

Heterobinuclear and Heterotrinuclear Metal μ -Allenyl Complexes Containing Platinum and One or Both of Iron and Ruthenium. Synthesis of Higher Nuclearity Metal Complexes from Mononuclear Metal η^1 -Propargyls and η^1 -Allenyls and from Binuclear Metal μ - $\eta^1:\eta^2_{\alpha,\beta}$ -Allenyls

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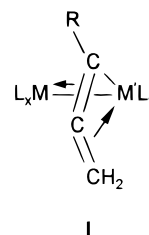
The reactions of $\text{Cp}(\text{CO})_2\text{MCH}_2\text{C}\equiv\text{CPh}$ with $\text{Pt}(\text{PPh}_3)_4$ or $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$ in THF at reflux and of $\text{Cp}(\text{CO})_2\text{MCH}=\text{C}=\text{CH}_2$ with $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$ in THF or hexane at -78°C to ambient temperature afforded the heterobinuclear metal μ -allenyl complexes $(\text{PPh}_3)_2\text{Pt}(\mu\text{-}\eta^1:\eta^2_{\alpha,\beta}\text{-C(Ph)=C=CH}_2)\text{M}(\text{CO})\text{Cp}$ ($\text{M} = \text{Ru}$, $\text{R} = \text{Ph}$ (**1a**); $\text{M} = \text{Fe}$, $\text{R} = \text{Ph}$ (**2a**); $\text{M} = \text{Ru}$, $\text{R} = \text{H}$ (**1b**); $\text{M} = \text{Fe}$, $\text{R} = \text{H}$ (**2b**)). The products reacted with $\text{Ru}_3(\text{CO})_{12}$ or $\text{Fe}_2(\text{CO})_9$ (Ru , $\text{Fe} = \text{M}'$) in THF at room temperature to yield open heterotrinuclear metal μ -allenyl complexes $(\text{PPh}_3)(\text{CO})\text{Pt}(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-C(R)=C=CH}_2)\text{M}'(\text{CO})_3\text{M}(\text{CO})\text{Cp}$ ($\text{M}' = \text{M} = \text{Ru}$, $\text{R} = \text{H}$ (**4**); $\text{M}' = \text{Ru}$, $\text{M} = \text{Fe}$, $\text{R} = \text{H}$ (**5**); $\text{M}' = \text{Fe}$, $\text{M} = \text{Ru}$, $\text{R} = \text{Ph}$ (**6a**); $\text{M}' = \text{Fe}$, $\text{M} = \text{Ru}$, $\text{R} = \text{H}$ (**6b**); $\text{M}' = \text{M} = \text{Fe}$, $\text{R} = \text{H}$ (**7**)), as well as $\text{M}'(\text{CO})_4\text{PPh}_3$. The reaction of **1a** with $\text{Fe}_2(\text{CO})_9$ also afforded the CO-for- PPh_3 substitution product $(\text{PPh}_3)(\text{CO})\text{Pt}(\mu\text{-}\eta^1:\eta^2_{\alpha,\beta}\text{-C(Ph)=C=CH}_2)\text{Ru}(\text{CO})\text{Cp}$ (**3**). Treatment of the μ -allenylcarbonyl $(\text{CO})_3\text{Fe}(\mu\text{-}\eta^3:\eta^2\text{-C(O)C(Ph)=C=CH}_2)\text{Ru}(\text{CO})\text{Cp}$ with $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$ in THF at 0°C with warming to ambient temperature gave three heterometallic products: **6a**, the PPh_3 -for-CO substituted $(\text{PPh}_3)(\text{CO})_2\text{Fe}(\mu\text{-}\eta^3:\eta^2\text{-C(O)C(Ph)=C=CH}_2)\text{Ru}(\text{CO})\text{Cp}$, and $(\text{PPh}_3)_2\text{Pt}(\mu_3\text{-}\eta^1:\eta^1:\eta^3\text{-C(Ph)CCH}_2)\text{Ru}(\text{CO})\text{Cp}(\mu_2\text{-CO})\text{Fe}(\text{CO})_2$ (**8**). All new products were characterized by a combination of IR and NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$) spectroscopy, FAB mass spectrometry, and elemental analysis; the structures of **1b**, **3**, **6a**, and **8** were elucidated by X-ray diffraction analysis. Complexes **1b** and **3** each contain a Pt–Ru bond and a μ -allenyl group that is η^1 ligated to Pt and η^2 ligated, through the internal $\text{C}=\text{C}$ bond, to Ru. **6a** contains an open Pt–Fe–Ru metal framework, with the $\mu\text{-C(Ph)=C=CH}_2$ ligand being attached η^1 to Pt, η^2 through the C(Ph)=C to Fe, and η^2 through the C=CH_2 to Ru. **8** is also an open, Pt–Fe–Ru bonded cluster; however, it contains an η^3 -allyl group ligated to Fe and metalated at CPh (Ru) and C_β (Pt). Possible mechanisms of formation of the new μ -allenyl-metal complexes are presented. Complexes **1** and **2** underwent fragmentation of the binuclear framework to yield $\text{Cp}(\text{CO})_2\text{MCH}=\text{C}=\text{CH}_2$ ($\text{M} = \text{Ru}$, Fe), $\text{Cp}(\text{CO})_2\text{RuC(Ph)=C=CH}_2$, or $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$, as appropriate, in addition to $\text{Pt}(\text{PPh}_3)_2(\text{CO})_2$, upon treatment with CO at room temperature. The reverse of these processes can be effected by sweeping the product solutions with Ar for the three η^1 -allenyl complexes, but not for $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$.

