Unusual reactions of cationic bridging carbyne complexes of dimethylsilane-bridged bis(η⁵-cyclopentadienyl)diiron tricarbonyl with carbonylmetal anions

Ruitao Wang [a], Jie Sun [a], Jiabi Chen [a],*, Qiang Xu [b],*, Yoshie Souma [b]

[a] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, People's Republic of China*
[b] *National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31, Midorigaoka, Ikeda, Osaka 563-8577, Japan*

Abstract

The reactions of the dimethylsilane-bridged cationic carbyne complexes of diiron, $[Fe_2(\mu\text{-CO})(\mu\text{-CAr})(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]BBr_4$ (**1**, Ar = C_6H_5; **2**, Ar = $p\text{-CF}_3C_6H_4$), with carbonylmetal anionic compounds $Na[M(CO)_5CN]$ (**4**, M = Cr; **5**, M = Mo; **6**, M = W) in THF at low temperature afford diiron bridging carbene complexes $[Fe_2(\mu\text{-CO})\{\mu\text{-}C(Ar)NCM(CO)_5\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**9**, M = Cr, Ar = C_6H_5; **10**, M = Mo, Ar = C_6H_5; **11**, M = W, Ar = C_6H_5; **12**, M = Cr, Ar = $p\text{-CF}_3C_6H_4$; **13**, M = Mo, Ar = $p\text{-CF}_3C_6H_4$; **14**, M = W, Ar = $p\text{-CF}_3C_6H_4$). In contrast to the reaction of **1** and **2**, cationic carbyne complex $[Fe_2(\mu\text{-CO})(\mu\text{-CC}_6H_4CH_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]BBr_4$ (**3**) reacts with **4**–**6** under the same conditions to produce novel cationic bridging carbene complexes $[Fe_2(\mu\text{-CO})(\mu\text{-CC}_6H_4CH_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]^+[M(CO)_5CN]^-$ (**15**, M = Cr; **16**, M = Mo; **17**, M = W). Analogous cationic bridging carbyne complex $[Fe_2(\mu\text{-CO})(\mu\text{-CC}_6H_4CH_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]^+[Fe(CO)_4CN]^-$ (**18**) can also be obtained from the reaction of **3** with $Na[Fe(CO)_4CN]$ (**7**). Complex **15** or **16** reacts with NaSR (R = CH_3, C_6H_5, $p\text{-CH}_3C_6H_4$) to give bridging mercaptocarbene complexes $[Fe_2(\mu\text{-CO})\{\mu\text{-}C(SR)C_6H_4CH_3\text{-}p\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**19**, R = CH_3; **20**, R = C_6H_5; **21**, R = $p\text{-CH}_3C_6H_4$) in high yields. The related reaction of **1** with $NaN(SiMe_3)_2$ affords a novel benzonitrile-coordinated diiron complex $[Fe_2(\mu\text{-CO})_2(CO)NCC_6H_5\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**22**). Unexpectedly, the reactions of **1** and **2** with **7** yield diiron bridging arylcarbene complexes $[Fe_2(\mu\text{-CO})\{\mu\text{-}C(H)Ar\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**23**, Ar = C_6H_5; **24**, Ar = $p\text{-CF}_3C_6H_4$). The products **23** and **24** and bridging p-tolyl-carbene complex $[Fe_2(\mu\text{-CO})\{\mu\text{-}C(H)C_6H_4CH_3\text{-}p\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (**25**) were also obtained from the reactions of **1**–**3** with $[(PPh_3)_2N][Cr(CO)_4NO]$ (**8**). The structures of **14**, **15**, **22**, and **23** have been established by X-ray crystallography. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Reaction; Diiron; Carbonylmetal anions; Bridging carbyne complexes

1. Introduction

Our interest in the chemistry of di- and polynuclear metal complexes with bridging carbene and bridging carbyne ligands stems from that many such complexes are themselves metal clusters or are the precursors of metal cluster complexes. A considerable number of dimetal complexes containing bridging carbene and carbyne ligands have been synthesized by Stone and co-workers by reactions [1–4] of carbene or carbyne complexes with low-valent metal species or by reactions [3,4] of neutral or anionic carbyne complexes with metal hydrides or cationic metal compounds. In continuation of our interest in developing the methodologies of the synthesis of transition metal bridging carbene and carbyne complexes, we have studied the reactions of the cationic carbyne complexes of transition metal with carbonylmetal anions. Recently, we have shown a convenient method for the preparation of dimetal bridging carbene and/or carbyne complexes: the reactions [5,6] of highly electrophilic cationic carbyne complexes of manganese and rhenium, [η⁵-

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* Corresponding authors. Fax: +86-21-64166128
E-mail addresses: chenjb@pub.sioc.ac.cn (J. Chen), q.xu@aist.go.jp (Q. Xu).

C$_5$H$_5$(CO)$_2$M≡CC$_6$H$_5$]BBr$_4$ (M = Mn, Re), with carbonylmetal anionic compounds. Most recently, we found a new method for the preparation of dimetal bridging carbene complexes that is the reactions of diiron cationic bridging carbyne complexes, [Fe$_2$(μ-CO)(μ-CAr)(CO)$_2$(η^5-C$_5$H$_5$)$_2$]BBr$_4$ (Ar = Ph, *p*-CH$_3$C$_6$H$_4$) and [Fe$_2$(μ-CO)(μ-CAr)(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}]-BBr$_4$ (Ar = C$_6$H$_5$, *p*-CH$_3$C$_6$H$_4$, *p*-CF$_3$C$_6$H$_4$), with nucleophiles. For instance, both diiron cationic carbyne complexes react with NaSR (R = alkyl or aryl) or Na[M(CO)$_5$CN] (M = Cr, Mo, W) to give a series of diiron bridging carbene complexes [Fe$_2$(μ-CO){μ-C(SR)Ar}(CO)$_2$(η^5-C$_5$H$_5$)$_2$] or [Fe$_2$(μ-CO){μ-C(C$_6$H$_4$CH$_3$-*p*)NCM(CO)$_5$}(CO)$_2$(η^5-C$_5$H$_5$)$_2$] [7] and [Fe$_2$(μ-CO){μ-C(SR)Ar}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}] [8], respectively. This offers useful method for the preparation and structural modification of dimetal bridging carbene complexes.

In order to explore the reactivity of different diiron cationic bridging carbyne complexes and the effect of different carbonylmetal anions on the reactivity of the diiron cationic carbyne complexes, and to further examine the scope of this preparation of dimetal bridging carbene and bridging carbyne complexes, we carried out the study of the reactivity of the dimethylsilane-bridged diiron cationic bridging carbyne complexes [Fe$_2$(μ-CO)(μ-CAr)(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}]BBr$_4$ (**1**, Ar = C$_6$H$_5$; **2**, Ar = *p*-CF$_3$C$_6$H$_4$; **3**, Ar = *p*-CH$_3$C$_6$H$_4$) with carbonylmetal anionic compounds containing a CN group, Na[M(CO)$_n$CN] (M = Cr, Mo, W, *n* = 5; M = Fe, *n* = 4), or a three-electron ligand of NO, [(PPh$_3$)$_2$N][Cr(CO)$_4$NO]. These reactions produce a series of novel di- or trimetal bridging carbene and cationic bridging carbyne complexes. Herein we report these unusual reactions and the structural characterizations of the resulting products.

2. Experimental

All procedures were performed under a dry, oxygen-free N$_2$ atmosphere using standard Schlenk techniques. All solvents employed were reagent grade and dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under a N$_2$ atmosphere. The tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl, while petroleum ether (30–60 °C) and CH$_2$Cl$_2$ were distilled from CaH$_2$. The neutral alumina used for chromatography was deoxygenated at room temperature (r.t.) under high vacuum for 16 h, deactivated with 5% w/w N$_2$-saturated water, and stored under N$_2$. Complexes [Fe$_2$(μ-CO){μ-CAr}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}]BBr$_4$ (**1**, Ar = C$_6$H$_5$; **2**, Ar = *p*-CF$_3$C$_6$H$_4$; **3**, Ar = *p*-CH$_3$C$_6$H$_4$) were prepared as previously described [8]. NaSCH$_3$, NaSC$_6$H$_5$, NaSC$_6$H$_4$CH$_3$-*p*, and NaN(SiMe$_3$)$_2$ (95%) were pur-

chased from Fluka Chemcal Co. and Aldrich Chemical Co., respectively. Compounds Na[Cr(CO)$_5$CN] (**4**) [9], Na[Mo(CO)$_5$CN] (**5**) [9], Na[W(CO)$_5$CN] (**6**) [9], Na[Fe(CO)$_4$CN] (**7**) [10], and [(PPh$_3$)$_2$N] [Cr(CO)$_4$NO] (**8**) [11] were prepared by literature methods.

IR spectra were measured on a Perkin–Elmer 983G spectrophotometer. All ^{1}H-NMR spectra were recorded at ambient temperature in acetone-d_6 solution with Me$_4$Si as the internal reference using a Bruker AM-300 spectrometer. Electron ionization mass spectra (EIMS) were run on a Hewlett–Packard 5989A spectrometer. Melting points obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

2.1. Reaction of [Fe$_2$(μ-CO)(μ-CC$_6$H$_5$)(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}]BBr$_4$ (1) with Na[Cr(CO)$_5$CN] (4) to give [Fe$_2$(μ-CO){μ-C(C$_6$H$_5$)NCCr(CO)$_5$}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}] (9)

To 0.400 g (0.494 mmol) of freshly prepared (in situ) compound **1** dissolved in 60 ml of THF at −100 °C was added 0.140 g (0.581 mmol) of Na[Cr(CO)$_5$CN] (**4**). The reaction mixture was stirred at −100 to −80 °C for 1 h, during which time the turbid solution gradually turned purple red. After stirring at −80 to −50 °C for an additional 4 h, the resulting solution was evaporated under high vacuum at −45 °C to dryness and the dark red residue was chromatographed on an alumina column (1.6 × 15–20 cm) at −25 °C with petroleum ether–CH$_2$Cl$_2$ (10:1) as the eluant. The red band was eluted and collected. After vacuum removal of the solvent, the residue was recrystallized from petroleum ether–CH$_2$Cl$_2$ (15:1) solution at −80 °C to give 0.286 g (84%, based on **1**) of purple–red crystals of **9**: melting point (decomposition) m.p. (dec.) 89–91 °C; IR (CH$_2$Cl$_2$)?(CO) 2047 (m), 1998 (s), 1936 (vs) 1811 (m), 1710 (m) cm^{-1}; ν(CN) 2057 (w) cm^{-1}; ^{1}H-NMR (CD$_3$COCD$_3$) δ 8.51–7.36 (m, 5H, C$_6$H$_5$), 6.84 (s, 2H, C$_5$H$_4$), 6.76 (s, 2H, C$_5$H$_4$), 6.08 (s, 2H, C$_5$H$_4$), 5.44 (s, 2H, C$_5$H$_4$), 0.64 (s, 3H, SiCH$_3$), 0.29 (s, 3H, SiCH$_3$); MS *m/e* 443 [M$^+$−Cr(CO)$_5$CN−CO], 415 [M$^+$−Cr(CO)$_5$CN−2CO], 387 [M$^+$−Cr(CO)$_5$CN−3CO], 218 [Cr(CO)$_5$CN$^+$], 192 [Cr(CO)$_5^+$]. Anal. Calc. for C$_{28}$H$_{19}$O$_8$NSiCrFe$_2$: C, 48.80; H, 2.78; N, 2.03. Found: C, 48.72; H, 3.05; N, 2.18%.

