

Reactions of Cationic Carbyne Complexes of Manganese and Rhenium with Carbonylmethyl Anions Containing Cyclopentadienyl, PPh₃, and NO Ligands. A Route to Dimetal Bridging Carbyne Complexes

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The reactions of cationic carbyne complexes of manganese and rhenium, $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{M}\equiv\text{CC}_6\text{H}_5]\text{BBr}_4$ (**1**, M = Mn; **2**, M = Re), with $\text{Na}[\eta\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]$ (**3**) in THF at low temperature afford η^1, η^2 -ketene complexes $[\text{MnMo}\{\text{C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (**8**) and $[\text{ReMo}\{\text{C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (**9**), respectively. Analogous reactions of $\text{Na}[\eta\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]$ (**4**) with **1** and **2** give the corresponding ketene complexes $[\text{MnW}\{\text{C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (**10**) and $[\text{ReW}\{\text{C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (**11**). $\text{Na}[\text{Co}(\text{CO})_3\text{PPh}_3]$ (**5**) also reacts with **1** and **2** to yield ketenyl-bridged complexes $[\text{MnCo}\{\text{C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_4(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$ (**12**) and $[\text{ReCo}\{\text{C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_4(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$ (**13**), respectively. However, compound $\text{Na}[\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]$ (**6**) reacts only with **2** to form a η^1, η^2 -ketene complex $[\text{ReFe}\{\text{C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)_2]$ (**14**), while the reactions of $(\text{Ph}_3\text{P})_2\text{N}[\text{Fe}(\text{CO})_3\text{NO}]$ (**7**) with **1** and **2** produce dimetal bridging carbyne complexes $[\text{MnFe}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_4(\text{NO})(\eta\text{-C}_5\text{H}_5)]$ (**15**) and $[\text{ReFe}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_4(\text{NO})(\eta\text{-C}_5\text{H}_5)]$ (**16**), respectively. Compound **15** treated with an excess of $\text{Fe}_2(\text{CO})_9$ gives a trimetallic bridging carbyne complex, $[\text{MnFe}_2(\mu_3\text{-CC}_6\text{H}_5)(\text{CO})_7(\text{NO})(\eta\text{-C}_5\text{H}_5)]$ (**17**). Complexes **12** and **13** also react with $\text{Fe}_2(\text{CO})_9$, leading to loss of the PPh_3 ligand to afford trimetallic bridging carbyne complexes $[\text{MnFeCo}(\mu_3\text{-CC}_6\text{H}_5)(\text{CO})_8(\eta\text{-C}_5\text{H}_5)]$ (**18**) and $[\text{ReFeCo}(\mu_3\text{-CC}_6\text{H}_5)(\text{CO})_8(\eta\text{-C}_5\text{H}_5)]$ (**19**), respectively. The structures of **10**, **13**, and **15** have been established by X-ray diffraction studies.

Introduction

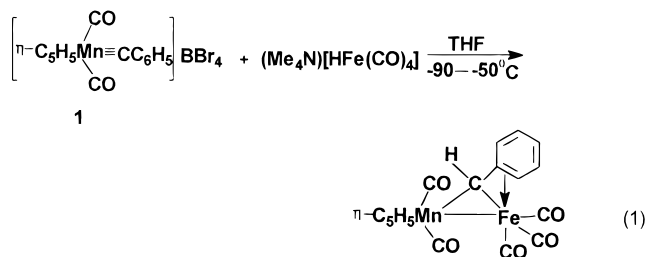
The current considerable interest in the synthesis and study of a variety of metal–metal-bonded cluster complexes is largely due to their important role in many catalytic processes.^{1–3} Since many transition metal bridging carbene and carbyne complexes are the metal clusters themselves or are the precursors of metal cluster complexes, the chemistry of transition metal bridging carbene and carbyne complexes are areas of current interest. In this regard, we are interested in developing the methodology of the synthesis of transition metal bridging carbene and carbyne complexes. The transition metal bridging carbene and carbyne complexes have been examined extensively by Stone and co-workers. A great number of dimetal bridging carbene and carbyne complexes have been synthesized by them by the reactions^{4–6} of carbene or alkylidyne complexes

with low-valent metal species or by reactions^{7–9} of neutral or anionic carbyne complexes with metal hydrides or cationic metal compounds. In our laboratory, one of the synthetic methods of bridging carbene and carbyne complexes is to conduct reactions of the highly electrophilic cationic carbyne complexes of manganese and rhenium, $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Mn}\equiv\text{CC}_6\text{H}_5]\text{BBr}_4$ (**1**) and $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}\equiv\text{CC}_6\text{H}_5]\text{BBr}_4$ (**2**), with carbonylmethyl anion compounds such as $\text{Na}_2[\text{Fe}(\text{CO})_4]$, $(\text{Et}_4\text{N})_2[\text{Fe}_2(\text{CO})_8]$, $(\text{Me}_4\text{N})[\text{HFe}(\text{CO})_4]$, $\text{Na}_2[\text{W}(\text{CO})_5]$, and $(\text{Ph}_3\text{P})_2\text{N}[\text{FeCo}(\text{CO})_8]$ or $(\text{Ph}_3\text{P})_2\text{N}[\text{WCo}(\text{CO})_9]$ to form the heteronuclear dimetal bridging carbene or bridging carbyne complexes.^{10–14} This represents a new route to dimetal

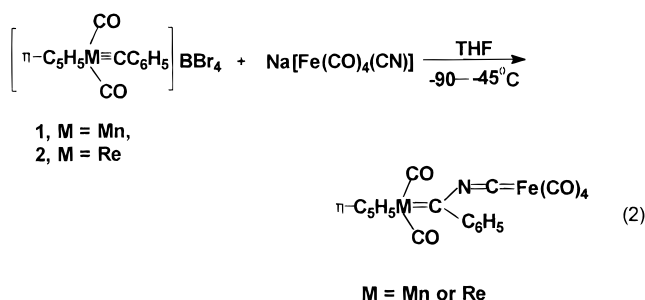
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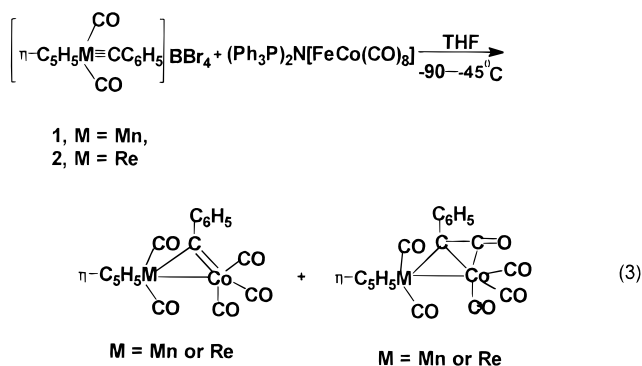
bridging carbene and bridging carbyne complexes. We found that the reactivity and resulting products depend not only on the central metal^{10,15} of the cationic carbyne complexes but also on the carbonylmethyl anions. For instance, the carbonyliron anion compound (Me₄N)[HFe(CO)₄] reacted with cationic carbyne complex **1** to give a novel Mn–Fe dimetal bridging carbene complex (eq 1), in which a hydride 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 atom to construct a dimetallocopropane ring,¹² whereas the reac-



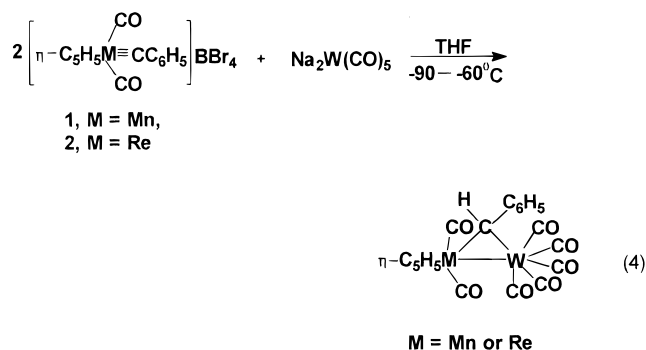
tions of the cyano-substituted carbonyliron anion compound Na[Fe(CO)₄CN] with cationic carbyne complexes **1** and **2** gave phenyl(tetracarbonylcyanoirron)carbenemanganese and -rhenium complexes [η-C₅H₅(CO)₂M=C(C₆H₅)NCFe(CO)₄] (M = Mn, Re) (eq 2),¹¹ respectively.