Introduction

Studies in this laboratory on reactions of transition metal η^1 -propargyl and η^1 -allenyl complexes with metal carbonyls have resulted in the preparation of heterobinuclear and heterotrinuclear metal μ -allenyl compounds, as well as other heterometallic products with bridging hydrocarbyl ligands.^{1,2} This synthetic methodology utilizes the multiple carbon–carbon bonds of the propargyl and allenyl as molecular templates for bring-

ing heterometallic nuclei into close proximity and thereby facilitating formation of metal–metal bonds.

Applications of this methodology to binuclear metal $\mu\text{-}\eta^3:\eta^2$ -allenyl/propargyl (**1**)³ and trinuclear metal $\mu_3\text{-}$

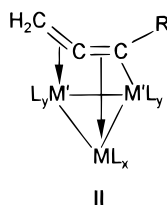


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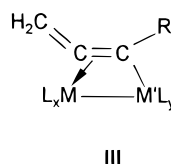
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$\eta^1:\eta^2:\eta^2$ -allenyl (**II**)^{3,4} compounds containing metal car-



bonyl and cyclopentadienylmetal carbonyl groups have already been reported. To further explore the scope of synthetic possibilities, we endeavored to examine reactions of iron and ruthenium η^1 -propargyl and η^1 -allenyl complexes with $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$ and $\text{Pt}(\text{PPh}_3)_4$. Both of these platinum(0) compounds readily undergo ligand dissociation and/or substitution,⁵ necessary for metal binding to the η^1 -attached propargyl or allenyl ligand. Furthermore, platinum forms strong metal-metal and metal-carbon bonds⁶ and therefore represents an excellent candidate for such nuclearity expansion reactions.

Reported herein is a full account of our studies⁷ on these reactions which afforded the first examples of heterometallic $\mu\text{-}\eta^1:\eta^2\text{-}\alpha,\beta$ -allenyl compounds (**III**), $(\text{PPh}_3)_2\text{-Pt}(\mu\text{-}\eta^1:\eta^2\text{-}\alpha,\beta\text{-C(R)=C=CH}_2)\text{M}(\text{CO})\text{Cp}$. Homometallic rep-



resentatives of **III** have been known for some time;⁸⁻¹⁰ however, they were prepared by completely different methods.

The availability of $(\text{PPh}_3)_2\text{Pt}(\mu\text{-}\eta^1:\eta^2\text{-}\alpha,\beta\text{-C(R)=C=CH}_2)\text{M}(\text{CO})\text{Cp}$ with an uncoordinated $\text{C}_\beta=\text{C}_\gamma$ bond of the allenyl ligand presented an opportunity to study possible expansion of molecular nuclearity by reaction with metal carbonyls. Indeed, compounds $(\text{PPh}_3)_2\text{Pt}(\mu\text{-}\eta^1:\eta^2\text{-}\alpha,\beta\text{-C(R)=C=CH}_2)\text{M}(\text{CO})\text{Cp}$ were found to react with $\text{Ru}_3(\text{CO})_{12}$ or $\text{Fe}_2(\text{CO})_9$ to afford heterotrinnuclear metal $\mu\text{-}\eta^1:\eta^2:\eta^2$ -allenyl products. All of these synthetic investigations, some reaction chemistry of the products, and X-ray structural studies on two binuclear and two trinnuclear products comprise the content of this paper.

Experimental Section

General Procedures and Measurements. All reactions and manipulations of air-sensitive compounds were carried out

under an atmosphere of argon by using standard procedures.¹¹ Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Chromatographic separations were effected on columns packed with Grade III (6% H_2O) alumina. Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared, NMR (^1H , ^{13}C , and ^{31}P), and mass spectra (FAB) were obtained as previously described.^{3,12}

Materials. All solvents were distilled under an argon atmosphere. Hexane was distilled from potassium, THF and diethyl ether were distilled from Na/K alloy and benzophenone, and dichloromethane was distilled from P_4O_{10} .

Reagents were obtained from various commercial sources and used as received, except as noted below. The compounds $\text{Pt}(\text{PPh}_3)_4$,¹³ $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$,¹⁴ $\text{Fe}_2(\text{CO})_9$,¹⁵ $\text{Ru}_3(\text{CO})_{12}$,¹⁶ and $(\text{CO})_3\text{-Fe}(\mu\text{-}\eta^3\text{-C}(\text{O})\text{C}(\text{Ph})=\text{C}=\text{CH}_2)\text{Ru}(\text{CO})\text{Cp}^4$ were synthesized according to the literature. $\text{Pt}(\text{PPh}_3)_2(\text{CO})_2$ was prepared quantitatively by exposure of THF solutions of $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$ to carbon monoxide atmosphere.¹⁷ The ruthenium propargyl and allenyl complexes $\text{Cp}(\text{CO})_2\text{RuCH}_2\text{C}\equiv\text{CPh}$ and $\text{Cp}(\text{CO})_2\text{-RuCH}=\text{C}=\text{CH}_2$, respectively, were prepared by literature procedures,¹⁸ and their iron analogues $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$ and $\text{Cp}(\text{CO})_2\text{FeCH}=\text{C}=\text{CH}_2$ were synthesized by a close adaptation of the literature procedure¹⁹ using Na/K alloy rather than sodium as a reducing agent.

