Unusual Reactions of Cationic Bridging Carbyne Complexes of Bis(η^5-cyclopentadienyl)diiron Tricarbonyl with Carbonylmetal Anions. A Route to Diiron Bridging Carbyne Complexes

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The reactions of cationic carbyne complexes of diiron, [$Fe_2(\mu$-CO)(μ-CPh)$(CO)_2(\eta^5$-$C_5H_5)_2$]-BBr_4 (**1**), with the anionic carbonylmetal compounds Na[$M(CO)_5CN$] (**3**, M = Cr; **4**, M = Mo; **5**, M = W) in THF at low temperature afford the novel bridging carbyne complexes [$Fe_2(\mu$-CO)(μ-CPh)$(CO)_2(\eta^5$-$C_5H_5)_2NCM(CO)_5$] (**6**, M = Cr; **7**, M = Mo; **8**, M = W). In contrast to the reaction of **1**, the cationic carbyne complex [$Fe_2(\mu$-CO)(μ-CC_6H_4Me-*p*)$(CO)_2(\eta^5$-$C_5H_5)_2$]BBr_4 (**2**) reacts with carbonylmetal anions **3**−**5** under the same conditions to produce the novel bridging *p*-tolyl(pentacarbonylcyanotungsten)carbene complexes [$Fe_2(\mu$-CO){μ-C(C_6H_4Me-*p*)$(CO)_2(\eta^5$-$C_5H_5)_2NCM(CO)_5$}] (**9**, M = Cr; **10**, M = Mo; **11**, M = W). However, the analogous reaction of Na[$Fe(CO)_4CN$] with **1** yields the diiron bridging phenylcarbene complex [Fe_2-(μ-CO){μ-C(H)Ph}$(CO)_2(\eta^5$-$C_5H_5)_2$] (**12**). The structures of **7**, **8**, and **11** have been established by X-ray crystallography.

Introduction

Metal−metal-bonded cluster complexes are well-known to have important roles in many catalytic reactions.[1,2] The current interest in the synthesis, structure, and chemistry of transition-metal bridging carbene and carbyne complexes stems from the fact that many such complexes are themselves metal clusters or are the precursors of metal cluster complexes. In recent years, we have been interested in developing the methodologies of the synthesis of transition-metal bridging carbene and carbyne complexes. A considerable number of dimetal complexes containing bridging carbene and carbyne ligands have been synthesized by Stone and coworkers by reactions[3−6] of carbene or carbyne complexes with low-valent metal species or by reactions[5,6] of neutral or anionic carbyne complexes with metal hydrides or cationic metal compounds. Recently, we have shown a convenient and useful method for the preparation of the bridging carbene and carbyne complexes: the reactions of highly electrophilic cationic carbyne complexes of manganese and rhenium, [(η^5-$C_5H_5)(CO)_2$-M≡CPh]BBr_4 (M = Mn, Re), with dianionic carbonylmetal compounds such as $Na_2[Fe(CO)_4]$, $(Et_4N)_2[Fe_2$-$(CO)_8]$, and $Na_2[W(CO)_5]$, monoanionic carbonylmetal compounds such as $(Me_4N)[HFe(CO)_4]$, Na[(η^5-C_5H_5)M-$(CO)_x$] (M = Mo, W, x = 3; M = Fe, x = 2), and Na[Co-$(CO)_3PPh_3$], or anionic mixed-dimetal carbonyl compounds such as $(Ph_3P)_2N[MCo(CO)_n]$ (M = Fe, W; n = 8, 9).[7,8] However, the reaction of carbonylmetal anionic compounds containing a CN group such as Na[Fe-$(CO)_4CN$] and Na[$W(CO)_5CN$] with cationic carbyne complexes [(η^5-$C_5H_5)(CO)_2$M≡CPh]BBr_4 (M = Mn, Re) did not give dimetal bridging carbene or bridging carbyne complexes but produced instead phenyl(carbonylcyanometal)carbene complexes, [(η^5-$C_5H_5)(CO)_2$-M=C(Ph)NCM′$(CO)_n$] (M = Mn, Re; M′ = Fe, W; n = 4, 5) (eq 1).[8a,f]

Most recently, we found a new method for the preparation of dimetal bridging carbene complexes: the reactions of diiron cationic carbyne complexes, [$Fe_2(\mu$-CO)(μ-CAr)$(CO)_2(\eta^5$-$C_5H_5)_2$]BBr_4 (**1**, Ar = Ph; **2**, Ar = *p*-MeC_6H_4), with anionic carbonylmetal nucleophiles. For instance, the cationic carbyne complexes **1** and **2**

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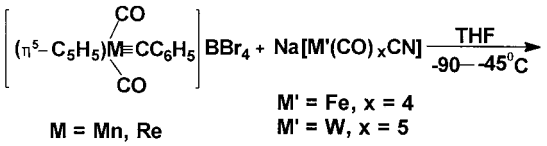
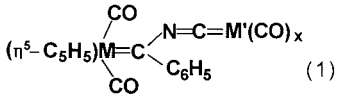
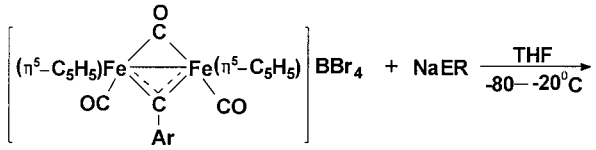
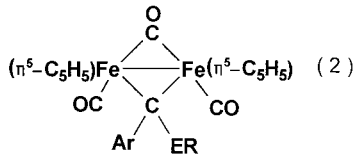




(1)

reacted with nucleophiles NaER (ER = SMe, SEt, SPh, SC_6H_4Me-*p*, $SC_6H_4NO_2$-*p*, OPh, $N(SiMe_3)_2$) to give the series of diiron bridging carbene complexes $[Fe_2(\mu\text{-CO})\{\mu\text{-C(ER)Ar}\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (eq 2).[9] This offers a new





(2)

and useful method for the preparation and structural modification of dimetal bridging carbene complexes.

To explore the reactivity of the cationic carbyne complexes of diiron and to further examine the scope of this preparation of dimetal bridging carbene and bridging carbyne complexes, we have studied the reactions of the cationic diiron bridging carbyne complexes **1** and **2** with anionic carbonylmetal compounds of the type $Na[M(CO)_5CN]$ (M = Cr, Mo, W). These reactions produced a series of novel trimetal bridging carbene and bridging carbyne complexes. Herein we report these unusual reactions and the structural characterizations of the resulting products.

