Novel Reactions of Cationic Carbyne Complexes of Manganese and Rhenium with $(Ph_3P)_2NW(CO)_5NCO$, $(Ph_3P)_2NW(CO)_5SCN$, and $NaW(CO)_5CN$

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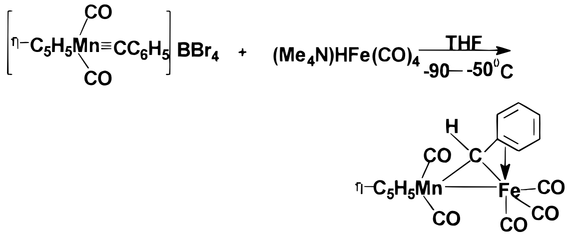
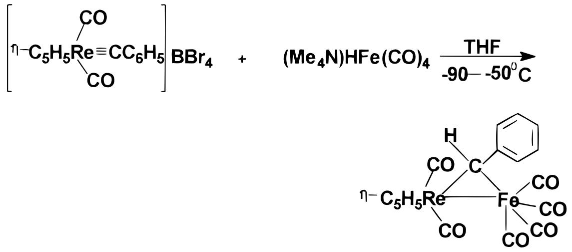
The reaction of a cationic carbyne complex of manganese, $[\eta\text{-}C_5H_5(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ (**1**), with $(Ph_3P)_2NW(CO)_5NCO$ (**3**) in THF at low temperature gave the novel chelated carbene complex $[\eta\text{-}C_5H_4(CO)_2Mn{=}C(NHC{=}O)C_6H_5]$ (**6**). The analogous reaction of a cationic carbyne complex of rhenium, $[\eta\text{-}C_5H_5(CO)_2Re{\equiv}CC_6H_5]BBr_4$ (**2**), with **3** afforded the azametallacyclic complex $[\eta\text{-}C_5H_5(CO)_2ReC(C_6H_5)(C{=}O)NW(CO)_5]$ (**7**). The reaction between **1** and $(Ph_3P)_2NW(CO)_5SCN$ (**4**) led to the loss of a sulfur atom to give the phenyl(pentacarbonylisocyanotungsten)carbene−manganese complex $[\eta\text{-}C_5H_5(CO)_2Mn{=}C(C_6H_5)CNW(CO)_5]$ (**8**). However, the reaction of **2** with **4** afforded the (isothiocyanato)phenylcarbene−rhenium complex $[\eta\text{-}C_5H_5(CO)_2Re{=}C(C_6H_5)SCN]$ (**9**). Complexes **1** and **2** react with $NaW(CO)_5CN$ (**5**) to produce novel phenyl(pentacarbonylcyanotungsten)carbene−manganese and −rhenium complexes, $[\eta\text{-}C_5H_5(CO)_2Mn{=}C(C_6H_5)NCW(CO)_5]$ (**10**) and $[\eta\text{-}C_5H_5(CO)_2Re{=}C(C_6H_5)NCW(CO)_5]$ (**11**), respectively. The structures of **6**, **7**, **8**, and **11** have been established by X-ray diffraction studies.

Introduction

The synthesis, structure, and chemistry of metal carbene and dimetal bridging carbene complexes are areas of current interest, stemming from the possible involvement of these species in some reactions catalyzed by organometallic compounds.[1,2] We have previously shown the reactions of the cationic carbyne complexes of manganese and rhenium $[\eta\text{-}C_5H_5(CO)_2M{\equiv}CC_6H_5]BBr_4$ (M = Mn, Re) with carbonyliron dianions such as $Na_2Fe(CO)_4$, $(NEt_4)_2Fe_2(CO)_8$, and $Na_2Fe_3(CO)_{11}$ to yield dimetal bridging carbene complexes.[3,4] This is a new route to dimetal bridging carbene complexes. We have recently reported the reactions of cationic carbyne complexes of manganese and rhenium with $(NMe_4)HFe(CO)_4$ to form the heteronuclear dimetal bridging carbene complexes $[MnFe\{\mu\text{-}C(H)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ and $[ReFe\{\mu\text{-}C(H)C_6H_5\}(CO)_6(\eta\text{-}C_5H_5)]$ (eqs 1 and 2), respectively, in which a negative hydrogen migrated from the Fe atom of the $HFe(CO)_4$ moiety to the bridging carbene carbon with the bonding of the Fe atom to the Mn or Re atom to construct a ferracyclopropane ring.[5] We are now interested in examining the transformation of the negative substituent and the effect of the carbonylmetal anions containing negative substituents such as NCO, SCN, and CN groups on the reactivities of the cationic carbyne complexes and the resulting products. Thus, we chose $(Ph_3P)_2NW(CO)_5NCO$ (**3**), $(Ph_3P)_2NW(CO)_5SCN$ (**4**), and $NaW(CO)_5CN$ (**5**) as the nucleophiles for the reactions with the cationic carbyne complexes of manganese and rhenium $[\eta\text{-}C_5H_5(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ (**1**) and $[\eta\text{-}C_5H_5(CO)_2Re{\equiv}CC_6H_5]BBr_4$ (**2**). These reactions afford the novel chelated metal carbene complex, azametallacyclic compound, or (pentacarbonylisocyanotungsten)carbene and (pentacarbonylcyanotungsten)carbene complexes of manganese and rhenium. Herein we describe these novel reactions and the structures of the resulting products.



