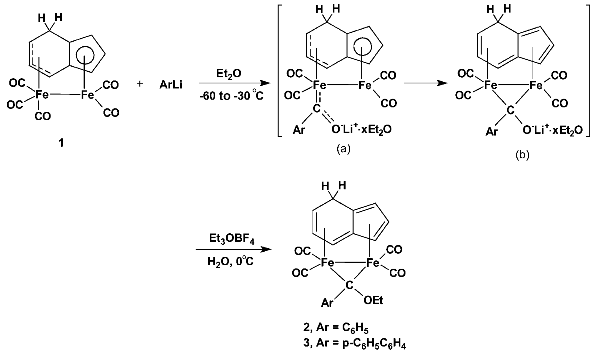
Results and discussion

Pentacarbonyl-7*H*-indenediiron, [$Fe_2(CO)_5$(η^3,η^5-C_9H_8)] (**1**), reacts with about 20% molar excess of the aryllithium reagents, ArLi (Ar = C_6H_5, *p*-$C_6H_5C_6H_4$), in ether at low temperature (−60 to −30 °C) for 3 h followed by alkylation with Et_3OBF_4. After removal of the solvent under high vacuum at low temperature, the residue was worked up as described in the Experimental Section to afford the 7*H*-indene-coordinated diiron bridging alkoxycarbene complexes [Fe_2{μ-C(OC_2H_5)Ar}$(CO)_4$(η^4,η^4-C_9H_8)] (**2**, Ar = C_6H_5; **3**, Ar = *p*-$C_6H_5C_6H_4$) (eqn (1)) in 79–86% yields.

Table 1 Crystal data and experimental details for complexes **2**, **6**, **8**, **14**, **18** and **22**

	2·0.5CH$_2$Cl$_2$	**6**	**8**	**14**	**18**	**22**·CH$_2$Cl$_2$
Formula	$C_{22.5}H_{19}O_5ClFe_2$	$C_{20}H_{14}O_4Fe_2$	$C_{27}H_{20}O_4SFe_2$	$C_{26}H_{13}O_9NFe_2W$	$C_{24}H_{13}O_7NFeMo$	$C_{30}H_{24}O_6Cl_2Fe_2$
M_r	516.53	430.01	552.19	778.92	579.14	663.09
Space group (no.)	$C2/c$ (15)	$P2_1/n$ (14)	$P\bar{1}$ (2)	$P2_1/n$ (14)	$Pca2_1$ (29)	$P\bar{1}$ (2)
a/Å	20.8199(16)	9.2338(14)	9.1797(10)	8.2775(6)	30.716(3)	8.1399(7)
b/Å	16.9844(13)	16.086(3)	9.5684(10)	16.1260(11)	7.2926(6)	10.3465(9)
c/Å	14.2447(11)	11.8502(18)	14.1755(15)	20.0995(14)	21.0737(18)	17.0935(15)
α/°			86.611(2)		90	86.069(2)
β/°	116.1330(10)	97.343(3)	80.660(2)	92.648(2)	90	80.494(2)
γ/°			75.326(2)		90	89.464(2)
V/Å^3	4522.2(6)	1745.8(5)	1188.3(2)	2680.1(3)	4720.4(7)	1416.5(2)
Z	8	4	2	4	8	2
D_c/g cm^{-3}	1.517	1.636	1.543	1.930	1.630	1.555
F(000)	2104	872	564	1496	2304	676
μ(Mo-Kα)/cm^{-1}	14.31	16.84	13.41	54.03	11.90	12.55
No. orientation refl.	2659	899	1069	2808	4114	1675
Orientation range 2θ/°	5.173–48.278	5.278–34.567	4.401–39.176	4.780–47.548	4.688–43.946	4.488–44.513
Data coll. range, 2θ/°	3.24–54.00	4.30–54.00	2.92–54.00	3.24–54.00	2.66–54.00	3.84–54.00
No. unique data, total	4922	3793	5052	5820	9080	6017
with $I > 2.00\sigma(I)$	3470	1934	2489	4012	5328	3451
No. params. refined	269	235	308	352	638	374
Correct. factors, max. min.	0.75523–1.00000	0.86201–1.00000	0.75892–1.00000	0.75440–1.00000	0.80535–1.00000	0.84868–1.00000
R^a	0.0556	0.0565	0.0503	0.0608	0.0471	0.0509
$R_w{}^b$	0.1424	0.0782	0.0905	0.1250	0.0746	0.1069
S^c	1.007	0.809	0.772	0.987	0842	0.771
Max. shift/esd. final cycle	0.001	0.000	0.000	0.001	0.092	0.059
Largest peak/e Å^{-3}	1.048	0.571	0.482	1.743	0.617	0.713
Minimum peak/e Å^{-3}	−0.508	−0.345	−0.361	−1.643	−0.284	−0.444

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit, $S = [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.



