*Organometallics* **2005,** *24,* 5807−5816

# Unusual Reactions of Cationic Carbyne Complexes of Manganese and Rhenium with the Carbonylmetal Anions $[Ir(CO)_4]^-$ and $[Ru(CO)_4]^{2-}$. Novel Route to Heteropolymetallic Bridging Carbyne Complexes

Lei Zhang,[†] Nu Xiao,[†] Qiang Xu,[*,‡] Jie Sun,[†] and Jiabi Chen[*,†]

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

*Received February 11, 2005*

The reaction of a cationic carbyne complex of manganese, $[(\eta^5\text{-}C_5H_5)(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ (**1**), with $[(Ph_3P)_2N][Ir(CO)_4]$ (**3**) in THF at low temperature gives a novel $Mn_2{-}Ir_2$ mixed-tetrametal bridging carbyne complex with $\mu$ and $\mu_3$ bridging carbyne ligands, $[Mn_2Ir_2(\mu\text{-}CC_6H_5)(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_3(CO)_3(\eta^5\text{-}C_5H_5)_2]$ (**5**), and a related $Mn_2{-}Ir_2$ mixed-tetranuclear cluster with a $\mu$ bridging carbene ligand and a $\mu_3$ bridging carbyne ligand, $[Mn_2Ir_2\{\mu\text{-}C(CO)C_6H_5\}(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_3(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (**6**). A cationic carbyne complex of rhenium, $[(\eta^5\text{-}C_5H_5)(CO)_2Re{\equiv}CC_6H_5]BBr_4$ (**2**), reacts similarly with **3** to afford the corresponding $Re_2{-}Ir_2$ mixed-tetrametal cluster $[Re_2Ir_2\{\mu\text{-}C(CO)C_6H_5\}(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_3(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (**8**) and a novel $Re{-}Ir_2$ mixed-trimetal bridging carbyne complex with an allyl ligand, $[ReIr_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C_3H_5)(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_2(CO)_4(\eta^5\text{-}C_5H_5)]$ (**7**). The cationic carbyne complex **1** also reacts with the anionic compound $Na_2[Ru(CO)_4]$ (**4**) to give a heterotrimetal bridging carbyne complex with a $\mu$-H ligand, $[MnRu_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta^5\text{-}C_5H_5)]$ (**10**), and the manganese aminocarbene complex $[(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}C(C_6H_5)NH_2]$ (**11**), while the analogous reaction of the cationic carbyne complex **2** with **4** produces a novel $Re_2{-}Ru_2$ mixed-tetrametal cluster with a $\mu_3\text{-}C(CC_6H_5)(\mu\text{-}CC_6H_5)$ bridging carbene ligand, $[Re_2Ru_2\{\mu_3\text{-}C(CC_6H_5)(\mu\text{-}CC_6H_5)\}(\mu\text{-}CO)(CO)_8(\eta^5\text{-}C_5H_5)_2]$ (**13**), in addition to the corresponding heterotrimetal bridging carbyne complex $[ReRu_2(\mu_3\text{-}CC_6H_5)(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)]$ (**12**) and aminocarbene complex $[\eta^5\text{-}C_5H_5(CO)_2Re{=}C(C_6H_5)NH_2]$ (**14**). The structures of complexes **6**, **7**, **11**, **13**, and **14** have been established by X-ray diffraction studies.

## Introduction

It is well-known that mixed-metal-bonded cluster complexes play important roles in a variety of homogeneous catalytic reactions.[1] Since many dinuclear and polynuclear metal bridging carbene and carbyne complexes, where the metal atoms are directly bonded to each other, are themselves metal clusters or are the precursors of metal cluster complexes, the chemistry of transition-metal bridging carbene and carbyne complexes is an area of current interest. The first heterobimetallic carbyne complexes were synthesized by Fischer's group[2] in the 1970s, and a considerable number of heteronuclear di- and trimetal bridging carbyne complexes have been synthesized by Stone and coworkers.[3] In recent years, several new routes to di- and trimetal bridging carbene and carbyne complexes, which were carried out by the reactions of the cationic metal carbyne complexes with metal carbonyl anions, have been developed in our laboratory. One of the synthetic methods for trimetal bridging carbyne complexes is to conduct reactions[4,5] of highly electrophilic cationic carbyne complexes of manganese and rhenium, $[(\eta^5\text{-}C_5H_5)(CO)_2M{\equiv}CC_6H_5]BBr_4$ (**1**, M = Mn; **2**, M = Re), with di- or polymetal carbonyl anions of group VIII such as $[Fe_2(\mu\text{-}CO)(\mu\text{-}SeC_4H_9\text{-}n)(CO)_6]^-$, $[M_3(CO)_{11}]^{2-}$ (M = Ru, Os), and $[Fe_4(CO)_{13}]^-$. Recently, in a communication[6] we reported an unusual approach to polymetallic bridging carbyne complexes: the reactions of cationic carbyne complexes of manganese and rhenium, **1** and **2**, with the monoanionic metal carbonyl compound $[(Ph_3P)_2N][Rh(CO)_4]$ gave novel heteronuclear polymetal clusters

---

[†] Shanghai Institute of Organic Chemistry.

[‡] National Institute of Advanced Industrial Science and Technology.

(1) (a) Norton, J. H. In *Fundamental Research in Homogeneous Catalysis*; Tsutsui, M., Ugo, R., Eds.; Plenum Press: New York, 1977; Vol. 1, p 99. (b) Suess-Fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993**, *35*, 41. (c) Gladfelter, W. L.; Roesselet, K. J. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: Weinheim, Germany, 1990; p 392. (d) Braunstein, P.; Rose, J. In *Comprehensive Organometallic Chemistry*, 2nd ed.; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 10, Chapter 7, pp 351−385.

(2) Fischer, E. O.; Lindner, T. L.; Kreissl, F. R.; Braunstein, P. *Chem. Ber.* **1977**, *110*, 3139.

(3) (a) Stone, F. G. A. *Pure Appl. Chem.* **1986**, *58*, 529. (b) Busetto, L.; Green, M.; Howard, J. A. K.; Hessner, B.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 1101. (c) Busetto, L.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Went, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1984**, 101. (d) Jeffery, J. C.; Lewis, D. B.; Lewis, G. E.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1985**, 2001.

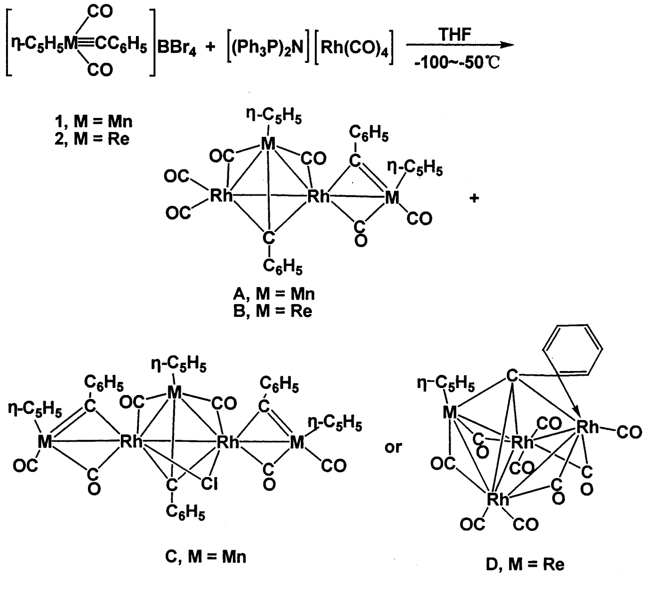
(4) Chen, J.-B.; Wang, R.-T. *Coord. Chem. Rev.* **2002**, *231*, 109.

(5) (a) Wang, R.-T.; Xu, Q.; Souma, Y.; Song, L.-C.; Sun, J.; Chen, J.-B. *Organometallics* **2001**, *20*, 2226. (b) Xiao, N.; Xu, Q.; Tsubota, S.; Sun, J.; Chen, J.-B. *Organometallics* **2002**, *21*, 2764.

(6) Zhang, L.; Zhu, B.-H.; Xiao, N.; Xu, Q.; Tsumori, N.; Sun, J.; Yin, Y.-Q.; Chen, J.-B.; *Organometallics* **2003**, *22*, 4369.

10.1021/om058008a CCC: $30.25

with $\mu$ and a $\mu_3$ bridging carbyne ligands, **A** and **B**, and the related polymetal cluster compound **C** or **D** (eq 1).



(1)

On the other hand, it was found that the different metal carbonyl anions involving those of the same group exhibit a different reactivity toward the cationic metal carbyne complexes and their reactions give different products.[4,7] To develop this new synthetic method for the preparation of polymetallic bridging carbyne complexes and further examine the reactivity of different carbonylmetal anions of group VIII toward the cationic carbyne complexes and their reaction products, we investigated the reactions of cationic carbyne complexes **1** and **2** with the monoanionic carbonyliridium compound $[(Ph_3P)_2N][Ir(CO)_4]$ and the dianionic carbonylruthenium compound $Na_2[Ru(CO)_4]$. These reactions yield a number of novel heteronuclear polymetallic bridging carbyne complexes and related polymetallic clusters or bridging carbene complexes. In this paper, we report these unusual reactions and the structures of the resulting products.

## Experimental Section

All reactions were performed under a dry, oxygen-free $N_2$ atmosphere using standard Schlenk techniques. All solvents employed were of reagent grade and were dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under $N_2$. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl, while petroleum ether (30−60 °C) and $CH_2Cl_2$ were distilled from $CaH_2$. Neutral alumina ($Al_2O_3$) was deoxygenated under high vacuum for 16 h, deactivated with 5% w/w $N_2$-saturated water, and stored under $N_2$. The compounds $[(\eta^5\text{-}C_5Me_5)Re(CO)_3]$ and $NaNH_2$ were purchased from Aldrich Chemical Co. The complexes $[(\eta^5\text{-}C_5H_5)(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ (**1**)[8a] and $[(\eta^5\text{-}C_5H_5)(CO)_2Re{\equiv}CC_6H_5]BBr_4$ (**2**)[8b] were prepared as previously described. The complex $[(\eta^5\text{-}C_5Me_5)(CO)_2Re{\equiv}CC_6H_5]BBr_4$ (**2-Cp***) was prepared[8] in a manner similar to that for complexes **1** and **2** from $[(\eta^5\text{-}C_5Me_5)(CO)_2Re{=}C(OC_2H_5)C_6H_5]$, which itself was prepared in a manner similar to that for $[(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(OC_2H_5)C_6H_4CF_3\text{-}p]$[9] from $[(\eta^5\text{-}C_5Me_5)Re(CO)_3]$. The compounds $[(Ph_3P)_2N][Ir(CO)_4]$ (**3**)[10] and $Na_2[Ru(CO)_4]$ (**4**)[11] were prepared by literature methods.