Reactions of Mononuclear Metal Propargyl and Allenyl Complexes with Platinum(0) Reagents. (i) $\text{Cp}(\text{CO})_2\text{-RuCH}_2\text{C}\equiv\text{CPh}$. To a stirred solution of $\text{Cp}(\text{CO})_2\text{RuCH}_2\text{C}\equiv\text{CPh}$ (0.550 g, 1.63 mmol) in THF (100 mL) at room temperature was added $\text{Pt}(\text{PPh}_3)_4$ (2.70 g, 2.17 mmol) as a solid. The resulting orange solution was heated at reflux temperature for 9 h, during which time its color turned deep red. The solution was allowed to cool to room temperature and was concentrated in vacuo to about 10 mL and treated with 20 mL of hexane with stirring. It was then kept at -23°C for 12 h to yield yellow crystals of $(\text{PPh}_3)_2\text{Pt}(\mu\text{-}\eta^1:\eta^2\text{-}\alpha,\beta\text{-C}(\text{Ph})=\text{C}=\text{CH}_2)\text{-Ru}(\text{CO})\text{Cp}$ (**1a**), which were collected by filtration. Repeated concentration/crystallization procedures on the resultant mother liquors afforded a total 56% yield (0.931 g) of **1a**: dec pt 175°C ; IR (CH_2Cl_2) $\nu(\text{CO})$ 1912 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.9–6.5 (m, 35H, Ph), 5.43 (d, $J_{\text{HH}} = 2.2\text{ Hz}$, $J_{\text{PH}} = 17.8\text{ Hz}$, 1H of $=\text{CH}_2$), 4.89 (d, $J_{\text{HH}} = 2.2\text{ Hz}$, $J_{\text{PH}} = 13.5\text{ Hz}$, 1H of $=\text{CH}_2$), 4.26 (s, 5H, Cp); ^{13}C NMR (CDCl_3) δ 206.6 (s, $J_{\text{PtC}} = 48\text{ Hz}$, CO), 165.3 (s, $=\text{C}$), 149.1 (s, $=\text{CPh}$), 137.0–124.4 (m, Ph), 97.2 (dt, $J_{\text{PC}} = 2.3\text{ Hz}$, $J_{\text{CH}} = 160\text{ Hz}$, $J_{\text{PtC}} = 32\text{ Hz}$, $=\text{CH}_2$), 85.2 (m, Cp); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 23.6 (d, $J_{\text{PP}} = 4.2\text{ Hz}$, $J_{\text{PtP}} = 2766\text{ Hz}$), 21.5 (d, $J_{\text{PP}} = 4.2\text{ Hz}$, $J_{\text{PtP}} = 3689\text{ Hz}$); MS (FAB), ^{102}Ru and ^{195}Pt isotopes, m/z 1029 (M^+), 1001 ($\text{M}^+ - \text{CO}$), 719 ($\text{Pt}(\text{PPh}_3)_2^+$). Anal. Calcd for $\text{C}_{51}\text{H}_{42}\text{O}_2\text{P}_2\text{PtRu}$: C, 59.53; H, 4.11. Found: C, 59.58; H, 3.75.

An alternative preparation of **1a** involves use of $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$ in place of $\text{Pt}(\text{PPh}_3)_4$. Thus, a solution of $\text{Cp}(\text{CO})_2\text{RuCH}_2\text{C}\equiv\text{CPh}$ (0.105 g, 0.311 mmol) and $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$ (0.300 g, 0.401 mmol) in 15 mL of ethylene-saturated THF was heated at reflux temperature for 20 h. Workup was as in the preceding procedure, except that only one crystallization was necessary. Yield: 0.28 g (87%).

(ii) $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$. A solution of $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$ (0.250 g, 0.856 mmol) and $\text{Pt}(\text{PPh}_3)_4$ (1.30 g, 1.04 mmol)

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in THF (80 mL) was heated at reflux temperature for 2 h before the orange solid $(\text{PPh}_3)_2\text{Pt}(\mu\text{-}\eta^1\text{-}\eta^2\text{-}\alpha,\beta\text{-C(Ph)=C=CH}_2\text{Fe(CO)Cp (2a)})$ was isolated as in the synthesis of **1a**: yield 0.675 g (80%); dec pt 160 °C; IR (CH_2Cl_2) $\nu(\text{CO})$ 1896 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.7–6.9 (m, 35H, Ph), 5.26 (d, $J_{\text{HH}} = 2.1$ Hz, $J_{\text{PH}} = 19.7$ Hz, 1H of $=\text{CH}_2$), 4.83 (d, $J_{\text{HH}} = 2.1$ Hz, $J_{\text{PH}} = 14.3$ Hz, 1H of $=\text{CH}_2$), 3.76 (s, 5H, Cp); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 220.4 (s, $J_{\text{PC}} = 8.0$ Hz, CO), 173.3 (s, $=\text{C=}$), 149.8 (s, $=\text{CPh}$), 96.9 (d, $J_{\text{PC}} = 3.5$ Hz, $J_{\text{PTC}} = 36$ Hz, $=\text{CH}_2$), 82.6 (s, Cp); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 27.7 (d, $J_{\text{PP}} = 1.0$ Hz, $J_{\text{PTP}} = 3500$ Hz), 26.0 (d, $J_{\text{PP}} = 1.0$ Hz, $J_{\text{PTP}} = 2813$ Hz); MS (FAB), ^{195}Pt isotope, m/z 984 ($\text{M}^+ + 1$), 956 ($\text{M}^+ - \text{CO} + 1$), 840 ($\text{M}^+ - \text{CO} - \text{CH}_2\text{CPh}$). Anal. Calcd for $\text{C}_{51}\text{H}_{42}\text{FeO}_2\text{Pt}$: C, 62.20; H, 4.40. Found: C, 62.41; H, 4.49.