Experimental Section

All procedures were performed under a dry, oxygen-free N_2 atmosphere using standard Schlenk techniques. All solvents employed were reagent grade and were dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under a N_2 atmosphere. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl, while petroleum ether (30−60 °C) and CH_2Cl_2 were distilled from CaH_2. The neutral alumina (Al_2O_3) 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. The complexes $[Fe_2(\mu\text{-CO})(\mu\text{-CPh})(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (**1**)[9] and $[Fe_2(\mu\text{-CO})(\mu\text{-}CC_6H_4Me\text{-}p)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (**2**)[9] were prepared as previously described. The compounds $Na[Cr(CO)_5CN]$ (**3**),[10] $Na[Mo(CO)_5CN]$ (**4**),[10] $Na[W(CO)_5CN]$ (**5**),[10] and $Na[Fe(CO)_4CN]$[11] were prepared by literature methods.

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

Reaction of $[Fe_2(\mu\text{-CO})(\mu\text{-CPh})(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (1) with $Na[Cr(CO)_5CN]$ (3) To Give $[Fe_2(\mu\text{-CO})(\mu\text{-CPh})(CO)_2(\eta^5\text{-}C_5H_5)_2NCCr(CO)_5]$ (6). To 0.270 g (0.362 mmol) of freshly prepared (in situ) **1** dissolved in 50 mL of THF at −90 °C was added 0.100 g (0.415 mmol) of $Na[Cr(CO)_5CN]$ (**3**). The reaction mixture was warmed slowly to −75 °C within 1 h, during which time the turbid red solution gradually turned brown-red. After it was stirred at −75 to −30 °C for an additional 3 h, the resulting solution was evaporated in vacuo at −30 °C to dryness, and the deep red residue was chromatographed on Al_2O_3 at −25 °C with petroleum ether/CH_2Cl_2 (10:1) as the eluant. After elution of a small light yellow band which contained $Cr(CO)_6$, a red band was collected. The solvent was removed under vacuum, and the residue was recrystallized from petroleum ether/CH_2Cl_2 (10:1) at −80 °C to give 0.140 g (64%, based on **1**) of purple-red crystals of **6**: mp 82−84 °C dec; IR (CH_2Cl_2) ν(CO) 2056 (s), 2016 (w),1987 (s), 1933 (vs),-1772 (m) cm^{-1}; ν(CN) 2059 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 8.36 (m, 2 H, C_6H_5), 7.74 (m, 2 H, C_6H_5), 7.36 (m, 1 H, C_6H_5), 5.84 (d, 2 H, C_5H_5), 5.62 (s, 1 H, C_5H_5), 5.48 (s, 1 H, C_5H_5), 5.34 (t, 3 H, C_5H_5), 4.90 (t, 3 H, C_5H_5); MS *m/e* 359 (M^+ − CO − $Cr(CO)_5CN$), 254 $[Fe_2(\eta^5\text{-}C_5H_5)_2C^+]$, 238 $[Fe(CO)(\eta^5\text{-}C_5H_5)\text{-}CPh^+]$, 218 $[Cr(CO)_5CN^+]$, 192 $[Cr(CO)_5^+]$. Anal. Calcd for $C_{25}H_{15}O_7NCrFe_2$: C, 49.62; H, 2.50; N, 2.31. Found: C, 49.40; H, 2.56; N, 2.60.

Reaction of 1 with $Na[Mo(CO)_5CN]$ (4) To Give $[Fe_2(\mu\text{-CO})(\mu\text{-CPh})(CO)_2(\eta^5\text{-}C_5H_5)_2NCMo(CO)_5]$ (7). Similar to the case for the reaction of **1** with **3**, compound **1** (0.270 g, 0.362 mmol) was treated with 0.124 g (0.430 mmol) of $Na[Mo(CO)_5CN]$ (**4**) at −90 to −30 °C for 4−5 h. Further treatment of the resulting mixture as described above for the preparation of **6** yielded 0.176 g (75%, based on **1**) of purple-red crystalline **7**: mp 96−97 °C dec; IR (CH_2Cl_2) ν(CO) 2053 (m), 2013 (w), 1998 (s), 1937 (vs), 1795 (s) cm^{-1}, ν(CN) 2060 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 8.34−7.26 (m, 5 H, C_6H_5), 5.85 (t, 3 H, C_5H_5), 5.63 (s, 1 H, C_5H_5), 5.50 (s, 1 H, C_5H_5), 5.24 (d, 2 H, C_5H_5), 5.22 (s, 1 H, C_5H_5), 5.14 (s, 1 H, C_5H_5), 5.07 (s, 1 H, C_5H_5), 4.91 (s, 1 H, C_5H_5); MS *m/e* 359 (M^+ − CO − $Mo(CO)_5\text{-}CN$), 254 $[Fe_2(\eta^5\text{-}C_5H_5)_2C^+]$, 238 $[Fe(CO)(\eta^5\text{-}C_5H_5)CPh^+]$, 262 $[Mo(CO)_5CN^+]$, 236 $[Mo(CO)_5^+]$. Anal. Calcd for $C_{25}H_{15}O_7\text{-}NMoFe_2$: C, 46.27; H, 2.33; N, 2.16. Found: C, 46.22; H, 2.55; N, 2.56.

Reaction of 1 with $Na[W(CO)_5CN]$ (5) To Give $[Fe_2(\mu\text{-CO})(\mu\text{-CPh})(CO)_2(\eta^5\text{-}C_5H_5)_2NCW(CO)_5]$ (8). The procedure used in the reaction of **1** (0.270 g, 0.362 mmol) with $Na[W(CO)_5CN]$ (**5**) (0.162 g, 0.430 mmol) was the same as that described for the reaction of **1** with **3** at −90 to −30 °C for 4−5 h. Further treatment as described for the preparation of **6** gave 0.213 g (80%, based on **1**) of blackish red crystals of **8**: mp 90−92 °C dec; IR (CH_2Cl_2) ν(CO) 2045 (s), 2022 (m), 1998 (s), 1926 (vs), 1771 (s) cm^{-1}; ν(CN) 2051 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 8.47 (m, 2 H, C_6H_5), 7.73 (m, 2 H, C_6H_5), 7.34 (m, 1 H, C_6H_5), 5.90 (d, 2 H, C_5H_5), 5.78 (d, 2 H, C_5H_5), 5.49 (s, 1 H, C_5H_5), 5.34 (s, 1 H, C_5H_5), 5.30 (m, 2 H, CH_2Cl_2), 5.24 (s, 1 H, C_5H_5), 5.14 (s, 1 H, C_5H_5), 5.05 (s, 1 H, C_5H_5), 4.90 (s, 1 H, C_5H_5); MS *m/e* 359 [M^+ − CO − $W(CO)_5CN$], 254 $[Fe_2(\eta^5\text{-}$

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$C_5H_5)_2C^+$], 238 [Fe(CO)(η^5-C_5H_5)CPh$^+$], 350 [W(CO)$_5$CN$^+$], 84 ($CH_2Cl_2^+$). Anal. Calcd for $C_{25}H_{15}O_7NWFe_2 \cdot CH_2Cl_2$: C, 38.00; H, 2.09; N, 1.70. Found: C, 38.61; H, 2.44; N, 2.01.