The following complexes were prepared by similar reactions.

2.2. [Fe$_2$(μ-CO){μ-C(C$_6$H$_5$)NCMo(CO)$_5$}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}] (10)

Purple–red crystals (82% yield); m.p. (dec.) 75–76 °C; IR (CH$_2$Cl$_2$) ν(CO) 2014 (m), 1993 (w), 1929 (vs, br), 1854 (m), 1784 (w) cm^{-1}; ν(CN) 2043 (m) cm^{-1}; ^{1}H-NMR (CD$_3$COCD$_3$) δ 8.37–7.36 (m, 5H, C$_6$H$_5$), 6.82 (s, 2H, C$_5$H$_4$), 6.76 (s, 2H, C$_5$H$_4$), 6.08 (s,

2H, C_5H_4), 5.45 (s, 2H, C_5H_4), 0.64 (s, 3H, $SiCH_3$), 0.29 (s, 3H, $SiCH_3$); MS m/e 443 [$M^+ - Mo(CO)_5CN - CO$], 415 [$M^+ - Mo(CO)_5CN - 2CO$], 387 [$M^+ - Mo(CO)_5CN - 3CO$], 262 [$Mo(CO)_5CN^+$], 236 [$Mo(CO)_5^+$]. Anal. Calc. for $C_{28}H_{19}O_8Fe_2NSiMo$: C, 45.87; H, 2.61; N, 1.75. Found: C, 45.58; H, 2.82; N, 1.94%.

2.3. $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(C_6H_5)NCW(CO)_5\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (11)

Purple–red crystals (79% yield); m.p. (dec.) 90–92 °C; IR (CH_2Cl_2) $\nu(CO)$ 2012 (w), 1972 (m), 1920 (vs, br), 1792 (w) cm^{-1}; $\nu(CN)$ 2046 (m) cm^{-1}; ^{1}H-NMR (CD_3COCD_3) δ 8.22–7.64 (m, 5H, C_6H_5), 6.82 (s, 2H, C_5H_4), 6.75 (s, 2H, C_5H_4), 6.08 (s, 2H, C_5H_4), 5.44 (s, 2H, C_5H_4), 0.63 (s, 3H, $SiCH_3$), 0.29 (s, 3H, $SiCH_3$); MS m/e 443 [$M^+ - W(CO)_5CN - CO$], 415 [$M^+ - W(CO)_5CN - 2CO$], 387 [$M^+ - W(CO)_5CN - 3CO$], 350 [$W(CO)_5CN^+$]. Anal. Calc. for $C_{28}H_{19}O_8N$-$SiWFe_2$: C, 40.96; H, 2.33; N, 1.70. Found: C, 40.67; H, 2.61; N, 1.85%.

2.4. $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(C_6H_4CF_3\text{-}p)NCCr(CO)_5\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (12)

Purple–red crystals (80% yield); m.p. (dec.) 98–102 °C; IR (CH_2Cl_2) $\nu(CO)$ 2039 (m), 1997 (s), 1951 (vs) 1798 (m) cm^{-1}; $\nu(CN)$ 2050 (w) cm^{-1}; ^{1}H-NMR (CD_3COCD_3) δ 7.56–7.16 (m, 4H, $C_6H_4CF_3$), 6.52 (s, 4H, C_5H_4), 6.16 (s, 2H, C_5H_4), 5.60 (s, 2H, C_5H_4), 0.62 (s, 3H, $SiCH_3$), 0.28 (s, 3H, $SiCH_3$); MS m/e 757 [M^+], 511 [$M^+ - Cr(CO)_5CN - 2CO$], 483 [$M^+ - Cr(CO)_5CN - 3CO$], 218 [$Cr(CO)_5CN^+$]. Anal. Calc. for $C_{29}H_{18}O_8F_3NSiCrFe_2$: C, 46.00; H, 2.40; N, 1.85. Found: C, 45.75; H, 2.59; N, 1.99%.

2.5. $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(C_6H_4CF_3\text{-}p)NCMo(CO)_5\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (13)

Purple–red crystals (78% yield); m.p. (dec.) 92–94 °C; IR (CH_2Cl_2) $\nu(CO)$ 2045 (m), 1998 (s), 1953 (vs, br), 1799 (m) cm^{-1}; $\nu(CN)$ 2058 (w) cm^{-1}; ^{1}H-NMR (CD_3COCD_3) δ 7.74–7.54 (m, 4H, $C_6H_4CF_3$), 6.74 (s, 4H, C_5H_4), 5.59 (s, 4H, C_5H_4), 0.57 (s, 3H, $SiCH_3$), 0.30 (s, 3H, $SiCH_3$); MS m/e 539 [$M^+ - Mo(CO)_5CN$], 511 [$M^+ - Mo(CO)_5CN - CO$], 482 [$M^+ - Mo(CO)_5CN - 2CO$], 262 [$Mo(CO)_5CN^+$]. Anal. Calc. for $C_{29}H_{18}O_8F_3NSiMoFe_2$: C, 43.48; H, 2.26; N, 1.75. Found: C, 43.19; H, 2.38; N, 1.99%.

2.6. $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(C_6H_5CF_3\text{-}p)NCW(CO)_5\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (14)

Purple–red crystals (83% yield); m.p. (dec.) 90–92 °C; IR (CH_2Cl_2) $\nu(CO)$ 2041 (m), 1996 (s), 1943

(vs, br), 1800 (m), 1706 (m) cm^{-1}; $\nu(CN)$ 2055 (w) cm^{-1}; ^{1}H-NMR (CD_3COCD_3) δ 8.74–8.18 (m, 4H, $C_6H_4CF_3$), 6.91 (s, 2H, C_5H_4), 6.79 (s, 2H, C_5H_4), 6.16 (s, 2H, C_5H_4), 5.53 (s, 2H, C_5H_4), 0.67 (s, 3H, $SiCH_3$), 0.31 (s, 3H, $SiCH_3$); MS m/e 539 [$M^+ - W(CO)_5CN$], 511 [$M^+ - W(CO)_5CN - CO$], 483 [$M^+ - W(CO)_5CN - 2CO$], 350 [$W(CO)_5CN^+$]. Anal. Calc. for $C_{29}H_{18}O_8F_3Nsi$-$WFe_2 \cdot CH_2Cl_2$: C, 39.18; H, 2.04; N, 1.58. Found: C, 38.98; H, 2.20; N, 1.74%.

2.7. Reaction of $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4CH_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]BBr_4$ (3) with 4 to give $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4CH_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]^+[Cr(CO)_5CN]^-$ (15)

To a stirred, turbid solution of freshly prepared (in situ) 3 (0.391 g, 0.475 mmol) dissolved in 50 ml of THF at -100 °C was added 0.136 g (0.565 mmol) of 4. The reaction mixture was slowly warmed to -80 °C within 1 h, during which time the turbid red solution gradually turned brown–red. After being stirred at -80 to -50 °C for an additional 4 h, the resulting red solution was evaporated in vacuo at -45 °C to dryness, and the brown–red residue was chromatographed on Al_2O_3 at -25 °C with petroleum ether–CH_2Cl_2 (1:1) as the eluant. A purple–red band was eluted and collected. After vacuum removal of the solvent, the crude product was recrystallized from petroleum ether–CH_2Cl_2 (2:1) solution at -80 °C to yield 0.264 g (79%, based on 3) of 15 as deep red crystals: m.p. (dec.) 122–124 °C; IR (CH_2Cl_2) $\nu(CO)$ 2040 (vs), 2012 (m), 1966 (m), 1922 (vs), 1890 (m), 1849 (m) cm^{-1}; $\nu(CN)$ 2090 (w) cm^{-1}; ^{1}H-NMR (CD_3COCD_3) δ 8.37–7.70 (m, 4H, $C_6H_4CH_3$), 6.73 (s, 2H, C_5H_4), 6.70 (s, 2H, C_5H_4), 6.01 (s, 2H, C_5H_4), 5.38 (s, 2H, C_5H_4), 2.56 (s, 3H, $C_6H_4CH_3$), 0.59 (s, 3H, $SiCH_3$), 0.25 (s, 3H, $SiCH_3$); MS m/e 485 [$M^+ - Cr(CO)_5CN$], 457 [$M^+ - Cr(CO)_5CN - CO$], 401 [$M^+ - Cr(CO)_5CN - 3CO$], 218 [$Cr(CO)_5CN^+$], 192 [$Cr(CO)_5^+$]. Anal. Calc. for $C_{29}H_{21}O_8NSiCrFe_2$: C, 49.53; H, 3.01; N, 1.99. Found: C, 49.54; H, 3.18; N, 2.16%.

The following complexes were prepared by similar reactions.

2.8. $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4CH_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]^+[Mo(CO)_5CN]^-$ (16)

Deep red crystals (78% yield); m.p. (dec.) 103–105 °C; IR (CH_2Cl_2) $\nu(CO)$ 2061 (s), 2043 (s), 2014 (s), 1930 (vs, br), 1852 (m), 1810 (m) cm^{-1}; $\nu(CN)$ 2100 (w) cm^{-1}; ^{1}H-NMR (CD_3COCD_3) δ 8.37–7.70 (m, 4H, $C_6H_4CH_3$), 6.71 (s, 4H, C_5H_4), 6.01 (s, 2H, C_5H_4), 5.38 (s, 2H, C_5H_4), 2.56 (s, 3H, $C_6H_4CH_3$), 0.59 (s, 3H, $SiCH_3$), 0.26 (s, 3H, $SiCH_3$); MS m/e 747 [M^+], 485 [$M^+ - Mo(CO)_5CN$], 457 [$M^+ - Mo(CO)_5CN - CO$], 262 [$Mo(CO)_5CN^+$]. Anal. Calc. for $C_{29}H_{21}O_8NSi$-

MoFe$_2$: C, 46.62; H, 2.83; N, 1.87. Found: C, 46.30; H, 2.98; N, 1.98%.

2.9. $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4CH_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]^+[W(CO)_5CN]^-$ (17)

Deep red crystals (76% yield); m.p. (dec.) 118–120 °C; IR (CH$_2$Cl$_2$) v(CO) 2056 (w), 2040 (s), 2012 (w), 1966 (m), 1917 (vs), 1853 (m) cm^{-1}; v(CN) 2096 (w) cm^{-1}; ^{1}H-NMR (CD$_3$COCD$_3$) δ 8.37–7.70 (m, 4H, C$_6$H$_4$CH$_3$), 6.73 (s, 2H, C$_5$H$_4$), 6.71 (s, 2H, C$_5$H$_4$), 6.01 (s, 2H, C$_5$H$_4$), 5.38 (s, 2H, C$_5$H$_4$), 5.26 (m, 2H, CH$_2$Cl$_2$), 2.56 (s, 3H, C$_6$H$_4$CH$_3$), 0.58 (s, 3H, SiCH$_3$), 0.25 (s, 3H, SiCH$_3$); MS m/e 835 [M$^+$], 485 [M$^+$ $-$ W(CO)$_5$CN], 457 [M$^+$ $-$ W(CO)$_5$CN], 350 [W(CO)$_5$CN$^+$], 84 (CH$_2$Cl$_2$). Anal. Calc. for C$_{29}$H$_{21}$O$_8$NSiWFe$_2$·CH$_2$Cl$_2$: C, 39.26; H, 2.52; N, 1.52. Found: C, 39.80; H, 2.65; N, 1.85%.

