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Remarkable Reactions of Cationic Carbyne Complexes of Manganese and Rhenium with the Carbonylrhodium Anion $[Rh(CO)_4]^-$. A Novel Route to Heteropolymetallic Bridging Carbyne Complexes with μ- and μ_3-Carbyne Ligands

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*Summary: The reaction of 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 $[(Ph_3P)_2N][Rh(CO)_4]$ in THF at low temperature gives the novel $Mn_2{-}Rh_2$ mixed-tetrametal bridging carbyne complexes **3** and **5** and $Mn_3{-}Rh_2$ mixed-pentametal bridging carbyne complex **4** or the $Re{-}Rh_3$ mixed-tetrametal cluster **6**, respectively. The structures of **3**, **4**, and **6** have been established by X-ray diffraction studies.*

The mixed-metal-bonded cluster complexes are well-known to have important roles in a variety of homogeneous catalytic reactions.[1] Since many dinuclear and polynuclear metal bridging carbene and carbyne complexes 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. A considerable number of heteronuclear di- and trimetal bridging carbyne complexes have been synthesized by Stone and co-workers.[2,3] In recent years, our laboratory has synthesized and characterized a great number of di- and trimetal bridging carbene and carbyne complexes by the reactions of the cationic metal carbyne complexes with carbonylmetal anions. 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 $[Fe_4(CO)_{13}]^-$. It is found that the different carbonylmetal anions of the same group exert great effects on the reactivity of the cationic metal carbyne complexes and resulting products.[4,6] Moreover, it has been found that rhodium, a metal of group VIII, is implicated in a number of catalytic organic reactions.[7] To further develop this new synthetic method for polymetal bridging carbene and bridging carbyne complexes and further examine the effect of different carbonylmetal anions of group VIII on the reactivity of the cationic carbyne complexes and reaction products, we investigated the reactions of cationic carbyne complexes of manganese and rhenium, **1** and **2**, with the anionic carbonylrhodium compound $[(Ph_3P)_2N][Rh(CO)_4]$, which produced novel heteronuclear polymetal clusters with μ- and μ_3-carbyne ligands. In this communication we report these unusual reactions and the structures of the resulting products.

A cationic carbyne complex of manganese, $[\eta^5\text{-}C_5H_5\text{-}(CO)_2Mn{\equiv}CC_6H_5]BBr_4$ (**1**), was treated with an equimolecular amount of $[(Ph_3P)_2N][Rh(CO)_4]$ 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 low temperature and the crude products were recrystallized from petroleum ether/CH_2Cl_2 at −80 °C to give a novel $Mn_2{-}Rh_2$ mixed-tetrametal bridging carbyne complex with μ- and μ_3-carbyne ligands, $[Mn_2Rh_2(\mu\text{-}CC_6H_5)(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_3(CO)_3(\eta^5\text{-}C_5H_5)_2]$ (**3**), and a novel $Mn_3{-}Rh_2$ mixed-pentametal bridging carbyne complex with two μ-carbyne ligands and one μ_3-carbyne ligand, $[Mn_3Rh_2(\mu\text{-}CC_6H_5)_2(\mu_3\text{-}CC_6H_5)(\mu\text{-}Cl)(\mu\text{-}CO)_3(CO)_2(\eta^5\text{-}C_5H_5)_3]$ (**4**), in 64% and 16% isolated yields, respectively (eq 1).

A cationic carbyne complex of rhenium, $[\eta^5\text{-}C_5H_5(CO)_2\text{-}Re{\equiv}CC_6H_5]BBr_4$ (**2**), reacts similarly with $[(Ph_3P)_2N][Rh(CO)_4]$ to afford the corresponding $Re_2{-}Rh_2$ mixed-tetrametal bridging carbyne complex $[Re_2Rh_2(\mu\text{-}CC_6H_5)(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_3(CO)_3(\eta^5\text{-}C_5H_5)_2]$ (**5**) and a novel $Re{-}Rh_3$ mixed-tetrametal cluster with a $\mu_4\text{-}CC_6H_5$ carbide-like

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(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) Maire, G. In *Metal Clusters in Catalysis*; Gates, B. C., Guczi, L., Knoezinger, H., Eds.; Elsevier: Amsterdam, The Netherlands, 1986; p 509.