Reaction of [Fe$_2$(μ-CO)(μ-CC$_6$H$_4$Me-*p*)(CO)$_2$(η^5-C$_5$H$_5$)$_2$]-BBr$_4$ (2) with 3 To Give [Fe$_2$(μ-CO){μ-CC$_6$H$_4$Me-*p*)NCCr(CO)$_5$}(CO)$_2$(η^5-C$_5$H$_5$)$_2$] (9). To 0.240 g (0.316 mmol) of freshly prepared (in situ) **2** dissolved in 50 mL of THF at −90 °C was added 0.081 g (0.336 mmol) of **3**. The reaction mixture was slowly warmed to −65 °C within 1 h, during which time the turbid red solution gradually turned brown-red. After it was stirred at −65 to −30 °C for an additional 3 h, the resulting clear deep red solution was evaporated in vacuo at −30 °C to dryness, and the brown-red residue was chromatographed on Al_2O_3 at −25 °C with petroleum ether/CH_2Cl_2 (15:1) 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 (10:1) solution at −80 °C to give 0.116 g (57%, based on **2**) of purple-red crystals of **9**: mp 157−158 °C dec; IR (CH_2Cl_2) ν(CO) 2057 (m), 2015 (s), 1993 (s), 1933 (vs), 1927 (s), 1772 (w) cm^{-1}, ν(CN) 2127 (w) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 8.29−7.36 (m, 4 H, $C_6H_4CH_3$), 5.80 (s, 10 H, C_5H_5), 2.54 (s, 3 H, $C_6H_4CH_3$); MS *m*/*e* 373 (M$^+$ − CO − Cr(CO)$_5$CN), 254 [Fe$_2$(η^5-$C_5H_5)_2C^+$], 252 [Fe(CO)(η^5-C_5H_5)(C_6H_4Me-*p*)$^+$], 218 [Cr(CO)$_5$CN$^+$], 192 [Cr(CO)$_5^+$]. Anal. Calcd for $C_{27}H_{17}O_8NCrFe_2$: C, 50.11; H, 2.65; N, 2.16. Found: C, 50.18; H, 2.58; N, 2.24.

Reaction of 2 with 4 To Give [Fe$_2$(μ-CO){μ-CC$_6$H$_4$Me-*p*)NCMo(CO)$_5$}(CO)$_2$(η^5-C$_5$H$_5$)$_2$] (10). Similar to the reaction of **2** with **3**, 0.230 g (0.302 mmol) of **2** reacted with 0.091 g (0.320 mmol) of **4** at −90 to −30 °C for 4−5 h. Further treatment of the resulting mixture as described for the preparation of **9** yielded 0.150 g (70%, based on **2**) of **10** as purple-red crystals: mp 65−66 °C dec; IR (CH_2Cl_2) ν(CO) 2054 (s), 2015 (s), 1998 (s), 1935 (vs, br), 1792 (w) cm^{-1}, ν(CN) 2125 (w) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 8.30−7.36 (m, 4 H, C_6H_4-CH_3), 5.81 (s, 10 H, C_5H_5), 3.29 (s, 2 H, H_2O), 2.54 (s, 3 H, $C_6H_4CH_3$); MS *m*/*e* 373 (M$^+$ − CO − Mo(CO)$_5$CN), 254 [Fe$_2$-(η^5-$C_5H_5)_2C^+$], 252 [Fe(CO)(η^5-C_5H_5)(C_6H_4Me-*p*)$^+$], 262 [Mo-(CO)$_5$CN$^+$]. Anal. Calcd for $C_{27}H_{17}O_8NMoFe_2 \cdot H_2O$: C, 45.73; H, 2.70; N, 1.97. Found: C, 45.45; H, 2.52; N, 2.07.

Reaction of 2 with 5 To Give [Fe$_2$(μ-CO){μ-CC$_6$H$_4$Me-*p*)NCW(CO)$_5$}(CO)$_2$(η^5-C$_5$H$_5$)$_2$] (11). As described for the reaction of **2** with **3**, compound **2** (0.240 g, 0.316 mmol) was treated with **5** (0.125 g, 0.335 mmol) at −90 to −30 °C for 4−5 h. Further treatment of the resulting mixture similar to that used in the reaction of **2** with **3** gave 0.191 g (76%, based on **2**) of purple-red crystalline **11**: mp 64−65 °C dec; IR (CH_2Cl_2) ν(CO) 2051 (m), 2015 (s), 1995 (s), 1933 (vs), 1926 (vs), 1791 (w) cm^{-1}, ν(CN) 2125 (w) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 8.37−7.37 (m, 4 H, $C_6H_4CH_3$), 5.81 (s, 10 H, C_5H_5), 3.32 (s, 2 H, H_2O), 2.59 (s, 3 H, $C_6H_4CH_3$); MS *m*/*e* 373 (M$^+$ − CO − W(CO)$_5$CN), 254 [Fe$_2$(η^5-$C_5H_5)_2C^+$], 252 [Fe(CO)(η^5-C_5H_5)(C_6H_4Me-*p*)$^+$], 350 [W(CO)$_5$CN$^+$]. Anal. Calcd for $C_{27}H_{17}O_8NWFe_2 \cdot H_2O$: C, 40.69; H, 2.40; N, 1.76. Found: C, 40.45; H, 2.31; N, 1.75.