(1)



(2)

Experimental Section

All reactions were performed under a dry, oxygen-free N_2 atmosphere by using standard Schlenk techniques. All solvents

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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) was distilled from CaH_2 and CH_2Cl_2 from P_2O_5. The neutral SiO_2 (Scientific Adsorbents Inc., 40 μm Flash) used for chromatography was deoxygenated at room temperature under high vacuum for 12 h and stored under N_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 [η-$C_5H_5(CO)_2Mn{\equiv}CC_6H_5$]$BBr_4$ (**1**)[6] and [η-$C_5H_5(CO)_2Re{\equiv}CC_6H_5$]$BBr_4$ (**2**)[7] were prepared as previously described. The compounds $(Ph_3P)_2NW(CO)_5NCO$ (**3**),[8] $(Ph_3P)_2NW(CO)_5SCN$ (**4**),[9] and $NaW(CO)_5CN$ (**5**)[10] 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 pointings obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

Reaction of [η-$C_5H_5(CO)_2Mn{\equiv}CC_6H_5$]$BBr_4$ (1) with $(Ph_3P)_2NW(CO)_5NCO$ (3) To Give [η-$C_5H_4(CO)_2Mn{=}C(NHC{=}O)C_6H_5$] (6). To 0.35 g (0.39 mmol) of $(Ph_3P)_2NW(CO)_5NCO$ dissolved in 50 mL of THF at −90 °C was added portionwise 0.24 g (0.40 mmol) of **1** with vigorous stirring. Immediately the orange-red solution turned red. The reaction mixture was stirred at −90 to −45 °C for 4−5 h, during which time the red solution turned gradually dark red. After the resulting solution was evaporated under high vacuum at −50 to −45 °C to dryness, the dark red residue was chromatographed on a silica gel column (1.6 × 15 cm) at −25 °C with petroleum ether/CH_2Cl_2 (10:1) as the eluant. After elution of a small yellow band from the column, an orange-red band was eluted with petroleum ether/CH_2Cl_2/Et_2O (10:1:1) 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 0.092 g (74%, based on **1**) of red crystals of **6**: mp 88−89 °C dec; IR (CH_2Cl_2) ν(CO) 1963 (vs), 1902 (vs) cm^{-1}, ν(C=O) 1717 (s) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.49 (m, 3H, C_6H_5), 7.43 (m, 2H, C_6H_5), 5.79 (m, 2H, C_5H_4), 5.06 (m, 2H, C_5H_4), 3.64 (m, 1H, NH); MS *m/e* 307 (M^+), 279 (M^+ − CO), 251 (M^+ − 2CO), 224 (M^+ − 3CO + 1). Anal. Calcd for $C_{15}H_{10}O_3NMn$: C, 58.65; H, 3.28; N, 4.60. Found: C, 58.16; H, 3.50; N, 4.80.

Reaction of [η-$C_5H_5(CO)_2Re{\equiv}CC_6H_5$]$BBr_4$ (2) with 3 To Give [η-$C_5H_5(CO)_2ReC(C_6H_5)(C{=}O)NW(CO)_5$] (7). To 0.38 g (0.53 mmol) of **2** dissolved in 50 mL of THF at −90 °C was added 0.38 g (0.53 mmol) of **3** with vigorous stirring. Immediately the orange solution turned orange-red. The reaction mixture was stirred at −90 to −45 °C for 5−6 h, during which time the orange-red solution turned gradually dark red. The resulting solution was evaporated under high vacuum at −50 to −45 °C to dryness. The dark red residue was chromatographed on a silica gel column with petroleum ether/CH_2Cl_2 (5:1) followed by petroleum ether/CH_2Cl_2/Et_2O (2:1:1). A red band was eluted and collected. After vacuum removal of the solvent, the crude product was recrystallized from petroleum ether/CH_2Cl_2 solution at −80 °C to afford 0.32 g (80%, based on **2**) of deep red crystals of **7**: mp 86−87 °C dec; IR (CH_2Cl_2) ν(CO) 2066 (w), 2039 (s), 1974 (s), 1924 (vs), 1882 (sh) cm^{-1}, ν(C=O) 1721 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.70 (m, 1H, C_6H_5), 7.54 (m, 3H, C_6H_5), 7.32 (m, 1H, C_6H_5), 6.24 (s, 5H, C_5H_5); MS *m/e* 734 (M^+ − CO), 334 [$C_5H_5Re(CO)_3^+$], 250 [$CNW(CO)_5^+$], 224 [$W(CO)_5^+$]. Anal. Calcd for $C_{20}H_{10}O_8NReW$: C, 31.51; H, 1.32; N, 1.84. Found: C, 31.80; H, 1.45; N, 1.86.

Reaction of 1 with $(Ph_3P)_2W(CO)_5SCN$ (4) To Give [η-$C_5H_5(CO)_2Mn{=}C(C_6H_5)CNW(CO)_5$] (8). Similar to the procedures for the reaction of **1** with **3**, compound **1** (0.43 g, 0.73 mmol) was treated with 0.67 g (0.73 mmol) of $(Ph_3P)_2W(CO)_5SCN$ at −90 to −45 °C for 4 h; during this time the orange-yellow solution gradually turned purple-red. The solvent was removed at −45 to −40 °C in vacuo. The blackish green residue was chromatographed on SiO_2 at −25 °C with petroleum ether/CH_2Cl_2 (5:1) as the eluant. A blue-purple band was eluted and collected. The solvent was removed, and the residue was recrystallized from petroleum ether/CH_2Cl_2 solution at −80 °C to yield 0.31 g (70%, based on **1**) of dark purple-red crystalline **8**: mp 119−120 °C dec; IR (CH_2Cl_2) ν(CO) 2055 (m), 1956 (s), 1917 (vs, br) cm^{-1}, ν(CN) 2072 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.73 (m, 2H, C_6H_5), 7.44 (m, 3H, C_6H_5), 5.12 (s, 5H, C_5H_5); MS *m/e* 615 (M^+, based on ^{184}W), 559 (M^+ − 2CO), 503 (M^+ − 4CO), 475 (M^+ − 5CO), 447 (M^+ − 6CO), 419 (M^+ − 7CO). Anal. Calcd for $C_{20}H_{10}O_7NMnW{\cdot}CH_2Cl_2$: C, 36.03; H, 1.73; N, 2.00. Found: C, 36.46; H, 1.77; N, 2.56.