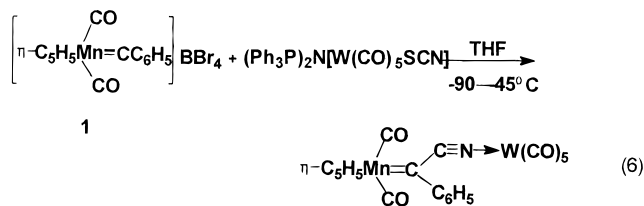
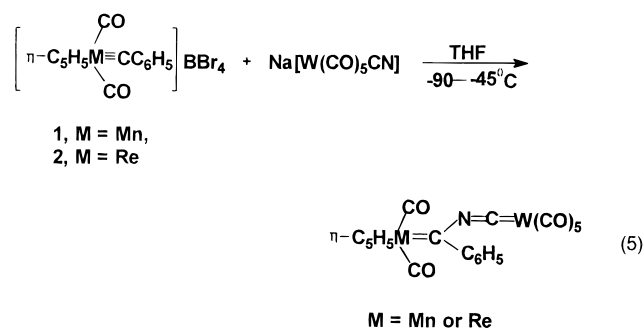
In contrast to monometal carbonyl anion, the mixed-dimetal carbonyl anion compounds such as (PPh₃)₂N[FeCo(CO)₈] reacted with complex **1** and **2** to yield heteronuclear dimetal bridging carbyne complexes [MCo(μ-CC₆H₅)(CO)₅(η-C₅H₅)] (M = Mn, Re) and bridging carbene complexes [MCo(μ-C(CO)C₆H₅)(CO)₅(η-C₅H₅)] (M = Mn, Re) (eq 3).¹⁴



In addition, compound Na₂[W(CO)₅] also reacted with **1** and **2** to yield Mn–W and Re–W dimetal bridging carbene complexes [MW{μ-C(H)C₆H₅}(CO)₇(η-C₅H₅)] (M = Mn or Re) (eq 4),¹³ respectively, whereas Na[W(CO)₅CN] reacted with complex **1** and **2** to afford no



similar bridging carbene complexes but phenyl(pentacarbonylcyanotungsten)carbenemanganese and -rhenium complexes [η-C₅H₅(CO)₂M=C(C₆H₅)NCW(CO)₅] (M = Mn or Re) (eq 5).¹⁵ Unexpectedly, the reaction of the isothiocyano-substituted carbonyltungsten anion compound (Ph₃P)₂N[W(CO)₅SCN] with **1** led to loss of the sulfur atom to give a novel phenyl(pentacarbonyl-isocyanotungsten)carbenemanganese complex [η-C₅H₅(CO)₂Mn=C(C₆H₅)CNW(CO)₅] (eq 6),¹⁵ but the analogous reaction with **2** yielded an (isothiocyanato)phenyl-carbenerrhenium complex [η-C₅H₅(CO)₂Re=C(C₆H₅)SCN].¹⁵



To investigate the scope of this new synthetic method for dimetal bridging carbene and carbyne complexes and further examine the effect of different metacarbonyl anions containing a bulky substituent of cyclopentadienyl and PPh₃ or a three-electron ligand of NO on the reactivity of the cationic carbyne complexes and reaction products, we chose metacarbonyl anion compounds of group VIB, such as Na[η-C₅H₅Mo(CO)₃] (**3**) and Na[η-C₅H₅W(CO)₃] (**4**), and of group VIII, such as Na[Co(CO)₃PPh₃] (**5**), Na[η-C₅H₅Fe(CO)₂] (**6**), and (Ph₃P)₂N[Fe(CO)₃NO] (**7**), as nucleophiles for the reactions with cationic carbyne complexes of manganese and rhenium, **1** and **2**. In this paper we describe these unusual

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reactions and the structural characterizations of the resulting products.

Experimental Section

All reactions were performed under a dry, oxygen-free N₂ atmosphere by using standard Schlenk techniques. All solvents employed were reagent grade and dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under N₂. The tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium benzophenone ketyl, while petroleum ether (30–60 °C) and CH₂Cl₂ were distilled from CaH₂. The neutral SiO₂ (Scientific Adsorbents Incorporated, 40 microns Flash) used for chromatography was deoxygenated at room temperature under high vacuum for 12 h, and the neutral alumina (Al₂O₃) was deoxygenated under high vacuum for 16 h, deactivated with 5% w/w N₂-saturated water, and stored under N₂. Complexes [η-C₅H₅(CO)₂Mn≡C C₆H₅]BBr₄ (**1**)¹⁶ and [η-C₅H₅(CO)₂Re≡C C₆H₅]BBr₄ (**2**)¹⁷ were prepared as previously described. Compounds Na[η-C₅H₅Mo(CO)₃] (**3**),¹⁸ Na[η-C₅H₅W(CO)₃] (**4**),¹⁸ Na[Co(CO)₃PPh₃] (**5**),¹⁹ Na[η-C₅H₅Fe(CO)₂] (**6**),^{20,21} and (Ph₃P)₂N[Fe(CO)₃NO] (**7**)²² 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 points obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

Reaction of [η-C₅H₅(CO)₂Mn≡C C₆H₅]BBr₄ (1**) with Na[η-C₅H₅Mo(CO)₃] (**3**) To Give [MnMo{C(CO)C₆H₅}(CO)₄(η-C₅H₅)₂] (**8**).** To a 5 mL of 0.8% Na/Hg in 50 mL of THF was added 0.107 g (0.22 mmol) of [η-C₅H₅Mo(CO)₃]₂. The mixture was stirred at room temperature for 2 h. The resulting light yellow solution of Na[η-C₅H₅Mo(CO)₃]¹⁸ was cooled to –90 °C, then poured rapidly on to 0.259 g (0.43 mmol) of **1** previously cooled to –90 °C. Immediately the orange-red solution turned deep red. The mixture was stirred at –90 to –45 °C for 7 h, during which time the solution gradually turned dark red. The resulting solution was evaporated under high vacuum at –45 to –40 °C to dryness. The residue was chromatographed on an alumina column (1.6 × 15 cm) at –25 °C with petroleum ether as the eluant. After elution of a small pink band which contained unreacted [η-C₅H₅Mo(CO)₃]₂ from the column, the brown-red band was eluted with petroleum ether/CH₂Cl₂/Et₂O (10:1:1) and collected. The solvent was removed under vacuum, and the residue was recrystallized from petroleum ether/CH₂Cl₂ solution at –80 °C to give 0.22 g (93%, based on **1**) of brown-red crystals of **8**: mp 73–74 °C dec; IR (CH₂Cl₂) ν CO 2051 (s), 2022 (m), 1988 (s), 1934 (vs, br), 1888 (sh) cm^{–1}; ¹H NMR (CD₃COCD₃) δ 7.44 (m, 2H, C₆H₅), 7.33 (m, 2H, C₆H₅), 7.16 (m, 1H, C₆H₅), 5.45 (s, 5H, C₅H₅), 4.73 (s, 5H, C₅H₅); MS *m/e* 510 (M⁺), 482 (M⁺ – CO), 426 (M⁺ – 3CO), 398 (M⁺ – 4CO), 370 (M⁺ – 5CO), 204 [C₅H₅Mn(CO)₃]⁺, 176 [C₅H₅Mn(CO)₂]⁺. Anal. Calcd for C₂₂H₁₅O₅MnMo: C, 51.79; H, 2.96. Found: C, 51.73; H, 3.03.

Reaction of [η-C₅H₅(CO)₂Re≡C C₆H₅]BBr₄ (2**) with **3** To Give [ReMo{C(CO)C₆H₅}(CO)₄(η-C₅H₅)₂] (**9**).** A fresh Na[η-C₅H₅Mo(CO)₃] solution prepared by reaction of [η-C₅H₅Mo(CO)₃]₂ (0.051 g, 0.10 mmol) with 2.5 mL of 0.8% Na/Hg in 50 mL of THF was reacted in a manner similar to that described

above with 0.153 g (0.21 mmol) of **2** at –90 to –45 °C for 6 h. Further treatment of the resulting solution as described in the reaction of **1** with **3** afforded 0.14 g (90%, based on **2**) of **9** as brown-red crystals: mp 81–82 °C dec; IR (CH₂Cl₂) ν CO 2054 (m), 2023 (sh), 1984 (s), 1945 (vs, br), 1911 (s), 1886 (w) cm^{–1}; ¹H NMR (CD₃COCD₃) δ 7.37 (m, 2H, C₆H₅), 7.28 (m, 2H, C₆H₅), 7.25 (m, 1H, C₆H₅), 5.63 (s, 5H, C₅H₅), 5.39 (s, 5H, C₅H₅); MS *m/e* 642 (M⁺), 558 (M⁺ – 3CO), 530 (M⁺ – 4CO), 502 (M⁺ – 5CO), 336 [C₅H₅Re(CO)₃]⁺, 308 [C₅H₅Re(CO)₂]⁺, 280 [C₅H₅Re(CO)⁺]. Anal. Calcd for C₂₂H₁₅O₅ReMo: C, 41.19; H, 2.36. Found: C, 41.40; H, 2.14.