Reaction of 1 with Na[Fe(CO)$_5$CN] To Give [Fe$_2$(μ-CO){μ-C(H)Ph}(CO)$_2$(η^5-C$_5$H$_5$)$_2$] (12). Freshly prepared compound **1** (0.260 g, 0.348 mmol) was treated, in a manner similar to that for the reaction of **1** with **3**, with Na[Fe(CO)$_5$CN] (0.089 g, 0.410 mmol) at −90 to −30 °C for 4 h, during which time the turbid red solution gradually turned clear brown-red. After removal of the solvent at −40 °C in vacuo, the dark red residue was chromatographed on Al_2O_3 at −25 °C with petroleum ether/CH_2Cl_2 (15:1) as the eluant. A purple-red band was eluted and collected. The solvent was removed, and the residue was recrystallized from petroleum ether/CH_2Cl_2 (15:1) solution at −80 °C to give 0.078 g (54%, based on **1**) of **12**[9] as purple-red crystals: mp 78−79 °C dec; IR (CH_2Cl_2) ν(CO) 1973 (vs), 1934 (m), 1773 (s) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 12.39 (s, 1 H, μ-CH), 7.56 (m, 2 H, C_6H_5), 7.36 (m, 1 H, C_6H_5), 7.21−7.06 (m, 2 H, C_6H_5), 4.95 (s, 10 H, C_5H_5); MS *m*/*e* 388 (M$^+$ − CO), 360 (M$^+$ − 2CO), 332 (M$^+$ − 3CO), 254 (M$^+$ − 3CO − Ph − H). Anal. Calcd for $C_{20}H_{16}O_3Fe_2$: C, 57.74; H, 3.88. Found: C, 57.57; H, 3.73.

X-ray Crystal Structure Determinations of Complexes 7, 8, and 11. The single crystals of **7**, **8**, and **11** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH_2Cl_2 solution at −80 °C. Single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data for 3557, 3343, and 3281 independent reflections, of which 2071 and 2276 with $I > 2.00\sigma(I)$ for **7** and **11** and 2554 with $I > 3.00\sigma(I)$ for **8** were observable, were collected with a Rigaku AFC7R diffractometer at 20 °C using Mo Kα radiation with an $\omega-2\theta$ scan mode within the ranges $5° \le 2\theta \le 50°$ for **7** and $5° \le 2\theta \le 45°$ for **8** and **11**, respectively.

The structures of **7** and **11** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was respectively based on 2071 and 2276 observed reflections and 325 and 361 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.049$ and $R_w = 0.050$ for **7** and $R = 0.056$ and $R_w = 0.071$ for **11**, respectively. The structure of **8** was solved by heavy-atom Patterson methods and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. The hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2554 observed reflections and 337 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.056$ and $R_w = 0.067$. All of the calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp.

The details of the crystallographic data and the procedures used for data collection and reduction information for **7**, **8**, and **11** are given in Table 1. Selected bond lengths and angles are listed in Table 2. The atomic coordinates and B_{iso}/B_{eq} values, anisotropic displacement parameters, all bond lengths and angles, and least-squares planes for **7**, **8**, and **11** are given in the Supporting Information. The molecular structures of **7**, **8**, and **11** are given in Figures 1−3, respectively.

Results and Discussion

In principle, the highly electrophilic cationic carbyne complexes of diiron [Fe$_2$(μ-CO)(μ-CAr)(CO)$_2$(η^5-C$_5$H$_5$)$_2$]$^+$ should be highly reactive toward nucleophiles, which is indeed the case. The freshly prepared (in situ) complex [Fe$_2$(μ-CO)(μ-CPh)(CO)$_2$(η^5-C$_5$H$_5$)$_2$] (**1**) was treated with about 10−15% molar excess of the anionic carbonylmetal compounds Na[M(CO)$_5$CN] (**3**, M = Cr; **4**, M = Mo; **5**, M = W) in THF at low temperature (−90 to −30 °C) for 4−5 h. After workup as described in the Experimental Section, novel bridging carbyne complexes [Fe$_2$(μ-CO)(μ-CPh)(CO)$_2$(η^5-C$_5$H$_5$)$_2$NCM(CO)$_5$] (**6**−**8**) (eq 3) were obtained in 64−80% yields.

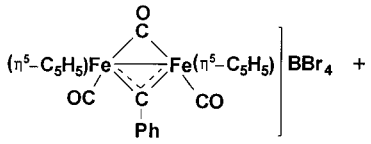
On the basis of elemental analyses and spectroscopic evidence, as well as X-ray crystallography, products **6**−**8** are formulated as novel diiron bridging carbyne complexes with an M(CO)$_5$CN (M = Cr, Mo, W) moiety bonded to an Fe atom through the N atom of the CN group.

Complexes **6**−**8** are readily soluble in polar organic solvents but only slightly soluble in nonpolar solvents. They are sensitive to air and temperature in solution but relatively stable in the solid state. The IR and ^{1}H NMR spectra of complexes **6**−**8** are consistent with the structures shown in eq 3. The IR spectra of complexes

Table 1. Crystal Data and Experimental Details for Complexes 7, 8, and 11

	7	**8**·CH_2Cl_2	**11**·H_2O
formula	$C_{25}H_{15}O_7NFe_2Mo$	$C_{26}H_{17}O_7NCl_2Fe_2W$	$C_{27}H_{19}O_9NFe_2W$
fw	649.03	821.87	796.99
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a (Å)	11.754(2)	11.045(3)	32.840(9)
b (Å)	11.988(3)	13.839(4)	10.907(2)
c (Å)	9.399(2)	10.351(4)	22.494(6)
α (deg)	98.13(2)	111.42(2)	
β (deg)	107.39(2)	104.13(1)	125.82(2)
γ (deg)	80.20(2)	93.14(3)	
V (Å^3)	1239.7(5)	1410.1(8)	6532(2)
Z	2	2	8
D_{calcd} (g/cm^3)	1.739	1.936	1.621
F(000)	644.00	792.00	3088.00
μ(Mo Kα) (cm^{-1})	16.96	53.21	44.38
radiation (monochromated in incident beam)	MoKα (λ = 0.71069 Å)	MoKα (λ = 0.71069 Å)	MoKα (λ = 0.71069 Å)
diffractometer	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R
temp (°C)	20	20	20
orientation rflns: no.; range (2θ) (deg)	16; 13.3−24.5	20; 14.0−21.6	15; 12.5−21.4
scan method	ω−2θ	ω−2θ	ω−2θ
data collecn range, 2θ (deg)	5−50	5−45	5−45
unique data: total, no. with $I > 2.00\sigma(I)$	3557, 2071	3343, 2554 ($I > 3.00\sigma(I)$)	3281, 2276
no. of params refined	325	337	361
cor factors: max−min	0.8673−1.0000	0.6668−1.0934	0.8477−1.0000
R^a	0.049	0.056	0.056
$R_w{}^b$	0.050	0.067	0.071
quality-of-fit indicator^c	1.28	2.44	2.26
max shift/esd final cycle	0.00	0.00	0.02
largest peak, (e/Å^3)	0.58	2.13	1.64
min peak (e/Å^3)	−0.47	−1.02	−0.79

^{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 = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.