The IR spectra were measured on a Perkin-Elmer 983G spectrophotometer. All $^1H$ NMR and $^{13}C$ NMR spectra were recorded in acetone-$d_6$ at ambient temperature with TMS as the internal reference using a Bruker AM-300 spectrometer. However, the $^{13}C$ NMR spectra for all of the compounds were not obtained, due to their sensitivity to temperature and/or poor solubility. 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 $[(\eta^5\text{-}C_5H_5)(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ (1) with $[(Ph_3P)_2N][Ir(CO)_4]$ (3) To Give $[Mn_2Ir_2(\mu\text{-}CC_6H_5)(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_3(CO)_3(\eta^5\text{-}C_5H_5)_2]$ (5) and $[Mn_2Ir_2\{\mu\text{-}C(CO)C_6H_5\}(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_3(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (6).** To 0.52 g (0.87 mmol) of freshly prepared compound **1** dissolved in 60 mL of THF previously cooled to −100 °C was added 0.75 g (0.89 mmol) of $[(Ph_3P)_2N][Ir(CO)_4]$ (**3**). The solution turned immediately from blackish brown to brown. The reaction mixture was stirred at −100 to −50 °C for 4 h, during which time the brown solution turned dark purple. The resulting mixture was evaporated to dryness under high vacuum at −50 to −45 °C, and the dark purple residue was chromatographed on an alumina (neutral, 100−200 mesh) column (1.6 × 15−25 cm) at −25 °C with petroleum ether/$CH_2Cl_2$ (2:1) as the eluant. The blue-green band which eluted first was collected, and then a blackish band was eluted with petroleum ether/$CH_2Cl_2$/$Et_2O$ (2:1:0.5). The solvents were removed from the above two eluates under vacuum at −20 °C, and the residues were recrystallized from petroleum ether/$CH_2Cl_2$ solution at −80 °C. From the first fraction, 0.20 g (22%, based on **1**) of dark red crystals of **6** was obtained: mp 133−135 °C dec; IR ($CH_2Cl_2$) $\nu$(CO) 2077 (vs), 2027 (s), 2014 (sh), 1977 (m), 1941 (vs, br),-1889 (s, br), 1835 (m), 1759 (w) cm$^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.74−7.60 (m, 3H, $C_6H_5$), 7.46−7.44 (m, 2H, $C_6H_5$), 7.24−7.18 (m, 3H, $C_6H_5$), 7.16−7.00 (m, 2H, $C_6H_5$), 5.53 (m, 1H, $CH_2Cl_2$), 4.98 (s, 2H, $C_5H_5$), 4.87 (d, 2H, $C_5H_5$), 4.71(d, 3H, $C_5H_5$), 4.50 (d, 3H, $C_5H_5$); MS *m/e* 595 $[MnIr_2(CC_6H_5)(C_5H_5)]^+$, 506 $[MnIr_2(C_5H_5)]^+$, 204 $[Mn(CO)_3(C_5H_5)]^+$, 176 $[Mn(CO)_2(C_5H_5)]^+$, 148 $[Mn(CO)(C_5H_5)]^+$, 84 ($CH_2Cl_2^+$). Anal. Calcd for $C_{32}H_{20}O_8Mn_2Ir_2{\cdot}0.5CH_2Cl_2$: C, 36.50; H, 1.93. Found: C, 36.14; H, 2.16. From the second fraction, 0.45 g (56%, based on **1**) of blackish green cryatalline **5** was obtained: mp >250 °C dec; IR ($CH_2Cl_2$) $\nu$(CO) 2041 (vs), 1994 (vs, br), 1803 (s, br), 1759 (m) cm$^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.62−7.59 (m, 2H, $C_6H_5$), 7.47−7.42 (m, 3H, $C_6H_5$), 7.21−7.16 (m, 3H, $C_6H_5$), 7.03−6.99 (m, 2H, $C_6H_5$), 5.65 (m, 1H, $CH_2Cl_2$), 5.33 (s, 2H, $C_5H_5$), 5.24 (d, 2H, $C_5H_5$), 4.67 (d, 3H, $C_5H_5$), 4.62 (d, 3H, $C_5H_5$); MS *m/e* 595 $[MnIr_2(CC_6H_5)(C_5H_5)]^+$, 571 $[MnIr_2(C_5H_5)_2]^+$, 204 $[Mn(CO)_3(C_5H_5)]^+$, 176 $[Mn(CO)_2(C_5H_5)]^+$, 84 ($CH_2Cl_2^+$). Anal. Calcd for $C_{30}H_{20}O_6Mn_2Ir_2{\cdot}0.5CH_2Cl_2$: C, 37.73; H, 2.18. Found: C, 37.70; H, 2.39.

**Reaction of $[(\eta^5\text{-}C_5H_5)(CO)_2Re{\equiv}CC_6H_5]BBr_4$ (2) with 3 To Give $[ReIr_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C_3H_5)(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_2(CO)_4(\eta^5\text{-}C_5H_5)]$ (7) and $[Re_2Ir_2\{\mu\text{-}C(CO)C_6H_5\}(\mu_3CC_6H_5)(\mu\text{-}CO)_3(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (8).** Similar to the procedures used in the reaction of **1** with **3**, freshly prepared compound **2** (0.63 g, 0.86 mmol) was treated with **3** (0.83 g, 0.98 mmol) at −100 to −50 °C for 4 h, during which time the dark green solution turned brown. After removal of the solvent in vacuo at −50 to −45 °C, the dark brown residue was chromatographed on $Al_2O_3$ at −25 °C with petroleum ether/$CH_2Cl_2$ (5:1) as the eluant. A

---

[7] Tang, Y.-Y.; Sun, J.; Chen, J.-B. *Organometallics* **2000**, *19*, 72.

[8] (a) Fischer, E. O.; Meineke, E. W.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 1140. (b) Fischer, E. O.; Chen, J.-B.; Scherzer, K. *J. Organomet. Chem.* **1983**, *253*, 231.

[9] Fischer, E. O.; Chen, J.-B.; Scherzer, K. *J. Organomet. Chem.* **1983**, *253*, 231.

[10] Garlaschelli, L.; Chini, P.; Martinengo, S. *Gazz. Chim. Ital.* **1982**, *112*, 285.

[11] Cotton, J. D.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2162.

yellow-green band was eluted first; then a blackish band was eluted with petroleum ether/$CH_2Cl_2$ (4:1). The solvents were removed from the above two eluates under vacuum, and the residues were recrystallized from petroleum ether/$CH_2Cl_2$ at −80 °C. From the first fraction, 0.055 g (22%, based on **2**) of **7** as dark yellow crystals was obtained: mp 136−138 °C dec; IR ($CH_2Cl_2$) $\nu(CO)$ 2046 (s), 2021 (s), 1985 (s), 1875 (m), 1829 (m) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.20 (m, 5H, $C_6H_5$), 5.54 (m, 1H, $CH_2Cl_2$), 5.33 (s, 5H, $C_5H_5$), 4.75 (m, 1H, $=CH$), 3.07 (m, 2H, $=CH_2$), 1.66−1.61 (m, 2H, $-CH_2$); MS *m/e* 849 [$M^+ - 4CO$], 821 [$M^+ - 5CO$], 793 [$M^+ - 6CO$], 336 $[Re(CO)_3(C_5H_5)]^+$, 308 $[Re(CO)_2(C_5H_5)]^+$, 280 $[Re(CO)(C_5H_5)]^+$, 252 $[Re(C_5H_5)]^+$, 84 ($CH_2Cl_2^+$), 41 ($C_3H_5^+$). Anal. Calcd for $C_{21}H_{14}O_6ReIr_2 \cdot CH_2Cl_2$: C, 25.96; H, 1.58. Found: C, 25.97; H, 1.61. From the second fraction, 0.251 g (41%, based on **2**) of blackish red crystals of **8** was obtained: mp 135−138 °C dec; IR ($CH_2Cl_2$) $\nu(CO)$ 2068 (vs), 2029 (vs), 2016 (vs), 1996 (m), 1932 (m), 1863 (m), 1794 (w) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.73−7.068 (m, 5H, $C_6H_5$), 5.54 (s, 5H, $C_5H_5$), 5.424 (s, 5H, $C_5H_5$); MS *m/e* 727 $[ReIr_2(CC_6H_5)(C_5H_5)]^+$, 638 $[ReIr_2(C_5H_5)]^+$, 336 $[Re(CO)_3(C_5H_5)]^+$, 308 $[Re(CO)_2(C_5H_5)]^+$, 280 $[Re(CO)(C_5H_5)]^+$. Anal. Calcd for $C_{30}H_{20}O_6Re_2Ir_2$: C, 29.81; H, 1.56. Found: C, 30.11; H, 1.35.

**Reaction of $[(\eta^5\text{-}C_5Me_5)(CO)_2Re\equiv CC_6H_5]BBr_4$ (2-Cp*) with 3 To Give $[Re_2Ir_2(\mu\text{-}CC_6H_5)(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_3(CO)_3(\eta^5\text{-}C_5Me_5)_2]$ (9).** To 0.59 g (0.75 mmol) of the complex $[(\eta^5\text{-}C_5Me_5)(CO)_2Re\equiv CC_6H_5]BBr_4$, freshly prepared (in situ) by the reaction of $[(\eta^5\text{-}C_5Me_5)(CO)_2Re{=}C(OC_2H_5)C_6H_5]$ (0.40 g, 0.78 mmol) with $BBr_3$ at −70 °C, dissolved in 60 mL of THF previously cooled to −100 °C was added 0.63 g (0.75 mmol) of **3**. The green-yellow solution was stirred at −100 to −90 °C for 1 h; during this time no color change was observed. The reaction mixture was warmed to −80 °C and stirred at −80 to −50 °C for 4 h, during which time the green solution gradually turned dark brown. The resulting mixture was evaporated to dryness under high vacuum at −50 to −45 °C, and the dark purple residue was chromatographed on $Al_2O_3$ at −25 °C with petroleum ether/$CH_2Cl_2$ (5:1) as the eluant. A brown 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 0.53 g (52%, based on **2-Cp***) of blackish cryatalline **9**: mp 108−110 °C dec; IR ($CH_2Cl_2$) $\nu(CO)$ 2021 (s), 2027 (s), 1972 (vs), 1765 (s), 1732 (m, br) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.40−7.03 (m, 10H, $2C_6H_5$), 1.99 (s, 15H, $C_5Me_5$), 1.85 (m, 15H, $C_5Me_5$); MS *m/e* 406 $[Re(CO)_3(C_5Me_5)]^+$, 378 $[Re(CO)_2(C_5Me_5)]^+$, 350 $[Re(CO)(C_5Me_5)]^+$. Anal. Calcd for $C_{40}H_{40}O_6Re_2Ir_2$: C, 34.96; H, 2.94. Found: C, 34.92; H, 3.26.