Reaction of **1 with Na[η-C₅H₅W(CO)₃] (**4**) To Give [MnW{C(CO)C₆H₅}(CO)₄(η-C₅H₅)₂] (**10**).** To 5 mL of 0.8% Na/Hg in 50 mL of THF was added 0.268 g (0.40 mmol) of [η-C₅H₅W(CO)₃]₂. The mixture was stirred at room temperature for 2 h. The resulting light yellow solution of Na[η-C₅H₅W(CO)₃]¹⁸ was cooled to –90 °C, then poured rapidly on to 0.432 g (0.73 mmol) of **1** previously cooled to –90 °C. Immediately the orange-red solution turned deep red. The mixture was stirred at –90 to –45 °C for 5 h, during which time the solution gradually turned dark red. Further treatment of the resulting solution as described in the reaction of **1** with **3** gave 0.22 g (92%, based on **1**) of reddish-brown crystalline **10**: mp 109–111 °C dec; IR (CH₂Cl₂) ν CO 2054 (w), 2008 (sh), 1985 (s), 1940 (vs, br), 1916 (s), 1886 (w) cm^{–1}; ¹H NMR (CD₃COCD₃) δ 7.46 (m, 2H, C₆H₅), 7.34 (m, 2H, C₆H₅), 7.13 (m, 1H, C₆H₅), 5.62 (s, 5H, C₅H₅), 4.71 (s, 5H, C₅H₅); MS *m/e* 598 (M⁺), 570 (M⁺ – CO), 542 (M⁺ – 2CO), 514 (M⁺ – 3CO), 204 [C₅H₅Mn(CO)₃]⁺. Anal. Calcd for C₂₂H₁₅O₅MnW: C, 44.18; H, 2.53. Found: C, 44.18; H, 2.58.

Reaction of **2 with **4** To Give [ReW{C(CO)C₆H₅}(CO)₄(η-C₅H₅)₂] (**11**).** Similar to that described for the reaction of **1** with **4**, compound **2** (0.153 g, 0.21 mmol) was treated with a fresh Na[η-C₅H₅Mo(CO)₃] solution prepared by reaction of [η-C₅H₅W(CO)₃]₂ (0.070 g, 0.11 mmol) with 1.5 mL of 0.8% Na/Hg in 40 mL of THF at –90 to –45 °C for 6 h. Further treatment of the resulting solution as described in the reaction of **1** with **3** afforded 0.14 g (90%, based on **2**) of reddish-brown crystals of **11**: mp 81–82 °C dec; IR (CH₂Cl₂) ν CO 2048 (m), 1985 (s), 1942 (vs, br), 1908 (s), 1860 (w) cm^{–1}; ¹H NMR (CD₃COCD₃) δ 7.36 (m, 2H, C₆H₅), 7.30 (m, 2H, C₆H₅), 7.05 (m, 1H, C₆H₅), 5.63 (s, 5H, C₅H₅), 5.38 (s, 5H, C₅H₅); MS *m/e* 729 (M⁺), 701 (M⁺ – CO), 673 (M⁺ – 2CO), 645 (M⁺ – 3CO), 617 (M⁺ – 4CO), 589 (M⁺ – 5CO), 336 [C₅H₅Re(CO)₃]⁺, 308 [C₅H₅Mn(CO)₂]⁺. Anal. Calcd for C₂₂H₁₅O₅ReW: C, 36.23; H, 2.07. Found: C, 36.36; H, 2.11.

Reaction of **1 with Na[Co(CO)₃PPh₃] (**5**) To Give [MnCo{C(CO)C₆H₅}(CO)₄(PPh₃)(η-C₅H₅)] (**12**).** To 6 mL of 0.8% Na/Hg in 50 mL of THF was added 0.391 g (0.48 mmol) of [Co(CO)₃PPh₃]₂. The mixture was stirred at room temperature for 2 h. The resulting yellow solution of Na[Co(CO)₃PPh₃]¹⁹ was cooled to –90 °C, then poured rapidly onto 0.518 g (0.87 mmol) of **1** previously cooled to –90 °C. The red solution turned immediately dark red. The mixture was stirred at –90 to –45 °C for 5 h, during which time the solution gradually turned blackish red. The resulting solution was evaporated under vacuum at –50 to –40 °C to dryness, and the residue was chromatographed on silica gel at –25 °C with petroleum ether followed by petroleum ether/CH₂Cl₂ (5:1) as the eluant. A blackish-green band was eluted and collected. After removal of the solvent in vacuo, the dark green residue was recrystallized from petroleum ether/CH₂Cl₂ solution at –80 °C to give 0.62 g (89%, based on **1**) of blackish-green crystals of **12**: mp 80–81 °C dec; IR (CH₂Cl₂) ν CO 2054 (m), 2018 (s), 1957 (vs, br), 1905 (w), 1863 (sh), 1766 (m) cm^{–1}; ¹H NMR (CD₃COCD₃) δ 7.52 (m, 5H, C₆H₅), 7.36 (m, 10H, C₆H₅), 7.10 (m, 5H, C₆H₅), 5.62 (s, 5H, C₅H₅); MS *m/e* 670 (M⁺), 614 (M⁺ – 2CO), 586 (M⁺ – 3CO), 204 [C₅H₅Mn(CO)₃]⁺, 176 [C₅H₅Mn(CO)₂]⁺. Anal. Calcd for C₃₅H₂₅O₅PMnCo·CH₂Cl₂: C, 57.24; H, 3.60. Found: C, 57.29; H, 3.80.

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Reaction of 2 with 5 To Give [ReCo{C(CO)C₆H₅}(CO)₄(PPh₃)(η -C₅H₅)] (13). Compound **2** (0.460 g, 0.63 mmol) was treated, in a manner similar to that in the reaction of **1** with **5**, with a fresh solution of Na[Co(CO)₃PPh₃] prepared by the reaction of [Co(CO)₃PPh₃]₂ (0.283 g, 0.35 mmol) with 4.5 mL of 0.8% Na/Hg in 50 mL of THF at -90 to -45 °C for 6 h. The resulting mixture was treated as described for the reaction of **1** with **5** to give 0.29 g (81%, based on **2**) of **13** as blackish-green crystals: mp 77–78 °C dec; IR (CH₂Cl₂) ν CO 2054 (w), 2018 (vs), 1956 (vs, br), 1894 (vs), 1852 (sh), 1750 (m) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.41 (m, 5H, C₆H₅), 7.29 (m, 10H, C₆H₅), 7.06 (m, 5H, C₆H₅), 5.49 (s, 5H, C₅H₅); MS *m/e* 802 (M⁺), 774 (M⁺ - 2CO), 662 (M⁺ - 5CO), 336 [C₅H₅Re(CO)₃]⁺, 308 [C₅H₅Re(CO)₂]⁺. Anal. Calcd for C₃₅H₂₅O₅ReCo·CH₂Cl₂: C, 48.77; H, 3.07. Found: C, 48.49; H, 3.06.

Reaction of 2 with Na[η -C₅H₅Fe(CO)₂] (6) To Give [ReFe{C(CO)C₆H₅}(CO)₃(η -C₅H₅)₂] (14). To 0.50 mL of 0.8% Na/Hg in 50 mL of THF was added 0.074 g (0.21 mmol) of [η -C₅H₅Fe(CO)₂]₂. The mixture was stirred at room temperature for 2 h. The resulting light yellow solution of Na[η -C₅H₅Fe(CO)₂]₂^{20,21} was cooled to -90 °C, then poured rapidly onto 0.306 g (0.42 mmol) of **2** previously cooled to -90 °C. The orange-red solution turned rapidly dark red. After stirring at -90 to -40 °C for 5–6 h, further treatment of the resulting mixture as described in the reaction of **1** with **3** gave 0.18 g (75%, based on **2**) of brown-red crystals of **14**: mp 92–95 °C dec; IR (CH₂Cl₂) ν CO 2053 (s), 2008 (sh), 1968 (vs, br), 1925 (m), 1896 (m), 1884 (s) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.46 (m, 2H, C₆H₅), 7.34 (m, 2H, C₆H₅), 7.13 (m, 1H, C₆H₅), 5.62 (s, 5H, C₅H₅), 4.71 (s, 5H, C₅H₅); MS *m/e* 572 (M⁺), 544 (M⁺ - CO), 516 (M⁺ - 2CO), 488 (M⁺ - 3CO), 460 (M⁺ - 4CO), 336 [C₅H₅Re(CO)₃]⁺, 308 [C₅H₅Mn(CO)₂]⁺. Anal. Calcd for C₂₁H₁₅O₄ReFe: C, 43.99; H, 2.64. Found: C, 44.25; H, 2.91.

Reaction of 1 with (Ph₃P)₂N[Fe(CO)₃NO] (7) To Give [MnFe(μ -CC₆H₅)(CO)₄(NO)(η -C₅H₅)] (15). To 0.605 g (1.02 mmol) of **1** dissolved in 50 mL of THF at -90 °C was added 0.719 g (1.02 mmol) of (Ph₃P)₂N[Fe(CO)₃NO] with stirring. The brick-red solution turned rapidly green. The mixture was stirred at -90 to -45 °C for 6 h, during which time the green solution turned blackish-green. After vacuum removal of the solvent at -45 to -40 °C, the residue was chromatographed on Al₂O₃ at -25 °C with petroleum ether/CH₂Cl₂ (5:1) as the eluant, the blackish-green band was eluted. The solvent was removed in vacuo, and the residue was recrystallized from petroleum ether/CH₂Cl₂ solution at -80 °C to give 0.384 g (93%, based on **1**) of blackish-green crystals of **15**: mp 86–87 °C dec; IR (CH₂Cl₂) ν CO 2054 (s), 1994 (m), 1970 (s), 1885 (w) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.80 (m, 2H, C₆H₅), 7.61 (m, 2H, C₆H₅), 7.19 (m, 1H, C₆H₅), 5.07 (s, 5H, C₅H₅); MS *m/e* 379 (M⁺ - CO), 323 (M⁺ - 3CO), 204 [C₅H₅Mn(CO)₃]⁺, 176 [C₅H₅Mn(CO)₂]⁺. Anal. Calcd for C₁₆H₁₀O₅NMnFe: C, 47.21; H, 2.48; N, 3.44. Found: C, 46.97; H, 2.36; N, 3.23.