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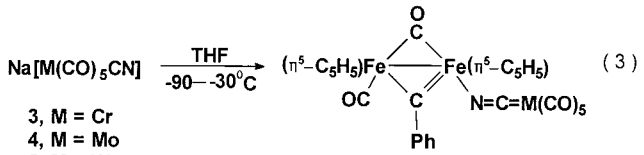

(3)

3, M = Cr
4, M = Mo
5, M = W

6, M = Cr
7, M = Mo
8, M = W

6−**8** in the ν(CO) region showed an absorption band at 1771−1795 cm^{-1} attributed to the bridging CO ligand, in addition to four terminal CO absorption bands at 2056−1926 cm^{-1}, which signified an $Fe_2(\mu\text{-}CO)_2(CO)_6$ and an $M(CO)_5$ (M = Cr, Mo, W) moiety in these complexes. It is interesting to note that the ^{1}H NMR spectra of **6**−**8** showed a multiplet resonance attributed to the cyclopentadienyl protons at about 5.90−4.90 ppm, instead of the normal singlet signal. The explanation for this might be that the C_{5v} symmetry of the Cp ring is destroyed when there exist different substituents on the Cp rings or that the cyclopentadienyl-coordinated metals are bonded to different ligands, which could lead to partial localization of electrons on the Cp ring.[12] In **6**−**8**, the C_{5v} symmetry of the Cp rings was destroyed by bonding of the $M(CO)_5CN$ ligand to the Fe(1) atom. This increased π-localization of electrons on the two Cp

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Table 2. Selected Bond Lengths (Å)^a and Angles (deg)^a for Complexes 7, 8, and 11

	7 (M = Mo)	**8** (M = W)	**11** (M = W)
Fe(1)−Fe(2)	2.501(2)	2.495(3)	2.507(4)
Fe(1)−C(1)	1.755(10)	1.81(8)	1.98(2)
Fe(2)−C(1)	1.854(9)	1.84(2)	1.99(2)
Fe(1)−C(10)	1.94(1)	1.95(2)	1.89(2)
Fe(2)−C(10)	1.95(1)	1.99(2)	1.89(2)
C(1)−C(2)	1.46(1)	1.44(2)	1.53(2)
Fe(1)−N	1.941(9)	1.95(1)	
C(1)−N			1.47(2)
N−C(23)	1.15(1)	1.11(2)	1.15(2)
M−C(23)	2.18(1)	2.20(2)	2.13(2)
C(10)−O(2)	1.16(1)	1.17(2)	1.20(2)
Fe(1)−C(Cp) (av)	2.12	2.10	2.12
Fe(2)−C(Cp) (av)	2.10	2.09	2.12
Fe(1)−C(1)−Fe(2)	87.7(4)	86.4(7)	78.3(7)
C(1)−Fe(1)−Fe(2)	47.8(3)	47.3(5)	50.9(5)
C(1)−Fe(2)−Fe(1)	44.5(3)	46.4(5)	50.8(6)
C(1)−Fe(1)−C(10)	98.0(4)	97.2(8)	97.6(8)
C(1)−Fe(2)−C(10)	94.2(4)	94.9(8)	97.7(8)
Fe(1)−C(10)−Fe(2)	80.1(4)	78.6(10)	83.0(9)
C(10)−Fe(1)−Fe(2)	50.2(3)	51.5(6)	48.4(7)
C(10)−Fe(2)−Fe(1)	49.7(3)	49.9(6)	48.6(6)
Fe(1)−C(10)−O(2)	140.7(9)	142(1)	138(1)
Fe(2)−C(10)−O(2)	139.1(9)	139(1)	138(1)
Fe(1)−N−C(23)	175.3(9)	167(1)	
Fe(1)−C(1)−N			114(1)
Fe(2)−C(1)−N			111(1)
C(1)−N−C(23)			178(1)
M−C(23)−N	177.5(9)	169(1)	176(1)
Fe(2)−Fe(1)−N	95.3(2)	99.6(4)	
C(1)−Fe(1)−N	95.7(4)	89.8(6)	
C(10)−Fe(1)−N	92.9(4)	89.9(6)	
C(10)−Fe(1)−C(1)	98.0(4)	97.2(8)	97.6(8)
C(10)−Fe(2)−C(1)	94.2(4)	94.9(8)	97.7(8)
Fe(1)−C(1)−C(2)	138.8(7)	134(1)	123(1)
Fe(2)−C(1)−C(2)	133.4(7)	138(1)	124(1)
C(2)−C(1)−N			103(1)

^{a} Estimated standard deviations in the least significant figure are given in parentheses.

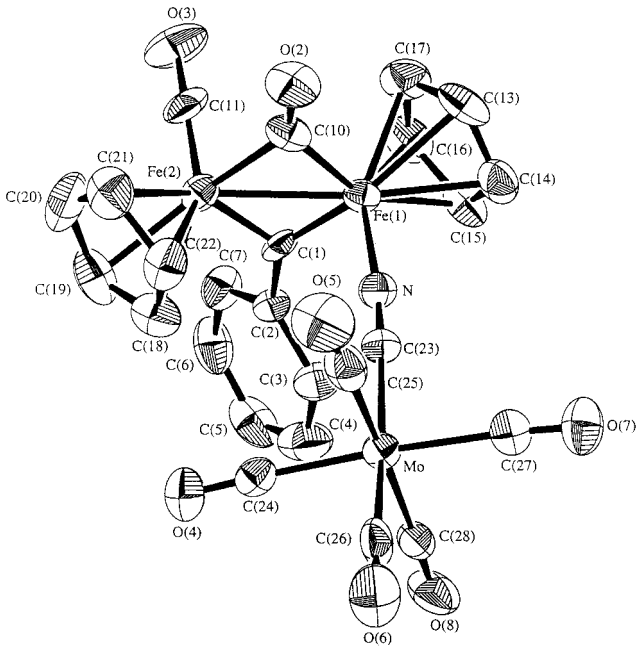

Figure 1. Molecular structure of **7**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 40% probability.