**Reaction of 1 with $Na_2[Ru(CO)_4]$ (4) To Give $[MnRu_2(\mu_3\text{-}CC_6H_5)(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)]$ (10) and $[(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}C(C_6H_5)NH_2]$ (11).** To 0.90 g (1.51 mmol) of freshly prepared compound **1** dissolved in 60 mL of THF previously cooled to −100 °C was added 0.38 g (1.50 mmol) of $Na_2[Ru(CO)_4]$ (**4**). The solution immediately turned from yellow-brown to brown-red. The reaction mixture was stirred at −100 to −50 °C for 4 h, during which time the brown-red solution turned dark brown. The resulting mixture was evaporated to dryness under vacuum at −45 to −40 °C, and the dark brown residue was chromatographed on alumina at −25 °C with petroleum ether/$CH_2Cl_2$ (5:1) as the eluant. An orange-red band which eluted first was collected, and then a yellow band was eluted with petroleum ether/$CH_2Cl_2$/$Et_2O$ (5:1:0.5). The solvents were removed from the above two eluates under vacuum at −25 °C, and the residues were recrystallized from petroleum ether/$CH_2Cl_2$ solution at −80 °C. From the first fraction, 0.27 g (47%, based on **1**) of brown-red cryatalline **10**[5b] was obtained: mp 144−146 °C dec; IR ($CH_2Cl_2$) $\nu(CO)$ 2092 (vs), 2071 (vs), 2031 (vs), 2004 (s), 1932 (m), 1839 (m) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.84−7.21 (m, 5H, $C_6H_5$), 4.68 (s, 5H, $C_5H_5$), −18.06 (s, 1H, $\mu$-H); MS *m/e* 492 $[MnRu_2(CO)_6(C_5H_5)]^+$, 464 $[MnRu_2(CO)_5(C_5H_5)]^+$, 436 $[MnRu_2(CO)_4(C_5H_5)]^+$, 204 $[Mn(CO)_3(C_5H_5)]^+$, 176 $[Mn(CO)_2(C_5H_5)]^+$, 148 $[Mn(CO)(C_5H_5)]^+$. Anal. Calcd for $C_{20}H_{11}O_8MnRu_2$: C, 37.75; H, 1.74. Found: C, 37.31; H, 1.78. From the second fraction, 0.065 g (15%, based on **1**) of orange-yellow crystals of **11** was obtained: mp 84−86°C dec; IR ($CH_2Cl_2$) $\nu(CO)$ 1930 (vs), 1857 (vs) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 9.43 (s, 1H, $NH_2$), 8.88 (s, 1H, $NH_2$), 7.34−7.06 (m, 5H, $C_6H_5$), 4.49 (s, 5H, $C_5H_5$); MS *m/e*, 281 ($M^+$), 225 [$M^+ - 2CO$]. Anal. Calcd for $C_{14}H_{12}O_2NMn$: C, 59.80; H, 4.30; N, 4.98. Found: C, 60.06; H, 4.18; N, 4.89.

**Reaction of 2 with 4 To Give $[ReRu_2(\mu_3\text{-}CC_6H_5)(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)]$ (12), $[Re_2Ru_2\{\mu_3\text{-}C(CC_6H_5)(\mu\text{-}CC_6H_5)\}(\mu\text{-}CO)(CO)_8(\eta^5\text{-}C_5H_5)_2]$ (13), and $[(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(C_6H_5)NH_2]$ (14).** To freshly prepared **2** (0.94 g, 1.29 mmol) dissolved in 60 mL of THF at −100 °C was added 0.026 g (1.00 mmol) of **4**. The reaction mixture was stirred at −100 to −50 °C for 4 h, during which time the yellow solution turned brown-red. The resulting mixture was evaporated to dryness under vacuum at −45 to −40 °C, and the dark brown residue was chromatographed on $Al_2O_3$ at −25 °C with petroleum ether/$CH_2Cl_2$ (10:1) as the eluant. An orange-red band which eluted first was collected, and then a red band was eluted with petroleum ether/$CH_2Cl_2$ (5:1), A third orange-yellow band was eluted with petroleum ether/$CH_2Cl_2$/$Et_2O$ (5:1:0.5). The solvents were removed from the above three eluates in vacuo at −20 °C, and the residues were recrystallized from petroleum ether or petroleum ether/$CH_2Cl_2$ solution at −80 °C. From the first fraction, 0.154 g (40%, based on **2**) of brown-red crystals of **12**[5b] was obtained: mp 105−107 °C dec; IR ($CH_2Cl_2$) $\nu(CO)$ 2087 (m), 2065 (vs), 2023 (vs), 2000 (s), 1926 (m), 1870 (m) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.66−7.08 (m, 5H, $C_6H_5$), 5.39 (s, 5H, $C_5H_5$), −17.47 (s, 1H, $\mu$-H); MS *m/e* 336 $[Re(CO)_3(C_5H_5)]^+$, 308 $[Re(CO)_2(C_5H_5)]^+$, 280 $[Re(CO)(C_5H_5)]^+$. Anal. Calcd for $C_{20}H_{11}O_8ReRu_2$: C, 31.30; H, 1.45. Found: C, 31.41; H, 1.56. From the second fraction, 0.120 g (20%, based on **2**) of blackish red crystals of **13** was obtained: mp 80−82 °C dec; IR ($CH_2Cl_2$) $\nu(CO)$ 2076 (m), 2065 (m), 2021 (vs), 2009 (vs), 1983 (vs), 1949 (vs), 1928 (s), 1889 (m), 1872 (m) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.49−7.19 (m, 10H, $2C_6H_5$), 5.39 (s, 10H, $2C_5H_5$), 1.29−1.09 (m, 8H, $CH_3(\mathit{CH_2})_4CH_3$), 0.86 (m, 6H, $\mathit{CH_3}(CH_2)_4\mathit{CH_3}$); MS *m/e* 336 $[Re(CO)_3(C_5H_5)]^+$, 308 $[Re(CO)_2(C_5H_5)]^+$, 280 $[Re(CO)(C_5H_5)]^+$, 86 ($C_6H_{14}^+$). Anal. Calcd for $C_{34}H_{20}O_9Re_2Ru_2 \cdot C_6H_{14}$: C, 38.96; H, 2.78. Found: C, 38.63; H, 2.48. From the third fraction, 0.061 g (13%, based on **2**) of orange crystalline **14** was obtained: mp 128−130 °C dec; IR ($CH_2Cl_2$) $\nu(CO)$ 1928 (vs), 1848 (vs) $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 9.121 (m, 2H, $NH_2$), 7.35−7.13 (m, 5H, $C_6H_5$), 5.11 (s, 5H, $C_5H_5$); MS *m/e* 412 ($M^+$), 384 [$M^+ - CO$], 356 [$M^+ - 2CO$]. Anal. Calcd for $C_{14}H_{12}O_2NRe$: C, 40.77; H, 2.93; N, 3.40. Found: C, 40.15; H, 3.02; N, 2.90.

**Reaction of 1 with $NaNH_2$ To Give 11.** To 0.52 g (0.86 mmol) of freshly prepared **1** dissolved in 60 mL of THF previously cooled to −100 °C was added 0.035 g (0.90 mmol) of $NaNH_2$. The solution turned immediately from yellow-brown to red. The mixture was stirred at −100 to −50 °C for 5 h, during which time the red solution turned dark red. The resulting mixture was evaporated to dryness under vacuum at −45 to −40 °C, and the dark residue was chromatographed on $Al_2O_3$ at −25 °C with petroleum ether/$CH_2Cl_2$ (2:1) as the eluant. An 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 0.175 g (72%, based on **1**) of yellow crystals of **11**, which was identified by its IR and $^1H$ NMR spectra.

**Reaction of 2 with $NaNH_2$ To Give 14.** To 0.39 g (0.54 mmol) of freshly prepared **2** dissolved in 60 mL of THF previously cooled to −100 °C was added 0.023 g (0.59 mmol) of $NaNH_2$. The solution turned immediately from yellow to red. The reaction mixture was stirred at −100 to −50 °C for 5 h, during which time the red solution turned dark red. The resulting mixture was evaporated to dryness under vacuum at −45 to −40 °C, and the dark residue was chromatographed on $Al_2O_3$ at −25 °C with petroleum ether/$CH_2Cl_2$ (2:1) as the eluant. An orange-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 0.172 g (78%, based on **2**) of **14** as orange crystals, which was identified by its IR and $^1H$ NMR spectra.

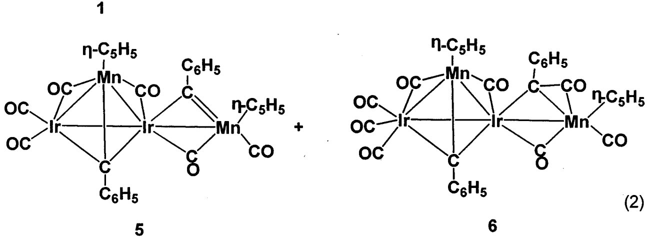
**X-ray Crystal Structure Determinations of Complexes 6, 7, 9, 11, 13, and 14.** The single crystals of complexes **6**, **7**, **9**, **11**, **13**, and **14** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether, petroleum ether/$CH_2Cl_2$, or petroleum ether/$Et_2O$ at −80 °C. Single crystals were mounted on a glass fiber and sealed with epoxy glue or placed in a sealed $N_2$-filled capillary. The X-ray diffraction intensity data of **6**, **7**, **9**, **11**, **13**, and **14** were collected with a Bruker Smart diffractometer at 20 °C using Mo Kα radiation with an $\omega-2\theta$ scan mode.

The structures of **6**, **7**, **9**, **11**, **13**, and **14** were solved by direct methods and expanded using Fourier techniques. For the six complexes, the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included but not refined. The absorption corrections were applied using SADABS. The final cycle of full-matrix least-squares refinement was based on the observed reflections and the variable parameters and converged with unweighted and weighted agreement to give agreement factors of $R = 0.0665$ and $R_w = 0.1430$ for **6**, $R = 0.0796$ and $R_w = 0.1976$ for **7**, $R = 0.0682$ and $R_w = 0.1790$ for **9**, $R = 0.0516$ and $R_w = 0.1238$ for **11**, $R = 0.0404$ and $R_w = 0.0613$ for **13**, and $R = 0.0574$ and $R_w = 0.1282$ for **14**.