2.10. $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4CH_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]^+[Fe(CO)_4CN]^-$ (18)

Deep red crystals (58% yield); m.p. (dec.) 207–209 °C; IR (CH$_2$Cl$_2$) v(CO) 2050 (w), 2038 (vs), 2012 (m), 1929 (vs), 1849 (m) cm^{-1}; v(CN) 2098 (m) cm^{-1}; ^{1}H-NMR (CD$_3$COCD$_3$) δ 8.36–7.64 (m, 4H, C$_6$H$_4$CH$_3$), 6.71 (s, 4H, C$_5$H$_4$), 6.01 (s, 2H, C$_5$H$_4$), 5.44 (s, 2H, C$_5$H$_4$), 2.56 (s, 3H, C$_6$H$_4$CH$_3$), 0.53 (s, 3H, SiCH$_3$), 0.30 (s, 3H, SiCH$_3$); MS m/e 485 [M$^+$ $-$ Fe(CO)$_4$CN], 457 [M$^+$ $-$ Fe(CO)$_4$ $-$ CO], 401 [M$^+$ $-$ Fe(CO)$_4$CN $-$ 3CO], 194 [Fe(CO)$_4$CN$^+$]. Anal. Calc. for C$_{28}$H$_{21}$O$_7$NSiFe$_3$: C, 47.83; H, 3.02; N, 1.99. Found: C, 47.62; H, 3.27; N, 2.09%.

2.11. Reaction of 16 with NaSCH$_3$ to give $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(SCH_3)C_6H_4CH_3\text{-}p\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (19)

To a brown–red solution of **16** (0.120 g, 0.161 mmol) in 50 ml of THF at -78 °C was added 0.012 g (0.171 mmol) of NaSCH$_3$. The reaction solution was stirred at -78 to -35 °C for 5 h, during which time the brown–red solution gradually turned purple red. After evaporation of the solvent under vacuum, the residue was chromatographed on Al$_2$O$_3$ at -25 °C with petroleum ether–CH$_2$Cl$_2$ (10:1) as the eluant. A purple–red band was eluted and collected. The solvent was removed in vacuo, and the residue was recrystallized from petroleum ether–CH$_2$Cl$_2$ (15:1) solution at -80 °C to yield 0.077 g (91% based on **16**) of **19** [8] as purple–red crystals: m.p. (dec.) 128–130 °C; IR (CH$_2$Cl$_2$) v(CO) 1982 (vs), 1949 (s), 1774 vs) cm^{-1}; ^{1}H-NMR (CD$_3$COCD$_3$) δ 7.35–6.83 (dd, 4H, C$_6$H$_4$CH$_3$), 6.13 (s, 2H, C$_5$H$_4$), 5.56 (s, 2H, C$_5$H$_4$), 5.22 (s, 2H, C$_5$H$_4$), 5.05 (s, 2H, C$_5$H$_4$), 2.19 (s, 3H, SCH$_3$), 2.03 (s, 3H, C$_6$H$_4$CH$_3$), 0.61 (s, 3H, SiCH$_3$), 0.47 (s, 3H, SiCH$_3$); MS m/e 532 [M$^+$], 504 [M$^+$ $-$ CO], 476 [M$^+$ $-$ 2CO], 448

[M$^+$ $-$ 3CO], 485 [M$^+$ $-$ SCH$_3$]. Anal. Calc. for C$_{24}$H$_{24}$O$_3$SFe$_2$Si: C, 53.23; H, 4.54. Found: C, 53.09; H, 4.70%.

2.12. Reaction of 15 with NaSC$_6$H$_5$ to give $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(SC_6H_5)C_6H_4CH_3\text{-}p\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (20)

As used for the reaction of **16** with NaSCH$_3$, **15** (0.049 g, 0.070 mmol) was treated with 0.010 g (0.071 mmol) of NaSC$_6$H$_5$ to yield 0.038 g (92%, based on **15**) of purple–red crystalline **20** [8]: m.p. (dec.) 134–135 °C; IR (CH$_2$Cl$_2$) v(CO) 1984 (vs), 1951 (s), 1778 (s) cm^{-1}; ^{1}H-NMR (CD$_3$COCD$_3$) δ 7.39–6.55 (m, 9H, C$_6$H$_5$ + C$_6$H$_4$CH$_3$), 6.24 (s, 2H, C$_5$H$_4$), 5.64 (s, 2H, C$_5$H$_4$), 5.27 (s, 2H, C$_5$H$_4$), 5.21 (s, 2H, C$_5$H$_4$), 2.01 (s, 3H, C$_6$H$_4$CH$_3$), 0.63 (s, 3H, SiCH$_3$), 0.52 (s, 3H, SiCH$_3$); MS m/e 594 [M$^+$], 538 [M$^+$ $-$ 2CO], 485 [M$^+$ $-$ SC$_6$H$_5$]. Anal. Calc. for C$_{29}$H$_{26}$O$_3$SFe$_2$Si: C, 58.60; H, 4.41. Found: C, 58.36; H, 4.62%.

2.13. Reaction of 15 with NaSC$_6$H$_4$CH$_3$-p to give $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(SC_6H_5CH_3\text{-}p)C_6H_4CH_3\text{-}p\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (21)

Using the same procedures for the reaction of **16** with NaSCH$_3$, compound **15** (0.070 g, 0.100 mmol) was treated with NaSC$_6$H$_4$CH$_3$-p (0.015 g, 0.100 mmol) to give 0.054 g (90%, based on **15**) of purple–red crystals of **21** [8]: m.p. (dec.) 109–110 °C; IR (CH$_2$Cl$_2$) v(CO) 1983 (vs), 1951 (m), 1773 (s) cm^{-1}; ^{1}H-NMR (CD$_3$COCD$_3$) δ 7.33–6.56 (m, 8H, 2C$_6$H$_4$CH$_3$), 6.22 (s, 2H, C$_5$H$_4$), 5.65 (s, 2H, C$_5$H$_4$), 5.26 (s, 2H, C$_5$H$_4$), 5.23 (s, 2H, C$_5$H$_4$), 2.25 (s, 3H, SC$_6$H$_4$CH$_3$), 2.03 (s, 3H, C$_6$H$_4$CH$_3$), 0.62 (s, 3H, SiCH$_3$), 0.50 (s, 3H, SiCH$_3$); MS m/e 608 [M$^+$], 580 [M$^+$ $-$ CO], 524 [M$^+$ $-$ 3CO], 485 [M$^+$ $-$ SC$_6$H$_4$CH$_3$]. Anal. Calc. for C$_{30}$H$_{28}$O$_3$SFe$_2$Si: C, 59.22; H, 4.64. Found: C, 58.87; H, 4.87%.

2.14. Reaction of 1 with NaN(SiMe$_3$)$_2$ to give $[Fe_2(\mu\text{-}CO)_2(CO)NCC_6H_5\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ (22)

To 0.400 g (0.494 mmol) of freshly prepared **1** dissolved in 60 ml of THF at -90 °C was added 0.106 g (0.581 mmol) of NaN(SiMe$_3$)$_2$. The reaction mixture was stirred at -80 °C for 1 h, during which time the turbid solution turned deep-red. After stirring at -70 to -50 °C for additional 4 h, the resulting solution was evaporated in vacuo at -45 °C to dryness and the dark red residue was chromatographed on Al$_2$O$_3$ at -25 °C with petroleum ether–CH$_2$Cl$_2$ (10:1) as the eluant. The red band was eluted and collected. After vacuum removal of the solvent, the residue was recrystallized from petroleum ether–CH$_2$Cl$_2$ (10:1) solution at -80 °C to yield 0.115 g (48%, based on **1**) of red crystals of **22**: m.p. (dec.) 122–123 °C; IR

$(CH_2Cl_2)\nu(CO)$ 1945 (s), 1795 (vs, br) cm^{-1}; $\nu(CN)$ 1993 cm^{-1}; ^{1}H-NMR (CD$_3$COCD$_3$) δ 7.56–7.26 (m, 5H, C$_6$H$_5$), 5.57 (s, 2H, C$_5$H$_4$), 5.47 (s, 2H, C$_5$H$_4$), 5.15 (s, 2H, C$_5$H$_4$), 5.02 (s, 2H, C$_5$H$_4$), 0.26 (s, 6H, SiCH$_3$); MS m/e 485 [M$^+$], 382 [M$^+$ $-$C$_6$H$_5$CN], 354 [M$^+$ $-$C$_6$H$_5$CN$-$CO], 298 [M$^+$ $-$C$_6$H$_5$CN$-$3CO]. Anal. Calc. for C$_{22}$H$_{19}$O$_3$NSiFe$_2$: C, 54.46; H, 3.95, N, 2.89. Found: C, 54.66, H, 4.02, N, 2.88%.

2.15. Reaction of 1 with 7 to give [Fe$_2$(μ-CO){μ-C(H)C$_6$H$_5$}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}] (23)

To a stirred, turbid red solution of **1** (0.400g, 0.494 mmol) in 50 ml of THF at -100 °C was added 0.126 g (0.581 mmol) of **7**. The reaction mixture was stirred at -100 to -50 °C for 5 h, during which time the turbid red solution gradually turned brown red. The resulting solution was evaporated in vacuo at -40 °C to dryness, and the dark-red residue was chromatographed on Al$_2$O$_3$ at -25 °C with petroleum ether–CH$_2$Cl$_2$ (5:1) as the eluant. A purple–red band was eluted and collected. The solvent was removed in vacuo, and the residue was recrystallized from petroleum ether–CH$_2$Cl$_2$ (5:1) solution at -80 °C to yield 0.120 g (51%, based on **1**) of purple–red crystals of **23**: m.p. (dec.) 228–230 °C; IR (CH$_2$Cl$_2$) $\nu(CO)$ 1971 (vs), 1938 (s), 1775 (vs) cm^{-1}; ^{1}H-NMR (CD$_3$COCD$_3$) δ 12.22 (s, 1H, μ-CH), 7.37–7.01 (m, 5H, C$_6$H$_5$), 5.70 (s, 2H, C$_5$H$_4$), 5.62 (s, 2H, C$_5$H$_4$), 5.35 (s, 2H, C$_5$H$_4$), 5.12 (s, 2H, C$_5$H$_4$), 0.58 (s, 3H, SiCH$_3$), 0.35 (s, 3H, SiCH$_3$); MS m/e 472 [M$^+$], 444 [M$^+$ $-$CO], 416 [M$^+$ $-$2CO], 388 [M$^+$ $-$3CO]. Anal. Calc. for C$_{22}$H$_{20}$O$_3$SiFe$_2$: C, 55.96; H, 4.27. Found: C, 55.70; H, 4.28%.

2.16. Reaction of 2 with 7 to give [Fe$_2$(μ-CO){μ-C(H)C$_6$H$_4$CF$_3$-p}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}] (24)

Similar to the reaction of **1** with **7**, **2** (0.389 g, 0.447 mmol) was treated with **7** (0.112 g, 0.513 mmol) to afford 0.110 g (46%, based on **2**) of purple–red crystalline **24**: m.p. (dec.) 212–214 °C; IR (CH$_2$Cl$_2$) $\nu(CO)$ 1975 (s), 1944 (m), 1781 (m) cm^{-1}; ^{1}H-NMR (CD$_3$COCD$_3$) δ 12.04 (s, 1H, μ-CH), 7.60–7.36 (m, 4H, C$_6$H$_4$CF$_3$), 5.69 (s, 2H, C$_5$H$_4$), 5.60 (s, 2H, C$_5$H$_4$), 5.35 (s, 2H, C$_5$H$_4$), 5.25 (m, 1H, CH$_2$Cl$_2$), 5.12 (s, 2H, C$_5$H$_4$), 0.59 (s, 3H, SiCH$_3$), 0.36 (s, 3H, SiCH$_3$); MS m/e 512 [M$^+$ $-$CO], 484 [M$^+$ $-$2CO], 456 [M$^+$ $-$3CO], 84 [CH$_2$Cl$_2^+$]. Anal. Calc. for C$_{23}$H$_{19}$O$_3$F$_3$SiFe$_2$ 0.5CH$_2$Cl$_2$: C, 48.47; H, 3.46. Found: C, 48.60; H, 4.00%.