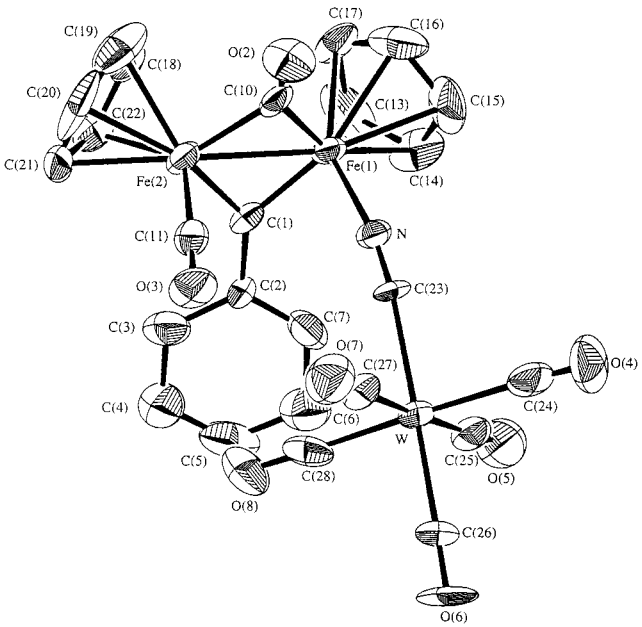

Figure 2. Molecular structure of **8**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 40% probability. CH_2Cl_2 has been omitted for clarity.

rings coordinated respectively to the Fe(1) and Fe(2) atoms. This would change the chemical environment of the cyclopentadienyl protons, resulting in the splitting of the singlet signal into a multiplet of cyclopentadienyl protons.

The structures of complexes **7** and **8** have been further confirmed by X-ray diffraction studies. The results of the X-ray diffraction work for both complexes are summarized in Table 1, and the structures are shown in Figures 1 and 2, respectively. Both structures are nearly identical, as illustrated by the following parameters. The distances of the Fe−Fe bond bridged by the μ-CPh ligand in **7** and **8** are 2.501(2) and 2.495(3) Å, respectively, which are slightly shorter than those in the bridging carbene complexes $[Fe_2(\mu\text{-CO})\{\mu\text{-C(OEt)Ph}\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (2.512(1) Å)[13] and $[Fe_2(\mu\text{-CO})\{\mu\text{-C(OEt)}C_6H_4\text{Me-}p\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (2.519(2) Å)[13] but significantly shorter than that found in the cycloheptatriene-coordinated bridging carbyne complex $[Fe_2\{\mu\text{-C(OEt)}\}\{\mu\text{-}\eta^4\text{:}\eta^3\text{-}C_7H_7C(OEt)(C_6H_4CF_3\text{-}p)\}(CO)_4]$ (2.6706(7) Å).[14] The alkylidyne carbon asymmetrically bridges the Fe−Fe bond with C(1)−Fe(1) = 1.755(10) Å and C(1)−Fe(2) = 1.854(9) Å in **7**. This asymmetry is more marked than that in **8** (C(1)−Fe(1) = 1.81(8) Å, C(1)−Fe(2) = 1.84(2) Å) and in the analogous bridging carbyne complex $[Fe_2\{\mu\text{-C(OEt)}\}\{\mu\text{-}\eta^4\text{:}\eta^3\text{-}C_7H_7C(OEt)C_6H_4CF_3\text{-}p\}(CO)_4]$ (Fe(1)−C(10) = 1.857(4) Å, Fe(2)−C(10) = 1.804(4) Å).[14] The Fe(1)−μ-C(1) distances in **7** and **8** not only are much shorter than the corresponding bonds in $[Fe_2(\mu\text{-CO})\{\mu\text{-C(OEt)Ph}\}(CO)_2\text{-}(\eta^5\text{-}C_5H_5)_2]$ (2.032(7) and 2.019(6) Å)[13] and $[Fe_2(\mu\text{-CO})\{\mu\text{-C(SEt)Ph}\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (2.03(1) and 2.00(1) Å)[9] but also significantly shorter than the Fe=$C_{carbene}$ bond in carbene complexes $[Fe\{C(OEt)C_6H_4\text{Me-}o\}(C_{10}H_{16})(CO)_2]$ (1.915(15) Å)[15] and $[Fe\{C(OEt)C_6H_4\text{Me-}o\}(C_6H_8)(CO)_2]$ (1.89(2) Å).[16] In the di- and trimetal bridging carbyne complexes $[MoFe(\mu\text{-}CC_6H_4\text{Me-4})(CO)_2(\eta^5\text{-}C_5H_5)]$[17a] and $[CrReFe(\mu\text{-}CC_6H_4\text{-Me-4})(CO)_{12}]$,[17b] the Fe−$\mu$-C distances, 2.008(5) and 1.872(8) Å, respectively, are longer than those in **7** and **8**. These data strongly suggest that the Fe(1)−μ-C(1) linkage in **7** and **8** is a double bond, thus giving the Fe(1) atom an 18-electron configuration.

The $M(CO)_5CN$ (M = Mo, W) moiety in **7** and **8** is bonded to the Fe(1) atom through the N atom. The Fe(1)−N bond lengths in **7** and **8** are 1.941(9) and 1.95(1) Å, respectively, which are much shorter than that in the complex $[Fe\{Me_2NCH_2C_6H_4C(OEt)CH_2C_6H_4CH_2\}\text{-}(CO)_3]$ (2.158(3) Å)[18] but are the same within experimental error as in $[Fe_2(CO)_6(N{=}CHCH_3)_2]$ (1.942(7) Å),[19] 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 bonds. The shorter Fe(1)−N distance suggests that there exists some double-bond character in the Fe(1)−N bond in both complexes. C(23)−N has a bond length of 1.15(1) Å for **7** and 1.11(2) Å for **8**, which indicates high triple-bond character, and is essentially the same as that found (1.15(1) Å) in $[(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(Ph)NCW(CO)_5]$ (1.16(1) Å)[8f] and is comparable with that of the corresponding C−N bond in $[Fe_2(\mu\text{-CNEt})_3(CNEt)_6]$ (1.13−1.19 Å).[20] The shorter M−C(23) distance (Mo−C(23) = 2.18(1) Å for **7**, W−C(23) = 2.20(2) Å for **8**) indicates a high double-bond character of the M−C(23) bond in both complexes. This distance is nearly the same as that in $[(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(Ph)\text{-}NCW(CO)_5]$ (W−C(8) = 2.13(1) Å)[8f] and is comparable