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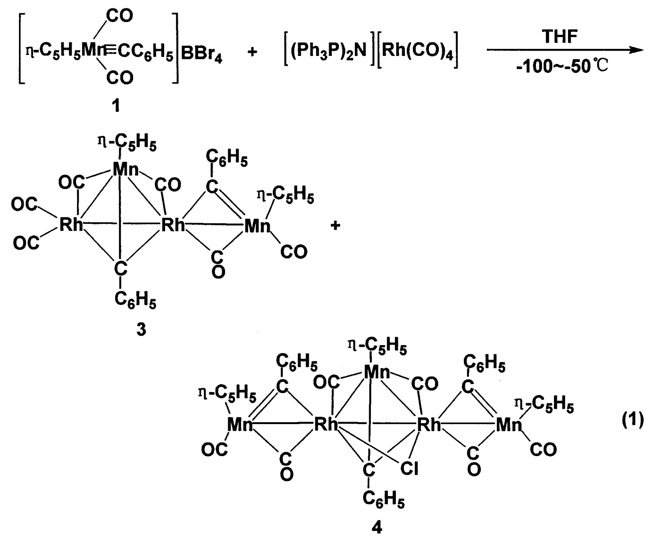
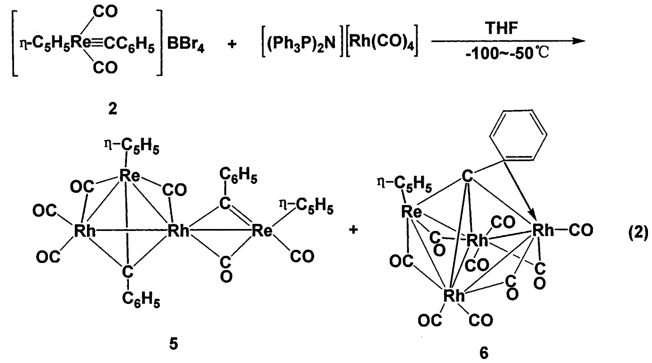


ligand, [ReRh$_3$(μ_4-CC$_6$H$_5$)(μ-CO)$_4$(CO)$_5$(η^5-C$_5$H$_5$)] (**6**), in 59% and 22% yields, respectively (eq 2); the structure of **6** has been confirmed by an X-ray diffraction study.



Complexes **3**−**6** are soluble in polar organic solvents but slightly soluble in nonpolar solvents. They are very sensitive to air and temperature in solution but relatively stable as the solid. Elemental analyses and spectroscopic data[8] are consistent with their compositions and assigned structures. The infrared studies of complexes **3**−**6** showed the presence of the terminal and bridging carbonyl groups, and the ^{1}H NMR spectra indicated the absence of a hydride proton for each complex, which showed only the proton signals attributed to the phenyl and cyclopentadienyl protons.