Reaction of 2 with 4 To Give [η-$C_5H_5(CO)_2Re{=}C(C_6H_5)SCN$] (9). In a manner similar to the procedure described for the reaction of **1** with **4**, compound **2** (0.28 g, 0.39 mmol) was treated with 0.35 g (0.39 mmol) of $(Ph_3P)_2W(CO)_5SCN$ at −90 to −45 °C for 9 h; during this time the orange-red solution gradually turned dark red. The solvent was removed at −45 to −40 °C in vacuo. The dark residue was chromatographed on Al_2O_3 (neutral) at −25 °C with petroleum ether/CH_2Cl_2 (5:1) as the eluant. An orange-red band was eluted and collected. The solvent was removed, and the residue was recrystallized from petroleum ether/CH_2Cl_2 solution at −80 °C to give 0.11 g (64%, based on **2**) of dark red crystalline **9**:[11] mp 90−91 °C dec; IR (CH_2Cl_2) ν(CO) 1970 (vs), 1902 (vs) cm^{-1}, ν(CN) 2081 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.79 (m, 2H, C_6H_5), 7.57 (m, 1H, C_6H_5), 7.34 (m, 2H, C_6H_5), 6.02 (s, 5H, C_5H_5); MS *m/e* 455 (M^+, based on ^{185}Re), 427 (M^+ − CO), 399 (M^+ − 2CO). Anal. Calcd for $C_{15}H_{10}O_2NSRe$: C, 39.64; H, 2.22; N, 3.08. Found: C, 39.66; H, 2.16; N, 3.04.

Reaction of 2 with KSCN To Give 9. To a solution of **2** (0.23 g, 0.32 mmol) in 50 mL of THF at −90 °C was added 0.031 g (0.32 mmol) of KSCN with stirring. Immediately the orange solution turned orange-red. The reaction mixture was stirred at −90 to −45 °C for 6 h, during which time the orange-red solution turned gradually dark red. Further treatment of the resulting solution in a manner similar to that described in the reaction of **1** with $(Ph_3P)_2NW(CO)_5SCN$ afforded 0.13 g (92%, based on **2**) of dark red crystals of **9**, which was identified by its melting point and IR and ^1H NMR spectra.

Reaction of 1 with $NaW(CO)_5CN$ (5) To Give [η-$C_5H_5(CO)_2Mn{=}C(C_6H_5)NCW(CO)_5$] (10). Compound **1** (0.518 g, 0.87 mmol) was treated, in a manner similar to that described in the reaction of **1** with **3**, with 0.324 g (0.87 mmol) of $NaW(CO)_5CN$ (**5**) at −90 to −45 °C for 6 h. The resulting purple-red mixture was evaporated to dryness under high vacuum at −50 to −40 °C. The dark purple-red residue was chromatographed on Al_2O_3 with petroleum ether/CH_2Cl_2 (10:1) as the eluant. A purple band was eluted and collected. After vacuum removal of the solvent, the crude product was recrystallized from petroleum ether/CH_2Cl_2 solution at −80 °C to give 0.39 g (89%, based on **1**) of dark purple-red crystals of **10**: mp 108−109 °C dec; IR (CH_2Cl_2) ν(CO) 2054 (w), 2030 (m), 1951 (vs, br) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.95 (m, 2H, C_6H_5), 7.56 (m, 3H, C_6H_5), 5.44 (s, 5H, C_5H_5); MS *m/e* 615 (M^+, based on ^{184}W), 559 (M^+ − 2CO), 503 (M^+ − 4CO), 475 (M^+ − 5CO), 447 (M^+

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Table 1. Crystal Data and Experimental Details for Complexes $6\cdot{}^1/_2C_6H_6$, 7, 8, and 11

	$6\cdot{}^1/_2C_6H_6$	7	8	11
formula	$C_{18}H_{13}O_3NMn$	$C_{20}H_{10}O_8NReW$	$C_{20}H_{10}O_7NMnW$	$C_{20}H_{10}O_7NReW$
fw	346.24	762.36	615.09	746.36
space group	$P2_1/n$ (No. 14)	$P4_12_1$ (No. 92)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	9.631(3)	9.580(3)	11.064(2)	11.212(9)
b (Å)	10.997(6)		11.147(3)	11.279(5)
c (Å)	14.532(3)	46.01(2)	9.483(4)	9.488(4)
α (deg)			113.98(2)	113.85(3)
β (deg)	92.23(2)		99.31(2)	101.16(5)
γ (deg)			74.56(1)	73.90(5)
V (Å^3)	1538.0(10)	4222(2)	1028.1(5)	1049(1)
Z	4	8	2	2
d_{calcd} (g/cm^3)	1.495	2.398	1.987	2.361
cryst size (mm)	0.10 × 0.22 × 0.20	0.15 × 0.20 × 0.25	0.25 × 0.22 × 0.20	0.15 × 0.20 × 0.20
μ (Mo Kα) (cm^{-1})	8.72	112.29	62.51	112.85
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)
diffractometer	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R
temp (°C)	20	20	20	20
orientation rflns: no.; range (2θ) (deg)	18; 10.3−19.8	15; 13.6−15.8	21; 14.2−21.4	19; 16.1−25.9
scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
data collecn range, 2θ (deg)	5−45	5−45	5−49.7	5−49.9
total no. of unique data	1702	1281	2714	2779
no. of data with $I > 2.50\sigma(I)$	718 ($I > 2.00\sigma(I)$)	1025	2265 ($I > 3.00\sigma(I)$)	2287
no. of params refined	194	180	271	272
cor factors, max min	0.7877−1.0000	0.9256−1.1630	0.7329−1.0000	0.4887−1.0000
R^a	0.068	0.042	0.032	0.031
$R_w{}^b$	0.064	0.045	0.040	0.037
quality-of-fit indicator^c	1.66	1.42	1.57	1.72
largest shift/esd in final cycle	0.01	0.00	0.00	0.03
largest peak (e/Å^3)	0.44	1.26	1.30	1.45
minimum peak, (e/Å^3)	−0.50	−0.91	−1.26	−1.16

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

− 6CO), 419 (M$^+$ − 7CO). Anal. Calcd for $C_{20}H_{10}O_7NMnW$: C, 39.05; H, 1.64; N, 2.27. Found: C, 38.86; H, 1.68; N, 2.16.

Reaction of 2 with 5 To Give $[\eta\text{-}C_5H_5(CO)_2Re{=}C(C_6H_5)NCW(CO)_5]$ (11). The reaction of 0.306 g (0.42 mmol) of **2** with 0.157 g (0.42 mmol) of **5** was as described in the reaction of **2** with **3** at −90 to −45 °C for 6 h, during which time the orange-red solution turned dark red. Further treatment of the resulting mixture as described for the reaction of **1** with **5** afforded 0.28 g (92%, based on **2**) of **11** as dark purple-red crystals: mp 120−121 °C dec; IR (CH_2Cl_2) ν(CO) 2053 (m), 2032 (s), 1951 (vs, br) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.99 (m, 2H, C_6H_5), 7.59 (m, 3H, C_6H_5), 6.09 (s, 5H, C_5H_5); MS m/e 745 (M$^+$, based on ^{185}Re and ^{184}W), 717 (M$^+$ − CO), 605 (M$^+$ − 5CO). Anal. Calcd for $C_{20}H_{10}O_7NReW$: C, 31.19; H, 1.35; N, 1.88. Found: C, 30.96; H, 1.38; N, 1.91.