(13) Chen, J.-B.; Li, D.-S.; Yu, Y.; Chen, C.-G. *Organometallics* **1994**, *13*, 3581.
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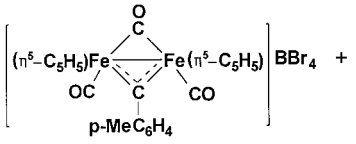
with the W−$C_{carbene}$ bond distance in the analogous carbene complex $[(CO)_5W{=}C(OEt)C_5H_4RuC_5H_5]$ (2.23(2) Å)[21] but is markedly longer than the W−$C_{carbyne}$ bond distance in the carbyne complex $[CrPPh_2(2,2'\text{-bipy})WCNEt_2(CO)_7]$ (1.877(8) Å).[22] The Fe(1), N, C(23), and Mo or W atoms are coplanar with an Fe(1)−N−C(23) angle of 175.3(9)° and a N−C(23)−Mo angle of 177.5(9)° for **7** and an Fe(1)−N−C(23) angle of 167(1)° and a N−C(23)−W angle of 169(1)° for **8**, which shows that the Fe(1)−N−C(23)−M fragment is approximately linear; thus, the Fe(1), N, C(23), and Mo or W atoms form a conjugate chain. Moreover, C(1)−C(2) bond lengths in **7** and **8** are 1.46(1) and 1.44(2) Å, respectively, which are intermediate between C−C single-bond and C=C double-bond distances. The shorter C(1)−C(2) distance suggests some π-bond character between the C(1) atom and C(2) atom of the benzene ring in complexes **7** and **8**.

The formation of complexes **6**−**8** could involve initial formation of the cationic bridging carbyne intermediate $[Fe_2(\mu\text{-CO})(\mu\text{-CPh})(CO)(\eta^5\text{-}C_5H_5)_2]^+$ by loss of a CO ligand from an Fe atom (e.g. Fe(1)) accompanied by formation of a $M(CO)_6$ (M = Cr, Mo, W) compound in the presence of the carbonylmetal anion. Then the $(CO)_5M{=}C{=}N^-$ (M = Cr, Mo, W) anion (a representation of the same electronic structure of the $^-M(CO)_5CN$ anion) attacks the unsaturated Fe(1) center of the carbyne intermediate to produce products **6**−**8**. Indeed, we have isolated small amounts of compound $M(CO)_6$ in the course of the column chromatography.

Although a number of dimetal bridging carbyne complexes have been prepared by Stone et al. and by us as mentioned in the Introduction, complexes **6**−**8** as dimetal bridging carbyne complexes were synthesized first by the reaction of a cationic carbyne complex of diiron with carbonylmetal anions.

In contrast to the reaction of complex **1**, the cationic carbyne complex $[Fe_2(\mu\text{-CO})(\mu\text{-}CC_6H_4Me\text{-}p)(CO)_2(\eta^5\text{-}C_5H_5)_2]BBr_4$ (**2**) reacts with carbonylmetal anions **3**−**5** under the same conditions to give not analogous bridging carbyne complexes but rather the novel bridging *p*-tolyl(pentacarbonylcyanotungsten)carbene complexes $[Fe_2(\mu\text{-CO})\{\mu\text{-}C(C_6H_4Me\text{-}p)NCM(CO)_5\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (**9**−**11**) (eq 4) in 57−76% isolated yields.



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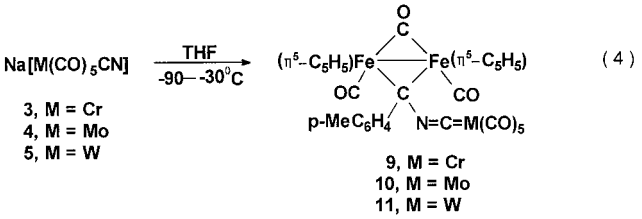

3, M = Cr
4, M = Mo
5, M = W

9, M = Cr
10, M = Mo
11, M = W

(4)

The composition and structure of complexes **9**−**11** are supported by their elemental analyses, spectroscopic data, and the X-ray diffraction study of **11**. The IR and ^{1}H NMR spectra of complexes **9**−**11** are different from those of **6**−**8** (see the Experimental Section). The IR spectra of **9**−**11** in the ν(CO) region showed four to six CO absorption bands at 2057−1772 cm^{-1}, similar to **6**−**8**, whereas the characteristic ν(CN) stretching vibration occurs at ca. 2059−2051 cm^{-1} for complexes **6**−**8** but at ca. 2127−2125 cm^{-1} for complexes **9**−**11**, shifting to high vibration frequency by about 70 cm^{-1}. This may be due to the coordination of the $M(CO)_5CN$ (M = Cr, Mo, W) moiety to the Fe(1) atom through a CN group leading to a weakening of the C−N bond to a greater extent in complexes **6**−**8,** as compared to that of complexes **9**−**11**, in which the $M(CO)_5CN$ moiety is bonded to the μ-carbene carbon through the CN group. The ^{1}H NMR spectra of **6**−**8** showed five to seven sets of proton signals attributed to the cyclopentadienyl protons at 5.90−4.90 ppm, while complexes **9**−**11** showed only a singlet cyclopentadienyl proton signal at ca. 5.81 ppm, since the $W(CO)_5CN$ moiety is bonded to the Fe(1) atom in **6**−**8** but to the μ-carbene carbon in the latter. In complexes **9**−**11**, the C_{5v} symmetry of the Cp rings has not been destroyed. This suggests that the structures of complexes **9**−**11** are quite different from those of complexes **6**−**8**, a fact that is further confirmed by an X-ray diffraction study of **11**.