Reaction of 2 with 7 To Give [ReFe(μ -CC₆H₅)(CO)₄(NO)(η -C₅H₅)] (16). Compound **2** (0.205 g, 0.28 mmol) was treated, in a manner similar to that in the reaction of **1** with **7**, with (Ph₃P)₂N[Fe(CO)₃NO] (0.20 g, 0.28 mmol) at -90 to -45 °C for 6 h. Further treatment of the resulting solution as described in the reaction of **1** with **7** gave 0.130 g (86%, based on **2**) of blackish-green crystals of **16**: mp 96–97 °C dec; IR (CH₂Cl₂) ν CO 2053 (s), 2024 (m), 1963 (vs, br), 1900 (w), cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.90 (m, 1H, C₆H₅), 7.62 (m, 3H, C₆H₅), 7.57 (m, 1H, C₆H₅), 5.26 (s, 5H, C₅H₅); MS *m/e* 539 (M⁺), 511 (M⁺ - CO), 483 (M⁺ - 2CO), 455 (M⁺ - 3CO), 427 (M⁺ - 4CO), 397 (M⁺ - 4CO - NO), 336 [C₅H₅Re(CO)₃]⁺. Anal. Calcd for C₁₆H₁₀O₅NMnFe: C, 47.21; H, 2.48; N, 3.44. Found: C, 46.97; H, 2.36; N, 3.23.

Reaction of 15 with Fe₂(CO)₉ To Give [MnFe₂(μ -CC₆H₅)(CO)₇(NO)(η -C₅H₅)] (17). To 0.025 g (0.061 mmol) of **15** dissolved in 50 mL of THF at -20 °C was added 0.085 g (0.234 mmol) of Fe₂(CO)₉. The mixture was stirred at -5 to 0 °C for 6 h, during which time the blackish-green solution

gradually turned dark red. After the solution was evaporated at 0 °C under vacuum to dryness, the dark red residue was chromatographed on SiO₂ at -20 °C with petroleum ether/CH₂Cl₂ (10:1) as the eluant. The purple-red band was eluted and collected. The solvent was removed from the red eluate in vacuo, and the crude product was recrystallized from petroleum ether/CH₂Cl₂ at -80 °C to give 0.026 g (76%, based on **15**) of purple-red crystals of **17**: mp 81–82 °C dec; IR (CH₂Cl₂) ν CO 2065 (s), 2023 (vs), 2012 (sh), 1985 (w), 1963 (m), 1925 (w), 1840 (m) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.92 (m, 2H, C₆H₅), 7.62 (m, 2H, C₆H₅), 7.36 (m, 1H, C₆H₅), 4.96 (s, 5H, C₅H₅); MS *m/e* 547 (M⁺), 491 (M⁺ - 2CO), 351 (M⁺ - 7CO), 321 (M⁺ - 7CO - NO). Anal. Calcd for C₁₉H₁₀O₈NMnFe₂: C, 41.73; H, 1.84; N, 2.56. Found: C, 41.48; H, 1.91; N, 2.37.

Reaction of 12 with Fe₂(CO)₉ To Give [MnFeCo(μ -CC₆H₅)(CO)₈(η -C₅H₅)] (18). To 0.025 g (0.037 mmol) of **12** dissolved in 50 mL of THF at -20 °C was added 0.042 g (0.115 mmol) of Fe₂(CO)₉. The mixture was stirred at -20 to 5 °C for 6–7 h, during which time the orange-red solution gradually turned brown-red. After removal of the solvent at 0 °C, the dark red residue was chromatographed on SiO₂ at -15 to -20 °C with petroleum ether/CH₂Cl₂ (10:1) as the eluant. The purple-red band was eluted. The solvent was removed from the red eluate in vacuo, and the crude product was recrystallized from petroleum ether/CH₂Cl₂ at -80 °C to yield 0.020 g (70%, based on **12**) of purple-red crystals of **18**:¹⁴ mp 91–92 °C dec; IR (CH₂Cl₂) ν CO 2078 (vs), 2054 (w), 2031 (vs), 1984 (w), 1963 (m), 1890 (s), 1831 (m) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.72 (m, 2H, C₆H₅), 7.51 (m, 2H, C₆H₅), 7.32 (m, 1H, C₆H₅), 4.89 (s, 5H, C₅H₅); MS *m/e* 548 (M⁺), 492 (M⁺ - 2CO), 464 (M⁺ - 3CO), 408 (M⁺ - 5CO), 380 (M⁺ - 6CO). Anal. Calcd for C₂₀H₁₀O₈MnFeCo: C, 43.83; H, 1.84. Found: C, 43.59; H, 2.04.

Reaction of 13 with Fe₂(CO)₉ To Give [ReFeCo(μ -CC₆H₅)(CO)₈(η -C₅H₅)] (19). Compound **13** (0.040 g, 0.050 mmol) was treated as described in the reaction of **12** with Fe₂(CO)₉ with 0.073 g (0.201 mmol) of Fe₂(CO)₉ at -20 to 5 °C for 7–8 h, during which time the orange-red solution gradually turned dark red. Further treatment of the resulting solution similar to that in the reaction of **12** with Fe₂(CO)₉ yielded 0.025 g (74%, based on **13**) of blackish-red crystalline **19**:¹⁴ mp 85–87 °C dec; IR (CH₂Cl₂) ν CO 2073 (s), 2052 (w), 2025 (vs), 1970 (w), 1954 (w), 1908 (m), 1854 (m, br) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.53 (m, 2H, C₆H₅), 7.45 (m, 2H, C₆H₅), 7.22 (m, 1H, C₆H₅), 5.62 (s, 5H, C₅H₅); MS *m/e* 650 (M⁺ - CO). Anal. Calcd for C₂₀H₁₀O₈ReFeCo: C, 35.36; H, 1.48. Found: C, 35.36; H, 1.41.

X-Ray Crystal Structure Determinations of Complexes 10, 13, and 15. Single crystals of complexes **10**, **13**, and **15** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH₂Cl₂ solution at -80 °C. Single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data for 3485, 6273, and 3271 independent reflections, of which 1852 and 3871 with *I* > 2.50 σ (*I*) for **10** and **13** and 2532 with *I* > 3.00 σ (*I*) for **15** were observable, were collected with a Rigaku AFC7R diffractometer at 20 °C using Mo K α radiation with an ω - 2θ scan mode within the ranges 5° ≤ 2θ ≤ 50° for **10** and **13**, 5° ≤ 2θ ≤ 52° for **15**, respectively.

The structures of **10**, **13**, and **15** were solved by direct methods and expanded using Fourier techniques. For **10** and **15**, the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of **10** were included but not refined, while the hydrogen atoms of **15** were refined isotropically. For **13**, the some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. The hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was respectively based on 1852, 3871, and 2532 observed reflections and 263, 410, and 258 variable parameters and converged with unweighted and weighted agreement factors of *R* = 0.046 and *R*_w = 0.046 for **10**, *R* = 0.046 and *R*_w = 0.052 for **13**, and *R* = 0.032 and *R*_w = 0.039

Table 1. Crystal Data and Experimental Details for Complexes 10, 13, and 15

	10	13 ·CH ₂ Cl ₂	15
formula	C ₂₂ H ₁₅ O ₅ MnW	C ₃₆ H ₂₇ O ₅ Cl ₂ PreCo	C ₁₆ H ₁₀ O ₅ NFeMn
fw	598.15	886.63	407.04
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>a</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> (Å)	9.582(2)	15.835(3)	7.684(2)
<i>b</i> (Å)	12.966(3)	12.552(3)	14.802(3)
<i>c</i> (Å)	15.807(2)	17.131(2)	14.202(3)
β (deg)	99.09(1)	95.11(1)	99.65(3)
<i>V</i> (Å ³)	1939.2(6)	3391(1)	1592.5(7)
<i>Z</i>	4	4	4
<i>D</i> _{calcd} (g/cm ³)	2.049	1.736	1.689
<i>F</i> (000)	1144.00	1736.00	816.00
μ (Mo K α) (cm ⁻¹)	66.17	43.03	17.27
radiation (monochromated in incident beam)	Mo K α (λ = 0.71069 Å)	Mo K α (λ = 0.71069 Å)	Mo K α (λ = 0.71069 Å)
diffractometer	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R
temperature (°C)	20	20	20
orientation reflections: no.; range (2 θ) (deg)	18; 14.0–16.2	17; 13.5–21.3	25; 18.3–21.6
scan method	ω –2 θ	ω –2 θ	ω –2 θ
data coll. range, 2 θ (deg)	5–50	5–50	5–52
no. of unique data, total	3485	6273	3271
with <i>I</i> > 2.50 σ (<i>I</i>)	1852	3871	2532 (<i>I</i> > 3.00 σ (<i>I</i>))
no. of params refined	263	410	258
correction factors, max. min.	0.7016–1.0000	0.9283–1.0000	0.8145–1.0000
<i>R</i> ^a	0.046	0.046	0.032
<i>R</i> _w ^b	0.046	0.052	0.039
quality-of-fit indicator ^c	1.25	1.43	1.53
largest shift/esd final cycle	0.00	0.02	0.00
largest peak, e ⁻ /Å ³	0.86	1.50	0.47
min. peak, e ⁻ /Å ³	–1.36	–1.72	–0.56