(iii) $\text{Cp(CO)}_2\text{RuCH=C=CH}_2$. To a stirred suspension of $\text{Pt(PPh}_3)_2\text{C}_2\text{H}_4$ (1.58 g, 2.11 mmol) in hexane (40 mL) at -20 °C was added a solution of $\text{Cp(CO)}_2\text{RuCH=C=CH}_2$ (0.500 g, 1.91 mmol) in hexane. The resulting mixture was allowed to warm to room temperature over 1 h. The color of the suspended material gradually changed from white to yellow. The reaction was complete in 2 h at room temperature as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The yellow solid of $(\text{PPh}_3)_2\text{Pt}(\mu\text{-}\eta^1\text{-}\eta^2\text{-}\alpha,\beta\text{-CH=C=CH}_2)\text{Ru(CO)Cp (1b)}$ was collected on a frit, washed with hexane (3×10 mL), and dried in vacuo: yield 1.58 g (87%); dec pt 160 °C; IR (CH_2Cl_2) $\nu(\text{CO})$ 1912 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.0–7.2 (m, 30H, Ph), 6.61 (m, $J_{\text{PH}} = 33.0$ Hz, 1H, $=\text{CH}$), 5.44 (d, $J_{\text{HH}} = 2.5$ Hz, $J_{\text{PH}} = 19.2$ Hz, 1H of $=\text{CH}_2$), 4.66 (d, $J_{\text{HH}} = 2.5$ Hz, $J_{\text{PH}} = 15.0$ Hz, 1H of $=\text{CH}_2$), 4.52 (s, 5H, Cp); ^{13}C NMR (CDCl_3) δ 206.9 (s, $J_{\text{PC}} = 38.4$ Hz, CO), 168.0 (s, $=\text{C=}$), 136.6–126.2 (m, Ph), 114.7 (dd, $J_{\text{PC}} = 84.7$ Hz, $J_{\text{CH}} = 161$ Hz, $J_{\text{PTC}} = 725$ Hz, $=\text{CH}$), 95.6 (dt, $J_{\text{PC}} = 3.1$ Hz, $J_{\text{CH}} = 160$ Hz, $J_{\text{PTC}} = 36.5$ Hz, $=\text{CH}_2$), 82.3 (m, Cp); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 27.7 (d, $J_{\text{PP}} = 4.3$ Hz, $J_{\text{PTP}} = 2852$ Hz), 21.8 (d, $J_{\text{PP}} = 4.3$ Hz, $J_{\text{PTP}} = 3620$ Hz); MS (FAB), ^{102}Ru and ^{195}Pt isotopes, m/z 953 (M^+), 886 ($\text{M}^+ - \text{CO} - \text{C}_3\text{H}_3$), 719 ($\text{Pt(PPh}_3)_2^+$). Anal. Calcd for $\text{C}_{45}\text{H}_{38}\text{OP}_2\text{PtRu}$: C, 56.72; H, 3.99. Found: C, 56.74; H, 4.08.

(iv) $\text{Cp(CO)}_2\text{FeCH=C=CH}_2$. Solid $\text{Pt(PPh}_3)_2\text{C}_2\text{H}_4$ (1.0 g, 1.3 mmol) was added to a stirred solution of $\text{Cp(CO)}_2\text{FeCH=C=CH}_2$ (0.33 g, 1.5 mmol) in 50 mL of THF at -15 °C. After the solid dissolved within 30 min, the resulting orange solution was allowed to warm to room temperature in 1 h. It was then concentrated in vacuo to ca. 10 mL, and hexane (20 mL) was added with vigorous stirring. The contents were cooled at -23 °C for 12 h, and the orange crystals of $(\text{PPh}_3)_2\text{Pt}(\mu\text{-}\eta^1\text{-}\eta^2\text{-}\alpha,\beta\text{-CH=C=CH}_2)\text{Fe(CO)Cp (2b)}$ were collected on a frit, washed with hexane (2×20 mL), and dried in vacuo: yield 0.730 g (60%); dec pt 140 °C; IR (CH_2Cl_2) $\nu(\text{CO})$ 1899 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.1–7.2 (m, 30H, Ph), 7.03 (m, $J_{\text{PH}} = 36.8$ Hz, 1H, $=\text{CH}$), 5.43 (d, $J_{\text{HH}} = 1.0$ Hz, $J_{\text{PH}} = 10.0$ Hz, 1H of $=\text{CH}_2$), 4.67 (d, $J_{\text{HH}} = 1.0$ Hz, $J_{\text{PH}} = 10.1$ Hz, 1H of $=\text{CH}_2$), 4.05 (s, 5H, Cp); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 220.2 (d, $J_{\text{PC}} = 8.6$ Hz, $J_{\text{PTC}} = 84.6$ Hz, CO), 176.4 (s, $=\text{C=}$), 122.3 (dd, $J_{\text{PC}} = 4.5$, 80.2 Hz, $J_{\text{PTC}} = 715$ Hz, $=\text{CH}$), 94.3 (d, $J_{\text{PC}} = 2.9$ Hz, $J_{\text{PTC}} = 41.7$ Hz, $=\text{CH}_2$), 79.7 (s, Cp); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 30.9 (d, $J_{\text{PP}} = 1.0$ Hz, $J_{\text{PTP}} = 2925$ Hz), 27.7 (d, $J_{\text{PP}} = 1.0$ Hz, $J_{\text{PTP}} = 3415$ Hz); MS (FAB), ^{195}Pt isotope, m/z 908 ($\text{M}^+ + 1$), 880 ($\text{M}^+ - \text{CO} + 1$), 840 ($\text{M}^+ - \text{CO} - \text{C}_3\text{H}_3$), 719 ($\text{Pt(PPh}_3)_2^+$). Anal. Calcd for $\text{C}_{45}\text{H}_{38}\text{FeO}_2\text{Pt}$: C, 59.55; H, 4.22. Found: C, 59.82; H, 4.21.