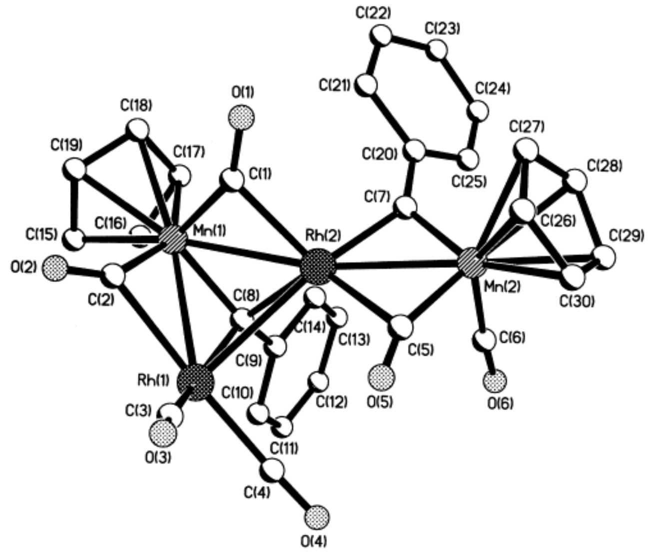


Figure 1. ORTEP diagram of **3**. Selected bond lengths (Å): Mn(1)−Rh(1) = 2.643(3), Mn(1)−Rh(2) = 2.606(3), Rh(1)−Rh(2) = 2.7749(18), Mn(2)−Rh(2) = 2.584(3), Mn(1)−C(8) = 1.882(16), Rh(1)−C(8) = 2.052(17), Rh(2)−C(8) = 2.071(17), Mn(2)−C(7) = 1.84(2), Rh(2)−C(7) = 1.896(16).

The structure of complex **3** was determined by a single-crystal X-ray diffraction study.[9] An ORTEP diagram is given in Figure 1, which also provides bond length data for the metal framework and metal−C$_{\text{carbyne}}$ bonds. The structure of **3** revealed that the cluster compound contains two bridging carbyne units, (μ-CC$_6$H$_5$)Mn(2)Rh(2) and (μ_3-CC$_6$H$_5$)Mn(1)Rh(1)Rh(2), in which the four vertical 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 the different electron environments for the four metal atoms. In the (μ_3-CC$_6$H$_5$)Mn(1)Rh(1)Rh(2) portion, the three metal atoms construct an approximately isosceles triangle (Mn(1)−Rh(1) = 2.643(3) Å, Mn(1)−Rh(2) = 2.606(3) Å, and Rh(1)−Rh(2) = 2.7749(18) Å). The μ-C(8)−Mn(1), μ-C(8)−Rh(1), and μ-C(8)−Rh(2) distances are 1.882(16), 2.052(17), and 2.071(17) Å, respectively. However, in the (μ-CC$_6$H$_5$)Mn(2)Rh(2) portion the Mn(2)−Rh(2) bond is bridged by the CC$_6$H$_5$ ligand, giving a dimetallacyclopropene ring with the dimensions of Mn(2)−Rh(2) = 2.584(3) Å, μ-C(7)−Mn(2) = 1.84(2) Å, and μ-C(7)−Rh(2) = 1.896(16) Å. Complex **3** appears to be the first example of a species with two kinds of bridging carbyne units studied by X-ray crystallography.

The structure[10] of complex **4** (Figure 2) showed that the cluster compound consists of three bridging units: (μ-CC$_6$H$_5$)Mn(2)Rh(1), (μ-CC$_6$H$_5$)Mn(3)Rh(2), and (μ_3-CC$_6$H$_5$)Mn(1)Rh(1)Rh(2), which is, to our knowledge, the first example of a mixed-pentanuclear cluster with two μ-carbyne ligands and one μ_3-carbyne ligand. The structural features of the (μ_3-CC$_6$H$_5$)Mn(1)Rh(1)Rh(2) and (μ-CC$_6$H$_5$)Mn(2)Rh(1) or (μ-CC$_6$H$_5$)Mn(3)Rh(2) portions of **4** are very similar to those in **3**, except that the two Rh atoms are bridged by a Cl atom in the (μ_3-CC$_6$H$_5$)Mn(1)-