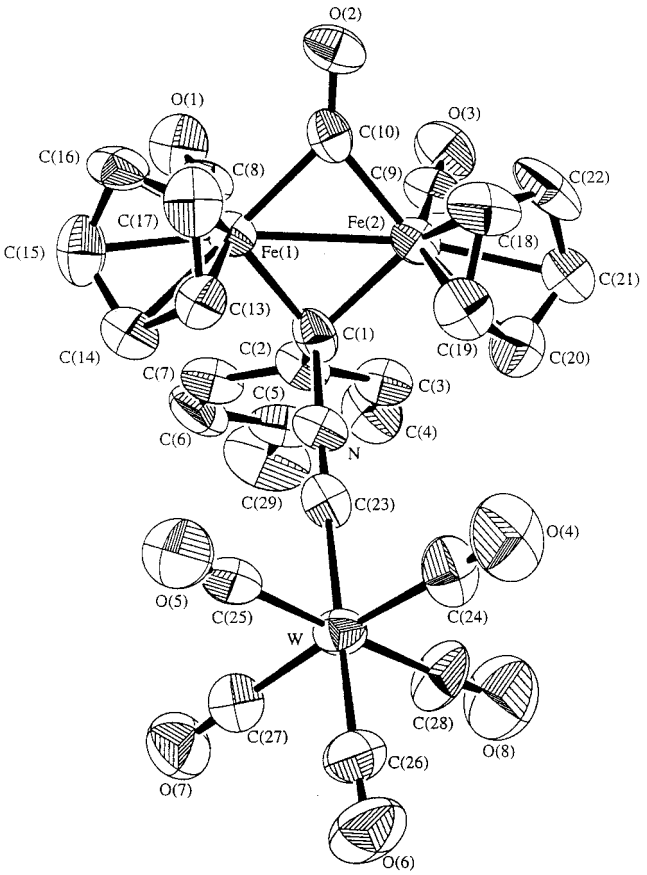

Figure 3. Molecular structure of **11**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 40% probability. H_2O has been omitted for clarity.

The structure of **11** (Figure 3) resembles that of the bridging complexes $[Fe_2(\mu\text{-CO})\{\mu\text{-}C(OEt)Ph\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$[13] and $[Fe_2(\mu\text{-CO})\{\mu\text{-}C(SEt)Ph\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$,[9] except that the substituent on the μ-carbene carbon is the $W(CO)_5CN$ group in **11** but an OEt or SEt group in

(21) Fischer, E. O.; Gammel, F. J.; Besenhard, J. O.; Frank, A.; Neugebauer, D. *J. Organomet. Chem.* **1980**, *191*, 261.
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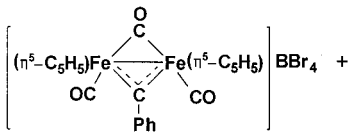
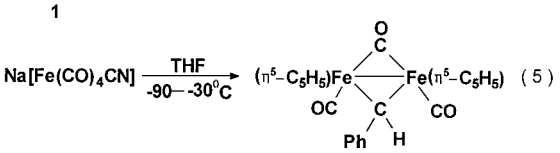
the latter. The structure of the principal portion of $[Fe_2(\mu\text{-CO})(\mu\text{-CAr})(CO)_2(\eta^5\text{-}C_5H_5)_2]$ in **11** is very similar to that in **7** and **8**. An apparent difference in the structures of **7** (or **8**) and **11** is the longer Fe−μ-C(1) bonds (Fe(1)−C(1) = 1.98(2) Å, Fe(2)−C(1) = 1.99(2) Å) and the longer C(1)−C(2) bond (1.53(2) Å) in **11**, as compared to **7** and **8**. The two C−N bond lengths in **11** are very different. C(23)−N has a bond length of 1.15(2) Å, which indicates high triple-bond character and is essentially the same as that found in **7** (1.15(1) Å) and **8** (1.11(2) Å). The other is C(1)−N with a bond length of 1.47(2) Å, which is between the normal C−N and C=N distances and is slightly shorter than the corresponding C−N distance in $[W{-}N(Bu^tCMe_2(Me)(NBu^t)\{N(Bu^t)\text{-}CMe{=}CMe_2\}]$ (1.438−1.521 Å).[23] The shorter W−C(23) distance (2.13(2) Å) in **11** signifies its high double-bond character, as in **7** and **8**. The C(1), N, C(23), and W atoms are coplanar with a C(1)−N−C(23) angle of 178(1)° and a N−C(23)−W angle of 176(1)°, indicating that the C(1)−N−C(23)−W fragment is almost linear; thus, the C(1), N, C(23), and W atoms form a conjugate chain.

The reaction pathway to complexes **9**−**11** could proceed via attack of the $(CO)_5M{=}C{=}N^-$ (M = Cr, Mo, W) anion (a representation of the same electronic structure of the $^-M(CO)_5CN$ anion) at the μ-carbyne carbon of **2**. In the reaction of **2**, no analogous cationic bridging carbyne intermediate $[Fe_2(\mu\text{-CO})(\mu\text{-}CC_6H_4Me\text{-}p)(CO)(\eta^5\text{-}C_5H_5)_2]^+$ would be formed as in the case of complex **1**, owing to the electron-pushing action of the *p*-tolyl group, which provides the partial charge for the μ-carbyne carbon to stabilize cationic **2**. Thus, the $(CO)_5M{=}C{=}N^-$ anion directly attacks the μ-carbyne carbon to produce complexes **9**−**11**.

Not all such carbonylmetal anions containing a CN group can react with cationic carbyne complex **1** or **2** to afford the bridging carbyne or bridging carbene complexes, since the analogous anionic carbonylmetal compound $Na[Fe(CO)_4CN]$ reacted with **1** under the same conditions to give a 54% yield of diiron bridging phenylcarbene complex $[Fe_2(\mu\text{-CO})\{\mu\text{-C(H)Ph}\}(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (**12**) (eq 5), instead of the expected bridging carbyne complex. This suggests that the metal atom in the carbonylmetal anionic compound is important; the Cr, Mo, and W atoms probably promote the reaction by forming a stable $(CO)_5M{=}C{=}NFe$ (M = Cr, Mo, W) core.



1



(5)

12

Complex **12** is a known compound[9] whose structure has been established by X-ray crystallography; it has been obtained by the reaction of **1** with the reactive salt $[Et_3NH][Fe_2(\mu\text{-CO})(\mu\text{-SPh})(CO)_6]$ or the carbonylmetal dianions $Na_2[W(CO)_5]$ and $Na_2[Fe(CO)_4]$. The formation of product **12** is unexpected, and we do not know the chemistry involved.

The title reaction shows the novel reactions between carbonylmetal anions and the cationic bridging carbyne complexes of diiron. The reaction results indicate that the different cationic bridging carbyne complexes exert great influence on the resulting products, and the different carbonylmetal anions exhibit great influence on the reactivity of cationic bridging carbyne complexes and the reaction products. The title reaction represents a new, convenient, and useful method for the preparation and structural modification of dimetal bridging carbene and bridging carbyne complexes.

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Supporting Information Available: Tables of the positional parameters and B_{iso}/B_{eq} values, H atom coordinates, anisotropic displacement parameters, all bond lengths and angles, and least-squares planes for **7**, **8**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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