2.17. Reaction of 1 with [(PPh$_3$)$_2$N][Cr(CO)$_4$NO] (8) to give 23

To a stirred solution of **1** (0.400 g, 0.494 mmol) in 50 ml of THF at -100 °C was added 0.340 g (0.494 mmol) of **8**. The reaction mixture was stirred at -100 to -50 °C for 5 h, during which time the turbid red solution gradually turned brown–red. After vacuum removal of the solvent, the brown–red residue was chromatographed on Al$_2$O$_3$ at -25 °C with petroleum ether–CH$_2$Cl$_2$ (5:1) as the eluant. A purple–red band was eluted and collected. The solvent was removed in vacuo, and the crude product was recrystallized from petroleum ether–CH$_2$Cl$_2$ (5:1) solution at -80 °C to yield 0.082 g (37%, based on **1**) of purple–red crystals of **23**, which was identified by its m.p., and IR, ^{1}H-NMR and mass spectra.

2.18. Reaction of 2 with 8 to give 24

Compound **2** (0.389 g, 0.447 mmol) was reacted with **8** (0.340 g, 0.447 mmol) as described for the reaction of **1** with **8** to produce 0.090 g (38%, based on **2**) of purple–red crystals of **24**, which was identified by its m.p., IR, and ^{1}H-NMR and mass spectra.

2.19. Reaction of 3 with 8 to give [Fe$_2$(μ-CO){μ-C(H)C$_6$H$_4$CH$_3$-p}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}] (25)

As used in the reaction of **1** with **8**, 0.313 g (0.380 mmol) of **3** was treated with **8** (0.289 g, 0.380 mmol) to give 0.087 g (47%, based on **3**) of **25** as purple–red crystals: m.p. (dec.) 220–222 °C; IR (CH$_2$Cl$_2$) $\nu(CO)$ 1971 (s), 1939 (m), 1770 (m) cm^{-1}; ^{1}H-NMR (CD$_3$COCD$_3$) δ 12.23 (s, 1H, μ-CH), 7.26–6.93 (m, 4H, C$_6$H$_4$CH$_3$), 5.63 (s, 2H, C$_5$H$_4$), 5.57 (s, 2H, C$_5$H$_4$), 5.30 (s, 2H, C$_5$H$_4$), 5.26 (m, 3H, CH$_2$Cl$_2$), 5.09 (s, 2H, C$_5$H$_4$), 2.23 (s, 3H, C$_6$H$_4$CH$_3$), 0.59 (s, 3H, SiCH$_3$), 0.34 (s, 3H, SiCH$_3$); MS m/e 557 [M$^+$], 529 [M$^+$ $-$CO], 501 [M$^+$ $-$2CO], 473 [M$^+$ $-$3CO], 84 [CH$_2$Cl$_2^+$]. Anal. Calc. for C$_{23}$H$_{22}$O$_3$SiFe$_2$ 1.5CH$_2$Cl$_2$: C, 47.95; H, 4.10. Found: C, 47.77; H, 4.22%.
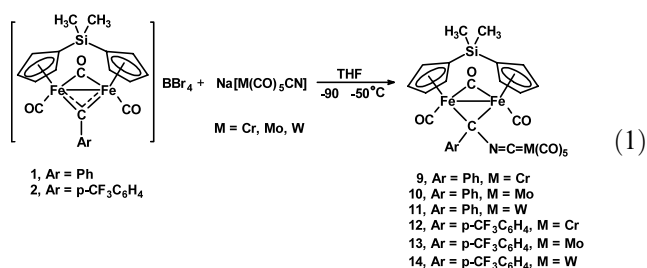
X-ray crystal structure determinations of complexes **14**, **15**, **22**, and **23**. The single crystals of **14**, **15**, **22**, and **23** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether–CH$_2$Cl$_2$ solution at -80 °C. Single crystals were mounted on a glass fibre and sealed with epoxy glue. The X-ray diffraction intensity data were collected with a Rigaku AFC7R or Brock Smart diffractometer.

The structures of **14**, **15**, **22**, and **23** were solved by direct methods and expanded using Fourier techniques. For **14**, some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. For **15**, **22**, and **23**, the non-hydrogen atoms were refined anisotropically. For the four complexes the hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement gave agreement factors of $R = 0.050$ and $R_w = 0.062$ for **14**, $R = 0.061$ and $R_w = 0.062$ for **15**, $R = 0.046$ and $R_w = 0.047$ for **22**, and $R = 0.0429$ and $R_w = 0.0514$ for **23**.

The details of the crystallographic data and the procedures used for data collection and reduction information for **14**, **15**, **22**, and **23** are given in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3. The atomic coordinates and B_{iso}/B_{eq}, anisotropic displacement parameters, complete bond lengths and angles, least-squares planes for **14**, **15**, **22**, and **23** are given in the supporting information. The molecular structures of **14**, **15**, **22**, and **23** are given in Figs. 1–4, respectively.

3. Results and discussion

The highly electrophilic dimethylsilane-bridged cationic carbyne complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}CAr\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]BBr_4$ should be highly reactive toward nucleophilic carbonylmetal anions, which is indeed the case. The freshly prepared (in situ) complex $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_5)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]BBr_4$ **(1)** was treated with about 10–15% molar excess of anionic carbonylmetal compounds $Na[M(CO)_5CN]$ (**4**, M = Cr; **5**, M = Mo; **6**, M = W) in THF at low temperature (-90 to $-50\ ^\circ$C) for 4–5 h. After work-up as described in the Section 2, the novel bridging phenyl(pentacarbonylcyanometal)carbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(C_6H_5)NCM(CO)_5\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ **(9–11)** (Eq. (1)) were obtained in 79–84% yields. Complex $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4CF_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]BBr_4$ **(2)** reacts similarly with **4–6** under the same conditions to give corresponding bridging aryl(pentacarbonylcyanometal)carbene complexes $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(C_6H_4CF_3\text{-}p)NCM(CO)_5\}(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]$ **(12–14)** (Eq. (1)) in similar yields (78–83%).

$$ (1) $$

1, Ar = Ph
2, Ar = p-CF₃C₆H₄

9, Ar = Ph, M = Cr
10, Ar = Ph, M = Mo
11, Ar = Ph, M = W
12, Ar = p-CF₃C₆H₄, M = Cr
13, Ar = p-CF₃C₆H₄, M = Mo
14, Ar = p-CF₃C₆H₄, M = W

In contrast to the reactions of cationic **1** and **2**, cationic carbyne complex $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4CH_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]BBr_4$ **(3)**, where the aryl substituent on the μ-carbyne carbon is a p-tolyl group, reacts with carbonylmetal anions **4–6** under the same conditions to give not analogous bridging carbene complexes but rather novel cationic carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4CH_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]^+[M(CO)_5CN]^-$ **(15–17)** (Eq. (2)) in 76–79% isolated yields. Analogous cationic bridging carbyne complex $[Fe_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4CH_3\text{-}p)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]^+[Fe(CO)_4CN]^-$ **(18)** can also

be obtained in somewhat lower yield (58%) from the reaction (Eq. (2)) of **3** with $Na[Fe(CO)_4CN]$ **(7)**.

$$ (2) $$

15, M = Cr, n = 5
16, M = Mo, n = 5
17, M = W, n = 5
18, M = Fe, n = 4
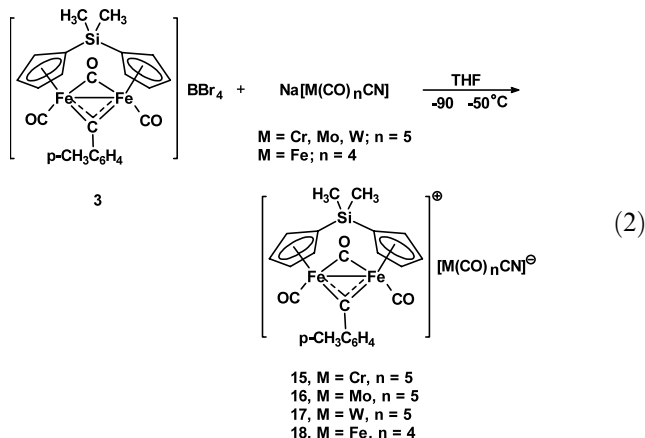
On the basis of elemental analyses and spectroscopic evidence, as well as X-ray crystallography, product **14** is formulated as diiron bridging carbene complexes with a $M(CO)_5CN$ (M = W) moiety bonded to bridging carbene carbon through the N atom of the CN group, while product **15** as novel cationic bridging carbyne complexes with a $[M(CO)_nCN]^-$ (M = Cr) anion as the counterion, respectively. Complexes **9–13** are assigned to similar structures since their spectral data and polarity are similar to those of complex **14**. Likely, complexes **16–18** are assigned to a similar structure since its spectral data and polarity are similar to those of complex **15**.

Complexes **9–14** are readily soluble in polar organic solvents but slightly soluble in non-polar solvents, while complexes **15–18** are only sparingly soluble in polar solvents, such as THF and CH_2Cl_2. The isolation of **9–14** was by chromatography on an alumina column with a 10:1 of petroleum ether–CH_2Cl_2 as the eluant and the further purification was recrystallized from a 15:1 of petroleum ether–CH_2Cl_2 solution, while for **15–18**, the chromatography isolation was with used an 1:1 of petroleum ether–CH_2Cl_2 as the eluant and the recrystallization was from a 2:1 of petroleum ether–CH_2Cl_2 solution, indicating larger polarity for **15–18** than for **9–14**. Complexes **9–14** and **15–18** are sensitive to air and temperature in solution but relatively stable in the solid states.