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[8] Data for **3** are as follows. Mp: 180 °C dec. Anal. Calcd for C$_{30}$H$_{20}$O$_6$Mn$_2$Rh$_2$: C, 45.49; H, 2.54. Found: C, 44.78; H, 2.56. IR (CH$_2$Cl$_2$): ν (CO) 2046 (vs), 2001 (v, br), 1822 (m), 1809 (s, br), 1772 (m) cm^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 7.58−7.00 (m, 10H, 2C$_6$H$_5$), 5.62 (s, 1H, C$_5$H$_5$), 5.25 (s, 1H, C$_5$H$_5$), 5.16 (d, 2H, C$_5$H$_5$), 4.53 (d, 3H, C$_5$H$_5$), 4.48 (d, 3H, C$_5$H$_5$). Data for **4** are as follows. Mp: 165−167 °C dec. Anal. Calcd for C$_{42}$H$_{30}$O$_6$ClMn$_3$Rh$_2$·2CH$_2$Cl$_2$: C, 43.79; H, 2.84. Found: C, 43.36; H, 3.10. IR (CH$_2$Cl$_2$): ν (CO) 1974 (vs, br), 1886 (s), 1837 (vs), 1799 (m) cm^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 7.32 (m, 10H, C$_6$H$_5$), 7.11 (m, 3H, C$_6$H$_5$), 6.91 (m, 2H, C$_6$H$_5$), 5.65 (m, 4H, CH$_2$Cl$_2$), 4.83 (s, 10H, C$_5$H$_5$), 4.04 (s, 5H, C$_5$H$_5$). Data for **5** are as follows. Mp: 166−168 °C dec. Anal. Calcd for C$_{30}$H$_{20}$O$_6$Re$_2$Rh$_2$·0.5CH$_2$Cl$_2$: C, 33.39; H, 1.93. Found: C, 33.47; H, 3.21. IR (CH$_2$Cl$_2$): ν (CO) 2038 (vs), 1991 (vs, br), 1825 (w), 1802 (m), 1765 (m) cm^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 7.64−7.53 (m, 6H, C$_6$H$_5$), 7.04−6.98 (m, 4H, C$_6$H$_5$), 5.84 (s, 3H, C$_5$H$_5$), 5.64 (s, 2H, C$_5$H$_5$), 5.54 (m, 1H, CH$_2$Cl$_2$), 5.20 (s, 5H, C$_5$H$_5$). Data for **6** are as follows. Mp: 150−151 °C dec. Anal. Calcd for C$_{21}$H$_{10}$O$_9$ReRh$_3$: C, 27.99; H, 1.12. Found: C, 27.95; H, 1.23. IR (CH$_2$Cl$_2$): ν (CO) 2079 (s), 2054 (vs) 2009 (vs, br), 1896 (s, br), 1859 (m), 1835 (m) cm^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 7.22 (m, 3H, C$_6$H$_5$), 6.75 (m, 2H, C$_6$H$_5$), 5.52 (s, 5H, C$_5$H$_5$).

[9] X-ray data for **3**: C$_{30}$H$_{20}$O$_6$Mn$_2$Rh$_2$, monoclinic, $P2_1/n$, a = 12.157(3) Å, b = 13.918(3) Å, c = 17.127(4) Å, β = 103.051(4)°, V = 2823.1(12) Å^3, F = 1552, R = 0.0773, R_w = 0.1467.

[10] X-ray data for **4**: C$_{44}$H$_{34}$O$_6$Cl$_5$Mn$_3$Rh$_2$, triclinic, $P\bar{1}$, a = 11.3354(16) Å, b = 12.9361(17) Å, c = 17.279(3) Å, α = 101.645(4)°, β = 97.034(3)°, γ = 111.972(3)°, V = 2245.9(5) Å^3, F = 1192, R = 0.0636, R_w = 0.0991.