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

Table 2. Selected Bond Lengths (Å)^a and Angles (deg)^a for Complexes 10 and 13

	10 (M = Mn, M' = W)	13 (M = Re, M' = Co)		10 (M = Mn, M' = W)	13 (M = Re, M' = Co)
M–M'	2.905(2)	2.717(2)	M–C(1)	1.78(2)	1.89(1)
M–C(8)	2.05(1)	2.136(10)	M–C(2)	1.81(2)	1.88(1)
M'–C(8)	2.15(1)	2.00(1)	M'–C(3)	1.94(2)	1.80(1)
M'–C(7)	2.25(2)	1.94(1)	M'–C(4)	1.92(2)	1.79(1)
C(7)–C(8)	1.38(2)	1.40(1)	M'–P		2.196(3)
C(7)–O(7)	1.21(2)	1.20(1)	M–C(Cp) (av)	2.14	2.30
C(8)–C(14)	1.48(2)	1.48(1)	M'–C(Cp) (av)	2.34	
M–M'–C(8)	44.9(3)	51.2(3)	M–C(8)–C(14)	129.8(9)	132.6(7)
M'–M–C(8)	47.5(4)	46.8(3)	M'–C(8)–C(14)	130.7(9)	131.3(7)
M–C(8)–M'	87.5(5)	82.0(3)	M–M'–P		160.51(9)
M–M'–C(7)	63.8(4)	71.6(3)	P–M'–C(8)		110.4(3)
M'–C(8)–C(7)	75.6(9)	66.8(6)	P–M'–C(7)		90.2(3)
C(8)–M'–C(7)	36.7(5)	41.7(4)	M–C(1)–O(1)	174(1)	176.4(10)
M'–C(7)–C(8)	67.7(8)	71.4(6)	M–C(2)–O(2)	170(1)	175(1)
C(8)–C(7)–O(7)	147(1)	147(1)	M'–C(3)–O(3)	178(1)	178(1)
M'–C(7)–O(7)	144(1)	140.7(9)	M'–C(4)–O(4)	178(1)	174(1)

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

for **15**, respectively. All the calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

The details of the crystallographic data and the procedures used for data collection and reduction information for **10**, **13**, and **15** are given in Table 1. The selected bond lengths and angles are listed in Tables 2 and 3, respectively. The atomic coordinates and *B*_{iso}/*B*_{eq}, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **10**, **13**, and **15** are given in the Supporting Information. The molecular structures of **10**, **13**, and **15** are given in Figures 1, 2, and 3, respectively.

Results and Discussion

The complex [η -C₅H₅(CO)₂Mn≡CC₆H₅][BBR₄] (**1**) was treated with equimolar quantity of Na[η -C₅H₅Mo(CO)₃] (**3**) in THF at low temperature (–90 to –45 °C) for 7 h.

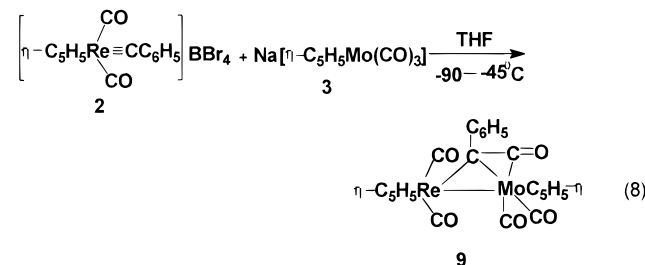
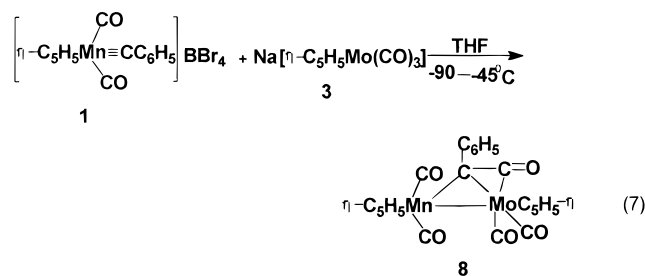
Table 3. Selected Bond Lengths (Å)^a and Angles (deg)^a for Complex 15

Mn–Fe	2.6494(3)	Mn–C(1)	1.796(3)
Mn–C(8)	1.865(3)	Mn–C(2)	1.816(3)
Fe–C(8)	1.853(3)	Fe–C(3)	1.787(3)
Fe–N	1.658(3)	Fe–C(4)	1.852(3)
N–O(5)	1.177(3)	Mn–C(Cp) (av)	2.15
C(8)–C(14)	1.455(3)	Mn–Fe–N	123.09(9)
Mn–Fe–C(8)	44.72(8)	Mn–C(1)–O(1)	179.2(3)
Fe–Mn–C(8)	44.37(2)	Mn–C(2)–O(2)	168.6(3)
Mn–C(8)–Fe	90.9(1)	Fe–C(3)–O(3)	176.0(3)
Mn–C(8)–C(14)	137.0(2)	Fe–C(4)–O(4)	179.5(3)
Fe–C(8)–C(14)	132.1(2)	C(8)–Fe–N	108.3(1)

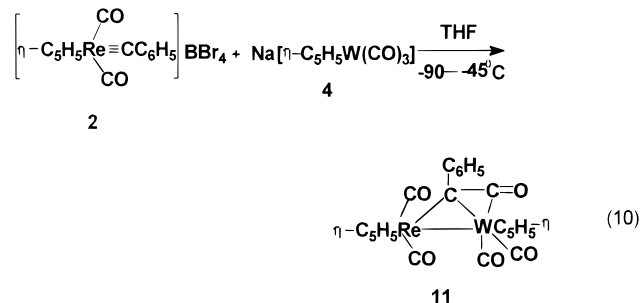
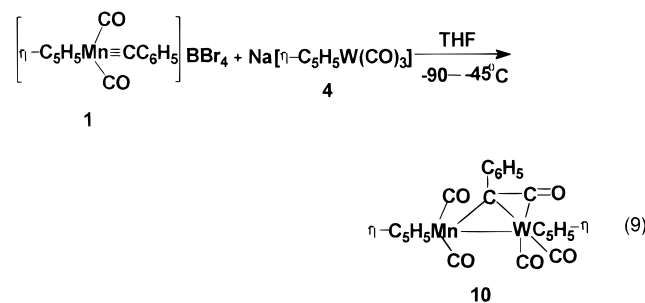
^a Estimated standard deviations in the least significant figure are given in parentheses.

After vacuum removal of the solvent, the residue was chromatographed on an alumina column at low temperature, and the crude products were recrystallized from petroleum ether/CH₂Cl₂ solution at –80 °C to give

a ketenyl-bridged Mn–Mo complex $[\text{MnMo}\{\text{C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (**8**) (eq 7) in 93% yield. The analogous reaction of $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Re}\equiv\text{CC}_6\text{H}_5]\text{BBr}_4$ (**2**) with **3** under the same conditions afforded a ketenyl-bridged Re–Mo complex $[\text{ReMo}\{\text{C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (**9**) (eq 8) in 90% yield.



Like **3**, compound $\text{Na}[\eta\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]$ (**4**) also reacted with complexes **1** and **2** under the same conditions to produce ketenyl-bridged Mn–W and Re–W complexes $[\text{MnW}\{\text{C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (**10**) (eq 9) and $[\text{ReW}\{\text{C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (**11**) (eq 10) in 92% and 90% yields, respectively.