X-ray Crystal Structure Determinations of Complexes 6, 7, 8, and 11. Single crystals of complexes **6**, **7**, **8**, and **11** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH_2Cl_2 or petroleum ether/benzene solution at −80 °C. Single crystals were mounted on glass fibers and sealed with epoxy glue. The X-ray diffraction intensity data for 1702, 1281, 2714, and 2779 independent reflections, of which 718 with $I > 2.00\sigma(I)$ for **6**, 1025 and 2287 with $I > 2.50\sigma(I)$ for **7** and **11**, and 2265 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° ≤ 2θ ≤ 45° for **6** and **7**, 5° ≤ 2θ ≤ 49.7° for **8**, and 5° ≤ 2θ ≤ 49.9° for **11**, respectively.

The structures of **6**, **7**, **8**, and **11** were solved by direct methods and expanded using Fourier techniques. For **6** and **7**, some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. The hydrogen atoms were included but not refined. For **8** and **11**, the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included but not refined. The final cycles of full-matrix least-squares refinement were respectively based on 718, 1025, 2265, and 2287 observed reflections and 194, 180, 271, and 272 variable parameters and converged with unweighted and weighted agreement factors of R = 0.068 and R_w = 0.064 for **6**, R = 0.042 and R_w = 0.045 for **7**, R = 0.032 and R_w = 0.040 for **8**, and R = 0.031 and R_w = 0.037 for **11**, respectively. All the calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp.

Table 2. Selected Bond Lengths (Å)^a and Angles (deg)^a for Complexes 6 and 7

Complex **6**			
Mn−C(9)	1.89(2)	N−C(8)	1.33(2)
Mn−C(6)	1.75(2)	N−C(9)	1.40(2)
Mn−C(7)	1.83(2)	C(8)−C(20)	1.50(2)
C(9)−C(10)	1.47(2)	O(8)−C(8)	1.24(2)
Mn−C(9)−C(10)	131(1)	Mn−C(20)−C(8)	110(1)
Mn−C(9)−N	116(1)	C(9)−Mn−C(20)	81.8(7)
N−C(9)−C(10)	112(1)	O(8)−C(8)−C(20)	123(1)
C(8)−N-C(9)	118(1)	Mn−C(6)−O(6)	178(2)
N−C(8)−C(20)	113(1)	Mn−C(7)−O(7)	177(2)
O(8)−C(8)−N	123(1)	C(9)−C(10)−C(11)	121(1)
Complex **7**			
Re−C(8)	2.16(3)	C(8)−O(8)	1.24(4)
Re−C(9)	2.09(3)	C(9)−C(10)	1.49(4)
N−C(8)	1.43(4)	Re−C(6)	1.86(4)
N−W	2.27(2)	Re−C(7)	1.98(4)
N−C(9)	1.30(3)	W−C(1)	2.11(3)
Re−C(9)−N	106(6)	Re−C(9)−C(10)	133(2)
C(8)−Re−C(9)	57(1)	N−C(9)−C(10)	119(2)
Re−C(8)−N	99(2)	O(8)−C(8)−N	126(2)
C(8)−N−C(9)	96(2)	W−N−C(8)	122(1)
Re−C(8)−O(8)	134(2)	W−N−C(9)	140(1)

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

The details of the crystallographic data and the procedures used for data collection and reduction information for **6**, **7**, **8**, and **11** are given in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3, respectively. The atomic coordi-

Table 3. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complexes 8 and 11

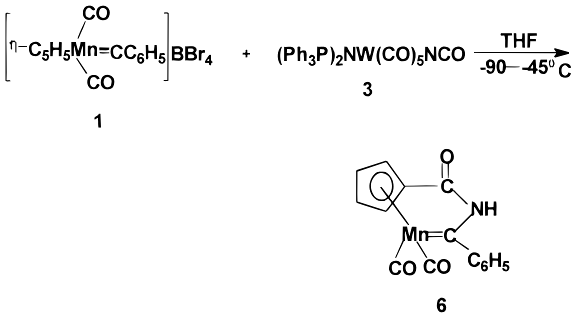
	8 (M = Mn)	**11** (M = Re)		**8** (M = Mn)	**11** (M = Re)
M−C(9)	1.897(8)	1.96(1)	N−W	2.161(8)	
N−C(9)		1.40(1)	C(8)−W		2.13(1)
C(8)−C(9)	1.44(1)		M−C(6)	1.80(1)	1.89(1)
C(9)−C(10)	1.48(1)	1.52(1)	M−C(7)	1.80(1)	1.90(1)
N−C(8)	1.15(1)	1.16(1)	W−C(1)	2.05(1)	2.03(1)
M−C(9)−C(8)	113.1(6)		C(8)−N−C(9)		176.8(10)
M−C(9)−N		117.4(6)	W−N−C(8)	171.9(7)	
M−C(9)−C(10)	134.2(6)	135.0(7)	W−C(8)−N		175.6(9)
C(8)−C(9)−C(10)	111.6(7)		M−C(6)−O(6)	177.9(10)	178(1)
N−C(9)−C(10)		106.6(8)	M−C(7)−O(7)	178.0(9)	176(1)
N−C(8)−C(9)	176.9(9)		C(9)−C(10)−C(11)	121.0(8)	123.2(9)

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

nates and B_{iso}/B_{eq} values, anisotropic displacement parameters, all bond lengths and angles, and least-squares planes for **6**, **7**, **8**, and **11** are given in the Supporting Information. The molecular structures of **6**, **7**, **8**, and **11** are given in Figures 1−4, respectively.

