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Remarkable Reactions of Cationic Carbyne Complexes of Manganese and Rhenium with Na[Fe(CO)$_4$CN] and Et$_4$N[Mn(CO)$_4$(CN)$_2$]

Yongjun Tang, Jie Sun, and Jiabi Chen*

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

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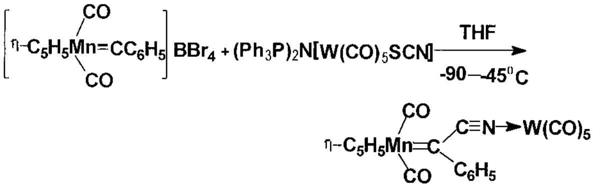
The reaction of a cationic carbyne complex of manganese, [(η-C$_5$H$_5$)(CO)$_2$Mn≡CC$_6$H$_5$]BBr$_4$ (**1**), with Na[Fe(CO)$_4$CN] (**3**) in THF at low temperature gives the phenyl(tetracarbonylcyanoiron)carbene−manganese complex [(η-C$_5$H$_5$)(CO)$_2$Mn═C(C$_6$H$_5$)NCFe(CO)$_4$] (**5**). The analogous reaction of a cationic carbyne complex of rhenium, [(η-C$_5$H$_5$)(CO)$_2$Re≡CC$_6$H$_5$]BBr$_4$ (**2**), with **3** affords the corresponding carbene−rhenium complex [(η-C$_5$H$_5$)(CO)$_2$Re═C(C$_6$H$_5$)NCFe(CO)$_4$] (**6**). Complex **1** reacts with Et$_4$N[Mn(CO)$_4$(CN)$_2$] (**4**) to yield the novel trinuclear metal dicarbene−manganese complex [{(η-C$_5$H$_5$)(CO)$_2$Mn═C(C$_6$H$_5$)NC}$_2$Mn(CO)$_3$CN] (**7**) and the novel tetranuclear metal dicarbene−manganese complex [{(η-C$_5$H$_5$)(CO)$_2$Mn═C(C$_6$H$_5$)NC}$_2$Mn(CO)$_3$CNMn(CO)$_2$(η-C$_5$H$_5$)] (**8**). Complex **2** reacts similarly with **4** to afford the corresponding trinuclear dicarbene−rhenium complex [{(η-C$_5$H$_5$)(CO)$_2$Re═C(C$_6$H$_5$)NC}$_2$Mn(CO)$_3$CN] (**9**). The structures of complexes **5**−**9** have been established by X-ray crystallography.

Introduction

Carbene complexes containing a conjugated cyanometal or isocyanometal ligand linked to the carbene carbon are interesting.[1] We have recently found that the reaction of the cationic carbyne complexes of manganese with metal salts containing an SCN substituent such as (Ph$_3$P)$_2$N[W(CO)$_5$SCN] led to loss of the S atom to give the novel phenyl(pentacarbonylisocyanotungsten)carbene−manganese complex [(η-C$_5$H$_5$)(CO)$_2$Mn═C(C$_6$H$_5$)CNW(CO)$_5$] (eq 1).[1] The reaction pathway to this complex was thought to proceed via a $^-$CN anion generated either by loss of the sulfur atom from the SCN group or by loss of the W(CO)$_5$ moiety from the $^-$CNW(CO)$_5$ species. The $^-$CN anion attacks at the carbyne carbon to form the carbene intermediate [(η-C$_5$H$_5$)(CO)$_2$Mn═C(C$_6$H$_5$)CN]; the N atom of its CN group then coordinates to the W atom of the W(CO)$_5$ moiety and provides two electrons for the W atom to satisfy an 18-electron configuration. However, when the cyano-containing carbonyltungsten anionic compound Na[W(CO)$_5$CN] was used as nucleophile for the reactions with the cationic carbyne complex of manganese or rhenium, the product was a phenyl(pentacarbonylcyanotungsten)carbene−manganese or −rhenium complex, [(η-C$_5$H$_5$)(CO)$_2$M═C(C$_6$H$_5$)NCW(CO)$_5$] (M = Mn, Re) (eq 2),[1] instead of the phenyl(pentacarbonylisocyanotungsten)carbene−manganese or −rhenium complex.



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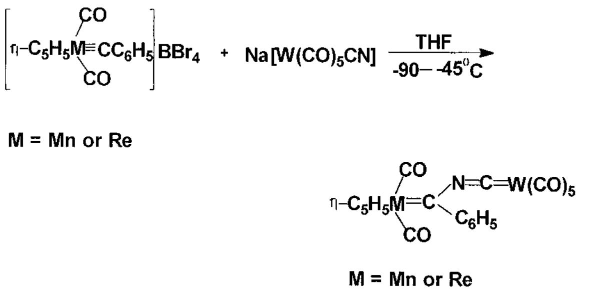

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In an extension of our research on reactions of the cationic carbyne complexes of transition metals with carbonylmetal anion compounds to form metal carbene complexes or dimetal bridging carbene and carbyne complexes, we have now studied the reactions of the cationic carbyne complexes of manganese and rhenium with carbonylmetal anions containing one and two CN groups in order to further investigate the effect of different carbonylmetal anion compounds on the reactivity of the cationic carbyne complexes and reaction products. Herein we report the unusual reaction of Na[Fe(CO)$_4$CN] (**3**) and Et$_4$N[Mn(CO)$_4$(CN)$_2$] (**4**) with cationic carbyne complexes of manganese and rhenium, [(η-C$_5$H$_5$)(CO)$_2$Mn≡CC$_6$H$_5$]BBr$_4$ (**1**) and [(η-C$_5$H$_5$)(CO)$_2$Re≡CC$_6$H$_5$]BBr$_4$ (**2**), to produce novel phenyl(tetracarbonylcyanoiron)carbene−manganese and −rhenium complexes or trinuclear and tetranuclear metal dicarbene complexes and the structural characterization of the resulting products.

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Experimental Section

All reactions were performed under a dry, oxygen-free N_2 atmosphere by 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 an 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 $[(\eta\text{-}C_5H_5)(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ (**1**)[2] and $[(\eta\text{-}C_5H_5)(CO)_2Re{\equiv}CC_6H_5]BBr_4$ (**2**)[3] were prepared as previously described. $Na[Fe(CO)_4CN]$ (**3**)[4] and $Et_4N[Mn(CO)_4(CN)_2]$ (**4**)[5] were prepared by literature methods.