Compounds **8–11** are readily soluble in polar organic solvents but sparingly soluble in nonpolar solvents. They are air-sensitive in solution but relatively stable as the solid. On the basis of elemental analyses, spectroscopic evidence, and X-ray crystallography, products **8–11** are formulated as possessing a ketenyl ligand bonded to a carbene carbon atom, similar to the complex $[\text{ReMn}\{\mu\text{-C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$ reported by

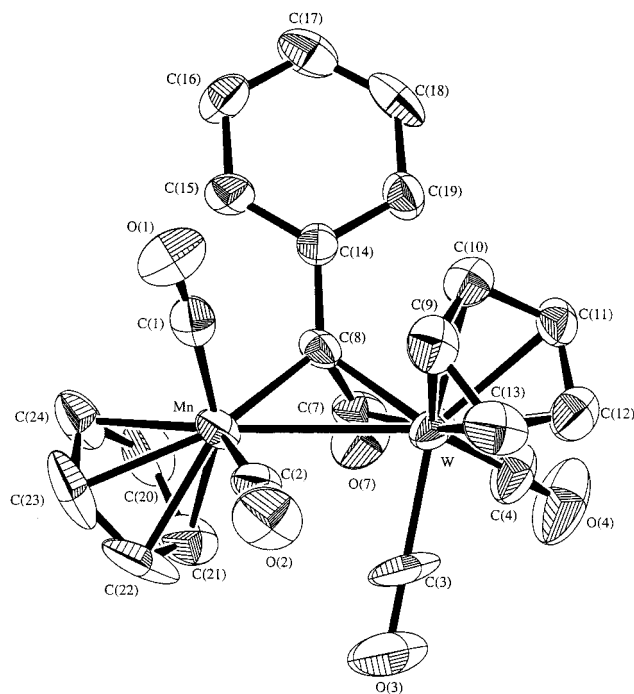


Figure 1. Molecular structure of **10**, showing the atom-numbering scheme.

Fischer et al.²³ by the reaction of $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{Mn}\equiv\text{CC}_6\text{H}_5]\text{BCl}_4$ with $\text{Na}[\text{Re}(\text{CO})_5]$ and $[\text{MMn}\{\mu\text{-C}(\text{CO})\text{C}_6\text{H}_4\text{Me-p}\}(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mn}$ or Re) reported by Stone and co-workers²⁴ by the reactions of $[\eta\text{-C}_5\text{H}_5(\text{CO})_2\text{M}\equiv\text{CC}_6\text{H}_4\text{Me-p}]\text{BF}_4$ ($\text{M} = \text{Mn}$ or Re) with $(\text{Ph}_3\text{P})_2\text{N}[\text{Mn}(\text{CO})_5]$. The X-ray diffraction study for complex **10** was carried out in order to firmly establish its structure. The results of the X-ray diffraction work are summarized in Table 1, and the structure is shown in Figure 1.

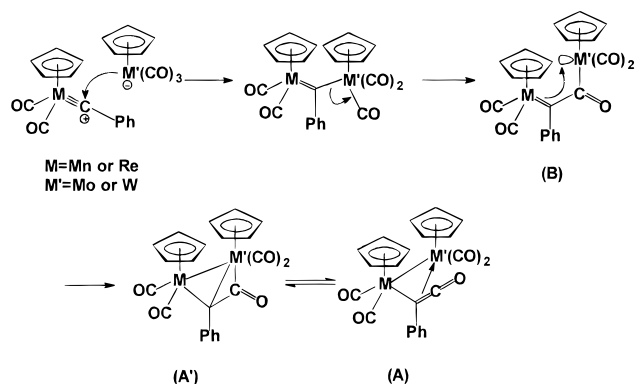
The structure of complex **10** resembled that of analogous complexes $[\text{ReMn}\{\mu\text{-C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$ ²³ and $[\text{Mn}_2\{\mu\text{-C}(\text{CO})\text{C}_6\text{H}_4\text{Me-p}\}(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$.²⁴ In **10** the Mn–W bond (2.905(2) Å) is asymmetrically bridged by the α -carbon atom of a phenyl ketenyl group [Mn–C(8) 2.05(1), W–C(8) 2.15(1) Å]. A unique feature of the structure is the presence of the C(7)O(7) group bonded to C(8) with a C(7)–O(7) distance of 1.21(2) Å and a C(8)–C(7) distance of 1.38(2) Å. The former distance might correspond either to a C=O or to a C \equiv O bond. The latter distance, however, suggests C=C character so that the $\text{C}(\text{CO})\text{C}_6\text{H}_5$ group might be regarded as a one-electron ketene bridge $\text{C}_6\text{H}_5\text{C}=\text{C}=\text{O}$ rather than a three-electron ylide bridge $\text{C}^-(\text{C}_6\text{H}_5)=\text{C}^+=\text{O}$ across the metal–metal bond.²⁴ Thus, complexes **8–11** might be better described as η^1, η^2 -ketene complexes (**A** or **A'**) (Scheme 1, see below).

The W–C(7) distance [2.25(2) Å] is much longer than the corresponding Co–C(7) distance in $[\text{ReCo}\{\mu\text{-C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (1.987(8) Å)¹⁴ since the radius of tungsten is larger than that of cobalt. Since the radii of Mn and Re atoms are nearly the same, the metal–metal bond distance in **10** is comparable with the longer Re–W separation in analogous bridging carbene complexes

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Scheme 1



[ReW{ μ -C(H)C₆H₅}(CO)₇(η -C₅H₅)} (3.0233(5) Å)¹³ and (PPh₃)₂N[ReW{ μ -C(H)C₆H₄Me-4}(CO)₉] (3.033(1) Å).²⁵ The C(8)–Mn linkage (2.05(1) Å) in **10** is close in value to the similar bond in the bridging carbene complex [MnFe{ μ -C(COEt)C₆H₅}(CO)₅(η -C₅H₅)} (2.021(4) Å)²⁶ but is obviously longer than the similar bond in bridging carbyne complexes [(CO)(η -C₅H₅)Fe(μ -COEt)(μ -CO)Mn-(η -C₅H₄Me)(CO)] (1.839(4) Å)²⁷ and [MnCo(μ -CC₆H₅)(CO)₅(η -C₅H₅)] (1.85(1) Å).¹⁴

The possible reaction pathway to complexes **8–11** (eqs 7–10) could involve initial formation of a carbene intermediate [η -C₅H₅(CO)₂M=C(C₆H₅)M'(CO)₃(η -C₅H₅)] (M = Mn or Re, M' = Mo or W), where the M'(CO)₃(η -C₅H₅) moiety is directly bonded to the carbene carbon through the M' atom, by attack of the [M'(CO)₃(η -C₅H₅)][−] anion on the cationic carbyne carbon of **1** or **2**. After initial metal–carbon bond formation, the migration of the M'=C bond of the carbene to a coordinated CO gives a coordinatively unsaturated ketene complex (**B**). Then addition of the M=C_{carbene} bond to the vacant site at M' completes the reaction to produce the η^1, η^2 -ketene complex (**A** or **A'**) (Scheme 1).

Interestingly, the PPh₃-substituted carbonylcobalt anion compound Na[Co(CO)₃PPh₃] (**5**) can also react with cationic carbyne complexes **1** and **2** to give PPh₃-coordinated ketenyl bridged complexes [MnCo{C(CO)-C₆H₅}(CO)₄(PPh₃)(η -C₅H₅)] (**12**) (eq 11) and [ReCo{C(CO)C₆H₅}(CO)₄(PPh₃)(η -C₅H₅)] (**13**) (eq 12) in 89% and 81% yields, respectively.

The formulas of complexes **12** and **13** are supported by microanalytical and spectroscopic data as well as X-ray crystallography. The formation pathway of complexes **12** and **13** could be analogous to that of cyclopentadienyl-substituted complexes **8–11**.

The crystal structure of complex **13** shown in Figure 2 resembled that of [MCo{ μ -C(CO)C₆H₅}(CO)₅(η -C₅H₅)] (M = Mn, Re) synthesized¹⁴ by the reactions of (Ph₃P)₂NFeCo(CO)₈ or (Ph₃P)₂NWCo(CO)₉ with complexes **1** and **2**, except that the substituents on the Co atom are two CO and one PPh₃ group in **13** but three CO ligands in the latter. As expected, two terminal carbonyl groups and one PPh₃ ligand are attached to the Co and two terminal CO to the Re atom. The Re–Co bond asym-