Results and Discussion

The complex [η-$C_5H_5(CO)_2Mn{\equiv}CC_6H_5$]$BBr_4$ (**1**) was treated with an equimolecular quantity of $(Ph_3P)_2NW(CO)_5NCO$ (**3**) in THF at low temperature (−90 to −45 °C) for 4−5 h. After removal of the solvent under high vacuum, the residue 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 novel chelated carbene complex [η-$C_5H_4(CO)_2Mn{=}C(NHC{=}O)C_6H_5$] (**6**) in 74% yield (eq 3). The analogous reaction of [η-$C_5H_5(CO)_2Re{\equiv}CC_6H_5$]$BBr_4$ (**2**) with **3** under the same conditions afforded the azametallacyclic complex [η-$C_5H_5(CO)_2ReC(C_6H_5)(C{=}O)NW(CO)_5$] (**7**) (eq 4) in 80% yield.



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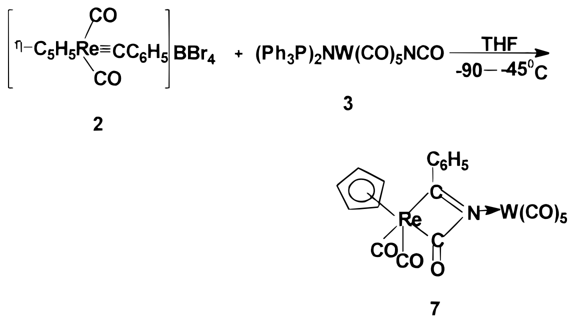

(4)

Complexes **6** and **7** are readily soluble in polar organic solvents but sparingly soluble in nonpolar solvents. They are sensitive to air and temperature in solution but relatively stable in the solid state. The formulas shown in eqs 3 and 4 for complexes **6** and **7** were established by elemental analysis and IR, ^{1}H NMR, and mass spectra (Experimental Section). Both structures have been confirmed by X-ray diffraction studies as well. The results of the X-ray diffraction work of complexes **6** and **7** are summarized in Table 1, and the structures are shown in Figures 1 and 2, respectively.

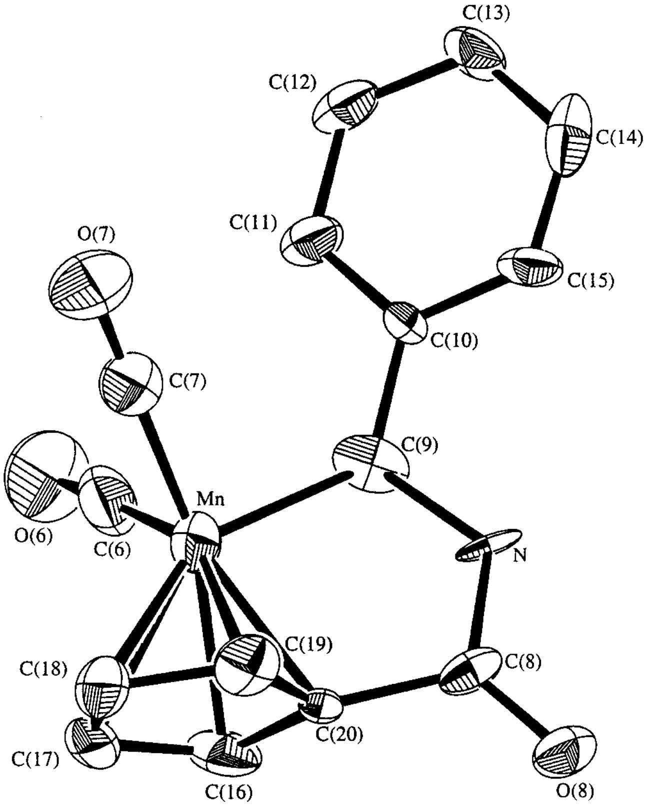

Figure 1. Molecular structure of **6**, showing the atom-numbering scheme.

In complex **6**, the Mn−C(9) distance is 1.89(2) Å, which signifies some double-bond character, and is the same within experimental error as those in the analogous carbene complexes [$C_5H_5\{(\eta^5$-$C_6H_6)(CO)_2Mn{=}C(OC_2H_5)C_6H_5\}$] (1.89(1) Å)[12] and [$C_5H_5\{(\eta^5$-$C_6H_6)(CO)_2$-$Mn{=}C(OC_2H_5)C_6H_4CH_3$-$o\}$] (1.881(4) Å)[12] but slightly longer than that in [$Mn(\eta^5$-$C_5H_5)(CO)_2\{C(OEt)Ph\}$] (1.865(4) Å).[13] The C(9)−N bond length of 1.40(2) Å is somewhat shorter than a normal C−N distance but is significantly longer than the corresponding C−N bond found in the analogous carbene complexes [$(CO)_4Fe{=}$

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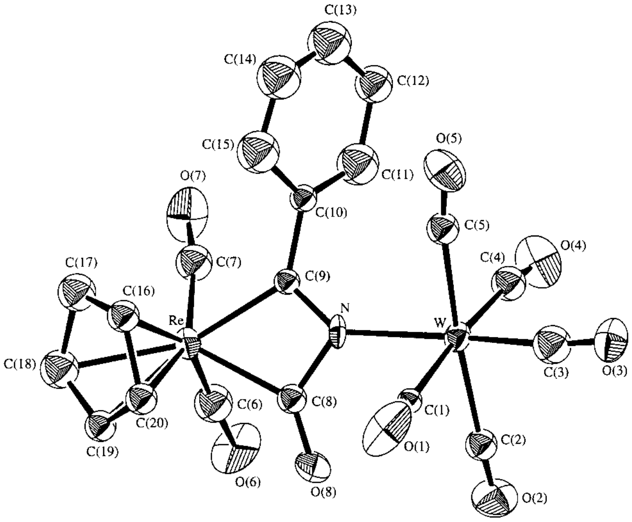

Figure 2. Molecular structure of **7**, showing the atom-numbering scheme.