(1)

Complexes **2** and **3** are soluble both in polar organic and nonpolar solvents. They are very sensitive to air and temperature in solution but relatively stable as the solid. The IR spectra of complexes **2** and **3** showed four CO absorption bands at *ca.* 2019, 1973, 1951 and 1911 cm^{-1} in the ν(CO) region, evidence an Fe$_2$(CO)$_4$ moiety in both complexes. The ^{1}H and ^{13}C NMR data for **2** and **3** were not obtained or assigned due to easy conversion or the broadened signals for the 7*H*-indene ligand bridged by the diiron center. The further characterization for their structures was obtained by X-ray analysis of **2**, which firmly confirmed the proposed structure for products **2** and **3** shown in eqn (1) and indicated that one terminal CO ligand of compound **1** has been converted into a bridging carbene ligand upon the reaction of **1** with nucleophilic aryllithium and subsequent alkylation with Et$_3$OBF$_4$.

A drawing of the molecular structure of **2** appears as Fig. 1. There are three important observations to be made from the crystallographic data on **2**. First, the Fe–Fe bond length is quite shorter, 2.6663(8) Å, as compared with that (2.782(1) Å[16b] of starting compound **1**. A short Fe–Fe bond, arising from the bridge of μ-carbene ligand, is characteristic for this type of molecule; [Fe$_2${μ-C(OEt)C$_6$H$_4$CF$_3$-*p*}(CO)$_4$(η^8-C$_8$H$_8$)] and

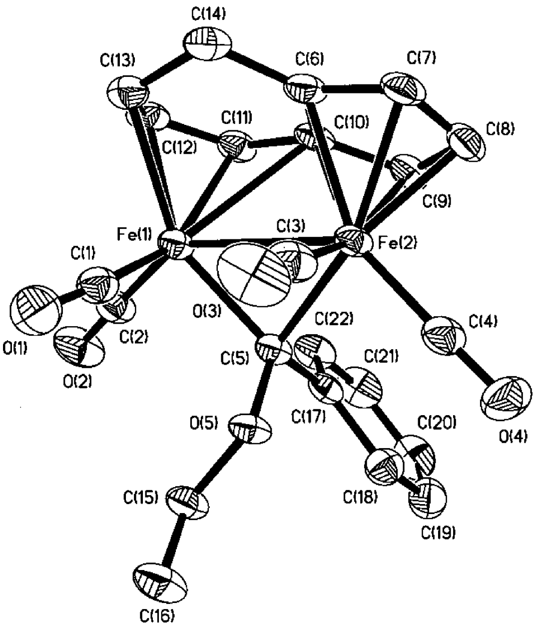
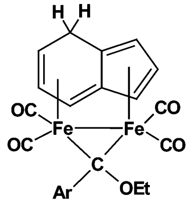
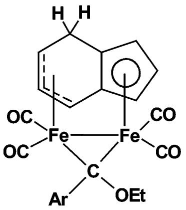


Fig. 1 Molecular structure of **2**, showing the atom-numbering scheme with 45% thermal ellipsoids.

$[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(OEt)C_6H_5\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ have Fe–Fe bond lengths of 2.686(1)[7] and 2.512(1) Å,[8] respectively. Second, the six-membered ring of the 7*H*-indene ligand is distorted away from planarity due to the methylene carbon atom (C(14)). The other five atoms in the ring, C(6) and C(10) through C(13), are roughly coplanar. Third, the coordination mode of 7*H*-indene ligand in **2** is essentially the same as that for compound **1**, even though the presence of some bonding interaction should be taken into account between Fe(1) and C(10), whose distance at 2.476(4) Å is considerably longer than the other Fe–C distances associated with 7*H*-indene ligand (Fe(1)–C(13) 2.202(4) Å, Fe(1)–C(12) 2.062(4) Å, Fe(1)–C(11) 2.116(4) Å), this may be explained by the existence of the contribution of the rare structure **B** toward the predominant structure **A** shown below.Both structures consist of 18e–18e diiron centers. Thus, in **2** the 7*H*-indene ligand is better to describe as an η^4,η^4-bonding coordinated to Fe(1) and Fe(2) (structure **A**), which is an interesting ring variation similar to the COT η^4,η^4 systems.[7]