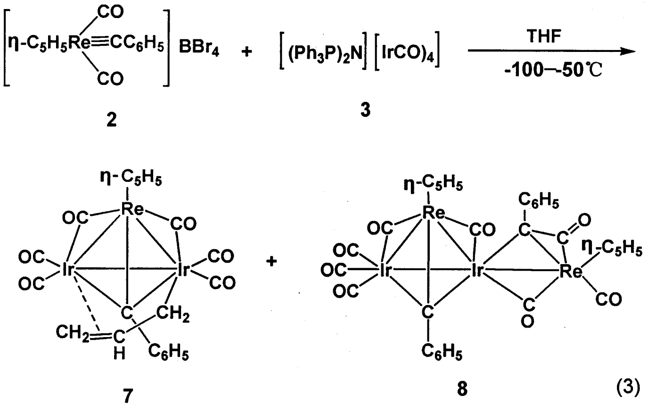
Crystallographic data and details of the procedures used for data collection and reduction information for **6**, **7**, **11**, **13**, and **14** are given in Table 1. Selected bond lengths and angles are listed in Table 2 for **6**, **7**, and **13** and in Table 3 for **11** and **14**. The molecular structures of **6**, **7**, **11**, **13**, and **14** are given in Figures 1−5, respectively. The atomic coordinates and $B_{iso}$/$B_{eq}$ values, anisotropic displacement parameters, all bond lengths and angles, and least-squares planes for **6**, **7**, **9**, **11**, **13**, and **14** are given in the Supporting Information. Crystallographic data and details of the procedures used for data collection and reduction information for **9** (Table 4) and the molecular structure of **9** (Figure 6) are also given in the Supporting Information.

## Results and Discussion

A cationic carbyne complex of manganese, $[(\eta^5\text{-}C_5H_5)(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ (**1**), was reacted with an equimolecular amount of the anionic carbonyliridium ionic compound $[(Ph_3P)_2N][Ir(CO)_4]$ (**3**) in THF at low temperature (−100 to −50 °C) for 4−5 h. After removal of the solvent under high vacuum, the residue was chromatographed on an alumina column at −25 °C and the crude products were recrystallized from petroleum ether/$CH_2Cl_2$ at −80 °C to give a novel $Mn_2-Ir_2$ mixed-tetrametal bridging carbyne complex with μ and a $\mu_3$ bridging carbyne ligands, $[Mn_2Ir_2(\mu\text{-}CC_6H_5)(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_3(CO)_3(\eta^5\text{-}C_5H_5)_2]$ (**5**), and a related $Mn_2-Ir_2$ mixed-tetranuclear cluster with a μ bridging carbene ligand and a $\mu_3$ bridging carbyne ligand, $[Mn_2Ir_2\{\mu\text{-}C(CO)C_6H_5\}(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_3(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (**6**), in 56 and 22% isolated yields, respectively (eq 2). A cationic carbyne complex of rhenium, $[(\eta^5\text{-}C_5H_5)(CO)_2Re{\equiv}CC_6H_5]BBr_4$ (**2**), reacts similarly with the anionic carbonyliridium compound **3** to afford the corresponding $Re_2-Ir_2$ mixed-tetrametal cluster $[Re_2Ir_2\{\mu\text{-}C(CO)C_6H_5\}(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_3(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (**8**) and a novel Re−$Ir_2$ mixed-trimetal bridging carbyne complex with an allyl ligand, $[ReIr_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C_3H_5)(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_2(CO)_4(\eta^5\text{-}C_5H_5)]$ (**7**), in 41 and 22% yields, respectively (eq 3), among which the structure of **7** has been confirmed by the X-ray diffraction study.



(2)



(3)

Complexes **5**−**8** are only soluble in polar organic solvents such as $CH_2Cl_2$ and THF. They are very sensitive to air and temperature in solution but relatively stable in the solid state. Elemental analyses and spectroscopic data are consistent with their compositions and assigned structures. The infrared studies of complexes **5**−**8** showed the presence of terminal and bridging carbonyl groups, and the $^1H$ NMR spectroscopic data indicated the absence of hydride protons for complexes **5**−**8**. For complex **7**, the $^1H$ NMR spectrum showed three unique resonances for the allyl ligand at δ 4.75 (m, 1H, =CH−), 3.07 (m, 2H, $=CH_2$), and 1.66−1.61 (m, 2H, $-CH_2$), in addition to the resonances for the phenyl and cyclopentadienyl protons.

The formulas of complexes **5** and **6** shown in eq 2 were based on the elemental analyses and spectral data, and the structure of **5** was established by comparison of its IR, $^1H$ NMR, and mass spectra with those of analogous complexes **A** and **B** (eq 1), while the structure of **6** has been further confirmed by a single-crystal X-ray diffraction study. The results of the X-ray diffraction work are summarized in Table 1, selected bond distances and angles are given in Table 2, and the molecular structure is shown in Figure 1.

The molecular structure of **6** revealed that the cluster compound contains the bridging carbyne unit $(\mu_3\text{-}CC_6H_5)$Mn(1)Ir(1)Ir(2) and the bridging carbene unit $\{\mu\text{-}C(CO)C_6H_5\}$Mn(2)Ir(2), in which the four metal atoms of the tetrametal framework lie in different coordination environments. In this cluster, the interactions between ligands and metals and between metals and metals provide different electron environments for the four metal atoms. In the $(\mu_3\text{-}CC_6H_5)$Mn(1)Ir(1)Ir(2) portion, the three metal atoms construct an approximately isosceles triangle (Mn(1)−Ir(1) = 2.694(3) Å, Mn(1)−Ir(2) = 2.626(3) Å, Ir(1)−Ir(2) = 2.7121(13) Å). The μ-C(7)−Mn(1), μ-C(7)−Ir(1), and μ-C(7)−Ir(2) distances are 1.996(19), 2.028(16), and 1.97(2) Å, respectively. In the $(\mu\text{-}CC_6H_5)$Mn(2)Ir(2) portion, the Mn(2)−Ir(2) bond

**Table 1. Crystal Data and Experimental Details for Complexes 6, 7, 11, 13, and 14**

| | **6**·1.5$CH_2Cl_2$ | **7** | **11** | **13**·$CH_2Cl_2$ | **14** |
|---|---|---|---|---|---|
| formula | $C_{33.5}H_{23}O_8Cl_3Mn_2Ir_2$ | $C_{21}H_{15}O_6Ir_2Re$ | $C_{14}H_{12}O_2NMn$ | $C_{35}H_{22}O_9Cl_2Re_2Ru_2$ | $C_{14}H_{12}O_2NRe$ |
| formula wt | 1154.15 | 933.93 | 281.19 | 1231.97 | 412.45 |
| space group | $P2_1/n$ (No. 14) | $P2_1/n$ (No. 14) | $Pn$ (No. 7) | $P2_1/n$ (No.14) | $P2_1/n$ (No. 14) |
| $a$ (Å) | 11.336(2) | 8.7448(8) | 6.0443(9) | 9.2216(7) | 7.6652(8) |
| $b$ (Å) | 13.548(3) | 20.6234(19) | 10.6127(15) | 33.276(3) | 14.3918(15) |
| $c$ (Å) | 23.138(5) | 12.0056(11) | 9.8443(14) | 11.4992(9) | 11.7411(12) |
| $\beta$ (deg) | 93.839(4) | 93.867(2) | 98.527(3) | 96.302(2) | 102.083(2) |
| $V$ (Å$^3$ ) | 3545.4(13) | 2160.3(3) | 624.50(16) | 3507.3(5) | 1266.5(2) |
| $Z$ | 4 | 4 | 2 | 4 | 4 |
| $D_{calcd}$ (g /cm$^3$) | 2.162 | 2.872 | 1.495 | 2.333 | 2.163 |
| $F$(000) | 2172 | 1672 | 288 | 2304 | 776 |
| $\mu$(Mo K$\alpha$) (cm$^{-1}$) | 84.54 | 179.14 | 10.48 | 79.31 | 95.86 |
| radiation | Mo K$\alpha$ (monochromated in incident beam; $\lambda$ = 0.710 73 Å) | | | | |
| diffractometer | Bruker Smart | | | | |
| temp (°C) | 20 | 20 | 20 | 20 | 20 |
| orientation rflns: range (2$\theta$) (deg) | 4.636−55.575 | 5.069−47.153 | 5.679−39.048 | 4.609−46.146 | 4.538−46.088 |
| scan method | $\omega-2\theta$ | $\omega-2\theta$ | $\omega-2\theta$ | $\omega-2\theta$ | $\omega-2\theta$ |
| data collecn range, 2$\theta$ (deg) | 3.48−51.00 | 3.94−51.00 | 3.84−55.00 | 4.32−54.00 | 4.54−55.00 |
| no. of unique data, total | 6593 | 4027 | 2244 | 7628 | 2860 |
| no. of data with $I > 2.00\sigma(I)$ | 3137 | 2909 | 1623 | 4769 | 2090 |
| no. of params refined | 412 | 272 | 163 | 446 | 172 |
| correction factors, max−min | 0.71710−1.00000 | 0.37403−1.00000 | 0.66288−1.00000 | 0.38028−1.00000 | 0.51098−1.00000 |
| $R^a$ | 0.0665 | 0.0796 | 0.0516 | 0.0404 | 0.0574 |
| $R_w{}^b$ | 0.1430 | 0.1976 | 0.1238 | 0.0613 | 0.1282 |
| quality of fit indicator$^c$ | 0.866 | 0.971 | 0.979 | 0.728 | 0.912 |
| max shift/esd, final cycle | 0.031 | 0.042 | 0.000 | 0.001 | 0.082 |
| largest peak, e/Å$^3$ | 2.123 | 5.029 | 0.489 | 1.301 | 3.051 |
| smalles peak, e/Å$^3$ | −1.587 | −2.960 | −0.272 | −0.974 | −1.972 |

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

is bridged by a $C(CO)C_6H_5$ ligand, giving a dimetallacyclopropane ring with the following dimensions: Mn(2)−Ir(2) = 2.565(3) Å, $\mu$-C(10)−Mn(2) = 2.07(2) Å, and $\mu$-C(10)−Ir(2) = 2.06(2) Å. In this portion, a unique feature of the structure is the presence of the C(26)O(8) group bonded to C(10) with a C(26)−O(8) distance of 1.30(3) Å and a C(26)−C(10) distance of 1.32(3) Å. The former distance might correspond either to a C═O or to a C≡O bond, and the latter distance suggests C═C double-bond character. Thus, the $C(CO)C_6H_5$ group in **6** might be also regarded as a ketenyl ligand, $C_6H_5C$═C═O, across the metal−metal bond.[12] Analogous structures were found in the complexes [MCo{$\mu$-C(CO)$C_6H_5$}(CO)$_5$($\eta^5$-$C_5H_5$)] (M = Mn, Re),[13] [MW{$\mu$-C(CO)$C_6H_5$}(CO)$_4$($\eta^5$-$C_5H_5$)$_2$] (M = Mn, Re),[7] and [MCo{$\mu$-C(CO)$C_6H_5$}(CO)$_4$($\eta^5$-$C_5H_5$)$_2$] (M = Mn, Re).[7] Evidently, as shown by X-ray crystallography, complex **6** is a novel cluster with a $\mu_3$ bridging carbyne unit and a bridging carbene unit (or ketene species).