Reactions of Heterobinuclear Metal Allenyl Complexes with $\text{Ru}_3(\text{CO})_{12}$. **(i) $(\text{PPh}_3)_2\text{Pt}(\mu\text{-}\eta^1\text{-}\eta^2\text{-}\alpha,\beta\text{-CH=C=CH}_2)\text{Ru(CO)Cp (1b)}$.** To a stirred solution of **1b** (0.414 g, 0.434 mmol) in THF (30 mL) at -78 °C was added solid $\text{Ru}_3(\text{CO})_{12}$ (0.320 g, 0.501 mmol). The orange suspension was allowed to warm to room temperature over 4 h, and the resulting red solution was stirred for an additional 12 h. Solvent was removed in vacuo, the red residue was dissolved in a minimum amount of CH_2Cl_2 , and the resulting solution was introduced onto a column of alumina (20×2 cm) packed in hexane. Elution with 25% diethyl ether in hexane gave $(\text{PPh}_3)(\text{CO})\text{Pt}(\mu_3\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-CH=C=CH}_2)\text{Ru(CO)}_3\text{Ru(CO)Cp (4)}$

(0.085 g, 22% yield) as a red solid upon solvent removal in vacuo: dec pt 107 °C; IR (CH_2Cl_2) $\nu(\text{CO})$ 2038 (s), 2015 (m), 2000 (w), 1971 (s) cm^{-1} ; ^1H NMR (CDCl_3) δ 7.9–7.0 (m, 30H, Ph), 4.96 (s, 5H, Cp), 2.66 (s, br, 1H of $=\text{CH}_2$), 2.32 (m, 1H of $=\text{CH}_2$) ($=\text{CH}$ signal masked in δ 7.9–7.0 region); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 201.1 (s, RuCO's), 200.7 (s, RuCO), 199.9 (s, PtCO), 196.9 (s, $=\text{C=}$), 166.6 (d, $J_{\text{PC}} = 4.0$ Hz, $=\text{CH}$), 89.4 (s, Cp), 44.4 (s, $=\text{CH}_2$); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 25.0 (s, $J_{\text{PTP}} = 2840$ Hz); MS (FAB), ^{102}Ru and ^{195}Pt isotopes, m/z 905 (M^+), consecutive loss of 5 CO's.

(ii) $(\text{PPh}_3)_2\text{Pt}(\mu\text{-}\eta^1\text{-}\eta^2\text{-}\alpha,\beta\text{-CH=C=CH}_2)\text{Fe(CO)Cp (2b)}$. A suspension of **2b** (0.300 g, 0.331 mmol) and $\text{Ru}_3(\text{CO})_{12}$ (0.215 g, 0.336 mmol) in hexane (30 mL) was heated at reflux temperature for 1 h, resulting in the formation of a red heterogeneous mixture. The contents were filtered through a pad of Celite while still hot, and solvent was removed from the solution to yield a red tar. The tar was dissolved in CH_2Cl_2 (3 mL) and added to a short column of alumina (10×5 cm) packed in hexane. Rapid elution with hexane removed unwanted side products (such as $\text{Ru(CO)}_4\text{PPh}_3$) as an orange band. Further elution with THF yielded a red band, which upon removal from the column and solvent evaporation afforded $(\text{PPh}_3)(\text{CO})\text{Pt}(\mu_3\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-CH=C=CH}_2)\text{Ru(CO)}_3\text{Fe(CO)Cp (5)}$. The product was purified by crystallization from THF/hexane: yield 0.095 g (34%); dec pt 97 °C; IR (CH_2Cl_2) $\nu(\text{CO})$ 2036 (s), 2010 (vs), 1994 (m), 1970 (m) cm^{-1} ; ^1H NMR (CDCl_3) δ 8.1–7.4 (m, 30H, Ph), 7.21 (d, $J_{\text{PH}} = 10.0$ Hz, $J_{\text{PH}} = 50.0$ Hz, 1H, $=\text{CH}$), 4.49 (s, 5H, Cp), 2.75 (s, br, 1H of $=\text{CH}_2$), 2.34 (d, $J_{\text{HH}} = 4.0$ Hz, $J_{\text{PH}} = 20.0$ Hz, 1H of $=\text{CH}_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 216.1 (s, $J_{\text{PC}} = 53.0$ Hz, FeCO), 208.0 (s, br, RuCO's), 199.7 (s, PtCO), 196.7 (s, $=\text{C=}$), 167.4 (d, $J_{\text{PC}} = 4.0$ Hz, $=\text{CH}$), 86.1 (s, Cp), 44.9 (s, $=\text{CH}_2$); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 24.1 ($J_{\text{PTP}} = 2854$ Hz); MS (FAB), ^{102}Ru and ^{195}Pt isotopes, m/z 859 (M^+), consecutive loss of 5 CO's. Anal. Calcd for $\text{C}_{31}\text{H}_{23}\text{FeO}_3\text{P}_2\text{Ru}$: C, 43.37; H, 2.70. Found: C, 43.35; H, 3.08.