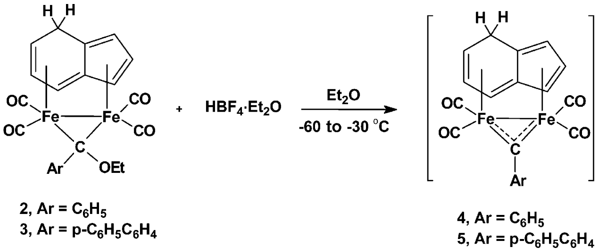
A



B

The reaction pathway to complexes **2** and **3** shown in eqn (1) is similar to that of the reactions of the cycloheptatriene-coordinated hexacarbonyldiiron compound $[C_7H_8Fe_2(CO)_6]$ with aryllithium reagents.[10] The Ar^- anion firstly attacks on a CO ligand of $Fe(CO)_3$ moiety of **1** to form an acylmetalate intermediate (a). This is a favorable attack since the electron density on a CO ligand in $Fe(CO)_3$ moiety is lower than that in $Fe(CO)_2$ moiety. The intermediate (a) can be converted into the intermediate (b),[22] which was subsequently alkylated with Et_3OBF_4 to afford bridging alkoxycarbene complex **2** or **3** (eqn (1)). It is strange that the other aryllithium reagents, such as *o*-, *m*-, *p*-$CH_3C_6H_4Li$, *p*-$CH_3OC_6H_4Li$ and *p*-$CF_3C_6H_4Li$ in which the aryl groups contain either an electron-pushing or an electron-withdrawing group, do not react with compound **1** to give the analogous bridging alkoxycarbene complexes. This could be arising from the lability of intermediates (a) or (b) formed from **1** and these aryllithiums due to electron effect of the aryl substituents, which occurred decomposition upon alkylation with Et_3OBF_4 in aqueous solution. To our knowledge, products **2** and **3** are the first examples of the dimetal bridging carbene complexes derived from a dimetal compound bearing only terminal CO ligands.

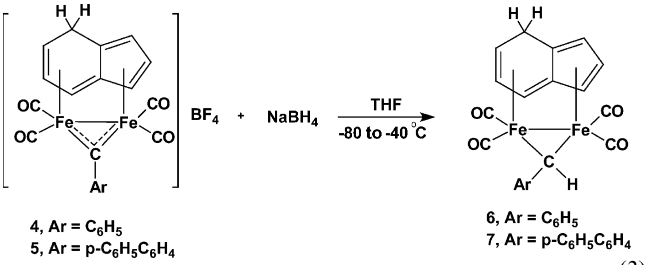
The bridging alkoxycarbene complexes **2** and **3** in ether was treated (eqn (2)) with an excess of $HBF_4{\cdot}Et_2O$ at low temperature (−60 to −30 °C) for 1 h to give 7*H*-indene-coordinated diiron cationic bridging carbyne complexes $[Fe_2(\mu\text{-}CAr)(CO)_4(\eta^4,\eta^4\text{–}C_9H_8)]BF_4$ (**4**, Ar = C_6H_5; **5**, Ar = *p*-$C_6H_5C_6H_4$) as brick red solids in 90–95% yields.



(2)

The cationic carbyne complexes **4** and **5** would be the 7*H*-indene-coordinated dimetal complexes with a bridging carbyne ligand as inferred from its reactivity (below) and previously reported analogous complexes,[13a,23] as well as their ^1H NMR and IR spectra. Complexes **4** and **5** are only sparingly soluble in polar organic solvents such as THF and CH_2Cl_2 and very sensitive to air, moisture and temperature and can be stored at low temperatures (below −60 °C) only for a short period of time. The carbyne structure is just a plausible proposal for both complexes, which are prepared *in situ* and not fully characterized.

The freshly prepared (*in situ*) diiron cationic carbyne complexes **4** and **5** react with $NaBH_4$ in THF at −80 to −40 °C for 3 h. After work-up as described in the Experimental section, arylcarbene complexes $[Fe_2\{\mu\text{-}C(H)Ar\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (**6**, Ar = C_6H_5; **7**, Ar = *p*-$C_6H_5C_6H_4$) were obtained in 73–85% isolated yields (eqn (3)).



(3)

The proposed structures for **6** and **7** were first supported by microanalytic and spectroscopic data. Their ^1H NMR spectra have a resonance at *ca.* 7.08–7.09 ppm for a μ-CHAr group. However, this resonance has undergone obviously upfield shift, as compared to that of analogous COT-coordinated bridging arylcarbene complex $[Fe_2\{\mu\text{-}C(H)C_6H_4CF_3\text{-}p\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (δ 9.17).[13a] This probably is arising from that the H atom is influenced by the ring current of the 7*H*-indene moiety. The further characterization for their structures was obtained by an X-ray diffraction study of **6**.

The structure of **6** (Fig. 2) is similar to that of **2**, except that OC_2H_5 group on the μ-carbene carbon in **2** is replaced by a H atom in **6**. Many structural features of **6** are nearly the same as those in **2**.

The cationic carbyne complexes **4** and **5** react similarly with $NaSC_6H_4CH_3\text{-}p$ to afford diiron bridging arylthiocarbene complexes $[Fe_2\{\mu\text{-}C(Ar)SC_6H_4CH_3\text{-}p\}(CO)_4(\eta^4,\eta^4\text{-}C_9H_8)]$ (**8**, Ar = C_6H_5; **9**, Ar = *p*-$C_6H_5C_6H_4$) (eqn (4)) in 71–87% yields,