The IR spectra were measured on a Shimadzu IR-440 spectrophotometer. All ^1H NMR spectra were recorded at ambient temperature in acetone-d_6 with TMS as the internal reference using a Bruker AM-300 spectrometer. Electron ionization mass spectra (EIMS) were run on a Hewlett-Packard 5989A spectrometer. Melting pointing obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

Reaction of $[(\eta\text{-}C_5H_5)(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ (1) with $Na[Fe(CO)_4CN]$ (3) To Give $[(\eta\text{-}C_5H_5)(CO)_2Mn{=}C(C_6H_5)NCFe(CO)_4]$ (5). To 0.19 g (0.88 mmol) of $Na[Fe(CO)_4CN]$ dissolved in 50 mL of THF at −90 °C was added portionwise 0.52 g (0.88 mmol) of **1** with vigorous stirring. Immediately the orange-red solution turned deep red. The reaction mixture was stirred at −90 to −45 °C for 6−7 h, during which time the solution turned gradually dark red. After the resulting solution was evaporated under high vacuum at −50 to −40 °C to dryness, the dark red residue was chromatographed on an alumina column (1.6 × 15−20 cm) at −25 °C with petroleum ether/CH_2Cl_2 (5:1) as the eluant. The brown-yellow band was eluted and collected. The solvent was removed under vacuum, and the residue was recrystallized from petroleum ether/CH_2Cl_2 solution at −80 °C to give 0.26 g (65%, based on **1**) of dark red crystals of **5**: mp 58−59 °C dec; IR (CH_2Cl_2) ν(CO) 2070 (w), 2054 (s), 2041 (s), 1970 (vs, br) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.88 (m, 1H, C_6H_5), 7.53 (m, 2H, C_6H_5), 7.35 (m, 2H, C_6H_5), 5.42 (s, 5H, C_5H_5); MS *m/e* 291 ($M^+ - Fe(CO)_4$), 204 $[C_5H_5Mn(CO)_3]^+$, 176 $[C_5H_5Mn(CO)_2]^+$, 168 $[Fe(CO)_4]^+$. Anal. Calcd for $C_{19}H_{10}O_6NMnFe$: C, 49.71; H, 2.20; N, 3.05. Found: C, 49.31; H, 2.28; N, 3.14.

Reaction of $[(\eta\text{-}C_5H_5)(CO)_2Re{\equiv}CC_6H_5]BBr_4$ (2) with 3 To Give $[(\eta\text{-}C_5H_5)(CO)_2Re{=}C(C_6H_5)NCFe(CO)_4]$ (6). To 0.306 g (0.42 mmol) of **2** dissolved in 50 mL of THF at −90 °C was added 0.091 g (0.42 mmol) of **3** with stirring. The orange solution turned immediately brown-red. The mixture was stirred at −90 to −45 °C for 6 h; during this time the solution turned gradually dark red. Further treatment of the resulting mixture as described in the reaction of **1** with **3** gave 0.17 g (68%, based on **2**) of **6** as blackish crystals: mp 68−69 °C dec; IR (CH_2Cl_2) ν(CO) 2078 (w), 2042 (s), 2023 (s), 1970 (vs, br), 1924 (vs) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.36 (m, 3H, C_6H_5), 7.18 (m, 1H, C_6H_5), 7.01 (m, 1H, C_6H_5), 5.63 (s, 5H, C_5H_5); MS *m/e* 589 (M^+), 588 ($M^+ - 1$), 560 ($M^+ - CO - 1$), 532 ($M^+ - 2CO - 1$), 504 ($M^+ - 3CO - 1$), 421 ($M^+ - Fe(CO)_4$). Anal. Calcd for $C_{19}H_{10}O_6NReFe{\cdot}{}^1/_2CH_2Cl_2$: C, 37.01; H, 1.75; N, 2.21. Found: C, 36.50; H, 1.78; N, 2.27.

Reaction of 1 with $Et_4N[Mn(CO)_4(CN)_2]$ (4) To Give $[\{(\eta\text{-}C_5H_5)(CO)_2Mn{=}C(C_6H_5)NC\}_2Mn(CO)_3CN]$ (7) and $[\{(\eta\text{-}C_5H_5)(CO)_2Mn{=}C(C_6H_5)NC\}_2Mn(CO)_3CNMn(CO)_2(\eta\text{-}C_5H_5)]$ (8). $Et_4N[Mn(CO)_4(CN)_2]$ (0.335 g, 0.96 mmol) was dissolved in 80 mL of THF and the solution cooled to −90 °C. To this solution was added 0.572 g (0.96 mmol) of **1** with stirring. Immediately the orange solution turned dark red. The mixture was stirred at −90 to −45 °C for 7 h; during this time the solution turned gradually brown. The resulting solution was evaporated under vacuum at −45 to −40 °C to dryness. The dark red residue was chromatographed on Al_2O_3 at −25 °C with petroleum ether/CH_2Cl_2 (10:1) as the eluant.The brown-yellow band was eluted, and then the yellow-green band was eluted with petroleum ether/CH_2Cl_2/Et_2O (5:1:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from petroleum ether/CH_2Cl_2 solution at −80 °C. From the first fraction, 0.23 g (0.25 mmol; 52% based on **4**) of dark green crystals of **8** were obtained: mp 93−94 °C dec; IR (CH_2Cl_2) ν(CO) 2086 (m), 2051 (w), 2035(s), 1991 (vs, br), 1936 (s), 1842 (w) cm^{-1}, ν(CN) 2086 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.97 (m, 2H, C_6H_5), 7.44 (m, 3H, C_6H_5), 5.44 (s, 5H, C_5H_5); MS *m/e* 204 $[C_5H_5Mn(CO)_3]^+$, 176 $[C_5H_5Mn(CO)_2]^+$. Anal. Calcd for $C_{41}H_{25}O_9N_3Mn_4$: C, 53.53; H, 2.71; N, 4.55. Found: C, 54.01; H, 3.00; N, 5.02. From the second fraction, 0.12 g (0.14 mmol; 30% based on **4**) of **7** as dark yellow crystals were obtained: mp 107−108 °C dec; IR (CH_2Cl_2) ν(CO) 2057 (w), 2034 (s), 1990 (vs, br), 1936 (s) cm^{-1}, ν(CN) 2085 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 8.00 (m, 2H, C_6H_5), 7.52 (m, 1H, C_6H_5), 7.41 (m, 2H, C_6H_5), 5.56 (s, 5H, C_5H_5); MS *m/e* 581 ($M^+ - 5CO - CN$), 204 $[C_5H_5Mn(CO)_3]^+$, 176 $[C_5H_5Mn(CO)_2]^+$. Anal. Calcd for $C_{34}H_{20}O_7N_3Mn_3{\cdot}CH_2Cl_2$: C, 50.51; H, 2.66; N, 5.05. Found: C, 50.40; H, 2.80; N, 4.98.