The structure of complex **8** was established by elemental analysis and by comparison of its IR, $^1$H NMR, and mass spectra with those of the analogous product **6**, while the structure of complex **7** was confirmed by a single-crystal X-ray diffraction study, in addition to elemental analysis and spectral analysis. The X-ray results confirm the novel structure of **7** (Figure 2), which has a triangular $ReIr_2$ arrangement with a capping $\mu_3$-$CC_6H_5$ ligand and an allyl ligand coordinated to the two Ir atoms through the three carbon atoms. The three metal atoms $ReIr_2$ construct an approximate isosceles triangle (Re(1)−Ir(1) = 2.7906(11) Å, Re(1)−Ir(2) = 2.8062(11) Å, and Ir(1)−Ir(2) = 2.6798(12) Å). Although an analogous bridging carbyne complex with a trimetallatetrahedrane $CReFe_2$ core, [$ReFe_2$($\mu$-H)($\mu$-CO)$_2$($\mu_3$-$CC_6H_5$)(CO)$_6$($\eta^5$-$C_5H_5$)], has been prepared[5b] from cationic **2** and [$(Ph_3P)_2N$]$_2$[$Fe_4(CO)_{13}$], no analogous bridging carbyne complex with a $CReIr_2$ core has been reported. Only a W−$Ir_3$ mixed-tetrametal cluster with a bridging carbyne ligand, [$WIr_3$($\mu_3$-CPh){$\mu_3$-$\eta^4$-C(Ph)C(Ph)C(Ph)C(Ph)}($\mu$-CPh)(CO)$_5$($\eta^5$-$C_5H_4Me$)], is known.[14] Complex **7** appears to be the first example of a species with Re−$Ir_2$ and Ir−Ir bonds studied by X-ray crystallography, and hence, comparison of the Re−Ir and Ir−Ir bond distances with others involving these elements is not possible. The two Re−Ir bond lengths, 2.7906(11) and 2.8062(11) Å, respectively, are nearly the same. The Ir−Ir bond length of 2.6798(22) Å in **7** is somewhat shorter than that in the W−$Ir_3$ mixed-tetrametal bridging carbyne complex [$WIr_3$($\mu_3$-CPh){$\mu_3$-$\eta^4$-C(Ph)C(Ph)C(Ph)C(Ph)}($\mu$-CPh)(CO)$_5$($\eta^5$-$C_5H_4Me$)] (average 2.724 Å)[14] but is significantly shorter than that in the related triiridium cluster compound [$NMe_3(CH_2Ph)$][$Ir_3$($\mu$-S)$_2$(CO)$_6$] (average 3.085 Å).[15] The $\mu$-C(7)−Re, $\mu$-C(7)−Ir(1), and $\mu$-C(7)−Ir(2) distances are 2.15(2), 2.09(2), and 2.064(19) Å, respectively, of which the $\mu$-C(7)−Re bond distance is close to that found in the related complexes [ReFeCo($\mu_3$-$CC_6H_5$)($\mu$-CO)$_2$(CO)$_6$($\eta^5$-$C_5H_5$)] (2.052(8) Å)[13] and [$ReFe_2$($\mu$-H)($\mu$-CO)$_2$($\mu_3$-$CC_6H_5$)(CO)$_5$($PPh_3$)($\eta^5$-$C_5H_5$)] 2.092(7) Å),[5b] and the two $\mu$-C(7)−Ir bond lengths are nearly the same, both being shorter than those found in [$WIr_3$($\mu_3$-CPh){$\mu_3$-$\eta^4$-C(Ph)C(Ph)C(Ph)C(Ph)}($\mu$-CPh)(CO)$_5$($\eta^5$-$C_5H_4Me$)] ($\mu$-C(40)−Ir(1) = $\mu$-C(40)−Ir(2) = 2.15(1) Å).[14]

In complex **7**, as anticipated from the $^1$H NMR spectrum, an allyl group is coordinated to the Ir(1) and Ir(2) atoms through the three carbon atoms, where the C(19) and C(20) atoms are bonded to the Ir(1) atom in

---

[12] Martin-Gil, J.; Howard, J. A. K.; Navarro, R.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1979**, 1168.

[13] Tang, Y.-J.; Sun, J.; Chen, J.-B. *Organometallics* **1998**, *17*, 2945.

[14] Notaras, E. G. A.; Lucas, N. T.; Blitz, J. P.; Humphrey, M. G. *J. Organomet. Chem.* **2001**, *631*, 143.

[15] Pergola, R. D.; Garlaschelli, L. *J. Chem. Soc., Dalton Trans.* **1986**, 2463.

**Table 2. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complexes 6, 7, and 13**

| | **6** (M = Mn, M′ = Ir) | **7** (M = Re, M′ = Ir) | **13** (M = Re, M′ = Ru) |
|---|---|---|---|
| M(1)−M′(1) | 2.694(3) | 2.7906(11) | |
| M(1)−M′(2) | 2.626(3) | 2.8062(11) | 2.9115(8) |
| M′(1)−M′(2) | 2.7121(13) | 2.6798(12) | 2.7705(8) |
| M(2)−M′(1) | | | 2.9157(7) |
| M(2)−M′(2) | 2.565(3) | | 2.8305(7) |
| M(1)−C(1) | 1.80(2) | 1.91(2) | 1.871(10) |
| M(1)−C(2) | 1.795(17) | 1.88(2) | 1.889(10) |
| M(2)−C(4) | 1.92(2) | | 2.030(8) |
| M(2)−C(10) | 2.07(2) | | 2.115(6) |
| M(1)−C(7) | 1.996(19) | 2.15(2) | 2.041(7) |
| M′(1)−C(7) | 2.028(16) | 2.09(2) | 2.310(7) |
| M′(2)−C(7) | 1.97(2) | 2.064(19) | 2.064(7) |
| M′(1)−C(10) | | | 2.203(7) |
| M′(2)−C(10) | 2.06(2) | | |
| M′(2)−C(4) | 2.05(2) | | 2.046(8) |
| M′(1)−C(1) | | 2.60(2) | |
| M′(2)−C(2) | | 2.50(2) | |
| M′(1)−C(19) | | 2.19(2) | |
| M′(1)−C(20) | | 2.51(3) | |
| M′(2)−C(21) | | 2.16(2) | |
| C(26)−O(8) | | | 1.30(3) |
| C(7)−C(8) | 1.51(3) | 1.47(3) | |
| C(7)−C(11) | | | 1.420(9) |
| C(10)−C(11) | | | 1.410(9) |
| C(10)−C(29) | 1.48(3) | | 1.525(9) |
| C(11)−C(23) | | | 1.500(9) |
| C(19)−C(20) | | 1.31(6) | 1.389(13) |
| C(20)−C(21) | 1.348(19) | 1.51(5) | 1.328(13) |
| C(26)−C(10) | | | 1.32(3) |
| M(1)−M′(1)−M′(2) | 58.12(7) | 61.69(3) | |
| M(1)−M′(2)−M′(1) | 60.60(7) | 61.10(3) | 91.77(2) |
| M′(1)−M(1)−M′(2) | 61.28(7) | 57.21(3) | |
| M(1)−M′(2)−M(2) | 143.51(10) | | 124.02(2) |
| M(2)−M′(1)−M′(2) | | | 59.64(2) |
| M′(1)−M(2)−M′(2) | | | 57.628(18) |
| M(2)−M′(2)−M′(1) | 155.72(8) | | 62.730(19) |
| M(1)−M′(1)−C(7) | 47.5(5) | 49.7(6) | |
| M(1)−M′(2)−C(7) | 48.9(5) | 49.5(6) | 44.52(19) |
| M′(1)−M(1)−C(7) | 48.5(5) | 47.9(5) | |
| M′(2)−M(1)−C(7) | 48.3(6) | 47.0(5) | 45.15(19) |
| M(1)−C(7)−M′(1) | 84.1(6) | 82.4(7) | 139.3(3) |
| M(1)−C(7)−M′(2) | 82.8(8) | 83.5(7) | 90.3(3) |
| M′(1)-−M′(2)−C(7) | 48.2(5) | 50.2(5) | 54.75(19) |
| M′(2)−M′(1)−C(7) | 46.5(6) | 49.4(5) | 46.87(17) |
| M(2)−M′(1)−C(10) | | | 46.26(17) |
| M(2)−M′(2)−C(10) | 51.8(7) | | |
| M′(1)−M(2)−C(10) | | | 48.82(19) |
| M′(2)−M(2)−C(10) | 51.3(7) | | 153.9(3) |
| M(2)−C(10)−M′(1) | | | 84.9(2) |
| M(2)−C(10)−M′(2) | 76.8(8) | | |
| M(2)−M′(2)−C(4) | 47.4(6) | | 45.8(2) |
| M′(2)−M(2)−C(4) | 52.1(6) | | 46.3(2) |
| M(2)−C(4)−M′(2) | 80.5(9) | | 88.0(3) |
| M′(1)−C(7)−M′(2) | 85.3(7) | 80.4(7) | 78.4(2) |
| M(1)−C(1)−O(1) | 149(2) | 165(2) | 176.3(8) |
| M′(1)−C(1)−O(1) | | 119(2) | |
| M′(2)−C(1)−O(1) | 123.9(17) | | |
| M(1)−C(2)−O(2) | 157.5(18) | 162.6(18) | 174.6(8) |
| M′(2)−C(2)−O(2) | | 118.8(14) | |
| M(1)−C(7)−C(11) | | | 139.6(5) |
| C(7)−M′(1)−C(11) | | | 36.2(2) |
| M(2)−C(10)−C(11) | | | 122.9(5) |
| M′(1)−C(19)−C(20) | | 88(2) | |
| M′(1)−C(20)−C(19) | | 60.5(13) | |
| M′(1)−C(20)−C(21) | | 106(2) | |
| M′(2)−C(21)−C(20) | | 95.9(19) | |
| C(7)−C(11)−C(10) | | | 118.1(6) |
| C(19)−C(20)−C(21) | | 128(3) | |

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

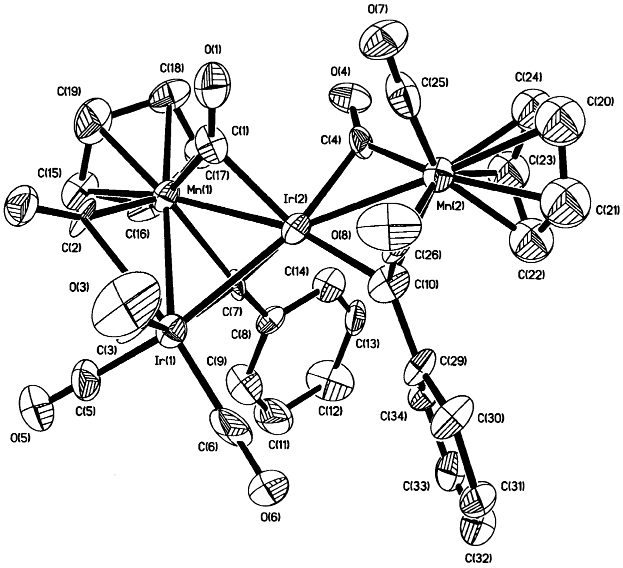


**Figure 1.** Molecular structure of **6**, showing the atom-numbering scheme with 45% thermal ellipsoids. $CH_2Cl_2$ has been omitted for clarity.