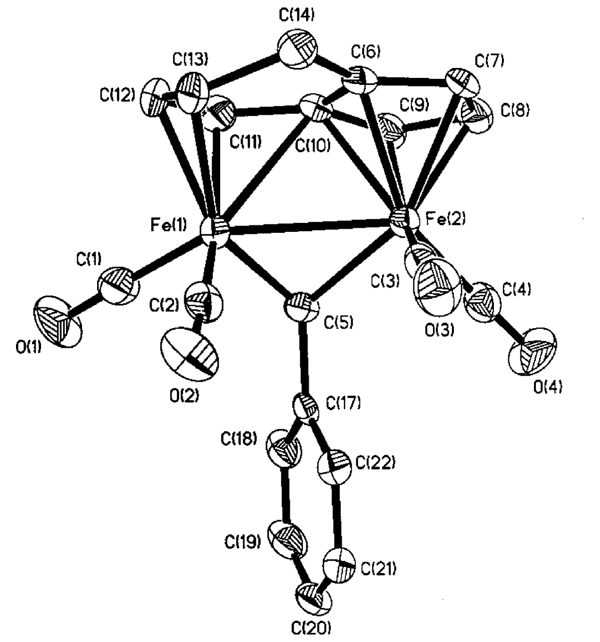
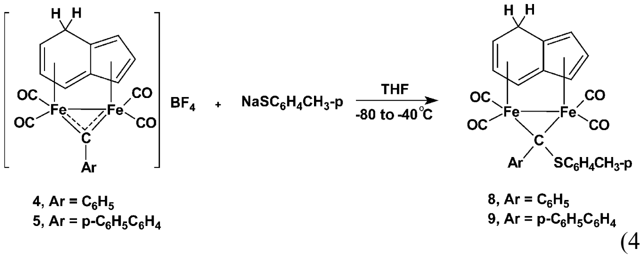


Fig. 2 Molecular structure of **6**, showing the atom-numbering scheme with 45% thermal ellipsoids.

of which the structure of **8** has been established by X-ray analysis.



(4)

The IR spectra of products **8** and **9** exhibit four absorption bands (at *ca.* 2017–218, 1981–1982, 1960–1961 and 1922–1939 cm^{-1}) in the ν(CO) region with a pattern similar to that of bridging alkoxycarbene complexes **2** and **3**. The site of nucleophilic attack of NaSC$_6$H$_4$CH$_3$-*p* resembles the reactions[11,12a,15] of cationic bridging carbyne complexes [Fe$_2$(μ-CO)(μ-CAr)(CO)$_2$(η^5-C$_5$H$_5$)$_2$]BBr$_4$ and [Fe$_2$(μ-CO)(μ-CAr)(CO)$_2${(η^5-C$_5$H$_4$)$_2$-Si(CH$_3$)$_2$}]BBr$_4$ with NaSR, which resulted in nucleophilic addition to the μ-carbyne carbon to give corresponding diiron bridging arylthiocarbene complexes.

The molecular structure of complex **8** (Fig. 3) is fundamentally the same as that of **2**, except that the substituent on the μ-carbene carbon is a *p*-CH$_3$C$_6$H$_4$S group in **8** but an OC$_2$H$_5$ group in the latter. The distance of the Fe–Fe bond in **8** is 2.6754(8) Å, very close to that in **2** and **6**. The μ-carbene carbon approximately symmetrically bridges the Fe–Fe bond with a C(5)–Fe(1) of 1.984(4) Å and a C(5)–Fe(2) of 2.103(4) Å distances. The C(5)–S bond length of 1.801(4) Å in **8** indicates that it is essentially single bond by comparison with standard C(sp^2)–S (1.76 Å)[24] single bond and C(sp^3)–S (1.81 Å)[24] single bond distances.

Complexes **4** and **5** can also react with anionic carbonylmetal compound containing a CN negative substituent, Na[M(CO)$_5$-(CN)] (M = Cr, Mo, W), to afford 7*H*-indene-coordinated diiron bridging aryl(pentacarbonylcyanometal)–carbene complexes [Fe$_2${μ-C(Ar)NCM(CO)$_5$}(CO)$_4$(η^4,η^4-C$_9$H$_8$)] (**10–15**) (eqn (5)) in 63–78% isolated yield.

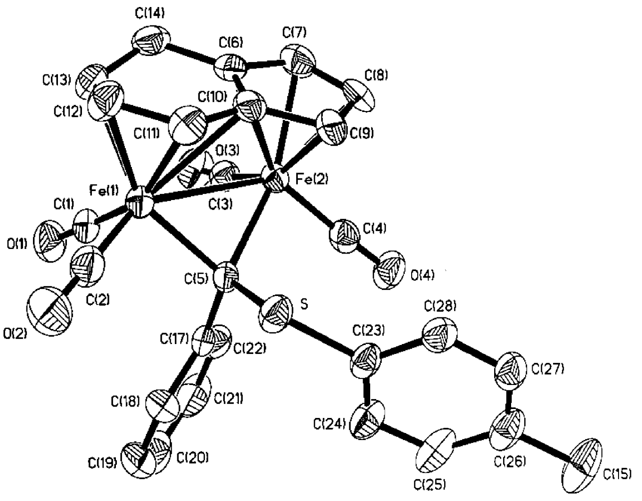
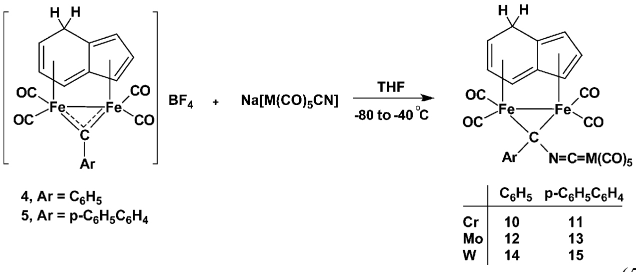


Fig. 3 Molecular structure of **8**, showing the atom-numbering scheme with 40% thermal ellipsoids.