Reactions of Heterobinuclear Metal Allenyl Complexes with $\text{Fe}_2(\text{CO})_9$. **(i) $(\text{PPh}_3)_2\text{Pt}(\mu\text{-}\eta^1\text{-}\eta^2\text{-}\alpha,\beta\text{-C(Ph)=C=CH}_2)\text{Ru(CO)Cp (1a)}$.** A stirred solution of **1a** (1.10 g, 1.07 mmol) in THF (100 mL) at room temperature was treated with solid $\text{Fe}_2(\text{CO})_9$ (0.518 g, 1.42 mmol). The color of the resulting suspension turned red over 36 h. Solvent was removed in vacuo to yield a red tar, which was dissolved in CH_2Cl_2 (2 mL), and the resulting solution was introduced onto a column of alumina (20×2 cm) packed in hexane. Elution with 4% diethyl ether in hexane afforded a yellow band, which upon removal from the column and evaporation of the solvent left a yellow solid, $(\text{PPh}_3)(\text{CO})\text{Pt}(\mu\text{-}\eta^1\text{-}\eta^2\text{-}\alpha,\beta\text{-C(Ph)=C=CH}_2)\text{Ru(CO)Cp (3)}$: yield 0.105 g (12%); dec pt 160 °C; IR (CH_2Cl_2) $\nu(\text{CO})$ 2018 (s), 1947 (s) cm^{-1} ; ^1H NMR (CDCl_3) δ 8.2–7.3 (m, 20H, Ph), 5.60 (s, $J_{\text{PH}} = 17.7$ Hz, 1H of $=\text{CH}_2$), 5.02 (s, $J_{\text{PH}} = 14.3$ Hz, 1H of $=\text{CH}_2$), 4.80 (s, 5H, Cp); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 204.2 (s, RuCO), 193.2 (d, $J_{\text{PC}} = 5.0$ Hz, PtCO), 163.3 (d, $J_{\text{PC}} = 5.0$ Hz, $=\text{C=}$), 148.2 (s, $=\text{CPh}$), 98.4 (s, $=\text{CH}_2$), 84.6 (s, Cp); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 24.4 (s, $J_{\text{PTP}} = 3277$ Hz); MS (FAB), ^{102}Ru and ^{195}Pt isotopes, m/z 795 (M^+), 767 ($\text{M}^+ - \text{CO}$), 739 ($\text{M}^+ - 2\text{CO}$). Anal. Calcd for $\text{C}_{34}\text{H}_{27}\text{O}_2\text{P}_2\text{Ru}$: C, 51.39; H, 3.42. Found: C, 51.23; H, 3.37.

Further elution with 15% diethyl ether in hexane yielded orange $(\text{PPh}_3)(\text{CO})\text{Pt}(\mu_3\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-C(Ph)=C=CH}_2)\text{Fe(CO)}_3\text{Ru(CO)Cp (6a)}$ after evaporation of the solvent: yield 0.175 g (17%); dec pt 180 °C; IR (CH_2Cl_2) $\nu(\text{CO})$ 2025 (s), 1996 (vs), 1954 (m) cm^{-1} ; ^1H NMR (CDCl_3) δ 7.7–7.0 (m, 20H, Ph), 4.82 (s, 5H, Cp), 3.86 (d, $J_{\text{HH}} = 5.1$ Hz, $J_{\text{PH}} = 12.7$ Hz, 1H of $=\text{CH}_2$), 2.82 (d, $J_{\text{HH}} = 5.1$ Hz, $J_{\text{PH}} = 21.1$ Hz, 1H of $=\text{CH}_2$); ^{13}C NMR (CDCl_3) δ 213.6 (d, $J_{\text{PC}} = 4.2$ Hz, $J_{\text{PTC}} = 50.0$ Hz, FeCO's), 203.5 (s, $J_{\text{PTC}} = 50.0$ Hz, RuCO), 191.7 (d, $J_{\text{PC}} = 4.9$ Hz, PtCO), 187.7 (d, $J_{\text{PC}} = 4.9$ Hz, $=\text{C=}$), 152.2 (d, $J_{\text{PC}} = 2.7$ Hz, $=\text{CPh}$), 84.7 (s, Cp), 13.4 (t, $J_{\text{CH}} = 156$ Hz, $=\text{CH}_2$); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 27.7 (s, $J_{\text{PTP}} = 3074$ Hz); MS (FAB), ^{102}Ru and ^{195}Pt isotopes, m/z 935 (M^+), 853 ($\text{M}^+ - 3\text{CO}$). Anal. Calcd for $\text{C}_{37}\text{H}_{27}\text{FeO}_3\text{P}_2\text{Ru}$: C, 47.54; H, 2.89. Found: C, 47.71; H, 2.87.