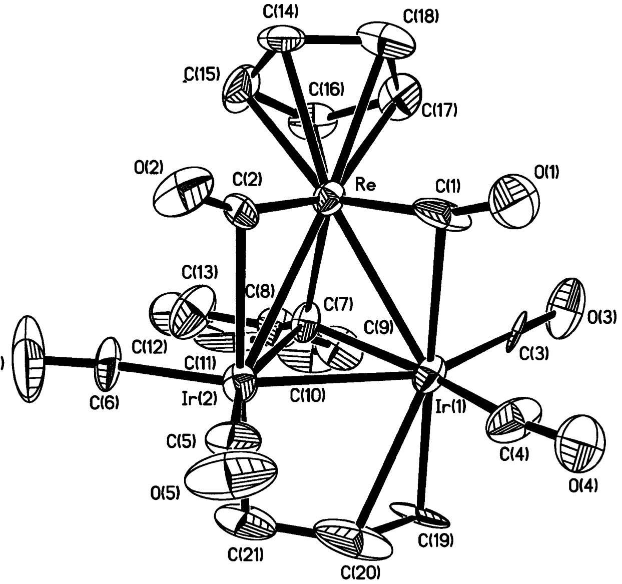


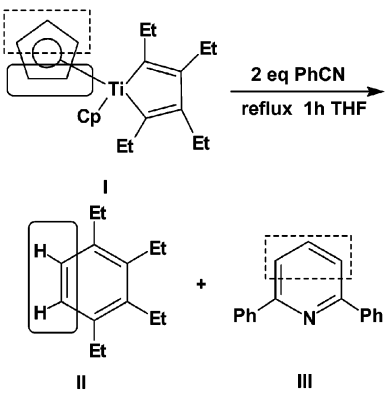
**Figure 2.** Molecular structure of **7**, showing the atom-numbering scheme with 45% thermal ellipsoids.

an $\eta^2$ bonding mode and the C(21) atom is $\eta^1$-bound to the Ir(2) atom with bond lengths Ir(1)−C(19) = 2.19(2) Å, Ir(1)−C(20) = 2.51(3) Å, and Ir(2)−C(21) = 2.16(2) Å, which are significantly longer than those found in an analogous diiridium complex with an $\eta^1$:$\eta^3$-allyl group, [($\eta^5$-$C_5Me_5$)($PMe_3$)Ir($\eta^1$:$\eta^3$-$C_3H_4$)Ir($\eta^5$-$C_5Me_5$)] (Ir(1)−C(1) = 2.046(7) Å, Ir(2)−C(1) = 2.139(6) Å, Ir(2)−C(2) = 2.107(7) Å, Ir(2)−C(3) = 2.112(7) Å).[16] The two C−C bond lengths of the allyl ligand in **7** are very different. C(20)−C(21) has a bond length of 1.51(5) Å, which is a normal C−C single-bond distance and is much longer than the corresponding C−C distance found in the analogous diiridium complex [($\eta^5$-$C_5Me_5$)($PMe_3$)Ir($\eta^1$:$\eta^3$-$C_3H_4$)Ir($\eta^5$-$C_5Me_5$)] (C(1)−C(2) = 1.421(11) Å).[16] The other is C(19)−C(20), with a bond length of 1.31(6) Å, which is between the C=C and C≡C distances and is somewhat shorter than the corresponding C−C distance in [($\eta^5$-$C_5Me_5$)($PMe_3$)Ir($\eta^1$:$\eta^3$-$C_3H_4$)Ir($\eta^5$-$C_5Me_5$)] (C(2)−C(3) = 1.453(11) Å).[16] The bond angle C(19)−C(20)−C(21) = 128(3)° in **7** is also much larger

---

[16] McGhee, M. D.; Hollander, F. J.; Bergmann, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8428.

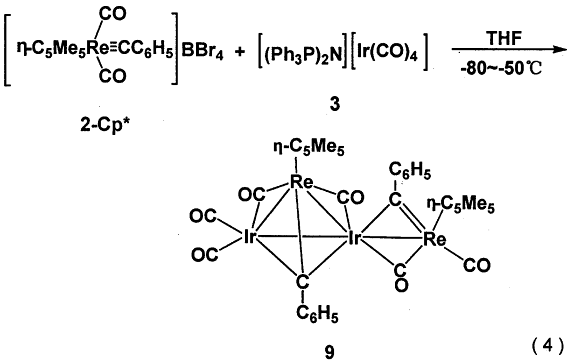
**Scheme 1**



than the corresponding angle in [($\eta^5$-$C_5Me_5$)($PMe_3$)Ir-($\eta^1$:$\eta^3$-$C_3H_4$)Ir($\eta^5$-$C_5Me_5$)] (C(1)−C(2)−C(3) = 117.5-(7)°).[16] These data indicate that the allyl ligand in **7** is an $\eta^1$:$\eta^2$-$C_3H_5$ ligand rather than an $\eta^1$:$\eta^3$-$C_3H_5$ ligand. The two Ir atoms each carry two terminal CO groups, and the Re atom carries two CO groups, being semibridging to the two Ir atoms, respectively (Re(1)−C(1)−O(1) = 165(2)°, Re(1)−C(1) = 1.91(2) Å; Re(1)−C(2)−O(2) = 162.6(18)°, Re(1)−C(2) = 1.88(2) Å). The semibridging CO ligands reveal themselves in the IR spectrum with a strong and a broad band at 1875 and 1829 $cm^{-1}$. Compound **7** is a 48-CVE (cluster valence electron) complex, where the Re (1), Ir(1), and Ir(2) atoms formally have 19, 18, and 17 electrons, respectively, which probably accounts for the presence of the semibridging carbonyls and a bridging allyl group. Analogous 48-valence-electron structures were found in the complexes [$MW_2$($\mu_3$-$C_2R_2$)$(CO)_7$($\eta^5$-$C_5H_5$)] (M = Ru, Os),[17] [ReFeCo($\mu_3$-$CC_6H_5$)$(CO)_8$($\eta^5$-$C_5H_5$)],[13] [$MnFe_2$($\mu$-H)($\mu$-CO)$_2$($\mu_3$-$CC_6H_5$)$(CO)_6$($\eta^5$-$C_5H_5$)],[5a] and [$MnRu_2$($\mu$-H)($\mu$-CO)$_2$($\mu_3$-$CC_6H_5$)$(CO)_6$($\eta^5$-$C_5H_5$)].[5b]

The formation of product **7** is unexpected. The origin of the allyl group ($C_3H_5$) in this product could be the cyclopentadienyl ligand ($C_5H_5$) of the cationic carbyne complex **2**. During the reaction of **2** with carbonylmetal anion **3**, two carbon−carbon bonds of the cyclopentadienyl ligand were cleaved and torn into two pieces, a two-carbon unit ($C_2H_2$) and a three-carbon unit ($C_3H_3$). The three CH moieties were trapped by cationic **2** and/or anionic **3** accompanied by the abstraction of two hydrogens from solvent THF to form an allyl ligand bonded to the Ir(1) and Ir(2) atoms in $\eta^2$ and $\eta^1$ modes, respectively, to construct the trimetal bridging carbyne complex **7**. Indeed, the transfer of a three-carbon unit from a cyclopentadienyl ligand to a complex has been documented: the reaction of titanacyclopentadiene (**I**) with 2 equiv of PhCN in THF at reflux for 1 h resulted in the formation of 1,2,3,4-tetraethylbenzene (**II**) and 2,6-diphenylpyridine (**III**), which were formed by respectively trapping a two-carbon unit and a three-carbon unit generated from cleavage of the two C−C bonds of a cyclopentadienyl ligand (Scheme 1).[18]

To explore the possibility of the allyl group ($C_3H_5$) in product **7** forming on cleavage of the cyclopentadienyl ligand in cationic **2**, the pentamethylcyclopentadienyl cationic carbyne complex [($\eta^5$-$C_5Me_5$)$(CO)_2$Re≡$CC_6H_5$]-$BBr_4$ (**2-Cp***) was prepared from [($\eta^5$-$C_5Me_5$)$(CO)_2$Re=C($OC_2H_5$)$C_6H_5$] and $BBr_3$ and used for the reaction with anion **3**. Unfortunately, the reaction of cationic **2-Cp*** gave only a $Re_2$−$Ir_2$ mixed-tetrametal bridging carbyne complex with $\mu$ and a $\mu_3$ bridging carbyne ligands, [$Re_2$-$Ir_2$($\mu$-$CC_6H_5$)($\mu_3$-$CC_6H_5$)($\mu$-CO)$_3$$(CO)_3$($\eta^5$-$C_5Me_5$)$_2$] (**9**), a pentamethylcyclopentadienyl analogue of complexes **B** and **5**, in 52% isolated yield (eq 4), instead of the expected Re−$Ir_2$ mixed-trimetal bridging carbyne complex with a trimethyl-substituted allyl ligand ($C_3H_2Me_3$) and the analogue of the $Re_2$−$Ir_2$ mixed-tetrametal cluster **8**. This might arise from the lower reactivity of pentamethylcyclopentadienyl cationic carbyne complex **2-Cp***, as compared with that of cationic **2**, due to the electron-pushing action and steric hindrance of the pentamethylcyclopentadienyl group in **2-Cp*** leading to a decrease in the electrophilicity of cationic **2-Cp***, which is indeed the case. The reaction of cationic **2** with anionic **3** can occur even below −100 °C, while the reaction of cationic **2-Cp*** occurred only over −80 °C (see Experimental Section). Although the reaction (eq 4) does not provide evidence for splitting of the pentamethylcyclopentadienyl ligand in **2-Cp*** to form a trimethyl-substituted allyl ligand to result in the expected $C_3H_2$-$Me_3$-coordinated mixed-trimetal bridging carbyne complex, an analogue of **7**, it cannot exclude the possibility of the cleavage of the cyclopentadienyl ligand in cationic **2** to form an allyl group in the reaction (eq 3), since cationic **2** has higher reactivity toward anionic **3** than does cationic **2-Cp***.