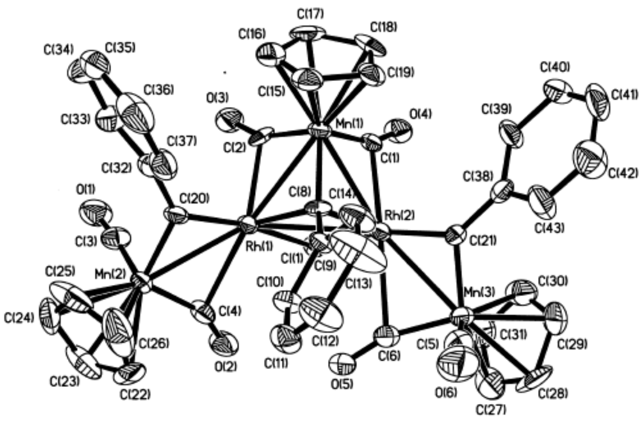

Figure 2. ORTEP diagram of **4**. Selected bond lengths (Å): Mn(1)−Rh(1) = 2.6615(15), Mn(1)−Rh(2) = 2.6567(15), Rh(1)−Rh(2) = 2.9450(11), Mn(2)−Rh(1) = 2.6551(15), Mn(3)−Rh(2) = 2.6090(18), Mn(1)−C(8) = 1.862(8), Rh(1)−C(8) = 2.019(9), Rh(2)−C(8) = 1.979(8), Mn(2)−C(20) = 1.820(8), Rh(1)−C(20) = 1.847(9), Mn(3)−C(21) = 1.847(8), Rh(2)−C(21) = 1.848(9).

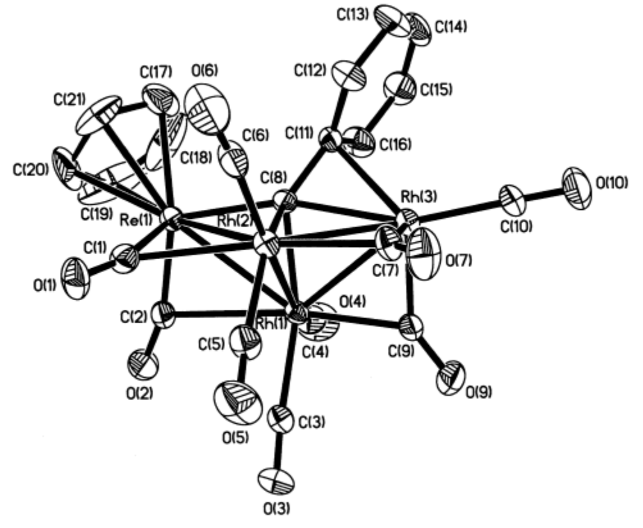

Figure 3. ORTEP diagram of **6**. Selected bond lengths (Å): Re(1)−Rh(1) = 2.8198(5), Re(1)−Rh(2) = 2.8104(5), Rh(1)−Rh(2) = 2.6602(6), Rh(1)−Rh(3) = 2.7663(6), Rh(2)−Rh(3) = 2.7648(6), Re(1)−C(8) = 2.081(5), Rh(1)−C(8) = 2.055(5), Rh(2)−C(8) = 2.087(5), Rh(3)−C(8) = 2.308(5), Rh(3)−C(11) = 2.345(6), C(8)−C(11) = 1.896(16).

Rh(1)Rh(2) unit. An apparent difference in the structures of **3** and **4** is the longer metal−metal bonds (average Mn−Rh = 2.658 Å and Rh−Rh = 2.9450(11) Å) and the shorter M−$C_{carbyne}$ bonds (average Mn−$C_{carbyne}$ = 1.843 Å, average Rh-μ_3-$C_{carbyne}$ = 1.999 Å and Rh-μ-$C_{carbyne}$ = 1.847 Å) in **4**, as compared to **3**. The mode of formation of complex **4** is not known. The source of the Cl atom could be $RhCl_3$ or $(Ph_3P)_2NCl$, which is a contaminant in the starting $[(Ph_3P)_2N][Rh(CO)_4]$ obtained from the reactants of $RhCl_3$ and $(Ph_3P)_2NCl$.

Of special interest is the structure of product **6**. The crystallographic investigation[11] of **6** reveals a highly unusual structure (Figure 3), which contains a butterfly $ReRh_3$ arrangement with a capping μ_4-CC_6H_5 ligand. In contrast to complexes **3** and **4**, the feature determining the structure of complex **6** is the ability of each metal atom to satisfy an 18-electron configuration, which is achieved in a remarkable and new way by additional bonding of the Re and Rh atoms to a carbide-like atom and of a carbon atom (C(11)) of the phenyl ring to a Rh atom with a C−Rh (C(11)−Rh(3)) distance of 2.345(6) Å and by both metal−metal and metal−carbonyl bonding. The carbide-like atom C(8) is at an average distance of 2.15 Å from the three Rh atoms and at a distance of 2.081(5) Å from the Re atom. No Re−Rh_3 heterotetranuclear clusters with a μ_4-CC_6H_5 carbide-like ligand have yet been structurally characterized, and indeed, this stereochemistry is rare. A related structure with a μ_4-CPh carbide ligand was found in a pentanuclear carbonyl cluster of ruthenium, $[Ru_5(CO)_{13}(CCPh)(PPh_2)]$.[12]