(5)

Complexes **10–15** are sensitive to air and temperature in both solution and the solid state. The spectroscopic data of complexes **10–15** are consistent with their structures shown in eqn (5). The IR spectra of **10–15** in the ν(CO) region showed five absorption bands of the CO groups at 2056–1944 cm^{-1}. The characteristic ν(CN) stretching vibration occurs at *ca.* 2114–2116 cm^{-1}, similar to those of analogous complex [Fe$_2${μ-C(Ar)NCM(CO)$_5$}(CO)$_4$(η^8-C$_8$H$_8$)] (at *ca.* 2117–2125 cm^{-1}).[13a] The ^{1}H NMR data for compounds **10–15** showed the proton signals attributed to the 7*H*-indene ligand at 6.40–2.86 ppm which are downfield of those in **6** and **7** (at 5.97–2.63 ppm) because of the stronger electron-accepting ability of (CO)$_5$MCN as compared with H group. The proposed structures for **10–15** are eventually confirmed by an X-ray diffraction study of **14**.

Complex **14** has a structure (Fig. 4) in which a W(CO)$_5$CN group is bound to the μ-carbene carbon through the N atom. The structural features of the principal portion of [Fe$_2$(μ-CC$_6$H$_5$)(CO)$_4$(η^4,η^4-C$_9$H$_8$)] of **14** are very similar to those of the same unit in **2** and **8**. The interesting structure of **14** is the μ-C(C$_6$H$_5$)W(CO)$_5$CN ligand, in which the two C–N bond lengths are very different. C(15)–N(1) has a bond length of 1.160(10) Å, which indicates high triple-bond character and is essentially the same as the corresponding distance in analogous complex [Fe$_2${μ-C(C$_6$H$_4$CF$_3$-*p*)NCW(CO)$_5$}(CO)$_4$(η^8-C$_8$H$_8$)] (1.174(13) Å).[13a] The

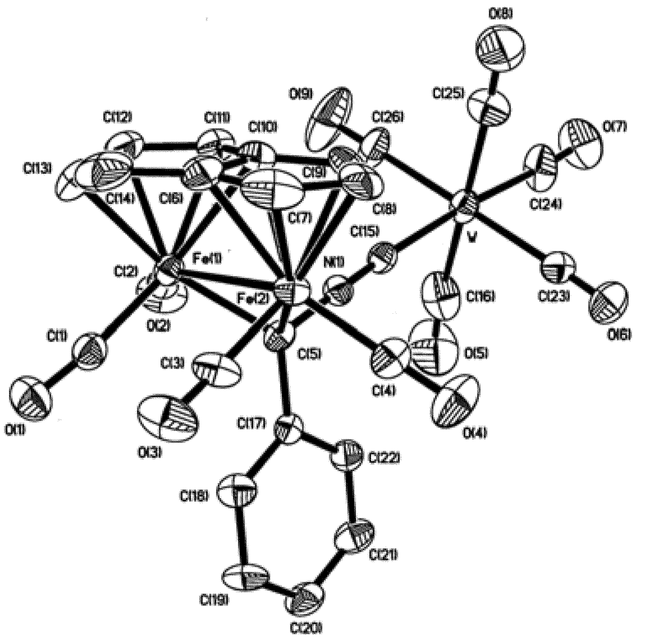
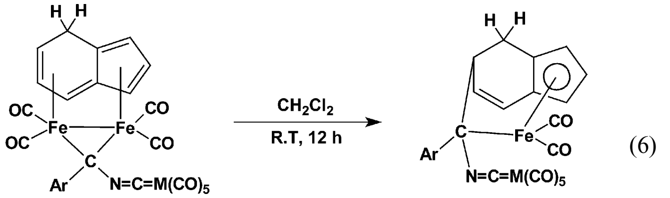


Fig. 4 Molecular structure of **14**, showing the atom-numbering scheme with 45% thermal ellipsoids.

other is C(5)–N(1) with the bond length of 1.404(10) Å, which is between the normal C–N and C=N distances and slightly shorter than the corresponding C–N distance in [$Fe_2\{\mu$-C($C_6H_4CF_3$-*p*)-NCW$(CO)_5\}(CO)_4(\eta^8$-$C_8H_8)$] (1.412(13) Å).[13a] The shorter W–C(15) distance of 2.139(9) Å in **14** signifies its high double bond character. The C(5), N(1), C(15) and W atoms are coplanar with a C(5)–N(1)–C(15) angle of 175.4(8)° and a N(1)–C(15)–W angle of 176.4(7)°, indicating that C(5)–N(1)–C(15)–W fragment is almost linear.

The reaction pathway to complexes **10–15** could proceed *via* attack of the $(CO)_5M{=}C{=}N^-$ (M = Cr, Mo, W) anion, a representation of the same electronic structure of the $^-M(CO)_5(CN)$ anion, on the μ-carbyne carbon of cationic **4** or **5** to produce the product.