The IR and ¹H-NMR spectra of complexes **9–14** and **15–18** are consistent with their structures shown in Eqs. (1) and (2), respectively. The IR spectra of **15–18** in the $v(CO)$ region shows that the absorption band of the bridging CO group appears at ca. 1810–1853 cm^{-1} for **15–18**, similar to complex **3** (at 1857 cm^{-1}) but very different from complexes **9–14** (at 1706–1799 cm^{-1}). The characteristic $v(CN)$ stretching vibration occurs at ca. 2043–2058 cm^{-1} for **9–14** but at ca. 2090–2100 cm^{-1} for **15–18**, shifting to high vibration frequency by about 45 cm^{-1}. The lower $v(CN)$ vibration frequency

Table 1
Crystal data and experimental details for complexes **14**, **15**, **22**, and **23**

	14	**15** CH_2Cl_2	**22**	**23**
Formula	$C_{29}H_{18}O_8NF_3SiWFe_2$	$C_{30}H_{23}O_8NCl_2SiCrFe_2$	$C_{22}H_{19}O_3NFe_2Si$	$C_{22}H_{20}O_3SiFe_2$
Formula weight	889.09	788.20	485.18	472.17
Space group	$P2_1/m$ (number 11)	$P2_1/n$ (number 14)	$P2_1/n$ (number 14)	$P2_12_12_1$
a (Å)	11.523(3)	9.474(3)	10.856(5)	8.4357(9)
b (Å)	11.028(3)	15.391(3)	14.992(4)	12.4388(14)
c (Å)	12.228(3)	23.028(4)	13.015(4)	19.011(2)
α (°)				90
β (°)	91.37(2)	90.39(2)	93.34(3)	90
γ (°)				90
V (Å^3)	1553.4(6)	3357(1)	2114(1)	1994.8(4)
Z	2	4	4	4
D_{calc} (g cm^{-3})	1.901	1.559	1.524	1.572
$F(000)$	860.00	1592.00	992.00	968
μ (Mo–K$_\alpha$) (cm^{-1})	47.24	14.12	14.50	15.35
Radiation (monochromated in incident beam)	Mo–K$_\alpha$ ($\lambda = 0.71069$ Å)	Mo–K$_\alpha$ ($\lambda = 0.71069$ Å)	Mo–K$_\alpha$ ($\lambda = 0.71069$ Å)	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å)
Diffractometer	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R	Brock Smart
Temperature (°C)	20	20	20	20
Orientation reflections: number; range (2θ) (°)	20; 14.5–21.1	19; 18.7–21.5	23; 14.4–19.3	2.95–28.82
Scan method	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
Data coll. range, 2θ (°)	5–55	5–50	5–51	3.92–56.6
Number of unique data, total with $I > 3.00\sigma(I)$	3675, 2565	6155, 406	3948, 2163 ($I > 2.50\sigma(I)$)	4643, 4643 ($I > 2.00\sigma(I)$)
Number of parameters refined	215	406	262	311
Corrected factors, max/min	0.9512–0.9999	0.7151–1.0000	0.8477–1.0000	0.8928–1.0000
R [a]	0.050	0.061	0.046	0.046
R_w [b]	0.062	0.062	0.047	0.0526
Quality of fit indicator [c]	1.88	1.80	1.25	0.713
Max shift/estimated S.D. final cycle	0.00	0.00	0.00	0.003
Largest peak (e Å^{-3})	2.08	1.03	0.40	0.788
Minimum peak (e Å^{-3})	-1.43	-0.47	-0.39	-0.320

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

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

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

for **9**–**14** may be due to the bonding of the M(CO)$_5$CN (M = Cr, Mo, W) moiety to the μ-carbene carbon through the CN group leading to a weakening of the C–N bond to a certain extent in **9**–**14**, as compared with that of complexes **15**–**18**. The ^{1}H-NMR spectra of **15**–**18** showed that the signals attributed to the cyclopentadienyl rings at 6.73–5.38 ppm which are different from those of **9**–**14** (at 6.91–5.44 ppm) but are similar to that of parent cationic carbyne complex **3** (at 6.78–5.42 ppm). These suggest that the structures of **15**–**18** are quite different from those of **9**–**14** and somewhat like parent complex **3**, a fact that is further confirmed by X-ray diffraction studies of **14** and **15**. The results of the X-ray diffraction work for both complexes are summarized in Table 1, and their structures are shown in Figs. 1 and 2, respectively.

The structure of **14** resembles that of bridging alkoxycarbene complex [Fe$_2$(μ-CO){μ-C(OC$_2$H$_5$)C$_6$H$_4$OCH$_3$-p}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}] [12] except that the substituents on the μ-carbene carbon are a p-CF$_3$C$_6$H$_4$ and a W(CO)$_5$CN group in **14** but a p-

CH$_3$OC$_6$H$_4$ and an OC$_2$H$_5$ group in the latter. The structural features of the principal portion of [Fe$_2$(μ-CO){μ-C(OC$_2$H$_5$)C$_6$H$_4$OCH$_3$-p}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}] of **14** are very similar to those of the same unit in complex [Fe$_2$(μ-CO){μ-C(OC$_2$H$_5$)C$_6$H$_4$OCH$_3$-p}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}]), as illustrated by the following parameters (the value for **14** is followed by the same parameters for [Fe$_2$(μ-CO){μ-C(OC$_2$H$_5$)-C$_6$H$_4$OCH$_3$-p}(CO)$_2${(η^5-C$_5$H$_4$)$_2$Si(CH$_3$)$_2$}]): Fe–Fe (2.502(3), 2.503(6) Å), average Fe–C(10) (1.914, 1.885 Å), average Fe–C(Cp) (2.117, 2.115 Å), C(1)–C(2) (1.51(1), 1.49(3) Å), Fe–C(1)–Fe (76.6(4)°, 75.4(9)°), Fe–C(10)–Fe (81.6(5)°, 82(1)°). The structure of W(CO)$_5$CN moiety bonded to the μ-carbene carbon is essentially the same as that in analogous complex [Fe$_2$(μ-CO){μ-C(C$_6$H$_4$CH$_3$-p)NCW(CO)$_5$}(CO)$_2$(η^5-C$_5$H$_5$)$_2$] [7]. The two C–N bond lengths in **14** are very different. C(18)–N has a bond length of 1.15(1) Å, which indicates high triple-bond character and is essentially the same as the corresponding distance found in [Fe$_2$(μ-CO){μ-C(C$_6$H$_4$CH$_3$-p)NCW(CO)$_5$}(CO)$_2$(η^5-

Table 2
Selected bond lengths (Å) [a] and angles (°) [a] for complexes **14** and **23**

	14	**23**		**14**	**23**
Bond lengths					
Fe–Fe	2.502(3)	2.5150(9)	C(9)–O(3)		1.170(4)
Fe–C(1)	2.019(9)		C(1)–N	1.43(1)	
Fe(1)–C(1)		1.996(5)	C(1)–C(2)	1.51(1)	1.453(6)
Fe(2)–C(1)		1.997(5)	N–C(18)	1.15(1)	
Fe–C(10)	1.914(9)		C(18)–W	2.13(1)	
Fe(1)–C(10)		1.913(5)	Si–C(17)	1.877(9)	1.863(5)
Fe(2)–C(10)		1.906(5)	Si–C(18)		1.866(5)
C(10)–O(2)	1.18(1)	1.181(5)	Si–C(23)	1.87(1)	1.849(5)
Fe(1)–C(8)	1.780(9)	1.700(5)	Si–C(24)	1.86(1)	1.852(4)
C(8)–O(1)	1.11(1)	1.178(5)	Fe(1)–C(Cp) (av)	2.117	2.107
Fe(2)–C(9)		1.689(5)	Fe(2)–C(Cp) (av)	2.117	2.115
Bond angles					
Fe(1)–Fe(2)–C(1)		50.93(15)	C(1)–N–C(18)	166.0(1)	
Fe–C(1)–Fe	76.6(4)	78.08(19)	N–C(18)–W	178.2(10)	
Fe(2)–Fe(1)–C(1)		50.98(15)	Fe–C(1)–C(2)	122.6(5)	
Fe(1)–Fe(2)–C(10)		48.92(14)	Fe(1)–C(1)–C(2)		130.3(4)
Fe–C(10)–Fe	81.6(5)	82.4(2)	Fe(2)–C(1)–C(2)		126.2(3)
Fe*–Fe–C(1)	51.7(2)		Fe–C(8)–O(1)	173.4(8)	
Fe*–Fe–C(10)	49.2(2)		Fe(1)–C(8)–O(1)		173.8(4)
Fe(2)–Fe(1)–C(10)		48.68(16)	Fe–C(10)–O(2)	139.2(2)	
C(1)–Fe–C(10)	97.6(3)		Fe(2)–C(9)–O(3)		175.9(4)
C(1)–Fe(1)–C(10)		97.3(2)	Fe–C(17)–Si	119.8(4)	
C(1)–Fe(2)–C(10)		97.5(2)	Fe(1)–C(17)–Si		120.5(2)
Fe(1)–C(10)–O(2)		137.9(4)	Fe(2)–C(18)–Si		119.5(2)
Fe(2)–C(10)–O(2)		139.7(4)	C(17)–Si–C(18)		106.4(2)
Fe–C(1)–N	116.7(5)				

[a] Estimated S.D. in the least significant figure are given in parentheses.

$C_5H_5)_2$] (C(23)–N 1.15(2) Å) [7]. The other is C(1)–N with the bond length of 1.43 (1) Å, which is between the normal C–N and C=N distances and slightly shorter than the corresponding C–N distance in complexes [$Fe_2(\mu$-CO){μ-C($C_6H_4CH_3$-*p*)NCW(CO)$_5$}(CO)$_2$-(η^5-$C_5H_5)_2$] (1.47(2) Å) and [W–N(Bu^{t}CMe$_2$(Me)-(NBu^t){N(Bu^t)CMe=CMe$_2$}] (1.438–1.521 Å) [13]. The shorter W–C(18) distance (2.13(1) Å) in **14** signifies its high double-bond character and is the same as the corresponding distance in [$Fe_2(\mu$-CO){μ-C($C_6H_4CH_3$-*p*)NCW(CO)$_5$}(CO)$_2$(η^5-$C_5H_5)_2$] (2.13(2) Å) [7]. The C(1), N, C(18), and W atoms are coplanar with a C(1)–N–C(18) angle of 166(1)° and a N–C(18)–W angle of 178.2(10)°, indicating that the C(1)–N–C(28)–W fragment is almost linear; thus C(1), N, C(28), and W atoms form a conjugate chain.

The X-ray study of **15** showed that its structure is formed by complex cations [$Fe_2(\mu$-CO)(μ-C$C_6H_4CH_3$-*p*)(CO)$_2${(η^5-$C_5H_4)_2$Si(CH$_3$)$_2$}]$^+$ and complex anions [Cr(CO)$_5$CN]$^-$; the anion being directed towards the cation, as shown in Fig. 2. The structure of the cationic [$Fe_2(\mu$-CO)(μ-C$C_6H_4CH_3$-*p*)(CO)$_2${(η^5-$C_5H_4)_2$-Si(CH$_3$)$_2$}]$^+$ fragment is very close to that of the similar unit [$Fe_2(\mu$-CO){μ-C($C_6H_4CF_3$-*p*)(CO)$_2${(η^5-$C_5H_4)_2$-Si(CH$_3$)$_2$}] in **14**. An apparent difference in the structures of **14** and **15** is the shorter Fe–Fe bond (2.495(2)

Å), shorter Fe-μ-C bonds (Fe(1)–C(1) = 1.83(1) Å, Fe(2)–C(1) = 1.83(1) Å), and shorter C(1)–C(2) bond (1.44(1) Å) but is longer Fe–C(10) bond (1.94(1) Å) and larger Fe-μ-C(1)–Fe angle (85.8(4)°) in **15**, as compared with **14**. The Fe-μ-C(1) distances in **15** not only are much shorter than that found (2.019(9) Å) in **14**, but also significantly shorter than the Fe=$C_{carbene}$ bond in carbene complexes [Fe{C(OC_2H_5)$C_6H_4CH_3$-*o*}-($C_{10}H_{16}$)(CO)$_2$] (1.915(15) Å) [14] and [Fe{C(OC_2H_5)-$C_6H_4CH_3$-*o*}(C_6H_8)(CO)$_2$] (1.89(2) Å) [15]. In the di- and trimetal bridging carbyne complexes [MoFe(μ-C$C_6H_4CH_3$-*p*)(CO)$_6$(η^5-C_5H_5)] [16a] and [CrReFe(μ-C$C_6H_4CH_3$-*p*)(CO)$_{12}$] [16b], the Fe-μ-C distances, 2.008(5) and 1.872(8) Å, respectively, are longer than those in **15**. These data strongly suggest that both Fe-μ-C(1) linkages in **15** are a double bond. Moreover, the shorter C(1)–C(2) bond length in **15**, which is intermediate between C–C single and C=C double bond distances, suggests some π-bond character between the C(1) atom and C(2) atom of the benzene ring in **15**.