(ii) **(PPh₃)₂Pt(μ - η^1 : η^2 $_{\alpha,\beta}$ -CH=C=CH₂)Ru(CO)Cp (1b).** A stirred solution of **1b** (0.900 g, 0.945 mmol) in THF (100 mL) at room temperature was treated with solid Fe₂(CO)₉ (0.360 g, 0.990 mmol). The original orange suspension slowly changed to a red solution as stirring was continued for 16 h. Solvent was removed in vacuo, and the red residue was chromatographed as in the preceding reaction. Elution with 25% diethyl ether in hexane and evaporation of the solvent afforded (PPh₃)-(CO)Pt(μ_3 - η^1 : η^2 : η^2 -CH=C=CH₂)Fe(CO)₃Ru(CO)Cp (**6b**) as a red solid in 20% yield (0.160 g): dec pt 176 °C; IR (CH₂Cl₂) ν (CO) 2027 (s), 1997 (s), 1953 (s) cm⁻¹; ¹H NMR (CDCl₃) δ 7.90 (d, J_{PH} = 10.7 Hz, J_{PtH} = 47.0 Hz, 1H, =CH), 7.8–7.2 (m, 15H, Ph), 4.64 (s, 5H, Cp), 3.54 (d, J_{HH} = 4.9 Hz, J_{PtH} = 11.4 Hz, 1H of =CH₂), 2.65 (dd, J_{HH} = 4.9 Hz, J_{PH} = 1.1 Hz, J_{PtH} = 19.2 Hz, 1H of =CH₂); ¹³C{¹H} NMR (CDCl₃) δ 214.5 (d, J_{PC} = 4.2 Hz, J_{PtC} = 48 Hz, FeCO's), 203.7 (s, J_{PtC} = 9.5 Hz, RuCO), 194.9 (d, J_{PC} = 2.5 Hz, PtCO), 194.1 (d, J_{PC} = 4.9 Hz, J_{PtC} = 61.4 Hz, =C=), 135.5 (d, J_{PC} = 5.4 Hz, J_{PtC} = 702 Hz, =CH), 85.1 (s, Cp), 13.8 (s, J_{PtC} = 42.3 Hz, =CH₂); ³¹P{¹H} NMR δ 28.3 (s, J_{PtP} = 3092 Hz); MS (FAB), ¹⁰²Ru and ¹⁹⁵Pt isotopes, m/z 859 (M⁺), 831 (M⁺ – CO), 803 (M⁺ – 2CO), 775 (M⁺ – 4CO), 747 (M⁺ – 5CO). Anal. Calcd for C₃₁H₂₃FeO₅P₂PtRu: C, 43.37; H, 2.70. Found: C, 43.27; H, 2.73.

(iii) **(PPh₃)₂Pt(μ - η^1 : η^2 $_{\alpha,\beta}$ -CH=C=CH₂)Fe(CO)Cp (2b).** The reaction was carried out similarly to the preceding one by using 0.335 g (0.369 mmol) of **2b** and 0.150 g (0.412 mmol) of Fe₂(CO)₉ in 30 mL of the THF. Stirring for 21 h at room temperature and chromatographic elution with 10% diethyl ether in hexane gave 0.078 g (26% yield) of the red solid (PPh₃)-(CO)Pt(μ_3 - η^1 : η^2 : η^2 -CH=C=CH₂)Fe(CO)₃Fe(CO)Cp (**7**): dec pt 110 °C; IR (CH₂Cl₂) ν (CO) 2024 (s), 1994 (vs), 1951 (m) cm⁻¹; ¹H NMR (CDCl₃) δ 8.04 (dt, J_{PH} = 10 Hz, J_{HH} = 1.2 Hz, J_{PtH} = 48.1 Hz, 1H, =CH), 7.8–7.1 (m, 15H, Ph), 4.20 (s, 5H, Cp), 3.41 (dd, J_{HH} = 1.2, 5.0 Hz, J_{PtH} = 18.3 Hz, 1H of =CH₂), 2.26 (dd, J_{HH} = 1.2, 5.0 Hz, J_{PtH} = 25.0 Hz, 1H of =CH₂); ¹³C{¹H} NMR (CDCl₃) δ 214.6 (s, J_{PtC} = 52 Hz, Fe(CO)'s), 210.3 (s, J_{PtC} = 13 Hz, FeCO), 194.7 (s, PtCO), 193.5 (d, J_{PC} = 4.0 Hz, =C=), 139.1 (d, J_{PC} = 5.0 Hz, =CH), 81.4 (s, Cp), 18.8 (s, J_{PtC} = 46.0 Hz, =CH₂); ³¹P{¹H} NMR (CDCl₃) δ 28.5 (s, J_{PtP} = 3062 Hz); MS (FAB), ¹⁹⁵Pt isotope, m/z 813 (M⁺), 785 (M⁺ – CO), 729 (M⁺ – 3CO), 701 (M⁺ – 4CO), 673 (M⁺ – 5CO). Anal. Calcd for C₃₁H₂₃Fe₂O₅P₂Pt: C, 45.78; H, 2.85. Found: C, 44.64; H, 3.06.

Reaction of (CO)₃Fe(μ - η^3 : η^2 -C(O)C(Ph)=C=CH₂)Ru(CO)Cp with Pt(PPh₃)₂C₂H₄. A solution of the RuFe title complex (0.050 g, 0.11 mmol) in THF (10 mL) at 0 °C was treated with solid Pt(PPh₃)₂C₂H₄ (0.078 g, 0.11 mmol), and the resulting orange mixture was stirred for 30 min and then allowed to warm to room temperature. After 1 h of reaction time, a ³¹P{¹H} NMR spectrum showed that the starting materials had been consumed and a new complex was present in solution. Continued stirring for an additional 5 h converted this complex into three major products, as observed by ³¹P{¹H} NMR spectroscopy. Solvent was then removed in vacuo, and the red residue was dissolved in CH₂Cl₂ (1 mL) and placed on a column of alumina (20 × 1 cm) packed in hexane. Elution with 5% diethyl ether in hexane separated a yellow band, which was removed from the column and evaporated to dryness to yield orange (PPh₃)(CO)Pt(μ_3 - η^1 : η^2 : η^2 -C(Ph)=C=CH₂)Fe(CO)₃Ru(CO)Cp (**6a**) (0.025 g, 25%). Continued elution removed a red band, which upon evaporation of the solvent afforded known⁴ (PPh₃)(CO)₂Fe(μ - η^3 : η^2 -C(O)C(Ph)=C=CH₂)-Ru(CO)Cp (0.015 g, 19% yield). Finally, a second red band was eluted off; solvent removal and evaporation to dryness gave a red solid, (PPh₃)₂Pt(μ_3 - η^1 : η^1 : η^3 -C(Ph)CCH₂)Ru(CO)Cp(μ_2 -CO)-Fe(CO)₂ (**8**): yield 0.025 g (19%); mp 159–162 °C; IR (THF) ν (CO) 2024 (w), 1979 (s), 1935 (vs), 1792 (m–s) cm⁻¹; ¹H NMR (CDCl₃) δ 7.36–6.85 (m, 35H, Ph), 4.74 (s, 5H, Cp), 3.05 (d, J = 4.9 Hz, J_{PtH} = 44.3 Hz, 1H of CH₂) (the other CH₂ signal was not observed); ¹³C{¹H} NMR (CDCl₃) δ 248.9 (s, μ -CO), 214.3 (s, FeCO's), 205.8 (s, RuCO), 182.3 (s, CCH₂), 156.4 (s,