Reaction of 2 with 4 To Give $[\{(\eta\text{-}C_5H_5)(CO)_2Re{=}C(C_6H_5)NC\}_2Mn(CO)_3CN]$ (9). Similar to the procedures for the reaction of **1** with **4**, compound **2** (0.383 g, 0.53 mmol) was treated with 0.184 g (0.53 mmol) of **4** at −90 to − 45 °C for 7 h; during this time the orange-yellow solution gradually turned orange-red. Further treatment of the resulting mixture as described in the reaction of **1** with **4** gave 0.21 g (0.18 mmol; 69% based on **4**) of dark red crystalline **9**: mp 98−99 °C dec; IR (CH_2Cl_2) ν(CO) 2036 (s), 2002 (sh), 1981 (vs, br), 1914 (vs) cm^{-1}, ν(CN) 2095 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 8.13 (m, 1H, C_6H_5), 8.04 (m, 2H, C_6H_5), 7.67 (m, 2H, C_6H_5), 6.11 (s, 5H, C_5H_5), 3.60−3.50 (m, 4H, $Br(CH_2)_4OH$), 2.25 (m, 1H, $Br(CH_2)_4OH$), 1.90 (m, 4H, $Br(CH_2)_4OH$); MS *m/e* 336 $[C_5H_5Re(CO)_3]^+$, 280 $[C_5H_5Re(CO)]^+$, 152 $[Br(CH_2)_4OH]^+$. Anal. Calcd for $C_{34}H_{20}O_7N_3Re_2Mn{\cdot}Br(CH_2)_4OH$: C, 39.25; H, 2.51; N, 3.61. Found: C, 39.49; H, 2.45; N, 3.78.

X-ray Crystal Structure Determinations of Complexes 5−9. Single crystals of **5**−**9** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH_2Cl_2 or petroleum ether/THF solution at −80 °C. Single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data for 2742, 2842, 6392, 5774, and 6900 independent reflections, of which 1885, 3055, 3354, and 3632 with $I > 2.00\sigma(I)$ for **5**, **7**, **8**, and **9** and 2170 with $I > 2.50\sigma(I)$ for **6** 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 range $5° \leq 2\theta \leq 50°$ for **5**−**9**, respectively.

The structures of **5**−**8** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1885, 2170, 3055, and 3354 observed reflections and 253, 253, 451, and 514 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.036$ and $R_w = 0.039$ for **5**, $R = 0.049$ and $R_w = 0.057$ for **6**, $R = 0.050$ and $R_w = 0.047$ for **7**, and $R = 0.062$ and $R_w = 0.063$ for **8**, respectively. The structure of **9** was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3632 observed reflections and 479

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Table 1. Crystal Data and Experimental Details for Complexes 5−9

	5	**6**	**7**·CH_2Cl_2	**8**	**9**·$Br(CH_2)_4OH$
formula	$C_{19}H_{10}O_6NMnFe$	$C_{19}H_{10}O_6NReFe$	$C_{35}H_{22}O_7N_3Mn_3Cl_2$	$C_{41}H_{25}O_9N_3Mn_4$	$C_{38}H_{29}O_8N_3MnRe_2Br$
fw	459.08	590.35	832.29	923.42	1162.92
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	10.019(3)	10.039(4)	10.604(3)	12.396(3)	13.130(4)
b (Å)	11.620(5)	11.607(4)	19.157(2)	14.123(4)	15.571(3)
c (Å)	8.651(3)	8.755(2)	17.403(2)	12.299(4)	18.792(4)
α (deg)	100.43(3)	101.27(2)		114.43(2)	
β (deg)	96.43(3)	96.36(2)	96.21(1)	100.88(2)	101.84(2)
γ (deg)	82.14(3)	84.07(3)		84.45(3)	
V (Å^3)	977.2(6)	990.9(5)	3514(1)	1924.7(10)	3760(1)
Z	2	2	4	2	4
d_{calcd} (g/cm^3)	1.560	1.978	1.573	1.593	2.054
F(000)	460.00	560.00	1672.00	928.00	2208.00
μ(Mo Kα) (cm^{-1})	14.21	68.71	12.65	13.42	78.78
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
diffractometer	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R
temp (°C)	20	20	20	20	20
orientation rflns: no.; range (2θ) (deg)	20; 13.6−21.4	18; 14.1−21.3	22; 13.5−21.6	19; 18.6−21.6	24; 13.5−20.7
scan method	ω-2θ	ω-2θ	ω-2θ	ω-2θ	ω-2θ
data collecn range, 2θ (deg)	5−50	5−50	5−50	5−50	5−50
no. of unique data					
total	2742	2842	6392	5774	6900
no. with $I > 2.00\sigma(I)$	1885	2170 ($I > 2.50\sigma(I)$	3055	3354	3632
no. of params refined	253	253	451	514	479
correction factors: min−max	0.9416−1.0000	0.8769−1.1177	0.7629−1.0000	0.9287−1.0000	0.6742−0.9995
R^a	0.036	0.049	0.050	0.062	0.055
$R_w{}^b$	0.039	0.057	0.047	0.063	0.052
quality-of-fit indicator^c	1.27	1.67	1.31	1.97	1.40
largest shift/esd, final cycle	0.00	0.01	0.00	0.07	0.04
largest peak (e/Å^3)	0.28	1.74	0.41	0.67	1.12
min peak (e/Å^3)	−0.21	−1.46	−0.53	−0.60	−1.86

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

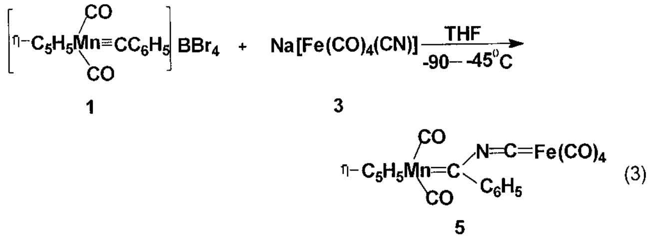
variable parameters and converged with unweighted and weighted agreement factors of R = 0.055 and R_w = 0.052 for **9**, All the calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp.