The molecular structure of **15** shows that in the direction of the cationic fragment [$Fe_2(\mu$-CO)(μ-C$C_6H_4CH_3$-*p*)(CO)$_2${(η^5-$C_5H_4)_2$Si(CH$_3$)$_2$}]$^+$, an anionic fragment of [Cr(CO)$_5$CN]$^-$ was located. The [Cr(CO)$_5$CN]$^-$ anion is a octahedral structure with the CO groups almost linear ($178 \geq$ Cr–C–O $\geq 176°$) in

Table 3
Selected bond lengths (Å) [a] and angles (°) [a] for complexes **15** and **22**

Complex 15

Bond lengths

Fe(1)–Fe(2)	2.495(2)	Fe(2)–C(9)	1.75(1)	Fe(2)–C(Cp) (av)	2.110
Fe(1)–C(1)	1.83(1)	C(9)–O(3)	1.15(1)	Cr–C(31)	1.92(2)
Fe(2)–C(1)	1.83(1)	C(1)–C(2)	1.44(1)	C(31)–N	1.13(1)
Fe(1)–C(10)	1.94(1)	Si–C(17)	1.86(1)	Cr–C(26)	1.85(1)
Fe(2)–C(10)	1.95(1)	Si–C(18)	1.86(1)	Cr–C(27)	2.02(1)
C(10)–O(2)	1.16(1)	Si–C(23)	1.85(1)	Cr–C(28)	1.92(1)
Fe(1)–C(8)	1.73(1)	Si–C(24)	1.85(1)	Cr–C(29)	1.89(1)
C(8)–O(1)	1.18(1)	Fe(1)–C(Cp) (av)	2.106	Cr–C(30)	1.90(2)

Bond angles

Fe(1)–Fe(2)–C(1)	47.0(3)	Fe(1)–C(10)–O(2)	141.4(9)	Fe(1)–Fe(2)–C(9)	104.5(3)
Fe(1)–C(1)–Fe(2)	85.8(4)	Fe(2)–C(10)–O(2)	138.9(9)	C(1)–Fe(2)–C(9)	88.3(5)
Fe(2)–Fe(1)–C(1)	47.2(3)	Fe(1)–C(1)–C(2)	136.1(9)	Cr–C(31)–N	175.0(1)
Fe(1)–Fe(2)–C(10)	50.0(3)	Fe(2)–C(1)–C(2)	137.9(9)	Cr–C(26)–O(4)	178.0(1)
Fe(1)–C(10)–Fe(2)	79.7(4)	Fe(1)–C(17)–Si	121.7(5)	Cr–C(27)–O(5)	176.0(1)
Fe(2)–Fe(1)–C(10)	50.3(3)	Fe(2)–C(18)–Si	121.5(5)	Cr–C(28)–O(6)	178.0(1)
C(1)–Fe(1)–C(10)	94.1(4)	Fe(2)–Fe(1)–C(8)	105.0(4)	Cr–C(29)–O(7)	178.0(1)
C(1)–Fe(2)–C(10)	93.7(5)	C(1)–Fe(1)–C(8)	89.2(5)	Cr–C(30)–O(8)	177.0(1)

Complex 22

Bond lengths

Fe(1)–Fe(2)	2.510(1)	C(10)–O(3)	1.183(7)	Si–C(24)	1.857(7)
Fe(1)–C(9)	1.933(6)	Fe(1)–C(8)	1.733(7)	Fe(2)–N	1.894(5)
Fe(2)–C(9)	1.905(7)	C(8)–O(1)	1.155(7)	N–C(1)	1.134(7)
Fe(1)–C(10)	1.946(6)	Si–C(17)	1.872(6)	C(1)–C(2)	1.435(9)
Fe(2)–C(10)	1.891(6)	Si–C(18)	1.869(6)	Fe(1)–C(Cp) (av)	2.1334
C(9)–O(2)	1.173(7)	Si–C(23)	1.858(7)	Fe(2)–C(Cp) (av)	2.1082

Bond angles

Fe(1)–Fe(2)–C(9)	49.6(2)	Fe(1)–C(9)–O(2)	138.3(5)	Fe(2)–Fe(1)–N	99.3(2)
Fe(1)–C(9)–Fe(2)	81.7(3)	Fe(2)–C(9)–O(2)	140.0(5)	C(9)–Fe(2)–N	90.1(2)
Fe(2)–Fe(1)–C(9)	48.7(2)	Fe(1)–C(10)–O(3)	136.6(5)	C(10)–Fe(2)–N	90.6(2)
Fe(1)–Fe(2)–C(10)	50.1(2)	Fe(2)–C(10)–O(3)	141.6(5)	Fe(2)–N–C(1)	179.2(5)
Fe(1)–C(10)–Fe(2)	81.7(2)	Fe(1)–C(8)–O(1)	178.7(6)	N–C(1)–C(2)	178.3(7)
Fe(2)–Fe(1)–C(10)	48.2(2)	Fe(1)–C(17)–Si	119.4(3)	C(1)–C(2)–C(3)	120.0(7)
C(9)–Fe(1)–C(10)	95.2(3)	Fe(2)–C(18)–Si	118.9(3)	C(1)–C(2)–C(7)	119.4(6)
C(9)–Fe(2)–C(10)	97.9(3)	Fe(1)–Fe(2)–N	101.5(2)		

[a] Estimated S.D. in the least significant figure are given in parentheses.

which one corner is occupied by a CN group. The average Cr–C(CO) bond length is 1.916 Å. The C–N bond has a bond length of 1.13(1) Å, which is a normal C≡N triple-bond distance and is comparable with that of corresponding C–N bonds in **14** (1.15(1) Å), [(PPh₃)₂N][Fe(CO)₄CN] (1.147(7) Å) [17], and [Fe₂(μ-CNEt)₃(CNEt)₆] (1.13–1.19 Å) [17]. The shorter Cr–C(CN) distance (1.92(2) Å) indicates a high double-bond character of the Cr–C(23) bond. Evidently, complex **15** is the first example of a dimetal cationic bridging carbyne complex with a carbonylmetal anion counterion studied by X-ray crystallography.

The formation of complexes **9–14** and **15–18** might involve initial formation of a cationic bridging carbyne intermediate [Fe₂(μ-CO)(μ-CAr)(CO)₂{(η⁵-C₅H₄)₂Si-(CH₃)₂}]⁺[M(CO)ₙCN]⁻ (M = Cr, Mo, W; n = 5; M = Fe, n = 4) by combination of **1** or **2** and **3** with [M(CO)ₙCN]⁻. In the case of cationic **1** and **2**, where

the aryl substituents on the μ-carbyne carbon are an electron-withdrawing phenyl and a p-(trifluoromethyl)phenyl group, respectively, the cationic carbyne intermediate [Fe₂(μ-CO)(μ-CAr)(CO)₂{(η⁵-C₅H₄)₂Si-(CH₃)₂}]⁺[M(CO)ₙCN]⁻ (Ar = C₆H₅ or p-CF₃C₆H₄) is not stably exist, and the (CO)₅M=C=N⁻ (M = Cr or Mo, W) anion (a representation of the same electronic structure of the ⁻M(CO)₅CN anion) further attacks the more positive μ-carbyne carbon of **1** or **2** to give bridging carbene complexes **9–14** due to the electron-withdrawing action of C₆H₅ or p-CF₃C₆H₄ group to increase the electron density on the μ-carbyne carbon; while in the case of **3**, where the aryl substituent on the μ-carbyne carbon is a electron-pushing p-tolyl group, the cationic carbyne intermediate [Fe₂(μ-CO)(μ-CC₆H₄CH₃-p)(CO)₂{(η⁵-C₅H₄)₂Si(CH₃)₂}]⁺[M(CO)ₙ-CN]⁻ formed can stably exist due to the electron-pushing action of the p-tolyl group, which provides its
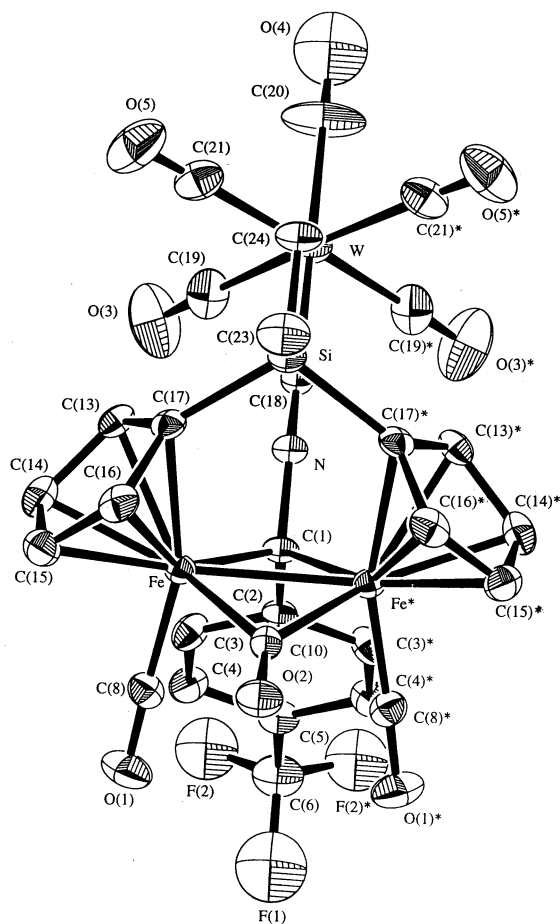
Fig. 1. Molecular structure of **14**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 45% probability.
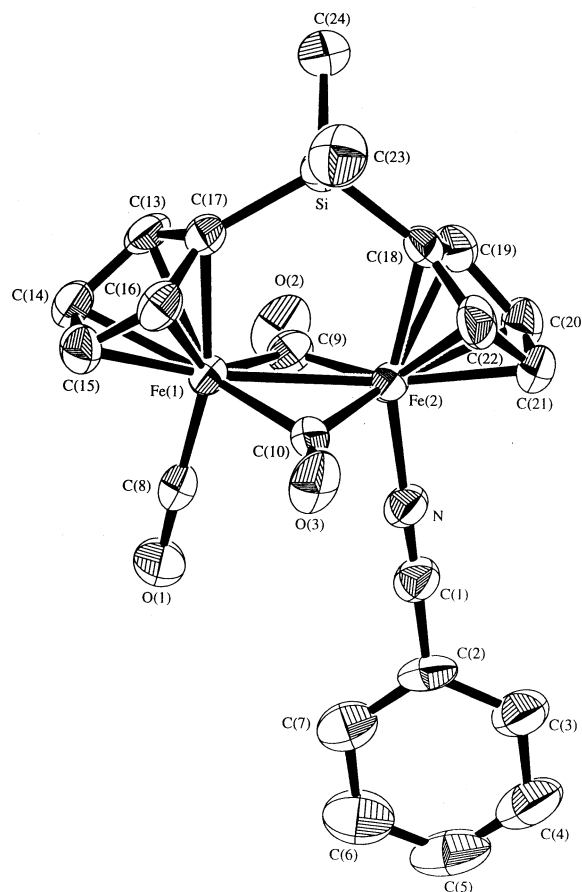
Fig. 3. Molecular structure of **22**, showing the atom-numbering scheme with 45% thermal ellipsoids.
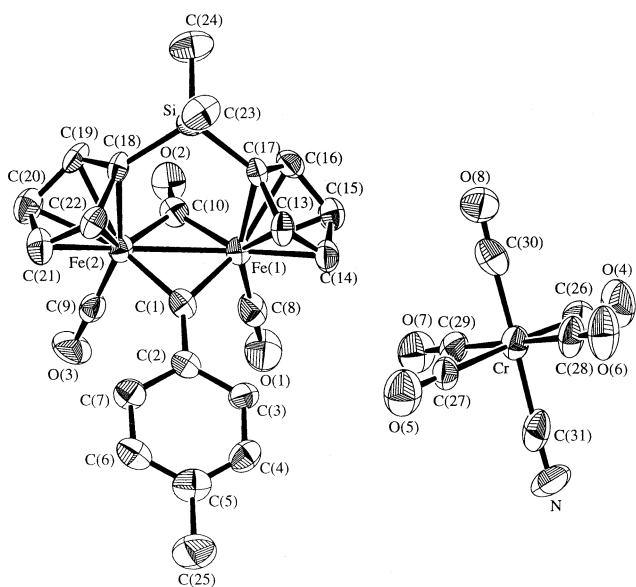
Fig. 2. Molecular structure of **15**, showing the atom-numbering scheme with 45% thermal ellipsoid. CH$_2$Cl$_2$ has been omitted for clarity.
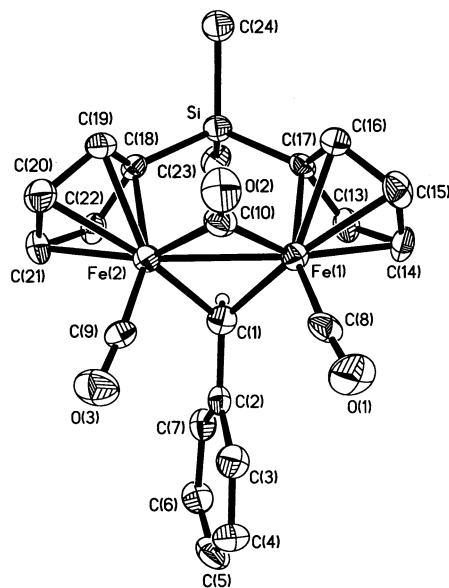
Fig. 4. Molecular structure of **23**, showing the atom-numbering scheme with 40% thermal ellipsoids.