Interestingly, when the solution of products **10–15** in CH_2Cl_2 was stirred at room temperature for 12 h, the deep red solution gradually turned yellow. After workup as described in the Experimental section, the isomerized 7*H*-indene-coordinated monoiron complexes with a C(Ar)NCM$(CO)_5$ group, [Fe$(CO)_2(\eta^5$-$C_9H_8)$C(Ar)NCM$(CO)_5$] (**16–21**), were obtained in lower (29–41%) yields (eqn (6)), of which the structure of **18** has been established by X-ray crystallography.



(6)

10 - 15

	C_6H_5	p-$C_6H_5C_6H_4$
Cr	16	17
Mo	18	19
W	20	21

The conversions of products **10–15** into complexes **16–21** were initially revealed by their ^{1}H NMR spectra. The acetone-d_6 solution of **10** or **11–15** whose NMR spectrum had been measured was kept at room temperature for about 1–2 h, during which time the solution changed from deep red to yellow. Their ^{1}H NMR spectra now showed only the proton signals attributable to the 7*H*-indene ring and aryl group of **16** or **17–21**. Further evidence for this conversion came from the isolation of crystals of **16–21** from the CH_2Cl_2 solution shown in eqn (6).

Complexes **16–21** were the corresponding decomposition products of **10–15**. The Fe$(CO)_2$ moiety coordinated to the six-membered ring of the 7*H*-indene ligand in **10–15** was lost and the original μ-carbene ligand became a C(Ar)NCM$(CO)_5$ group bonded to Fe(2) and a carbon atom (C(13)) of the six-membered ring through μ-carbene carbon (C(5)) in **16–21**.

The molecular structure of **18** (Fig. 5) shows that the configuration and bond distances of the 7*H*-indene ligand have been changed by comparison with analogous parent **14**, caused by the loss of the Fe$(CO)_2$ moiety and the transfer of the carbene ligand C(Ar)NCMo$(CO)_5$ from the lost Fe(1) atom to the C(13) atom of the indene ring. In the six-membered ring moiety, only C(10), C(11), C(12) and C(13) are in a plane (±0.0023 Å); C(14) is out of the C(10)C(11)C(12)C(13) plane by 1.0912 Å.

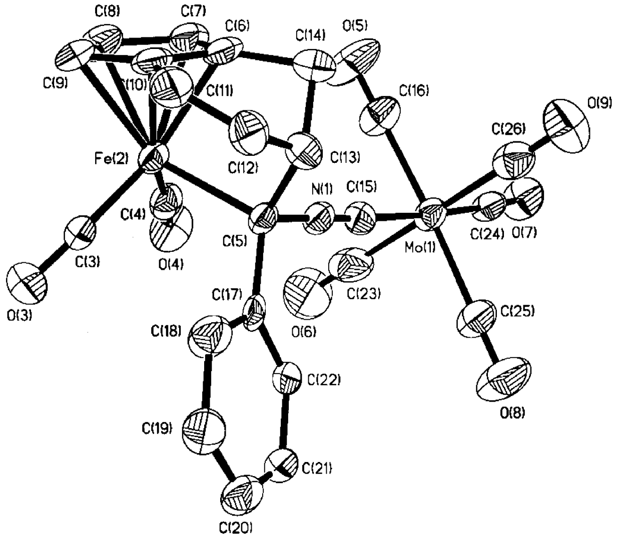


Fig. 5 Molecular structure of **18**, showing the atom-numbering scheme with 45% thermal ellipsoids.

In contrast to the nearly equal distances in C(10) to C(13) of the C_6 ring in **14**, in **18** the C(10)–C(11) (1.445(12) Å) and C(12)–C(13) (1.492(12) Å) bonds are much longer than C(11)–C(12) (1.287(12) Å), indicating that the latter is a double-bond. The structure of the Mo$(CO)_5$CN moiety in **18** are the same as those in **14**. An only difference for the Mo$(CO)_5$CN moiety in **14** and **18** is the larger C(5)–N(1)–C(15) (179.7(8)°) and N(1)–C(15)–Mo (178.0(7)°) bond angles in **18**, indicating an highly linear for the C(5)–N(1)–C(15)–W fragment.

Likewise interestingly, a CH_2Cl_2 solution of bridging alkoxycarbene complex **3** in a closed flask was stirred at room temperature for 12 h to give a novel ring addition product [$Fe_2\{C(OC_2H_5)C_6H_4C_6H_5$-*p*-$(\eta^2,\eta^5$-$C_9H_8)\}(CO)_5$] (**22**) in 53% yield