Crystallographic data and details of the procedures used for data collection and reduction information for **5**−**9** are given in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3, respectively. The atomic coordinates and B_{iso}/B_{eq} values, anisotropic displacement parameters, all bond lengths and angles, and least-squares planes for **5**−**9** are given in the Supporting Information. The structures of **5**−**9** are given in Figures 1−5, respectively.

Results and Discussion

The complex [(η-C_5H_5)(CO)$_2$Mn≡CC_6H_5]BBr_4 (**1**) was treated with an equimolar quantity of Na[Fe(CO)$_4$CN] (**3**) in THF at low temperature (−90 to − 45 °C) for 4−5 h. After removal of the solvent under high vacuum, the residue obtained was chromatographed on an alumina column at low temperature and the crude products were recrystallized from petroleum ether/CH_2Cl_2 at −80 °C to give the phenyl(tetracarbonylcyanoiron)carbene−manganese complex [(η-C_5H_5)(CO)$_2$Mn=C(C_6H_5)-NCFe(CO)$_4$] (**5**) (eq 3) in 65% yield. The analogous reaction of a cationic carbyne complex of rhenium, [(η-C_5H_5)(CO)$_2$-Re≡CC_6H_5]BBr_4 (**2**), with **3** under the same conditions afforded the phenyl(tetracarbonylcyanoiron)carbene−rhenium complex [(η-C_5H_5)(CO)$_2$Re=C(C_6H_5)NCFe(CO)$_4$] (**6**) (eq 4) in 68% yield.

The composition and structure of complexes **5** and **6** are supported by their element analysis and spectroscopic data and X-ray diffraction studies. The IR spectrum of **6** showed five ν(CO) stretching vibration bands at 2078, 2042, 2023, 1970, and 1924 cm^{-1}, but complex



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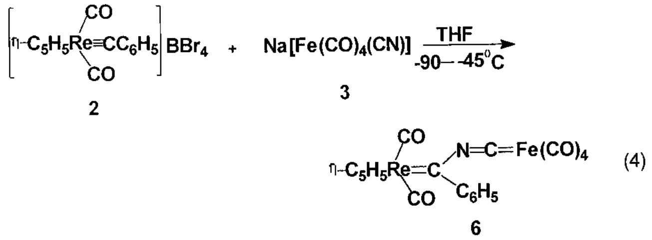

(4)

5 showed only four bands at 2070, 2054, 2041, and 1970 cm^{-1}, which indicates that the different central metal exerts an obvious effect on the vibrational frequency ν(CO). The ^{1}H NMR spectrum of **5** showed three sets of the proton signals attributed to the phenyl at 7.88, 7.53, and 7.35 ppm and a singlet signal attributed to the cyclopentadienyl proton at 5.42 ppm, while complex **6** showed three sets of phenyl proton signals at 7.36, 7.18, and 7.01 ppm and a singlet signal due to the cyclopentadienyl proton at 5.63 ppm. These suggest that the different central metal also exerts a significant effect on the chemical shifts of the phenyl and cyclopentadienyl protons. It is also noted that both ^{1}H NMR spectra are very different from those of the analogous phenyl(pentacarbonylcyanotungsten)carbene complexes [(η-C_5H_5)(CO)$_2$M=C(C_6H_5)NCW(CO)$_5$] (M = Mn, Re) (two

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Table 2. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complexes 5 and 6

	5 (M = Mn)	**6** (M = Re)		**5** (M = Mn)	**6** (M = Re)
M−C(16)	1.868(4)	1.99(1)	C(16)−C(17)	1.485(6)	1.46(2)
N−C(16)	1.410(5)	1.42(2)	Fe−C(1)	1.779(7)	1.79(2)
N−C(4)	1.165(5)	1.17(2)	Fe−C(2)	1.786(6)	1.77(2)
Fe−C(4)	1.859(5)	1.85(1)	Fe−C(3)	1.786(6)	1.76(2)
M−C(7)	1.786(6)	1.96(2)	Fe−C(5)	1.775(6)	1.78(2)
M−C(8)	1.785(5)	1.89(2)	M−C(Cp) (av)	2.149	2.294
M−C(16)−N	117.1(3)	115.1(9)	M−C(8)−O(5)	179.0(4)	176(1)
M−C(16)−C(17)	134.3(3)	134(1)	Fe−C(1)−O(1)	179.0(6)	177(2)
N−C(16)−C(17)	108.6(4)	109(1)	Fe−C(2)−O(2)	178.8(6)	177(2)
C(4)−N-C(16)	176.1(4)	175(1)	Fe−C(3)−O(3)	177.8(5)	177(1)
Fe−C(4)−N	178.9(4)	178(1)	Fe−C(5)−O(6)	177.9(7)	175(2)
M−C(7)−O(4)	179.0(5)	178(1)	C(16)−C(17)−C(22)	121.9(4)	122(1)

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

Table 3. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complexes 7−9

	7 (M = Mn)	**8** (M = Mn)	**9** (M = Re)		**7** (M = Mn)	**8** (M = Mn)	**9** (M = Re)
M(2)-C(16)	1.866(6)	1.871(10)	2.00(2)	Mn(1)−C(5)	1.927(7)	1.93(1)	1.97(2)
N(1)−C(16)	1.418(8)	1.42(1)	1.41(2)	C(28)−C(29)	1.488(9)	1.48(1)	1.52(2)
N(1)−C(4)	1.162(7)	1.16(1)	1.16(2)	Mn(1)−C(6)	2.002(9)	1.979(10)	2.01(2)
Mn(1)−C(4)	1.925(7)	1.933(10)	1.93(2)	N(3)−C(6)	1.129(9)	1.154(10)	1.13(2)
C(16)−C(17)	1.488(8)	1.52(1)	1.49(2)	Mn(4)−N(3)		1.970(8)	
M(3)-C(28)	1.872(7)	1.865(9)	1.99(2)	M(2)-C(Cp) (av)	2.153	2.16	2.306
N(2)−C(28)	1.390(8)	1.44(1)	1.37(2)	M(3)-C(Cp) (av)	2.155	2.139	2.286
N(2)−C(5)	1.164(7)	1.15(1)	1.15(2)	Mn(4)−C(Cp) (av)		2.122	
M(2)−C(16)−N(1)	117.2(4)	118.2(7)	115(1)	C(5)−N(2)−C(28)	177.9(7)	178.2(9)	175(1)
M(2)−C(16)−C(17)	133.9(5)	133.1(7)	132(1)	Mn(1)−C(5)−N(2)	178.0(6)	173.1(8)	175(1)
N(1)−C(16)−C(17)	108.7(5)	108.2(8)	111(1)	C(4)−Mn(1)−C(5)	88.0(3)	85.4(4)	89.6(7)
C(4)−N(1)−C(16)	175.1(7)	172(1)	178(1)	Mn(1)−C(6)−N(3)	179.0(7)	176.0(8)	176(1)
Mn(1)−C(4)−N(1)	177.0(7)	168.1(9)	176(1)	Mn(4)−N(3)−C(6)		177.6(8)	
M(3)−C(28)−N(2)	117.9(5)	117.7(6)	118(1)	C(4)−Mn(1)-C(6)	86.4(3)	87.1(4)	86.0(7)
M(3)−C(28)−C(29)	132.1(5)	132.7(7)	130(1)	C(5)−Mn(1)-C(6)	88.7(3)	92.0(4)	85.4(7)