$C(OEt)N^iPr_2]$ (1.326(4) Å),[14] $[(CO)_3Fe\{C(N^iPr_2)OCO(C_2H_5)\}]$ (1.329(7) Å),[14] and $[cis\text{-}(CO)_4W\{C(N^iPr_2)OEt\}_2]$ (1.340(12) Å),[15] arising from the ring tension. The other unusual feature is the C(8)−N bond length (1.33(2) Å) of the HNC═O group, which is the same within experimental error as a normal C═N distance. Both the C(9)−N and the C(8)−N bond lengths are obviously different from those found in the analogous chelated carbene complex $[(\eta^4\text{-}C_6H_5CH{=}CH)CH(\mu\text{-}CH_3C_6H_4)N(C_6H_5)C(OC_2H_5){=}]Fe(CO)_2$,[16] where the corresponding C(2)−N and C(12)−N distances are 1.329(4) and 1.474(4) Å,[16] respectively. The shorter C(8)−N distance in **6** signifies a double-bond character between the C(8) and N atoms. The Mn atom lies essentially in the plane composed of O(8), C(8), N, and C(9) (0.014 Å). The C_5H_4 ring plane is oriented at an angle of 90.54° with respect to the O(8)C(8)NC(9) plane; thus, the C_5H_4 ring and O(8)C(8)NC(9) planes are perpendicular to each other. The angle of 87.76° between the benzene ring and the C_5H_4 ring plane shows that the benzene ring plane is almost perpendicular to the C_5H_4 ring plane. The angle between the benzene ring and the O(8)C(8)NC(9) planes is 27.55°.

In complex **7**, the Re−C(8) and Re−C(9) bond lengths are 2.16(3) and 2.09(3) Å, respectively, which are slightly longer than the $Re{-}C_{carbene}$ distance found in the carbene complex $[\eta\text{-}C_5H_5(CO)_2Re{=}C(OC_2H_5)C_6H_5]$ (1.990(5) Å)[3] but significantly shorter than the Re−C σ-bond found in the complex $[\eta\text{-}C_5H_5(CO)_2BrReCH_2C_6H_5]$ (Re−C(3) = 2.315(6) Å).[3] This might be caused by the ring shrinkage. The C(8)−N bond length of 1.43(4) Å is much longer than that in **6**, while the C(9)−N distance of 1.30(3) Å is markedly shorter than that of **6**. The shorter C(9)−N distance signifies a high double-bond character. The W atom is coplanar with the Re, N, C(8), and C(9) atoms. The W−N distance of 2.27(2) Å is the same within experimental error as that of the corresponding W−N bond in $[(CO)_5CrPPh_3(CO)_2(2,2'\text{-}bipy)WCNEt_2]$ (2.22−2.25 Å)[17] and comparable with those in W(mpd) (mpd = 2-mercaptopyrimidinato) (2.16−2.17 Å)[18] and pentacarbonyl(4-phenyl-1,2,3-thiadiazole)tungsten (2.322(7) Å).[19] However, the W−N distance is somewhat longer than the corresponding W−N bond length in $[W{-}N(Bu^tCMe_2(Me)(NBu^t)\{N(Bu^t)CMe{=}CMe_2\}]$ (1.907−1.940 Å)[20] and is obviously longer than the W═N bond distance in $[W{-}N(Bu^tCMe_2(Me)(NBu^t)\{N(Bu^t)CMe{=}CMe_2\}]$ (1.757(12) Å),[20] which indicates that the W−N bond in **7** is a weaker coordinating bond.

The reaction pathways to complexes **6** and **7** are not yet clear. However, the formation of **6** might involve initial formation of the ^-NCO anion arising from breakage of the $^-W(CO)_5NCO$ anion; then, the ^-NCO anion attacks at the carbyne carbon of **1** with bonding of the N atom to the carbene carbon C(9) and the carbon atom C(8) to the cyclopentadienyl ring C(20) to form a chelated manganese carbene complex accompanied by migration of a hydrogen atom from the cyclopentadienyl ring to the N atom. Analogous results have been observed in the reactions of the cationic manganese carbyne complexes $[Cp(CO)_2Mn{\equiv}CR]^+$ (R = Ph, Tol) with imines Ph(H)C═NR′ (R′ = Me, −N═(H)Ph), which give the chelated carbene complexes $[\eta\text{-}C_5H_4(CO)_2Mn{=}C(R)N(R')C(H)Ph]$, in which the imine carbon has been coupled to the cyclopentadienyl ligand.[21,22] Similar metallacyclic carbene complexes $[\eta\text{-}C_5H_4(CO)_2Mn{=}C(NR_2)N{=}CPh]$ (R = Me, Et, i-Pr, i-Bu) have also been obtained[22,23] in the reaction between the cationic manganese carbyne complex $[Cp(CO)_2Mn{\equiv}CPh]^+$ and dialkylcyanamides $N{\equiv}CNR_2$.

The formation of **7** could involve initial formation of the carbene intermediate complex $[\eta\text{-}C_5H_5(CO)_2Re{=}C(C_6H_5)W(CO)_5NCO]$, where the $W(CO)_5NCO$ moiety is directly bonded to the carbene carbon through the W atom. Then the N═C bond of the NCO group is opened to respectively bond to the carbene carbon and the Re atom through the N atom and C(8) atom with dissociation of the $C_{carbene}{-}W$ bond, resulting in formation of an azametallacyclobutene ring. A similar intermediate has been observed in the reactions of the tungsten carbene complex $[(CO)_5W{=}C(R^1)C_6H_5]$ (R^1 = Ph, OMe) with carbodiimides $R^2N{=}C{=}NR^2$ (R^2 = *i*-Pr, c-Hex).[24] The reaction pathway to complex **7** is very similar to that of the reaction of the cationic rhenium carbyne complex $[Cp(CO)_2Re{\equiv}CTol]^+$ with imines Ph(H)C═NR (R = Me, −N═CHPh) to give the four-membered metallaazacycles $[Cp(CO)_2ReC(Tol)NRC(H)Ph]$, in which the nucleophilic nitrogen atom attacks the electrophilic

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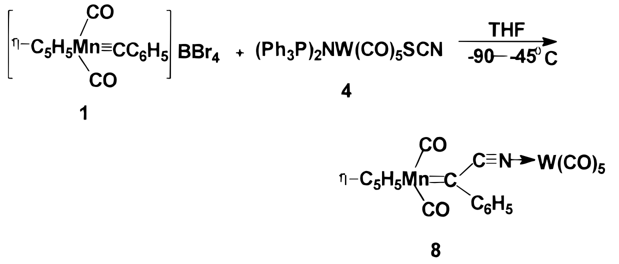
carbyne carbon.[21,22] The new carbene fragment then coordinates intramolecularly to the unsaturated metal center, thus forming a four-membered metallacycle in which the double bond is delocalized.