Since the cyclopentadienyl ligand ($C_5H_5$) in **2** does not contains enough H atoms to account for a splitting reaction to produce $C_2H_2$ and $C_3H_5$ units, the allyl group ($C_3H_5$) in product **7** is hypothesized to be derived by abstracting two H atoms from solvent THF. To prove this hypothesis, $CH_2Cl_2$, instead of THF, was used as the solvent for the reaction of cationic **2** with anionic **3** under the same conditions as those in THF, and no product **7** was obtained. This provided evidence that the two added H atoms of the allyl ligand in **7** could be from the solvent THF. A $^1H$ NMR tube reaction of cationic **2** with anionic **3** in THF-$d_8$ was also attempted. Unfortunately, no deuterium atoms of the allyl ligand in product **7** can be recognized from the complex $^1H$ NMR spectrum, since the reaction products were a mixture and the deuterated product **7**, a minor product, was hardly formed. Thus, there is not sufficient evidence to establish the origin of the two $H^-$ of the $C_3H_5$ ligand in product **7** at present.

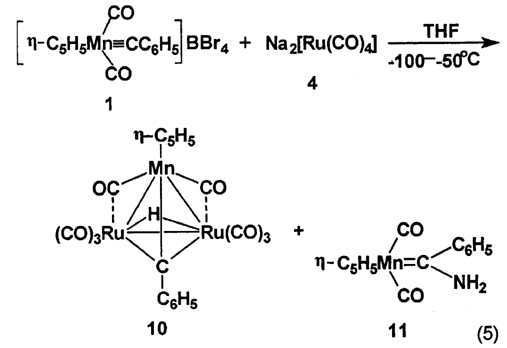
---

(17) Busetto, L.; Green, M.; Howard, J. A. K.; Hessner, B.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 1101.

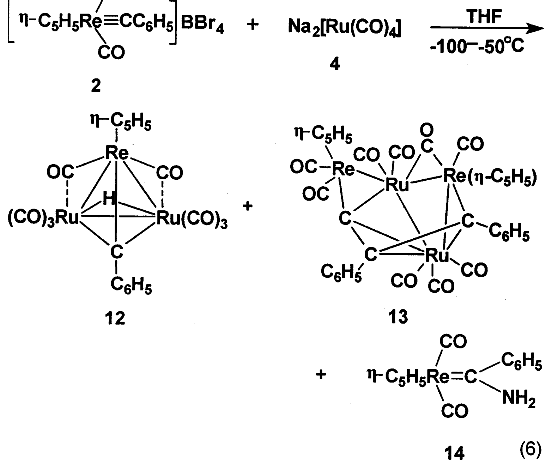
(18) Xi, Z.-F.; Sato, K.; Gao, Ye.; Lu, J.-M.; Takahashi, T. *J. Am. Chem. Soc.* **2003**, *125*, 9568.

Although several di- and polynuclear metal complexes with an $\eta^1$:$\eta^3$-allyl ligand have been reported,[16,19] only a dinuclear metal compound with an $\eta^1$:$\eta^2$-allyl ligand, $[(\eta^5\text{-}C_5Me_5)Ir(\eta^1{:}\eta^2\text{-}C_3H_5)(\eta^2{:}\eta^1\text{-}C_2H_3)Ir(\eta^5\text{-}C_5Me_5)]$, is known.[16] Evidently, compound **7** is the first example of a polymetallic bridging carbyne complex with an allyl ligand.

In contrast to the reaction of the carbonyliridium anion **3** to give the mixed-tetrametal bridging carbyne complexes or mixed-trimetal bridging carbyne complexes with an allyl ligand, the reaction of the dianionic carbonylruthenium compound $Na_2[Ru(CO)_4]$ (**4**) with cationic **1** under the same conditions as for **3** yields a mixed-trimetal bridging carbyne complex with a $\mu$-H ligand, $[MnRu_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta^5\text{-}C_5H_5)]$ (**10**), and a manganese aminocarbene complex, $[\eta^5\text{-}C_5H_5(CO)_2Mn{=}C(C_6H_5)NH_2]$ (**11**) (eq 5), in 47 and 15% yields, respectively. The analogous reaction of **4** with cationic **2** produces the analogous trimetal bridging carbyne complex $[ReRu_2(\mu_3\text{-}CC_6H_5)(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)]$ (**12**) and aminocarbene complex $[(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(C_6H_5)NH_2]$ (**14**) and a novel $Re_2{-}Ru_2$ mixed-tetrametal cluster with a $\mu_3$-$C(CC_6H_5)(\mu\text{-}CC_6H_5)$ carbene ligand, $[Re_2Ru_2\{\mu_3\text{-}C(CC_6H_5)(\mu\text{-}CC_6H_5)\}(\mu\text{-}CO)(CO)_8(\eta^5\text{-}C_5H_5)_2]$ (**13**), in 40, 13, and 20% yields, respectively (eq 6).



(5)



(6)

**Table 3. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complexes 11 and 14**

| | **11** (M = Mn) | **14** (M = Re) |
|---|---|---|
| M−C(1) | 1.729(8) | 1.880(11) |
| M−C(2) | 1.735(9) | 1.896(11) |
| M−C(8) | 1.938(8) | 2.042(10) |
| C(8)−N(1) | 1.312(9) | 1.313(14) |
| C(8)−C(9) | 1.465(9) | 1.509(14) |
| M−C(Cp) (av) | 2.146 | 2.307 |
| C(1)−O(1) | 1.183(9) | 1.171(13) |
| C(2)−O(2) | 1.184(11) | 1.162(12) |
| M−C(8)−N(1) | 125.4(5) | 127.9(9) |
| M−C(8)−C(9) | 122.6(5) | 121.3(7) |
| N(1)−C(8)−C(9) | 112.0(6) | 110.2(9) |
| M−C(1)−O(1) | 176.0(8) | 178.2(9) |
| M−C(2)−O(2) | 175.5(8) | 177.1(9) |

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

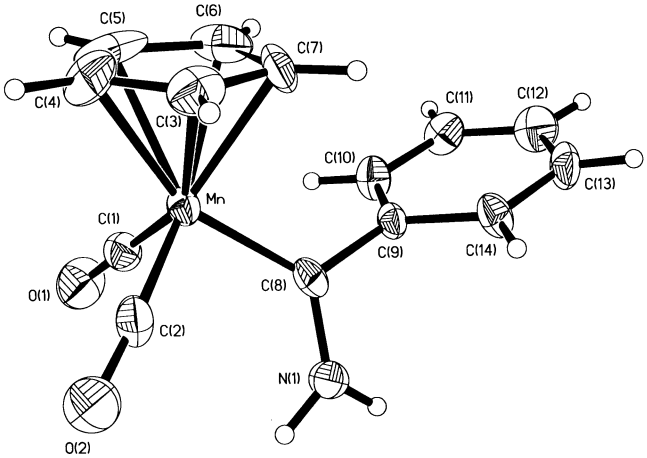


**Figure 3.** Molecular structure of **11**, showing the atom-numbering scheme with 40% thermal ellipsoids.

Products **10** and **12** are known compounds, which have been obtained from the reactions of $[(PPh_3)_2N][Ru_3(CO)_{11}]$ with the cationic carbine complexes **1** and **2**, respectively, among which product **10** has been structurally characterized by X-ray crystallography.[5b] The formulas of products **11**, **13**, and **14** were established by microanalytical data and IR, $^1H$ NMR, and mass spectra (Experimental Section), as well as X-ray crystallography.

Although several Fischer-type carbene complexes of chromium with an amino $NH_2$ group on the carbene carbon have been synthesized by Fischer et al.,[20] none of them have been studied by X-ray diffraction, and no aminocarbene complex of manganese or rhenium has ever been reported. Therefore, single-crystal X-ray diffraction studies were carried out on complexes **11** and **14** for comparison with analogous aminocarbene complexes. The results are given in Tables 1 and 3, and the molecules are illustrated in Figures 3 and 4, respectively.

The complexes **11** and **14** have the same molecular configurations as shown in Figures 3 and 4, respectively, and have many common features. In molecules **11** and **14**, the $M{-}C(8)_{carbene}$ distances are 1.938(8) and 2.042(10) Å, respectively, which are shorter than those found in the analogous aminocarbene complexes $[(CO)_5Cr{=}C(OC_2H_5)N(CH_3)_2]$ (2.133(4) Å)[21] and $[(CO)_5Cr{=}C(CH_3)N$-

---

(19) (a) McGhee, M. D.; Bergmann, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 5621. (b) Michaell, B.; Michaell, W. *J. Organomet. Chem.* **1985**, *288*, C55. (c) Housecroft, C. E.; Johnson, B. F. G.; Lewis, J.; Lunniss, J. A.; Owen, S. M.; Raithby, P. R. *J. Organomet. Chem.* **1991**, *409*, 271. (d) Chihara, T.; Yamazaki, H. *J. Organomet. Chem.* **1992**, *428*, 169. (e) Chihara, T.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1995**, 1369. (f) Chihara, T.; Kubota, H.; Fukumoto, M.; Orgawa, H.; Yamamoto, Y.; Wakatsuki, Y. *Inorg. Chem.* **1997**, *36*, 5488.

(20) (a) Fischer, E. O.; Kollmeier, H. J. *Chem. Ber.* **1971**, *104*, 1339. (b) Knauss, L.; Fischer, E. O. *J. Organomet. Chem.* **1971**, *31*, C68.