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

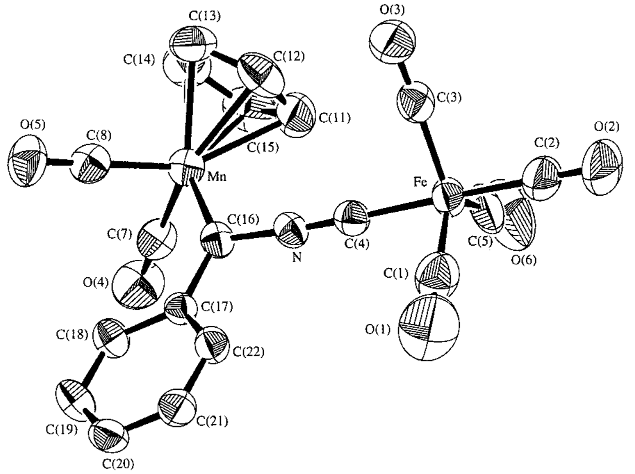

Figure 1. Molecular structure of **5**, showing the atom-numbering scheme.

sets of the phenyl proton signals at 7.95−7.99 and 7.56−7.59 ppm),[1] which shows that the carbonylcyanometal substituent on the carbene carbon has a certain effect on the chemical shifts of the phenyl and cyclopentadienyl protons as well.

The formation of complexes **5** and **6** could proceed via an attack of the $(CO)_4Fe{=}C{=}N^-$ anion, a representation of the electronic structure of the $^-Fe(CO)_4CN$ anion, on the carbyne carbon of complexes **1** and **2**, similar to that of analogous phenyl(pentacarbonylcyanotungsten)carbene−manganese and −rhenium complexes $[(\eta\text{-}C_5H_5)(CO)_2M{=}C(C_6H_5)NCW(CO)_5]$ (M = Mn, Re).[1]

The molecular structures of **5** and **6** established by the X-ray diffraction studies are shown in Figures 1 and 2, respectively. In **5** the Mn−C(16) bond length of 1.868(4) Å signifies a high double-bond character and is essentially the same as the corresponding $Mn{-}C_{carbene}$ bond distance in the analogous carbene complex [(η-

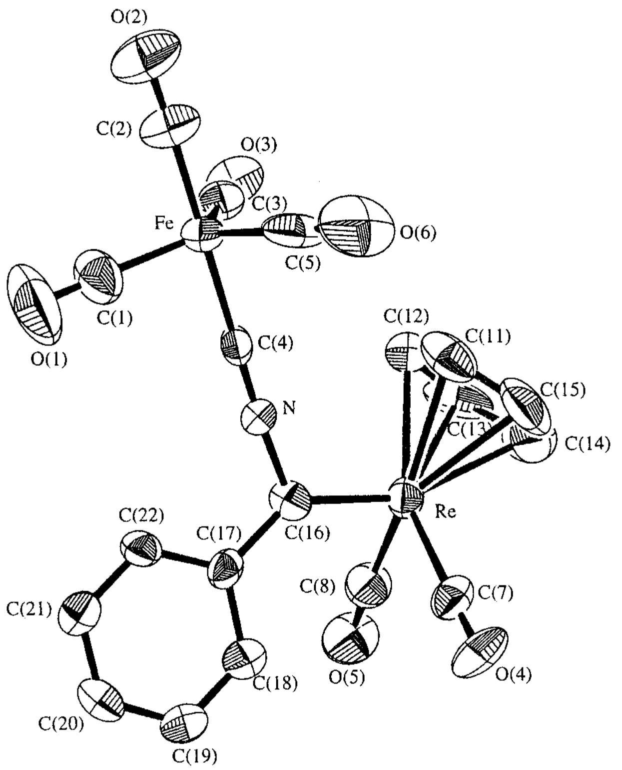

Figure 2. Molecular structure of **6**, showing the atom-numbering scheme.

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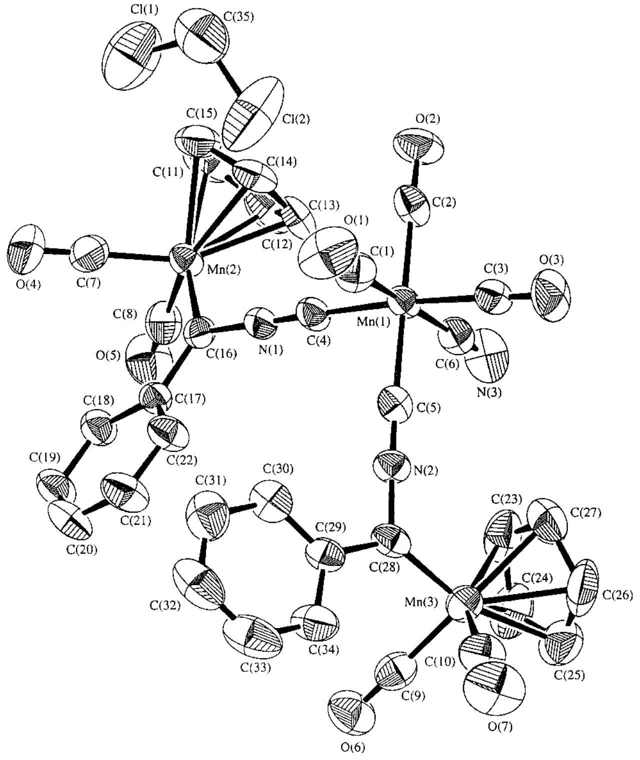

Figure 3. Molecular structure of **7**, showing the atom-numbering scheme.