Surprisingly, the reaction of compound **1** with $(Ph_3P)_2NW(CO)_5NCS$ (**4**) under similar conditions led to loss of the sulfur atom to give the phenyl(pentacarbonylisocyanotungsten)carbene–manganese complex [η-$C_5H_5(CO)_2Mn{=}C(C_6H_5)CNW(CO)_5$] (**8**) in 70% yield (eq 5), whose structure has been established by X-ray diffraction analysis. However, the reaction between compounds **2** and **4** under the same conditions gave no analogous product but rather the (isothiocyanato)phenylcarbene–rhenium complex **9**[11] in 64% yield (eq 6). The latter reaction showed that the SCN group was dissociated from the $W(CO)_5SCN$ moiety and bonded to the carbyne carbon of **1** to form carbene complex **9**. This was confirmed by the reaction of **2** with KSCN under the same conditions, which yields the same product **9** in 92% yield (eq 7). Complex **9** is a known compound and was obtained by Fischer and co-workers in the reaction of [η-$C_5H_5(CO)_2Re{\equiv}CC_6H_5$]$BCl_4$ with LiSCN, in lower yield (35%).[11]



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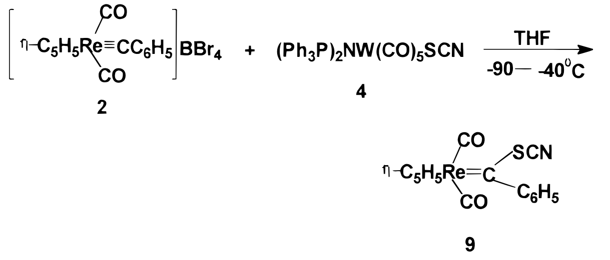


(6)

$$2 \quad + \quad \mathrm{KSCN} \xrightarrow[-90-\ -50^{\circ}C]{\mathrm{THF}} 9 \qquad (7)$$

The molecular structure of complex **8** is shown in Figure 3. The Mn–C(9) bond length of 1.897(8) Å is the same as that found (1.89(2) Å) in chelated carbene complex **6**. The C(9)–C(8) distance is 1.44(1) Å, which is between the normal C–C and C=C distances and indicates that there exists certain double-bond character in the C(9)–C(8) bond. The C(8)–N bond length (1.15(1) Å) is a normal C≡N distance, which is the same within experimental error as that in [$(PPh_3)_2N$][$Fe(CO)_4CN$] (1.147(7) Å).[25] The W–N distance (2.161(8) Å) in **8** is somewhat shorter than that found (2.27(2) Å) in **7**. The C(9), C(8), N, and W atoms are coplanar, and the angles C(9)–C(8)–N and C(8)–N–W are 176.9(9) and 171.9(7)°, respectively, which signifies that the C(9)–C(8)–N–W fragment is nearly linear; thus, the C(9)–C(8)–N–W chain is a conjugate system.

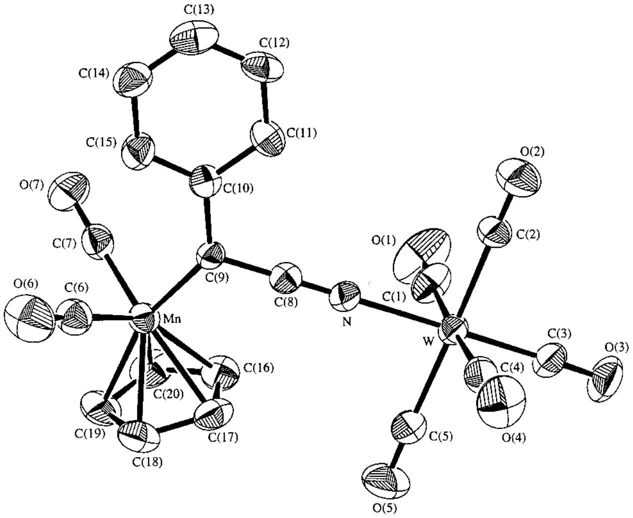
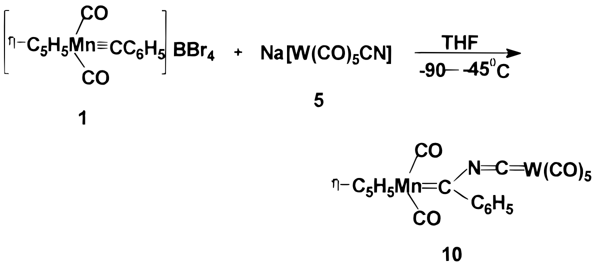


Figure 3. Molecular structure of **8**, showing the atom-numbering scheme.

It is not yet clear how the sulfur atom is lost and how the $^{-}CNW(CO)_5$ species becomes bonded to the carbene carbon atom during the reaction. We suppose that the formation pathway of complex **8** might involve initial formation of a "$(CO)_5WN{\equiv}C-$" species derived from loss of the sulfur atom of the $W(CO)_5NCS$ moiety, which then attacks at the carbyne carbon of **1**. We cannot exclude the possibility that a possible alternate formation pathway could proceed via a ^{-}CN anion produced by either loss of the sulfur atom from the SCN group or loss of the $W(CO)_5$ moiety from the $^{-}CNW(CO)_5$ species. The ^{-}CN anion attacks at the carbyne carbon to produce the carbene intermediate [η-$C_5H_5(CO)_2Mn{=}C(C_6H_5)CN$]; 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.

Interestingly, the reaction of $NaW(CO)_5CN$, where the negative CN group is directly bonded to the W atom, with complexes **1** and **2** gave the novel phenyl(pentacarbonylcyanotungsten)carbene–manganese and –rhenium complexes [η-$C_5H_5(CO)_2Mn{=}C(C_6H_5)NCW(CO)_5$] (**10**) (eq 8) and [$\eta$-$C_5H_5(CO)_2Re{=}C(C_6H_5)NCW(CO)_5$] (**11**) (eq 9) in 89% and 92% yields, respectively.