Like $Rh(CO)_4^-$, the $Ir(CO)_4^-$ anion can also reacts similarly with cationic carbyne complex **1** to give an analogous Mn_2−Ir_2 mixed-tetranuclear cluster[13] with μ- and μ_3-carbyne ligands, $[Mn_2Ir_2(\mu\text{-}CC_6H_5)(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_3(CO)_3(\eta^5\text{-}C_5H_5)_2]$ (**7**), and a related mixed-tetranuclear cluster[14] with a μ-carbene ligand and a μ_3-carbyne ligand, $[Mn_2Ir_2\{\mu\text{-}C(CO)C_6H_5\}(\mu_3\text{-}CC_6H_5)(\mu\text{-}CO)_3(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (**8**), in which a CO ligand is bridged to the Mn and μ-$C_{carbene}$ atoms in the MnIr{μ-$C(CO)C_6H_5$} portion. The structure of **8** has also been further confirmed by crystallography.[15] Further studies on the reactions of cationic carbyne complexes **1** and **2** with the $Ir(CO)_4^-$ anion are underway.

In conclusion, we have discovered new types of polymetallic bridging carbyne complexes with the μ- and μ_3-carbyne ligands synthesized by the reactions of cationic carbyne complexes **1** and **2** with a monometal carbonylrhodium anion and demonstrated that there are two different bonding modes of the bridging carbyne ligands on the M_2−Rh_2 or M_3−Rh_2 (M = Mn, Re) cluster framework. Furthermore, we have developed a remarkable and very useful methodology for the preparation of heteropolymetallic bridging carbyne complexes containing four or more metal atoms. Efforts are currently underway with complexes **3**−**5** to selectively catalyze carbonylation of olefins, such as the aldehydation of styrene.

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Supporting Information Available: Text giving full experimental details and characterization data for complexes **3**−**8** and tables giving X-ray crystallographic data for **3**, **4**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] X-ray data for **6**: $C_{21}H_{10}O_9ReRh_3$, monoclinic, $P2_1/n$, a = 9.8967(6) Å, b = 16.5945(10) Å, c = 14.6970(9) Å, β = 103.8960(10)°, V = 2343.1(2) Å^3, F = 1672, R = 0.0378, R_w = 0.0791.

[12] Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 2456.

[13] Data for **7** are as follows. Yield: 56%. Mp: >250 °C dec. 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. IR (CH_2Cl_2): ν (CO) 2041 (vs), 1994 (vs, br), 1803 (s, br), 1759 (m) cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 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).

[14] Data for **8** are as follows. Yield: 22%. Mp: 133−135 °C dec. Anal. Calcd for $C_{32}H_{20}O_8Mn_2Ir_2\cdot 1.5CH_2Cl_2$: C, 34.86; H, 2.00. Found: C, 35.14; H, 2.24. IR (CH_2Cl_2): ν (CO) 2077 (vs), 2027 (s), 2014 (sh), 1977 (m), 1941 (vs, br), 1889 (s, br), 1835 (m), 1759 (w) cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 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), 5.23 (m, 3H, 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).

[15] X-ray data for **8**: $C_{33.5}H_{23}O_8Cl_3Mn_2Ir_2$, monoclinic, $P2_1/n$, a = 11.336(2) Å, b = 13.548(3) Å, c = 23.138(95) Å, β = 93.839(4)°, V = 3545.4(13) Å^3, F = 2172, R = 0.0648, R_w = 0.1385.