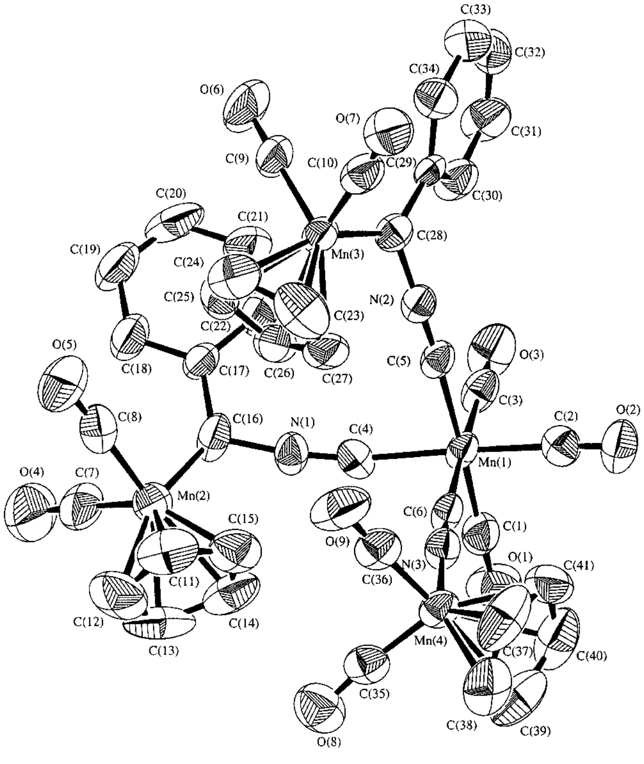

Figure 4. Molecular structure of **8**, showing the atom-numbering scheme.

$C_5H_5)(CO)_2Mn{=}C(OEt)Ph]$ (1.865(14) Å)[6] and is comparable with those in the carbene complexes $[C_5H_5\{(\eta^5\text{-}C_6H_6)(CO)_2Mn{=}C(OC_2H_5)C_6H_5\}]$ (1.89(1) Å)[7] and $[C_5H_5\{(\eta^5\text{-}C_6H_6)(CO)_2Mn{=}C(OC_2H_5)C_6H_4CH_3\text{-}o\}]$ (1.881(4) Å).[7]

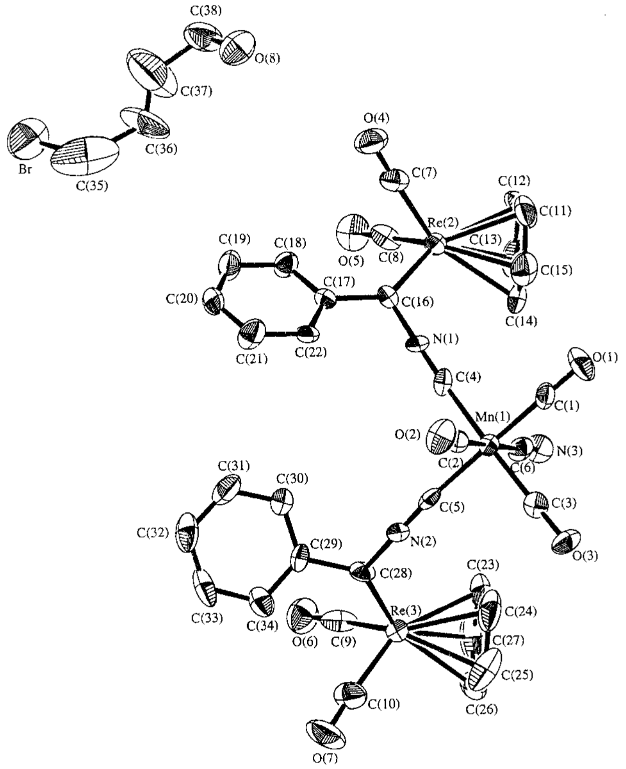

Figure 5. Molecular structure of **9**, showing the atom-numbering scheme.

The two C−N bond lengths in **5** are very different. C(4)−N has a bond length of 1.165(5) Å, which exhibits high triple-bond character and is nearly the same as that found in the analogous phenyl(pentacarbonylcyanotungsten)carbene−rhenium complex $[(\eta\text{-}C_5H_5)(CO)_2Re{=}C(C_6H_5)NCW(CO)_5]$ (1.16(1) Å)[1] and is comparable with the corresponding C−N distance in $[Fe_2(\mu\text{-}CNEt)_3(CNEt)_6]$ (1.13−1.19 Å).[8] The other, C(16)−N, has a bond distance of 1.410(5) Å, which is between the normal C−N and C=N distances and is slightly shorter than the corresponding C−N distance in $[W{-}N(Bu^tCMe_2\text{-}(Me)(NBu^t)\{N(Bu^t)CMe{=}CMe_2\}]$ (1.438−1.521 Å).[9] The shorter Fe−C(4) distance (1.859 (5) Å) indicates its high double-bond character, which is comparable with the Fe−$C_{carbene}$ bond in the carbene−iron complexes $[(CO)_4Fe{=}C(OC_2H_5)C_6Cl_5]$ (1.887(4) Å),[10] $[(\eta^4\text{-}C_{10}H_{16})(CO)_2Fe{=}C(OC_2H_5)C_6H_4CH_3\text{-}o\}]$ (1.915(15) Å),[11] and $[\{(\eta^4\text{-}C_6H_5CH{=}CH)CH(C_6H_4CH_3\text{-}m)N(C_6H_5)C(OC_2H_5){=}\}Fe(CO)_2]$ (1.918(3) Å).[12] The C(16), N, C(4), and Fe atoms are coplanar with a C(16)−N−C(4) angle of 176.1(4)° and N−C(4)−Fe angle of 178.9(4)°, which shows that the C(16)−N−C(4)−Fe fragment is almost linear; thus, the C(16), N, C(4), and Fe atoms form a conjugate chain.