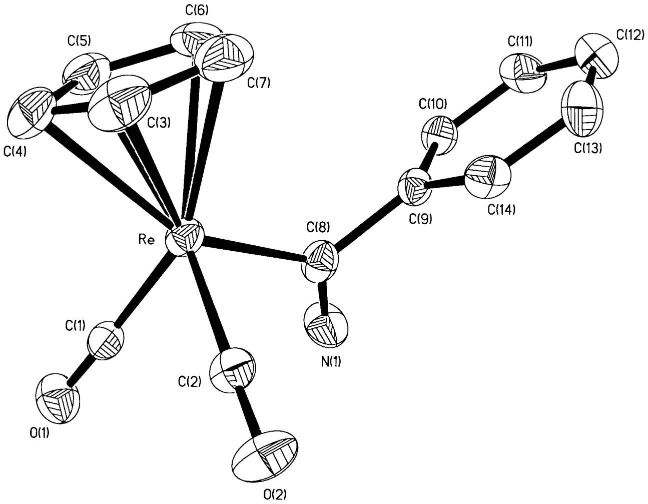


**Figure 4.** Molecular structure of **14**, showing the atom-numbering scheme with 40% thermal ellipsoids.

$(C_2H_5)_2]$ (2.16(1) Å).[22] The C(8)−N(1) bond lengths of **11** (1.312(9) Å) and **14** (1.313(19) Å) are the same within experimental error, which are somewhat shorter than the corresponding distance in $[(CO)_5Cr{=}C(OC_2H_5)N(CH_3)_2]$ (1.328(4) Å).[21] The M−C(8)−N(1) bond angles of 125.4(5)° for **11** and of 127.9(9)° for **14** are much smaller than the corresponding angle (129.4(1)°)[22] in $[(CO)_5Cr{=}C(CH_3)N(C_2H_5)_2]$. The carbene carbon atom (C(8)) is coplanar with the benzene ring in both complexes. The M, C(8), N(1), and C(9) atoms in **11** and **14** lie approximately in one plane, and the dihedral angles between this plane and the benzene ring plane in **11** and **14** are 67.62 and 57.92°, respectively. The plane of the cyclopentadienyl ring is inclined at an angle of 16.53° for **11** and of 17.98° for **14** to the plane of the benzene ring.

Of special interest is the structure of product **13**. The crystallographic investigation of **13** reveals a highly unusual structure (Figure 5), which contains a butterfly-like $Re_2Ru_2$ arrangement with a capping $\mu_3$-$C(CC_6H_5)$($\mu$-$CC_6H_5$) ligand. The $\mu_3$-C(7) atom is at a distance of 2.041(7) Å from the Re(1) atom, at distances of 2.310(7) and 2.064(7) Å from the Ru(1) and Ru(2) atoms, respectively, and at a distance of 1.420(9) Å from the C(11) atom. The structural features of the ($\mu$-$CC_6H_5$)Re(2)Ru(1) portion in **13** are very similar to those of the same unit in **6**, except the $\mu$-carbene carbon is linked to a carbon (C(11)) atom in the former but to a bridging CO group in the latter. In the ($\mu$-$CC_6H_5$)Re(2)Ru(1) portion, the Re(2)−Ru(1) bond is bridged by a $\mu$-$C(C_6H_5)$($\mu_3$-$CCC_6H_5$) ligand with the dimensions Re(2)−Ru(1) = 2.9157(7) Å, $\mu$-C(10)−Re(2) = 2.115(6) Å, and $\mu$-C(10)−Ru(1) = 2.203(7) Å. In this portion, a more interesting feature is the bonding of the $\mu$-carbene carbon (C(10)) to a carbon atom (C(11)) of the $\mu_3$-$C(CC_6H_5)$ moiety with a C(10)−C(11) distance of 1.410(9) Å. The shorter C(10)−C(11) and C(7)−C(11) bond distances in the $\mu_3$-$C(CC_6H_5)$($\mu$-$CC_6H_5$) moiety indicate that there is some double-bond character for both C−C bonds and that the C(7), C(11), and C(10) three carbon atoms are $\eta^3$-bound to the Ru(1) atom.

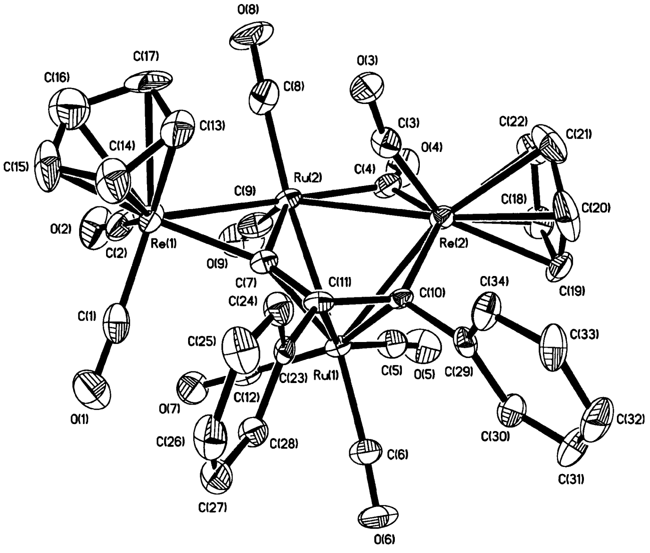


**Figure 5.** Molecular structure of **13**, showing the atom-numbering scheme with 45% thermal ellipsoids. $CH_2Cl_2$ has been omitted for clarity.

Complexes **10** and **12** could be produced via a $[Ru_2(CO)_6H]^-$ species generated from a dimerization of the dianion $[Ru(CO)_4]^{2-}$. The formed $[Ru_2(CO)_6H]^-$ anion then becomes bonded to the carbyne carbon of cationic **1** or **2** through the two Ru atoms with bonding of the Mn or Re atom to the two Ru atoms to give complex **10** or **12**. This reaction pathway is rather analogous to that of the reactions[5] of $[M'_3(CO)_{11}]^{2-}$ (M′ = Ru, Os) and $[Fe_2(\mu\text{-}CO)(\mu\text{-}SeC_4H_9\text{-}n)(CO)_6]^-$ anions with complex **1** or **2**. Those reactions were assumed to proceed via a $[M'_2(CO)_6H]^-$ (M′ = Ru, Os) and $[Fe_2(CO)_6H]^-$ species, respectively, which attacked at the carbyne carbon of cationic **1** or **2** to afford the bridging carbyne complexes $[MM'_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta^5\text{-}C_5H_5)]$ (M = Mn, Re; M′ = Ru, Os)[5b] and $[MFe_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta^5\text{-}C_5H_5)]$ (M = Mn),[5a] respectively. Since $[Ru(CO)_4]^{2-}$ is a dianion, its protonation could give the $[Ru(CO)_4H]^-$ anion in the presence of water, which is a trace contaminant in the solvent THF or from glassware. The formed $[Ru(CO)_4H]^-$ anion could be the species responsible for the origin of $H^-$ in these reactions. Thus, the heteronuclear trimetal bridging carbyne complexes $[MRu_2(\mu\text{-}H)(\mu\text{-}CO)_2(\mu_3\text{-}CC_6H_5)(CO)_6(\eta^5\text{-}C_5H_5)]$ (M = Mn, Re) can be obtained not only from the trimetallic carbonylruthenium anion[5b] but also from the monometallic carbonylruthenium anion by reactions with cationic carbyne complexes **1** and **2**.

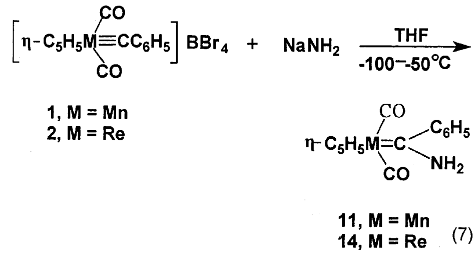
The route for the formation of product **13** is not clear. We speculate that it could proceed via a $[Ru_2(CO)_6]^{2-}$ species, derived by dimerization of the $[Ru(CO)_4]^{2-}$ dianion, which might become bonded to the carbyne carbons of two molecules of cationic **2** through the two Ru atoms to form the unstable dicarbene intermediate $[\{(\eta^5\text{-}C_5H_5)(CO)_2Re{=}CC_6H_5\}_2\{Ru_2(CO)_6\}]$. Then the linkage of the two Ru atoms to the two Re atoms, accompanied by an insertion of a CO ligand of a $Ru(CO)_3$ moiety into the Re−$\mu$-C bridging carbene bond (Re(1)−$\mu$-C(11)), occurred to the intermediate owing to its lability. Subsequently, the reduction−elimination of the oxygen atom from the inserted C=O group with the bonding of the Ru(1) atom of another $Ru(CO)_3$ moiety to the carbonyl carbon (C(7)) and the $\mu$-carbene carbon

---

[21] Fischer, E. O.; Winkler, E.; Kreiter, C. G.; Huttner, G.; Krieg, B. *Angew. Chem.* **1971**, 83, 1021; *Engl. Ed.* **1971**, *10*, 922.

[22] Connor, J. A.; Mills, O. S. *J. Chem. Soc. A* **1969**, 334.

(C(10)) to the C(11) atom could occur to eventually produce product **13**. However, the reaction pathway to aminocarbene complexes **11** and **14**, which are undesired byproducts, could be via a direct attack of $NH_2^-$ anion at the carbyne carbon of cationic **1** or **2**. The source of the $NH_2^-$ anion would be $NaNH_2$, which is a contaminant in the starting $Na_2[Ru(CO)_4]$ obtained[11] from $Ru_3(CO)_{12}$ and $NaNH_2$ prepared (in situ) by the reaction of ammonia and sodium and is difficult to remove from the starting $Na_2[Ru(CO)_4]$. This has been confirmed by the experimental fact that when $NaNH_2$ was reacted with cationic carbyne complexes **1** and **2** under the same conditions as those of **4**, the products **11** and **14** were obtained (eq 7) in 72 and 78% yields, respectively.



**1**, M = Mn
**2**, M = Re

**11**, M = Mn
**14**, M = Re (7)

In conclusion, we have discovered the remarkable reactions of cationic carbyne complexes **1** and **2** with the carbonyliridium monoanion $[Ir(CO)_4]^-$ and carbonylruthenium dianion $[Ru(CO)_4]^{2-}$. In the reactions of $[Ir(CO)_4]^-$, the products were novel polymetallic bridging carbyne complexes with $\mu$ and $\mu_3$ bridging carbyne ligands, with a $\mu_3$ bridging carbyne ligand and a $\mu$ bridging carbene ligand, or with a $\mu_3$ bridging carbyne ligand and an allyl ligand, while in the case of $[Ru(CO)_4]^{2-}$, the major products were the trimetal carbyne complexes with a $\mu$-H ligand or a novel $Re_2$–$Ru_2$ mixed-tetrametal cluster with a $\mu_3$-$C(CC_6H_5)(\mu$-$CC_6H_5)$ bridging carbene ligand. These results demonstrate the variety of the reactions of the cationic carbyne complexes with carbonylmetal anions. The title reaction may offer a convenient and useful method for the preparation of heteronuclear polymetallic bridging carbyne complexes.

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

**Supporting Information Available:** Tables of the positional parameters and $B_{iso}/B_{eq}$ values, H atom coordinates, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **6**, **7**, **9**, **11**, **13**, and **14** and a figure giving the molecular structure for **9** (Figure 6). This material is available free of charge via the Internet at http://pubs.acs.org.

OM058008A