partial charge for the μ-carbyne carbon to stabilize the cationic moiety of **3**. Thus, complexes **15**–**18** can be isolated in high yields.

Complexes **9**–**14** as dimetal bridging carbene complexes were conveniently synthesized by the reaction of the dimethylsilane-bridged diiron cationic carbyne complexes with CN-containing carbonylmetal anions; and these products are related to metal cyanide complexes which have been examined extensively and can be used as synthetic building blocks for syntheses of heterocycles [18]. On the other hand, the carbonylmetal anion as a counterion is quite unusual in the cationic carbyne complexes. Only the $[BF_4]^-$, $[BCl_4]^-$, $[BBr_4]^-$, and $[SbCl_6]^-$ salts are known in transition-metal cationic carbyne complexes [19]. To our knowledge, products **15**–**18** are the first samples of transition-metal cationic carbyne complexes with a carbonylmetal anion as a counterion obtained by the reactions of $[BBr_4]^-$ salt of **3** with the $[M(CO)_nCN]^-$ (M = Cr, Mo, W, n = 5; M = Fe, n = 4) anions.

It is noteworthy that cationic carbyne complexes **15**–**17** are more thermally stable than the parent complexes **1**–**3** and can be stored at below −20 °C for several months, while complexes **1**–**3** only can be stored at lower temperature (below −65 °C) for a short period. Like complexes **1**–**3**, cationic carbyne complexes **15**–**18** should be highly electrophilic and highly reactive toward nucleophiles. Indeed, when complex **15** or **16** was treated with an equimolar quantity of NaSR (R = CH_3, C_6H_5, p-$CH_3C_6H_4$) in THF at −70 to −35 °C for 4–5 h, after work up as described in the Section 2 the known bridging mercaptocarbene complexes $[Fe_2(\mu-CO)\{\mu-C(SR)C_6H_4CH_3-p\}(CO)_2\{(\eta^5-C_5H_4)_2Si(CH_3)_2\}]$ (**19**–**21**) (Eq. (3)) were obtained in > 90% yields, similar to the reaction of parent cationic carbyne complex **3** with NaSR which afforded the same products **19**–**21** in lower yields (64–73%), among which the structure of **20** has been established by X-ray crystallography [8].

(3)

15, M = Cr
or
16, M = Mo

19, R = CH_3
20, R = C_6H_5
21, R = p-$CH_3C_6H_4$
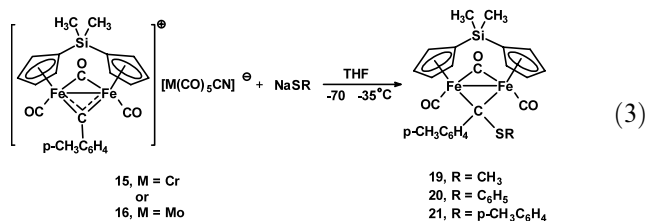
To further compare the reactivity of complexes **15**–**18** with that of parent cationic carbyne complexes **1**–**3**, the reactions of complexes **1**, **3**, and **16** with $NaN(SiMe_3)_2$ was also made. When $Na[N(SiMe_3)_2]$ was used as a nucleophile for the reaction with cationic carbyne complex **1** in THF at −70 to −30 °C for 5 h, no expected bridging carbene complex with a μ-$C(C_6H_5)N(SiMe_3)_2$ ligand bonded to the μ-carbene carbon but a novel transferred product of bridging carbene ligand, $[Fe_2(\mu-CO)_2(CO)NCC_6H_5\{(\eta^5-$

$C_5H_4)_2Si(CH_3)_2\}]$ (**22**), in 48% yield was obtained (Eq. (4)), whose structure has been established by its single crystal X-ray diffraction study.

(4)

22
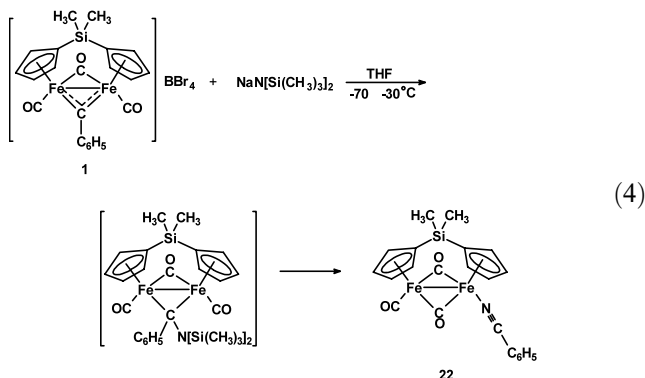
However, complexes **3** and **16** react with $Na[N(SiMe_3)_2]$ under the same conditions to give not similar arylnitrile-coordinated diiron complexes but rather an unidentified decomposition product. The identical reaction patterns of cationic complexes **3** and **16** with mercaptides and $NaN(SiMe_3)_2$ exhibit that both complexes have similar reactivity which is different from that of **1**. Moreover, in contrast to the reaction [7] of analogous cationic carbyne complex $[Fe_2(\mu-CO)(\mu-CC_6H_5)(CO)_2(\eta^5-C_5H_5)_2]BBr_4$ with $Na[N(SiMe_3)_2]$ which afforded a bridging carbene complex $[Fe_2(\mu-CO)\{\mu-C(C_6H_5)N(SiMe_3)_2\}(CO)_2(\eta^5-C_5H_5)_2]$, where the $N(SiMe_3)_2$ moiety is bonded to the μ-carbene carbon, the reaction of cationic carbyne complex **1** with $Na[N(SiMe_3)_2]$ gives benzonitrile-coordinated complex **22**. These reaction results indicate that the different aryl-substituents at the μ-carbyne carbon in the cationic carbyne complexes have a great influence on the reactivity of the cationic bridging carbyne complexes and the resulting products.

The molecular structure of **22** (Fig. 3) confirmed that the $C_6H_5C{\equiv}N$ moiety is bonded to an Fe atom through the N atom. The principal structure of the $[Fe_2(\mu-CO)(CO)\{(\eta^5-C_5H_4)_2Si(CH_3)_2\}]$ fragment of **22** is similar to that of the same unit in **14** and **15**. The Fe–Fe bond length of 2.510(1) Å is the same within experimental error as that found in **14**, but the average Fe–C(Cp) distance of 2.121 Å is slightly longer than those of **14** and **15** (average 2.108–2.117 Å). The Fe(2)–N bond length is 1.894(5) Å, which is somewhat shorter than that in complex $[Fe_2(CO)_6(N{=}CHCH_3)_2]$ (1.942(7) Å) [20], in which the closing of the Fe_2N_2 core with the shorter Fe–N bond distance results in partial double-bond character in the Fe–N bond. The shorter Fe(2)–N distance in **22** suggests that the Fe(2)–N bond is a more strongly coordinating bond and that there exists certain double-bond character in the Fe(2)–N bond. The C(1)–N has a bond length of 1.134(7) Å, which is a normal C≡N distance and significantly shorter than that in similar complexes $[\{(\eta^5-C_5H_5)(CO)_2Mn{=}C(C_6H_5)NC\}_2Mn-$

$(CO)_3CNMn(CO)_2(\eta^5-C_5H_5)]$ (1.154(10) Å) [6a] but is comparable with that of the corresponding C–N bond in $[Fe_2(\mu-CNEt)_3(CNEt)_6]$ (1.13–1.19 Å) [17]. The Fe(2), N, C(1), and C(2) atoms are coplanar with an Fe(2)–N–C(1) angle of 179.2(5)° and a N–C(1)–C(2) angle of 178.3(7)°, which shows that the Fe(2)–N–C(1)–C(2) fragment is nearly linear. Thus, the Fe(2), N, C(1), and C(2) atoms form a conjugate chain; the molecular of **22** is a stable conjugate system. Moreover, the C(1)–C(2) bond length is 1.435(9) Å, intermediate between C–C single and C=C double bond distances, which signify some π-bond character between the C(1) atom and C(2) atom of the benzene ring. In addition, it is interesting that the two bridging CO ligands in **22** are asymmetrically bridged by the two iron atoms C(9)–Fe(1) 1.933(6) Å, C(9)–Fe(2) 1.905(7) Å; C(10)–Fe(1) 1.946(6) Å, C(10)–Fe(2) 1.891(6) Å. The distances of Fe(1)–C(9) and Fe(1)–C(10) are obviously longer than those of Fe(2)–C(9) and Fe(2)–C(10). This might be caused by the stronger electron-withdrawing action of the $C_6H_5C\equiv N$ ligand, which formed a conjugated chain with the Fe(2) atom. Complex **22** appears to be the first example of a species with a ArCN–Fe bond studied by X-ray crystallography.

The formation of product **22** is unexpected and we do not know the chemistry involved. Presumably the reaction pathway to complex **22** could be proceeded via initial attack of the $[N(SiMe_3)_2]^-$ anion on the μ-carbyne carbon of **1** to form an unstable bridging carbene intermediate $[Fe_2(\mu-CO)\{\mu-C(Ar)N(SiMe_3)_2\}(CO)_2\{(\eta^5-C_5H_4)_2Si(CH_3)_2\}]$, which then formally lost two SiMe_3 group with the dissociation of the μ-C–Fe bonds and the coordination of the N atom to the Fe(2) atom and the terminal CO at Fe(2) to Fe(1) to yield product **22**. Such transformation from a bridging phenylcarbene ligand into a benzonitrile ligand to coordinate to a central metal is quite novel. To the best of our knowledge, there is no precedent for such transformation in the reaction of transition-metal carbyne complexes.