The structure of **6** resembles that of **5**. This investigation was carried out in order to extend the scope of the structural data available for the (carbonylcyanometal)−carbene complexes. In **6**, the Re−C(16) bond length of

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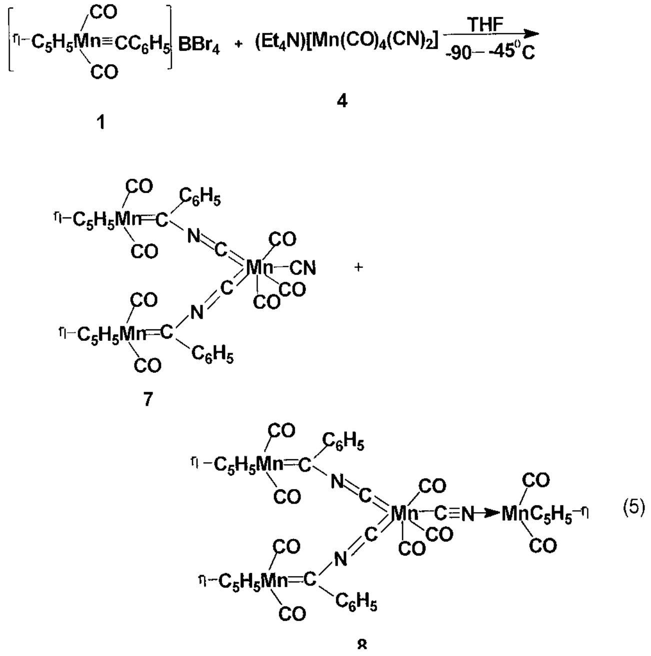
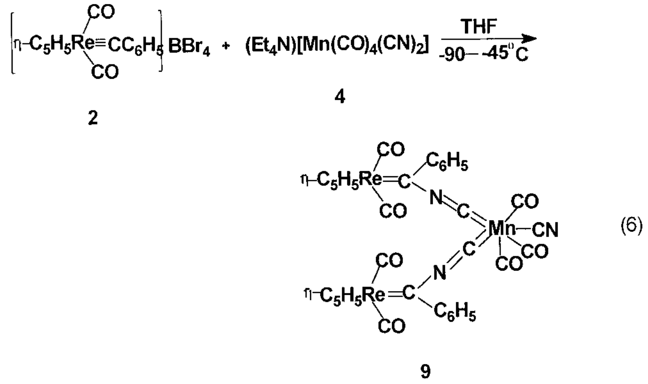
1.99(1) Å, which signifies a high double-bond character, is nearly the same as those of the Re$-$C$_{carbene}$ bond in the analogous carbene complexes [(η-C_5H_5)(CO)$_2$Re$=$C(C_6H_5)NCW(CO)$_5$] (1.96(1) Å)[1] and [(η-C_5H_5)(CO)$_2$Re$=$C(OC_2H_5)C_6H_5] (1.990(5) Å).[13] Similar to the case for **5** and [(η-C_5H_5)(CO)$_2$Re$=$C(C_6H_5)NCW(CO)$_5$], the two C$-$N bond distances in **6** are very different as well. The C(4)$-$N (1.17(2) Å) and C(16)$-$N (1.42(2) Å) bonds are nearly the same as those in **5** and [(η-C_5H_5)(CO)$_2$Re$=$C(C_6H_5)NCW(CO)$_5$] (C(8)$-$N = 1.16(1), C(9)$-$N = 1.40(1) Å).[1] As in **5**, the C(16)$-$N$-$C(4)$-$Fe chain is a nearly linear conjugate system.

Interestingly, the reaction of a carbonylmetal anion compound containing two CN groups, Et_4N[Mn(CO)$_4$(CN)$_2$] (**4**), with complex **1** under the same conditions gave the novel trinuclear dicarbene$-$manganese complex [{(η-C_5H_5)(CO)$_2$Mn$=$C(C_6H_5)NC}$_2$Mn(CO)$_3$CN] (**7**) and the tetranuclear dicarbene$-$manganese complex [{(η-C_5H_5)(CO)$_2$Mn$=$C(C_6H_5)NC}$_2$Mn(CO)$_3$CNMn(CO)$_2$(η-C_5H_5)] (**8**) (eq 5) in reasonable yields, respectively. Complex **2** reacts similarly with **4** to give the trinuclear dicarbene$-$rhenium complex [{(η-C_5H_5)(CO)$_2$Re$=$C(C_6H_5)NC}$_2$Mn(CO)$_3$CN] (**9**) (eq 6) in 69% yield.





The formation of complexes **7** and **9** could proceed via an attack of the (CO)$_4$(CN)Mn$=$C$=$N$^-$ anion, a representation of the electronic structure of the $^-$Mn(CO)$_4$(CN)$_2$ anion, on the carbyne carbon of cationic carbyne complex **1** or **2** to form the unstable carbene intermediate [(η-C_5H_5)(CO)$_2$M$=$C(C_6H_5)NCMn(CO)$_4$CN] (M = Mn, Re), similar to that of complexes **5** and **6**. This unstable intermediate was then converted into an [(η-C_5H_5)(CO)$_2$M$=$C(C_6H_5)NCMn(CO)$_3$(CN)$_2$]$^-$ (M = Mn, Re) anion by losing a CO ligand from the Mn(CO)$_4$CN moiety and abstracting a CN group from another molecule of (Et_4N)[Mn(CO)$_4$(CN)$_2$]. Subsequently, the [(η-C_5H_5)(CO)$_2$M$=$C(C_6H_5)NC(CO)$_3$(CN)Mn$=$C$=$N$^-$] anion, a representation of the electronic structure of [(η-C_5H_5)(CO)$_2$M$=$C(C_6H_5)NCMn(CO)$_3$(CN)$_2$]$^-$, attacked the carbyne carbon of another molecule of **1** or **2** to yield eventually the product **7** or **9**, while the formation of **8** might involve initial formation of the dicarbene intermediate complex [{(η-C_5H_5)(CO)$_2$Mn$=$C(C_6H_5)NC}$_2$Mn(CO)$_3$CN] (**7**). Then the N atom of its CN group coordinates to the Mn atom of the "(η-C_5H_5)Mn(CO)$_2$" moiety generated by loss of the carbyne ligand from **1** and provides two electrons for the Mn atom to satisfy an 18-electron configuration.