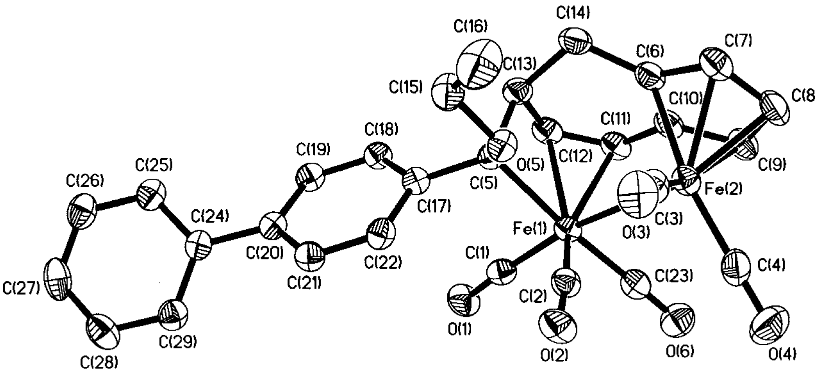
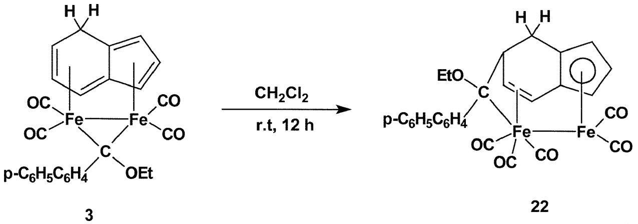


Fig. 6 Molecular structure of **22**, showing the atom-numbering scheme with 45% thermal ellipsoids.

(eqn (7)), whose structure has been established by its X-ray analysis.



3 **22**

(7)

The transformation of complex **3** into complex **22** was initially revealed by its IR spectrum. The CH_2Cl_2 solution of **3** whose IR spectrum had been recorded was kept at room temperature for about 5–10 min, its IR spectrum now showed only four absorption bands at 2031, 1987, 1964 and 1938 cm^{-1} attributable to **22**. Further evidence for this transformation came from its isolation of crystalline **22** from the CH_2Cl_2 solution shown in eqn (7).

The crystallographic investigation of **22** reveals an unusual structure (Fig. 6), which is quite different from that of **3**, arising from that the μ-C–Fe(2) bond in **3** was cleaved and the μ-carbene carbon (C(5)) is linked to a ring carbon (C(13)) of the 7*H*-indene ligand leading to formation of an η^2-bonding to coordinate to the $Fe(CO)_3$ moiety in **22**. Thus, the six-membered ring of the 7*H*-indene ligand carries a $C(OC_2H_5)C_6H_5C_6H_4$-*p* group on C(13) and its configuration and bond lengths have been changed, similar to that in **18**, caused by the migration of the μ-carbene ligand $C(OC_2H_5)C_6H_5C_6H_4$-*p* from Fe(2) to C(13) of the C_6 ring. In **22**, the ring carbons C(11) and C(12) are coordinated to Fe(1) in an η^2-bonding and C(5) is σ bound to Fe(2) and a CO group generated from the decomposition of **3** or an intermediate is also coordinated to the Fe(1) atom. The Fe–Fe distance (2.752(7) Å) is slightly longer than that (2.6663(8) Å) of **2**, a phenyl analogue of **3**. The Fe(1)–C bond lengths of C(11) and C(12) are 2.217(4) and 2.199(4) Å, respectively. The structure of the six-membered ring moiety of the 7*H*-indene ligand in **22** are similar to that in **18**. An apparent difference between **22** and **18** is the longer C(11)–C(12) bond distance (1.357(6) Å) in **22** owing to the coordination of Fe(1).

In summary, we have discovered the first examples of the dimetal bridging carbene complexes derived from a dimetal compound bearing only terminal CO ligands. A new type of the 7*H*-indene-coordinated diiron bridging alkoxycarbene complexes **2** and **3** were synthesized from pentacarbonyl-7*H*-indenediiron, a diiron compound bearing only terminal CO ligands and a series of novel 7*H*-indene-coordinated bridging carbene complexes have been obtained by reactions of their cationic bridging carbyne complexes with the nucleophiles involving carbonylmetal anions. This opens up a new route to synthesize dimetal bridging carbene complexes and provides an useful and convenient method for the preparation and structural modification of such bridging carbene complexes. The unusual transformation of complexes **3** and **10–15** have also been investigated. Further studies on the scope of the reaction and application in organic and organometallic synthesis are now being carried out in our laboratory.

Acknowledgements

We thank the National Natural Science Foundation of China, the Science Foundation of the Chinese Academy of Sciences and the JSPS of Japan for financial support of this research.

References

1 (*a*) F. G. A. Stone, in *Advances in Metal Carbene Chemistry*, ed. U. Schubert, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1989, p. 11; (*b*) G. A. Carriedo, J. A. K. Howard and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1555; (*c*) M. E. Garcia, J. C. Jeffery, P. Sherwood and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 1209; (*d*) D. Hodgson, J. A. K. Howard, F. G. A. Stone and M. J. Went, *J. Chem. Soc., Dalton Trans.*, 1985, 331; (*e*) M. U. Pilotti, F. G. A. Stone and L. Topaloglu, *J. Chem. Soc., Dalton Trans.*, 1991, 1621.

2 (*a*) J. B. Keister, M. W. Payne and M. J. Muscatella, *Organometallics*, 1983, **2**, 219; (*b*) J. B. Keister, *J. Chem. Soc., Chem. Commun.*, 1979, 214; (*c*) J. B. Keister, *Polyhedron*, 1988, **7**, 847.