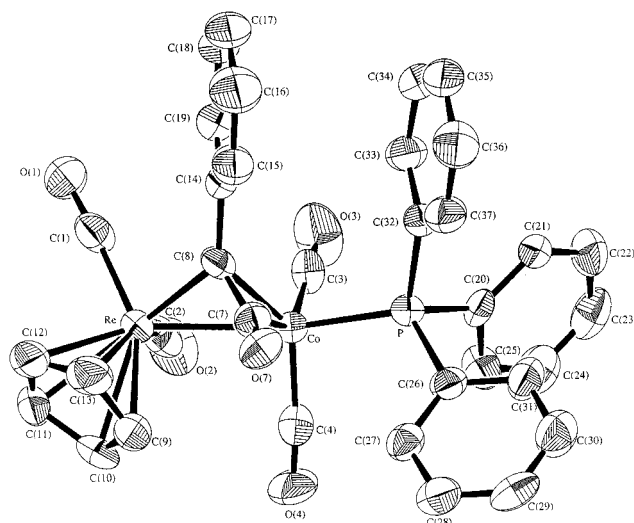
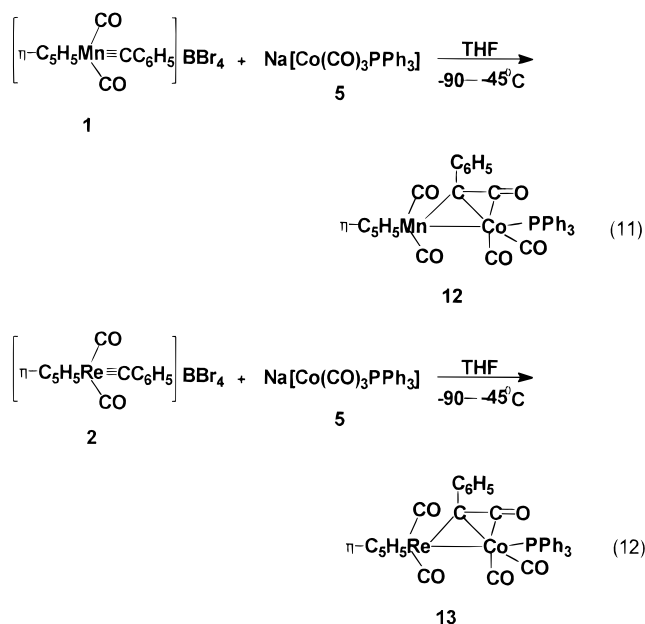


Figure 2. Molecular structure of **13**, showing the atom-numbering scheme. CH₂Cl₂ has been omitted for clarity.



metrically bridged by the α -carbon atom of the ketenyl group of C(CO)C₆H₅ [Re–C(8) 2.136(10), Co–C(8) 2.00(1) Å] has a length of 2.717(2) Å, which is nearly the same as that in [ReCo{ μ -C(CO)C₆H₅}(CO)₅(η -C₅H₅)] (2.720(1) Å).¹⁴ The C(7)–O(7) and C(8)–C(7) bond lengths are 1.20(1) and 1.40(1) Å, respectively, which are the same within experimental error as those in **10**. Thus, the C(CO)C₆H₅ group in **13** is also regarded as a ketenyl ligand. The C(8)–Re distance is close to those in bridging carbene complexes (PPh₃)₂N[ReW{ μ -C(H)C₆H₄Me-4}(CO)₉] (2.155(8) Å),²⁵ [Re₂(μ -H)₂(μ -CHBu^t)(η -C₆H₆)] (2.13(3) Å),²⁸ and [ReFe{ μ -C(H)C₆H₅}(CO)₆(η -C₅H₅)] (2.120(5) Å).^{10a}

Unlike Mo, W, and Co anionic compounds **3**, **4**, and **5**, the iron anion compound Na[η -C₅H₅Fe(CO)₂] (**6**) reacted only with **2** to form a ketenyl-bridged Re–Fe complex [ReFe{C(CO)C₆H₅}(CO)₃(η -C₅H₅)₂] (**14**) (eq 13) in a somewhat lower yield (75%), whose structure is supported by its elemental analysis and IR, ¹H NMR,

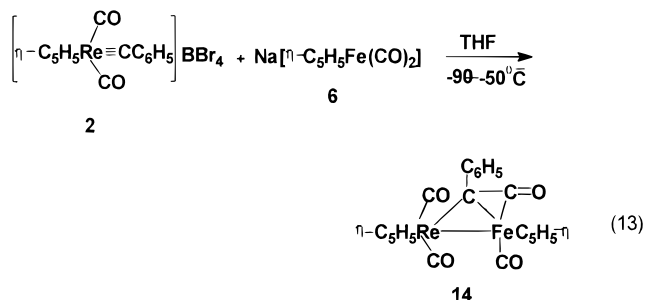
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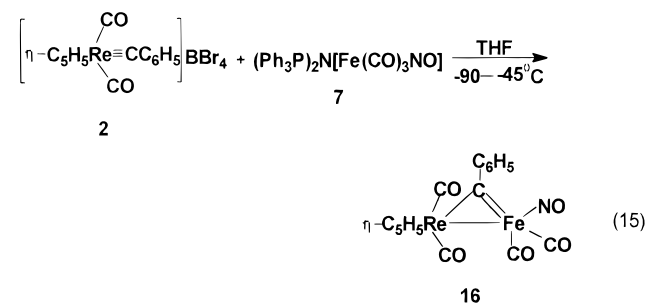
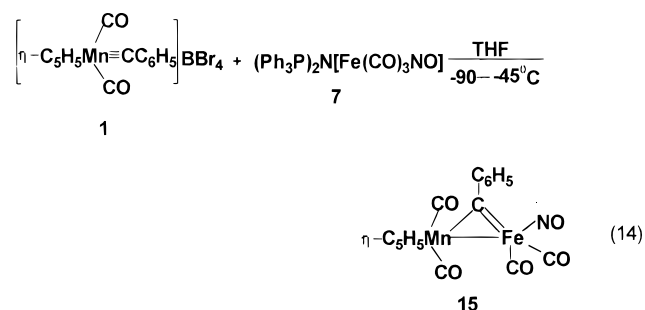
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and mass spectra and by comparison of the ^1H NMR spectrum of **14** with those of complexes **8–11**.



Of special interest are the reactions of compound $(\text{Ph}_3\text{P})_2\text{N}[\text{Fe}(\text{CO})_3\text{NO}]$ (**7**). The reactions of **7** with complexes **1** and **2** under similar conditions gave no expected bridging carbene or ketene complexes but heteronuclear dimetal bridging carbyne complexes $[\text{MnFe}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_4(\text{NO})(\eta\text{-C}_5\text{H}_5)]$ (**15**) (eq 14) and $[\text{ReFe}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_4(\text{NO})(\eta\text{-C}_5\text{H}_5)]$ (**16**) (eq 15) in 93% and 86% yields, respectively.



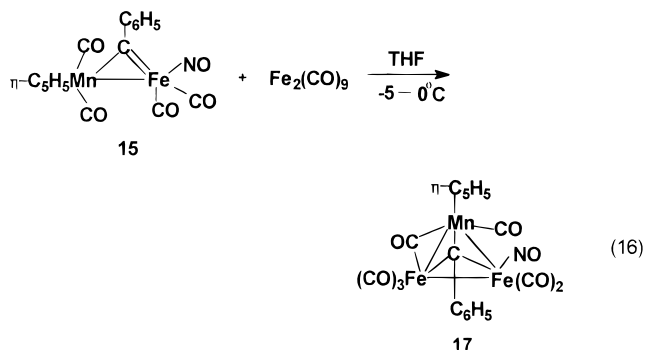
The formulas for complexes **15** and **16** shown in eqs 14 and 15 are based on elemental analysis and spectroscopic evidence. An X-ray study of **15** establishes its structure (Figure 3). The structural features of the dimetallacyclopentene part of **15** are very similar to that in analogous bridging carbyne complex $[\text{MnCo}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$,¹⁴ except the $\mu\text{-C-Fe}$ bond distance (1.853(3) Å) is slightly longer than the corresponding bond in $[\text{MnCo}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ ($\mu\text{-C-Co}$ 1.77(1) Å).¹⁴ The Mn–Fe bond (2.6494(3) Å) in **15** is somewhat longer than that in the analogous bridging carbyne complex $[(\text{CO})(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-COEt})(\mu\text{-CO})\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})]$ (2.572(1) Å)²⁷ but is slightly shorter than the similar bond in the bridging carbene complex $[\text{MnFe}\{\mu\text{-C}(\text{COEt})\text{C}_6\text{H}_5\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (2.6929(8) Å).²⁶ The C(8)–Mn linkage (1.865(3) Å) is slightly longer than that found in $[\text{MnCo}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (1.85(1) Å)¹⁴ but is obviously shorter than that in $[\text{MnFe}\{\mu\text{-C}(\text{COEt})\text{C}_6\text{H}_5\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (2.021(4) Å).²⁶ The C(8)–

Fe distance (1.853(3) Å) in **15** is as expected for a C=Fe bond, which is obviously shorter than the corresponding distance in $[\text{MnFe}\{\mu\text{-C}(\text{COEt})\text{C}_6\text{H}_5\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (2.020(4) Å).²⁶

The possible reaction pathway to complexes **15** and **16** (eqs 14 and 15) could proceed via a synthon for $[\text{Fe}(\text{CO})_2\text{NO}]^-$, analogous to the reactions¹⁴ of $(\text{PPh}_3)_2\text{N}[\text{FeCo}(\text{CO})_8]$ with complexes **1** and **2** (eq 3). The latter was assumed via a synthon for $\text{Co}(\text{CO})_3^-$, which attacked on the carbyne carbon of cationic **1** or **2** with bonding of the Co atom to the Mn or Re atom to construct a dimetallacyclopentene ring. The synthon of $[\text{Fe}(\text{CO})_2\text{NO}]^-$ could come from either an $[\text{Fe}(\text{CO})_3\text{NO}]^-$ anion that lost a CO ligand in the presence of **1** or **2** or a carbene intermediate $[\eta\text{-C}_5\text{H}_5\text{M}=\text{C}(\text{C}_6\text{H}_5)\text{Fe}(\text{CO})_3\text{NO}]$ (M = Mn or Re) formed by attack of the $[\text{Fe}(\text{CO})_3\text{NO}]^-$ anion on the carbyne carbon of **1** or **2**. The carbene intermediate then underwent cleavage of a CO group to generate the $[\text{Fe}(\text{CO})_2\text{NO}]^-$ species. We have indeed determined CO gas in the course of the reaction by gas chromatography.