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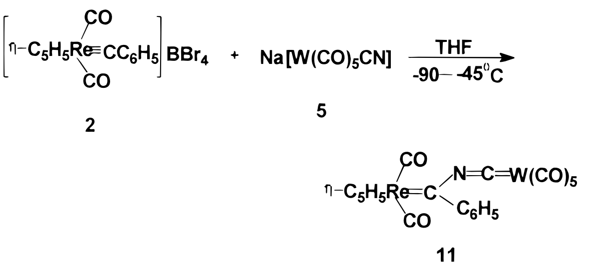

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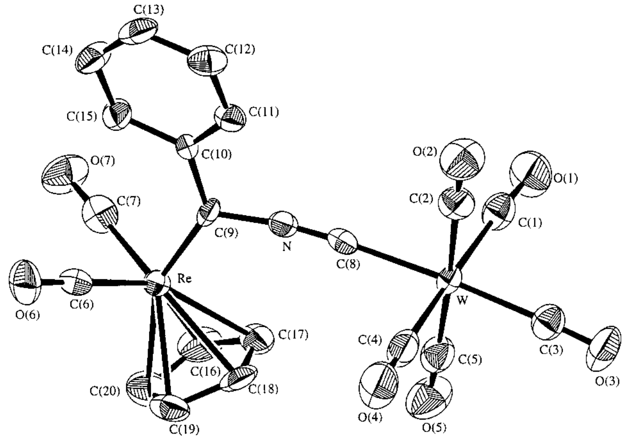

Figure 4. Molecular structure of **11**, showing the atom-numbering scheme.

The composition and structure of complexes **10** and **11** are supported by their elemental analysis and spectroscopic data and by the X-ray diffraction study of **11**. The elemental analysis and mass spectra of **10** show the same composition as complex **8**. The IR and ^{1}H NMR spectra of complex **10** are similar to those of **11** but are very different from those of **8** (see Experimental Section). The IR spectrum of **8** showed four ν(CO) stretching vibration bands at 2072, 2055, 1956, and 1917 cm^{-1}, but complexes **10** and **11** showed only three bands at ca. 2054, 2030, and 1951 cm^{-1}. The ^{1}H NMR spectrum of **8** showed two sets of proton signals attributed to the phenyl group at 7.73 and 7.44 ppm and a singlet signal attributed to cyclopentadienyl protons at 5.12 ppm, while complexes **10** and **11** showed two sets of the phenyl proton signals at ca. 7.95−7.99 and 7.56−7.59 ppm and the cyclopentadienyl proton signal at 5.44−6.09 ppm. These data indicate that the structures of complexes **10** and **11** are different from that of **8**. This has been further confirmed by the X-ray single-crystal determination of **11** (see below).

The formation of complexes **10** and **11** could proceed via attack of the $(CO)_5W{=}C{=}N^-$ anion, a representation of the same electronic structure of the $^-W(CO)_5CN$ anion, on the carbyne carbon of complexes **1** and **2**.

The structure of complex **11** resembles that of **8**, except that the substituent on the carbene carbon is a pentacarbonylcyanotungsten group in **11** but a pentacarbonylisocyanotungsten group in the latter, as can be visualized in the ORTEP diagrams of **8** and **11** represented in Figures 3 and 4. The Re−C(9) bond length of 1.96(1) Å signifies a high double-bond character and is nearly the same as that in the analogous carbene complex [η-$C_5H_5(CO)_2Re{=}C(OC_2H_5)C_6H_5$] (1.990(5) Å).[3] The two C−N bond lengths in **11** are very different. C(8)−N has a bond length of 1.16(1) Å, which exhibits high triple-bond character and is essentially the same as that found (1.15(1) Å) in **8** and is comparable with that of the corresponding C−N bond in [$Fe_2(\mu$-$CNEt)_3(CNEt)_6$] (1.13−1.19 Å).[25] The other, C(9)−N, has a bond distance of 1.40(1) 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^{t}CMe$_2$(Me)-(NBu^t){N(Bu^t)CMe=CMe$_2$}] (1.438−1.521 Å).[20] The shorter W−C(8) distance (2.13(1) Å) indicates a high double-bond character of the W−C(8) bond. This distance is comparable with the W−C$_{\text{carbene}}$ bond distance in the analogous carbene complexes [$(CO)_5W{=}C(OC_2H_5)$-$C_5H_4RuC_5H_5$] (2.23(2) Å)[26] and [*cis*-$(CO)_4W\{C(N^iPr_2)$-$OEt\}_2$] (2.30 Å)[15] but is markedly longer than the W−C$_{\text{carbyne}}$ bond distance in the carbyne complex [$(CO)_5CrPPh_2(CO)_2(2,2'$-bipy)$WCNEt_2$] (1.877(8) Å).[17] The C(9), N, C(8), and W atoms are coplanar with a C(9)−N−C(8) angle of 176.8(10)° and a N−C(8)−W angle of 175.6(9)°, which shows that the C(9)−N−C(8)−W fragment is almost linear; thus, the C(9), N, C(8), and W atoms form a conjugate chain.

The title reaction shows that the reactions of carbonyltungsten anions containing NCO, SCN, and CN groups with cationic carbyne complexes of manganese and rhenium, **1** and **2**, give the unexpected cyano-containing monometal carbene complexes or azametallacyclic compounds, instead of the expected dimetal bridging carbene complex having a negative substituent on the bridging carbene carbon, and these compounds are related to metal cyanide complexes. The metal cyanide complexes have been examined extensively and can be used as synthons for syntheses of heterocycles.[27] Carbonylmetal anions containing halogen such as $^-W(CO)_5Br$, $^-Cr(CO)_5I$, and $^-Co_4(CO)_{11}I$ do not react with complexes **1** and **2** under the same conditions. The reaction results show a variety of reactions between carbonylmetal anions and the cationic carbyne complexes and further indicate that the different carbonylmetal anions exert great influence on the reactivity of the cationic carbyne complexes.

Acknowledgment. Financial support from the National Natural Science Foundation of China and the Science Foundation of the Chinese Academy of Sciences is gratefully acknowledged.

Supporting Information Available: Tables of positional parameters and temperature factors, H atom coordinates, anisotropic displacement parameters, all bond lengths and angles, and least-squares planes for **6**, **7**, **8**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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