3 (*a*) L. Busetto and V. Zanotti, *J. Organomet. Chem.*, 2005, **690**, 5430; (*b*) L. Busetto, F. Marchetti, S. Zacchini and V. Zanotti, *Organometallics*, 2005, **24**, 2297; (*c*) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini and V. Zanotti, *Organometallics*, 2004, **23**, 3348.

4 (*a*) M. Akita, R. Hua, S. A. R. Knox, Y. Moro-oka, S. Nakanishi and M. I. Yates, *J. Organomet. Chem.*, 1990, **250**, 255; (*b*) S. A. R. Knox, *J. Organomet. Chem.*, 1990, **250**, 255; (*c*) R. E. Colborn, D. L. Davies, A. F. Dyke, S. A. R. Knox, K. A. Mead, A. G. Orpen, J. E. Guerchais and J. Roue, *J. Chem. Soc., Dalton Trans.*, 1989, 1799.

5 (*a*) J. R. Matachek, R. J. Angelici, K. A. Schugart, K. J. Haller and R. F. Fenske, *Organometallics*, 1984, **3**, 1038; (*b*) M. H. Quick and R. J. Angelici, *Inorg. Chem.*, 1981, **20**, 1123; (*c*) N. C. Schroeder, R. Funchness, R. A. Jacobson and R. J. Angelici, *Organometallics*, 1989, **8**, 521.

6 (*a*) D. Navarre, A. Parlier, H. Rudler and J. C. Daran, *J. Organomet. Chem.*, 1987, **322**, 103; (*b*) C. Alvarez-Toledano, A. Parlier,

F. Rose-Munch, H. Rudler, J. C. Daran, C. Knobler and Y. Jeannin, *J. Organomet. Chem.*, 1987, **323**, 371.

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

8 J.-B. Chen, D.-S. Li, Y. Yu and C. G. Chen, *Organometallics*, 1994, **13**, 3581.

9 R.-T. Wang, J. Sun and J.-B. Chen, *J. Organomet. Chem.*, 2001, **617–618**, 292.

10 Y. Yu, J.-B. Chen, J. Chen and P.-J. Zheng, *Organometallics*, 1993, **12**, 4731.

11 Y.-J. Liu, R.-T. Wang, J. Sun and J.-B. Chen, *Organometallics*, 2000, **19**, 3784.

12 (*a*) R.-T. Wang, Q. Xu, J. Sun, Li-C. Song and J.-B. Chen, *Organometallics*, 2001, **20**, 4092; (*b*) R.-T. Wang, J. Sun, J.-B. Chen, Q. Xu and Y. Souma, *J. Organomet. Chem.*, 2002, **658**, 214.

13 (*a*) S. Zhang, Q. Xu, J. Sun and J.-B. Chen, *Organometallics*, 2003, **22**, 1816; (*b*) S. Zhang, Q. Xu, J. Sun and J.-B. Chen, *Chem.–Eur. J.*, 2003, **9**, 5111.

14 (*a*) P.-H. Wang, R.-H. Li, J. Sun and J.-B. Chen, *Chem. Commun.*, 1998, 631; (*b*) Nu. Xiao, S. Zhang, Z.-L. Qiu, R.-H. Li, P.-H. Wang, Q. Xu, J. Sun and J.-B. Chen, *Organometallics*, 2002, **21**, 3709.

15 Y.-J. Liu, R.-T. Wang, J. Sun and J.-B. Chen, *Organometallics*, 2000, **19**, 3498.

16 (*a*) S. G. Davies, K. S. Holland, K. H. Sutton and J. P. McNally, *Isr. J. Chem.*, 1991, **31**, 25; (*b*) F. A. Cotton and B. E. Hanson, *Inorg. Chem.*, 1977, **16**, 1861.

17 E. E. Reid, *Organic Chemistry of Bivalent Sulfur*, Chemical Publishing Co. Inc., New York, NY, 1958, vol. 1, p. 127.

18 R. B. King, *Inorg. Chem.*, 1967, **6**, 25.

19 G. Wittig, *Angew. Chem.*, 1940, **53**, 243.

20 H. Gilman, W. Langham and F. W. Moore, *J. Am. Chem. Soc.*, 1940, **62**, 2327.

21 H. Meerwein, G. Hinze, P. Hofmann, E. Kroniny and E. Pfeil, *J. Prakt. Chem.*, 1937, **147**, 257.

22 According to the properties of di- or polymetal bridging carbene complexes, the intermediates (a) and (b) could be converted to each other, *i.e.* the monometal carbene ligand and dimetal bridging carbene ligand can be converted to each other, accompanied by the conversion between the terminal CO group and bridging CO group. For detailed review on fluxional metal carbonyls, see: F. A. Cotton, *Inorg. Chem.*, 2002, **41**, 643.

23 N. Xiao, Q. Xu, J. Sun and J.-B. Chen, *Dalton Trans.*, 2005, 3250.

24 (*a*) B. Rozsondai, G. Schultz and I. Hargittai, *J. Mol. Struct.*, 1981, **70**, 309; (*b*) S. Samdal, H. M. Seip and T. Torgrimsen, *J. Mol. Struct.*, 1979, **57**, 105.