Although a number of dimetal bridging carbyne complexes have been prepared by Stone et al. and us as mentioned in the Introduction, complexes **15** and **16**, as heteronuclear dimetal bridging carbyne complexes, were synthesized first by the reaction of the cationic carbyne complex with the monometal carbonyl anion. Undoubtedly, this is another new and convenient method for preparation of such bridging carbyne complexes.

Complex **15** reacted with an excess of $\text{Fe}_2(\text{CO})_9$ in THF at -5 to 0°C for 6 h. After workup as described in the Experimental Section, the purple-red heteronuclear trimetal bridging carbyne complex **17**, $[\text{MnFe}_2(\mu_3\text{-CC}_6\text{H}_5)(\text{CO})_7(\text{NO})(\eta\text{-C}_5\text{H}_5)]$, was isolated in 76% yield (eq 16).



The structure of complex **17** shown in eq 16 is established by an X-ray diffraction study,²⁹ which gave an *R* value of 0.15 due to serious decay. However, the elemental analysis and IR, ^1H NMR, and mass spectra are consistent with this geometry. The IR spectrum in the $\nu(\text{CO})$ region of **17** showed an absorption band at 1840 cm^{-1} attributed to a bridging or semibridging carbonyl ligand, in addition to six terminal CO absorption bands at 2065, 2023, 2012, 1985, 1963, and 1925 cm^{-1} , indicative of a $(\text{CO})_6\text{Fe}_2\text{Mn}(\mu\text{-CO})$ moiety. The ^1H NMR spectrum showed the expected proton signals due to the phenyl and cyclopentadienyl groups. The mass spectrum provided further structural information (Experimental Section) showing the molecular ion peak and

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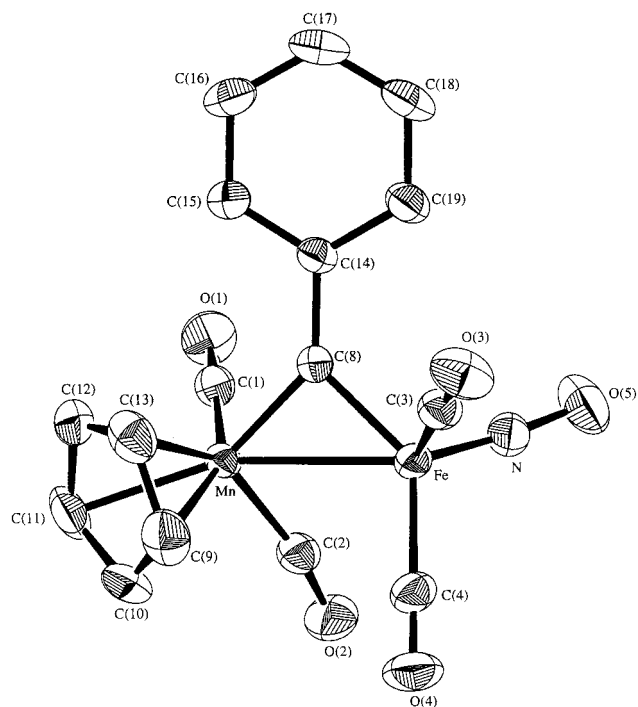
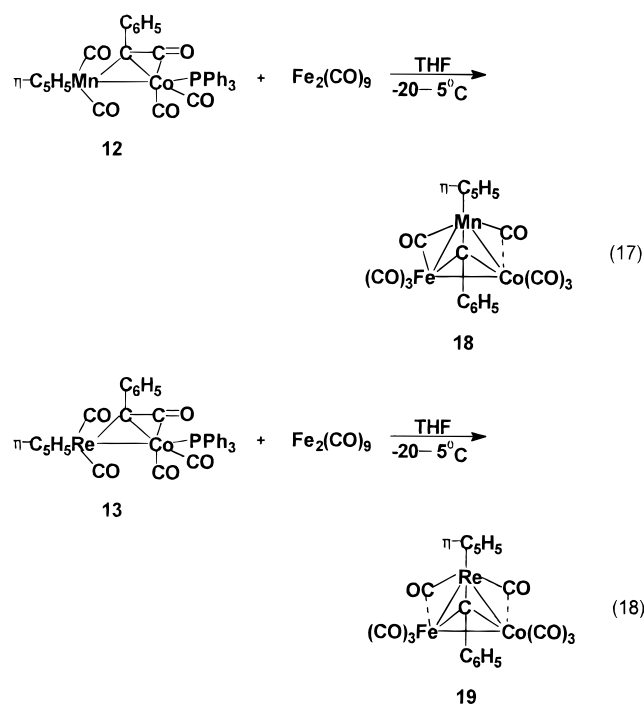


Figure 3. Molecular structure of **15**, showing the atom-numbering scheme.

the feature fragments generated by loss of CO ligands. The formation of **17** is not surprising since the analogous products **18** and **19** (see below) have been obtained in the reactions¹⁴ of the bridging carbyne complexes $[\text{MCo}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mn, Re}$) with $\text{Fe}_2(\text{CO})_9$.

Surprisingly, complexes **12** and **13** can also react with $\text{Fe}_2(\text{CO})_9$ under similar conditions, leading to loss of the PPh_3 ligand to produce trimetal bridging carbyne complexes $[\text{MnFeCo}(\mu_3\text{-CC}_6\text{H}_5)(\text{CO})_8(\eta\text{-C}_5\text{H}_5)]$ (**18**) (eq 17) and $[\text{ReFeCo}(\mu_3\text{-CC}_6\text{H}_5)(\text{CO})_8(\eta\text{-C}_5\text{H}_5)]$ (**19**) (eq 18) in >70% yields, respectively.



Complexes **18** and **19** are known compounds¹⁴ synthesized by the reactions of bridging carbyne complexes $[\text{MCo}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mn, Re}$) or bridging carbene complexes $[\text{MCo}\{\mu\text{-C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mn, Re}$) with $\text{Fe}_2(\text{CO})_9$. The possible formation pathway of **18** and **19** shown in eqs 17 and 18 could proceed either via a dimetal bridging carbene intermediate $[\text{MCo}\{\mu\text{-C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mn or Re}$) or via an unstable trimetal bridging carbyne intermediate $[\text{MnFeCo}(\mu_3\text{-CC}_6\text{H}_5)(\text{CO})_7(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mn or Re}$). The former, which is formed by displacement of a PPh_3 ligand of complex **12** or **13** by a CO ligand derived from $\text{Fe}_2(\text{CO})_9$, reacted¹⁴ with $\text{Fe}_2(\text{CO})_9$ to give compound **18** or **19**. The latter, which is formed directly by the reaction of **12** or **13** with $\text{Fe}_2(\text{CO})_9$ as in the reaction¹⁴ of $[\text{MCo}\{\mu\text{-C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mn or Re}$) with $\text{Fe}_2(\text{CO})_9$, occurred from PPh_3 ligand displacement by a CO ligand arising from the great steric hindrance of the PPh_3 ligand to afford stable product **18** or **19**. A series of trimetal bridging carbyne complexes have been synthesized by Stone et al. by reactions^{6a,c,30} of alkylidyne complexes with low-valent metal species as mentioned in the Introduction. However, the reaction of η^1, η^2 -ketene complex with low-valent metal species giving a trimetal bridging carbyne complex is unusual. This reaction was only found in the reaction¹⁴ of $[\text{MCo}\{\mu\text{-C}(\text{CO})\text{C}_6\text{H}_5\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mn, Re}$) with $\text{Fe}_2(\text{CO})_9$. Not all such η^1, η^2 -ketene complexes can react with $\text{Fe}_2(\text{CO})_9$ to produce trimetal bridging carbyne complexes since analogous ketene complexes **8–11** and **14** do not react similarly under the same conditions. This suggests that the Co moiety is important; it probably promotes this reaction by forming a stable trimetal $\mu_3\text{-CMFeCo}$ core.

The title reaction shows that the reactions of the carbonylmethyl anions containing cyclopentadienyl, PPh_3 , and NO ligands with the cationic carbyne complexes of manganese and rhenium, **1** and **2**, give the η^1, η^2 -ketene complexes or bridging carbyne complexes. Thus, the cationic carbyne complexes of manganese and rhenium reacted not only with the mixed-dimetal carbonyl anions¹⁴ but also with the substituted monometal carbonyl anions to yield the dimetal bridging carbyne complexes. This offers a convenient and useful method for the preparation of such dimetal bridging 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 the positional parameters and temperature factors, H atom coordinates, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **10**, **13**, and **15**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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