Complexes **7**$-$**9** are readily soluble in polar organic solvents. They are sensitive to air and temperature in solution but relatively stable as the solid. The formulas shown in eqs 5 and 6 for **7**$-$**9** were established by elemental analysis and spectroscopic data (Experimental Section). Surprisingly, complex **9** contains one molecule of Br(CH_2)$_4$OH, which cannot be separated from **9**, like the shadow following a person. It is not clear how the Br(CH_2)$_4$OH molecule is formed. We suppose that it might form by a ring-opening reaction of the solvent THF (C_4H_8O) companied by abstraction of a hydrogen from THF and a bromide ion from the BBr_4^- species during a reaction such as that in the reaction of **2** with (Et_4N)$_2$[Fe_2(CO)$_8$] giving [(η-C_5H_5)(CO)$_2$BrReCH$_2C_6H_5$].[13] The source of the H atom could be either the solvent THF itself or water, which is a trace contaminant in solvent THF, in the reactions[1,14] of **2** with (Et_4N)$_2$[Fe_2(CO)$_8$] and Na_2W(CO)$_5$ to form the bridging carbene complexes [ReFe{μ-C(H)C_6H_5}(CO)$_6$(η-C_5H_5)] and [ReW{μ-C(H)C_6H_5}(CO)$_7$(η-C_5H_5)], respectively. The existence of the Br(CH_2)$_4$OH molecule in **9** was initially revealed by its ^{1}H NMR and mass spectra. The ^{1}H NMR spectrum of **9** showed two sets of the signals attributed to the methylene protons at 3.60$-$3.50 and 1.90 ppm and a signal due to the hydroxy (OH) proton at 2.25 ppm, while the mass spectrum of **9** showed a peak at m/e 152 assigned to the Br(CH_2)$_4$OH molecular ion.

The structures of the complexes **7**$-$**9** have been strongly confirmed by X-ray diffraction studies. The structures are shown in Figures 3$-$5, respectively. The principal structural fragment [{(η-C_5H_5)(CO)$_2$Mn$=$C(C_6H_5)NC}$_2$Mn(CO)$_3$CN] of **8** is nearly the same as **7**, as illustrated by the following parameters. The M$-$C$_{carbene}$ bond distances Mn(2)$-$C(16) and Mn(3)$-$C(28), respectively, are 1.866(6) and 1.872(7) Å for **7** and 1.871(10) and 1.865(9) Å for **8**. Both distances in **7** and **8** signify a high double-bond character and are the same within experimental error as that found (1.868(4) Å) in **5**. The C(4)$-$N(1) and C(5)$-$N(2) distances are 1.162-

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(7), 1.164(7) Å and 1.16(1), 1.15(1) Å for **7** and **8**, respectively, very close to that of the corresponding bond in **5**, while the C(16)−N(1) and C(28)−N(2) distances are 1.418(8) and 1.390(8) Å for **7** and 1.42(1) and 1.44(1) Å for **8**. The distances of the Mn(1) atom to the C(4) and C(5) atoms, 1.925(7) and 1.927(7) Å for **7** and 1.933(10) and 1.93(1) Å for **8**, which indicates some double-bond character of the Mn(1)−C(4) and Mn(1)−C(5) bonds in both complexes, are somewhat shorter than the Mn(1)−C(6) distance of 2.002(9) Å for **7** and 1.979(10) Å for **8**. As in complexes **5** and **6**, the C(16)−N(1)−C(4)−Mn(1) and C(28)−N(2)−C(5)−Mn(1) fragments in **7** and **8** are almost linear conjugate chains. The angles between the two conjugate chains are 88.0(3) and 85.4(4)° for **7** and **8**, respectively. In **8**, the C(6)−N(3) bond length (1.154(10) Å), which is slightly longer than that found (1.129(9) Å) in **7**, is a normal C≡N distance and is the same within experimental error as those in the similar complexes [$(\eta\text{-}C_5H_5)(CO)_2Mn{=}C(C_6H_5)CNW(CO)_5$] (1.15(1) Å)[1] and [$(PPh_3)_2N][Fe(CO)_4CN$] (1.147(7) Å).[15] Complex **8** appears to be the first example of a species with a CN−Mn bond studied by X-ray crystallography and, hence, comparison of the Mn−N(CN) bond distance with others involving these elements is not possible. However, the Mn(4)−N(3) distance of 1.970(8) Å in **8** is markedly shorter than the Mn−N distances in [$C_6H_4CH_2N(CH_3)_2Mn(CO)_4$] (2.139(3) Å)[16] and [$Mn(CO)_3(C_5H_5N)_2(O_2CCF_3)$] (2.086−2.110 Å).[17] This suggests that the Mn(4)−N(3) bond in **8** is a more strongly coordinating bond. Thus, the molecule of **8** is a stable conjugate system.

The X-ray structure of **9** confirmed that there exists one molecule of $Br(CH_2)_4OH$ in the molecule of **9**. The configuration of **9** resembles that of **7**, as can be visualized in the ORTEP diagrams of **7** and **9** represented in Figures 3 and 5, respectively. In **9** the Re−$C_{carbene}$ distances are 2.00(2) and 1.99(2) Å for Re−C(16) and Re(3)−C(28), respectively, which are essentially the same as that (1.99(1) Å) in **6**. The C(16)−N(1) bond length (1.41(2) Å) is longer than that of C(28)−N(2) (1.37(2) Å), while the C(4)−N(1) distance of 1.16(2) Å is essentially the same as that of C(5)−N(2) (1.15(2) Å) but is slightly longer than that of C(6)−N(3) (1.13(2) Å). The distances of Mn(1) to the C(4) and C(5) atoms are 1.93(2) and 1.97(2) Å, respectively; both are somewhat shorter than that of Mn(1) to C(6) (2.01(2) Å). The bond angle data indicate that the C(16)−N(1)−C(4)−Mn(1) and C(28)−N(2)−C(5)−Mn(1) chains in **9** are nearly linear conjugate chains with an angle of 89.6(7)° between them.

The title reaction shows that the reactions of the cyano-containing carbonylmetal anionic compounds with the cationic carbyne complexes of manganese and rhenium give (carbonylcyanoiron)carbene−manganese and −rhenium complexes or (carbonylcyanomanganese)dicarbene−manganese and −rhenium complexes, and these products are related to metal cyanide complexes. The metal cyanide complexes have been examined extensively and can be used as synthetic building blocks for syntheses of heterocycles.[18] The title reaction may represent a new route to such metal cyanide complexes and further indicates that the different carbonylmetal anions exert great influence on the reactivity of the cationic carbyne complexes and resulting products.

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Supporting Information Available: Tables of the positional parameters and temperature factors, H atom coordinates, anisotropic displacement parameters, all bond lengths and angles, and least-squares planes for **5**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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