Unlike the reaction of **3**, the reactions of cationic carbyne complexes **1** and **2** with $Na[Fe(CO)_4CN]$ under the same conditions give neither bridging aryl(penta-carbo-nylcyanometal)carbene complexes nor cationic bridging carbyne complexes with the $[Fe(CO)_4CN]^-$ anion as a counterion; instead unexpected bridging arylcarbene complexes **23** and **24** (Eq. (5)) were obtained in 51 and 46% yield, respectively.

The products **23** and **24** and bridging *p*-tolylcarbene complex $[Fe_2(\mu-CO)\{\mu-C(H)C_6H_4CH_3-p\}(CO)_2(\eta^5-C_5H_4)_2]$ (**25**) were also obtained in 37–47% yields from the respective reaction (Eq. (6)) of **1**, **2**, and **3** with $[(PPh_3)_2N][Cr(CO)_4NO]$ (**8**), of which the structure of **23** has been established by X-ray diffraction studies.

The formulas of complexes **23**–**25** are also supported by microanalytical and spectroscopic data (Section 2).

Their ^{1}H-NMR spectra had a resonance at 12.22, 12.04 and 12.23 ppm, respectively, characteristic for a μ-C(H)Ar group.

Interestingly, this resonance has undergone a remarkable downfield, similar to that of analogous bridging arylcarbene complexes $[Fe_2(\mu-CO)\{\mu-C(H)Ar\}(CO)_2(\eta^5-C_5H_5)_2]$ (Ar = C_6H_5, δ 12.38; Ar = *p*-$CH_3C_6H_4$, δ 12.40) [21].

$$ (5) $$

$$ (6) $$
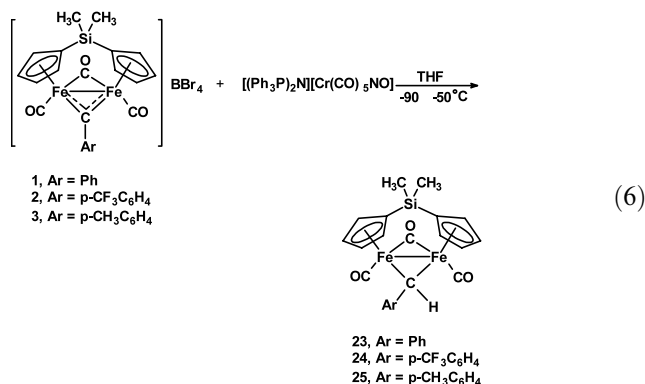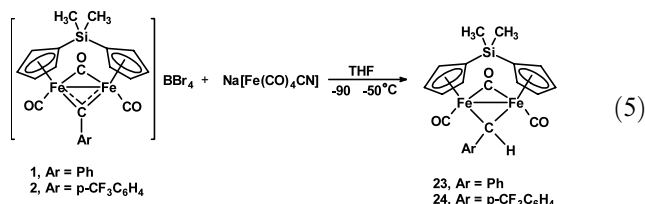
The structures of complexes **23** (Fig. 4) are very similar to that of **14** and $[Fe_2(\mu-CO)\{\mu-C(SCH_3)-C_6H_4CH_3-p\}(CO)_2\{(\eta^5-C_5H_4)_2Si(CH_3)_2\}]$ [8], except that the $W(CO)_5CN$ group in **14** or SCH_3 group in $[Fe_2(\mu-CO)\{\mu-C(SCH_3)C_6H_4CH_3-p\}(CO)_2\{(\eta^5-C_5H_4)_2Si(CH_3)_2\}]$ is replaced by a H atom in **23**. Many structural features of **23** are nearly the same as those of **14** and $[Fe_2(\mu-CO)\{\mu-C(SCH_3)C_6H_4CH_3-p\}(CO)_2\{(\eta^5-C_5H_4)_2Si(CH_3)_2\}]$: the Fe–Fe distance, the two μ-C(1)–Fe distances, and the μ-C(CO)–Fe distances, the angles between the planes of the benzene ring and the two cyclopentadienyl rings. An apparent difference in the structures of **14** or $[Fe_2(\mu-CO)\{\mu-C(SCH_3)C_6H_4-CH_3-p\}(CO)_2\{(\eta^5-C_5H_4)_2Si(CH_3)_2\}]$ and **23** is the shorter C(1)–C(2) bond in **23** (1.453(6) Å), which is intermediate between C–C single and C=C double bond distances, as compared with **14** (1.51(1) Å) (or $[Fe_2(\mu-CO)\{\mu-C(SCH_3)C_6H_4CH_3-p\}(CO)_2\{(\eta^5-C_5H_4)_2Si(CH_3)_2\}]$ 1.52(1) Å).

It is not clear by what pathway complexes **23**–**25** formed in reactions 5 and 6. These reactions possibly could involve the formation of $[MH(CO)_n]^-$ (M = Fe, n = 4; M = Cr, n = 5) species via dissociation of the $[Fe(CO)_4CN]^-$ or $[Cr(CO)_4NO]^-$ anion and protonation of $[M(CO)_n]^{2-}$ (M = Fe, n = 4; M = Cr, n = 5) formed. Hydride transfer from the $[MH(CO)_n]^-$ anion to the μ-carbyne carbon of the cationic bridging carbyne

complex could form the bridging arylcarbene complex. Indeed, the attack of $[MH(CO)_5]^-$ (M = Cr, W) species on unsaturated M≡C moiety has been documented [22]. An indirect evidence is the reaction 6b of $[\eta^5\text{-}C_5H_5(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ with $[NMe_4][FeH(CO)_4]$ to give bridging phenylcarbene complex $[MnFe\{\mu\text{-}C(H)C_6H_5\}(CO)_6(\eta^5\text{-}C_5H_5)]$ which was formed via a carbene intermediate $[\eta^5\text{-}C_5H_5(CO)_2Mn{=}(C_6H_5)FeH(CO)_6]$, then a hydrogen migration from Fe to the carbene carbon occurred to produce the phenylcarbene complex. The origin of the hydrogen could be THF or water, which is a trace contaminant in solvent THF or from glassware. Analogous H-abstracting reactions from THF solvent to form the arylcarbene complexes have been observed in the reactions of $[\eta^5\text{-}C_5H_5(CO)_2Re{\equiv}CC_6H_5]BBr_4$ with $Na_2[Fe(CO)_4]$ and $Na_2[W(CO)_5]$, which afforded $[ReFe\{\mu\text{-}C(H)C_6H_5\}(CO)_6(\eta^5\text{-}C_5H_5)]$ [5a] and $[WRe\{\mu\text{-}C(H)C_6H_5\}(CO)_7(\eta^5\text{-}C_5H_5)]$ [6c], respectively.

The title reaction shows the novel reactions between the dimethylsilane-bridged cationic carbyne complexes of diiron and carbonylmetal anions. The reactions of the carbonylmetal anions containing a CN group with diiron cationic carbyne complexes give diiron bridging aryl(pentacarbonylcyanometal)carbene complexes or cationic bridging carbyne complexes with a carbonylmetal anion as counterion or bridging arylcarbene complexes depending on the different aryl-substituents at the μ-carbyne carbon, while the reactions of carbonylmetal anion containing a NO group with the cationic carbyne complexes give only bridging arylcarbene complexes. These results indicate that different aryl-substituents at the μ-carbyne carbon in the cationic carbyne complexes and different carbonylmetal anions exhibit great influence on the reactivity of the cationic bridging carbyne complexes and the resulting products. The title reaction may represent a convenient and useful method for preparation and structural modification of dimetal bridging carbene and cationic bridging carbyne complexes.

4. Supplementary material

Tables of atomic coordinates, thermal parameters, H atom coordinates, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **14**, **15**, **22**, and **23** are available. Crystallographiic data for the structural analysis in this paper have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 178395, 178396, 178397 and 178398 respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] F.G.A. Stone, in: U. Schubert (Ed.), Advances in Metal Carbene Chemistry, Kluwer Academic Publishers, Dordrecht, The Netherlands, 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, Y. Yu, K. Liu, G. Wu, P.-J. Zheng, Organometallics 12 (1993) 1213;
(b) Y. Yu, J.-B. Chen, J. Chen, P.-J. Zheng, J. Chem. Soc. Dalton Trans. (1996) 1443.

[6] (a) Y.-J. Tang, J. Sun, J.-B. Chen, Organometallics 18 (1999) 4337;
(b) Y.-J. Tang, J. Sun, J.-B. Chen, J. Chem. Soc. Dalton Trans. (1998) 931;
(c) Y.-J. Tang, J. Sun, J.-B. Chen, J. Chem. Soc. Dalton Trans. (1998) 4003;
(d) Y.-J. Tang, J. Sun, J.-B. Chen, Organometallics 17 (1998) 2945;
(e) Y.-J. Tang, J. Sun, J.-B. Chen, Organometallics 19 (2000) 72;
(f) Y.-J. Tang, J. Sun, J.-B. Chen, Organometallics 18 (1999) 2459.

[7] Y.-J. Liu, R.-T. Wang, J. Sun, J.-B. Chen, Organometallics 19 (2000) 3784.

[8] R.-T. Wang, Q. Xu, J. Sun, L.-C. Song, J.-B. Chen, Organometallics 20 (2001) 4092.

[9] R.B. King, Inorg. Chem. 6 (1967) 25.

[10] U. Wannaga, H. Seyffert, Angew. Chem. 77 (1965) 457.

[11] D.R. Mantell, W.L. Gladfelter, J. Organomet. Chem. 347 (1988) 333.

[12] R.-T. Wang, J. Sun, J.-B. Chen, J. Organomet. Chem. 617–618 (2001) 292.

[13] K.W. Chiu, R.A. Jones, G. Wilkinson, J. Chem. Soc. Dalton Trans. (1981) 2088.

[14] J.-B. Chen, G.-X. Lei, Z.-S. Jin, L.-H. Hu, G.-C. Wei, Organometallics 7 (1988) 1652.

[15] J.-B. Chen, Y. Yu, L.-H. Hu, Z.-S. Jin, J. Organomet. Chem. 447 (1993) 113.

[16] (a) M.E. Garcia, J.C. Jeffery, P. Sherwood, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1987) 1209;
(b) D.G. Evans, J.A.K. Howard, J.C. Jeffery, G.E. Lewis, M.J. Grosse-Ophoff, M.J. Parrott, F.G.A. Stone,. J. Chem. Soc. Dalton Trans. (1986) 1723.

[17] S.A. Goldfield, K.N. Raymond, Inorg. Chem. 13 (1974) 770.

[18] W.P. Fehlhammer, M. Fritz, Chem. Rev. 93 (1993) 1243.

[19] (a) H. Fischer, P. Hofmann, F.R. Kreissl, R.R. Schrock, U. Schubert, K. Weiss, Carbyne Complexes, VCH Publishers, New York, 1988, p. 117;
(b) E.O. Fischer, R.L. Clough, P. Stueckler, J. Organomet. Chem. 120 (1976) C6;
(c) E.O. Fischer, R.L. Clough, G. Besl, F.R. Kreissl, Angew. Chem. 17 (1976) 584.

[20] G. Gervasio, P.L. Stanghellini, R. Rossetti, Acta Crystallogr. Sect. B 37 (1981) 1198.
[21] Y.-J. Liu, R.-T. Wang, J. Sun, J.-B. Chen, Organometallics 19 (2000) 3498.
[22] D. Hodgson, J.A.K. Howard, F.G.A. Stone, M.J. Went, J. Chem. Soc. Dalton Trans. (1985) 1331.