CPh), 135.0–123.9 (m, Ph), 91.9 (s, Cp), 69.8 (s, CH₂); ³¹P{¹H} NMR (CDCl₃) δ 24.1 (d, J_{PP} = 7.9 Hz, J_{PtP} = 4053 Hz), 22.2 (d, J_{PP} = 7.9 Hz, J_{PtP} = 2819 Hz); MS (FAB), ¹⁰²Ru and ¹⁹⁵Pt isotopes, m/z 1170 (M⁺ + 1), 719 (Pt(PPh₃)₂⁺). Anal. Calcd for C₅₄H₄₂FeO₄P₂PtRu: C, 55.48; H, 3.62. Found: C, 55.77; H, 3.89.

Reactions of Heterobinuclear Metal Allenyl Complexes with CO. Measured quantities (30–50 mg) of **1** or **2** were dissolved in 0.5 mL of C₆D₆ or CD₂Cl₂ in screw-cap NMR tubes equipped with pierceable septa. Carbon monoxide or argon was bubbled through the solution via an inlet needle through the septum. Excess gas was vented through another needle connected to a mineral oil bubbler.

Reactions of Metal Propargyl and Allenyl Complexes with Pt(PPh₃)₂(CO)₂. These reactions were carried out by using equimolar amounts of Pt(PPh₃)₂(CO)₂ and metal allenyl or propargyl complex in THF solution at room temperature (with metal allenyls) or reflux temperature (with metal propargyls). A detailed description of the reaction between Cp(CO)₂FeCH=C=CH₂ and Pt(PPh₃)₂(CO)₂ follows.

Solid Pt(PPh₃)₂(CO)₂ (0.250 g, 0.322 mmol) was added to a stirred solution of Cp(CO)₂FeCH=C=CH₂ (0.070 g, 0.324 mmol) in THF (25 mL) at room temperature. Stirring was continued for 2 h, at which time the reaction was complete as ascertained by NMR spectroscopy. Removal of the solvent in vacuo, followed by recrystallization of the residue from 2:1 hexane/THF, yielded 0.255 g (87%) of (PPh₃)₂Pt(μ - η^1 : η^2 $_{\alpha,\beta}$ -CH=C=CH₂)Fe(CO)Cp (**2b**).

Complex **1b** was obtained in an analogous manner in 90% yield from Pt(PPh₃)₂(CO)₂ and Cp(CO)₂RuCH=C=CH₂, whereas **1a** resulted (92% yield) from the reaction of Pt(PPh₃)₂(CO)₂ with Cp(CO)₂RuCH₂C≡CPh in THF at reflux for 2 h. Complex **2a** was not isolated, as the reaction of Pt(PPh₃)₂(CO)₂ with Cp(CO)₂FeCH₂C≡CPh did not proceed beyond 10% completion (NMR spectroscopy), even after 24 h in THF at reflux temperature.

Crystallographic Analysis of (PPh₃)₂Pt(μ - η^1 : η^2 $_{\alpha,\beta}$ -CH=C=CH₂)Ru(CO)Cp (1b), (PPh₃)(CO)Pt(μ - η^1 : η^2 $_{\alpha,\beta}$ -C(Ph)=C=CH₂)Ru(CO)Cp (3), (PPh₃)(CO)Pt(μ_3 - η^1 : η^2 : η^2 -C(Ph)=C=CH₂)Fe(CO)₃Ru(CO)Cp (6a), and (PPh₃)₂Pt(μ_3 - η^1 : η^1 : η^3 -C(Ph)CCH₂)Ru(CO)Cp(μ_2 -CO)Fe(CO)₂ (8). All crystals were mounted on glass fibers and coated with varnish. Measurements were done with Mo K α radiation (λ = 0.71073 Å) on a Nicolet R3m diffractometer with graphite monochromator. Unit-cell parameters were obtained from the angular settings of 25 reflections (20° ≤ 2 θ ≤ 25°). For **6a** and **8**, photographic evidence indicated 2/m Laue symmetry, and systematic absences in the data uniquely determined the monoclinic space groups shown. For **1b** and **3**, the indicated Laue symmetry was 1, and in both cases the centrosymmetric alternative was initially assumed to be correct and later confirmed by the refinement process. A summary of the crystal data and the details of the intensity data collection and refinement for all complexes are provided in Table 1.

All data sets were corrected for absorption by semiempirical ψ -scan methods, and for decay. Structures were solved by heavy-atom methods and subsequent difference Fourier syntheses. Non-hydrogen atoms were anisotropically refined, and hydrogen atoms were treated as idealized contributions. Phenyl rings were constrained to rigid planar hexagons with C–C distances = 1.395 Å.

All computations used SHELXTL (version 5.1), which also served as the source for the neutral-atom scattering terms used in refinement (G. Sheldrick, Nicolet (Siemens), Madison, WI).

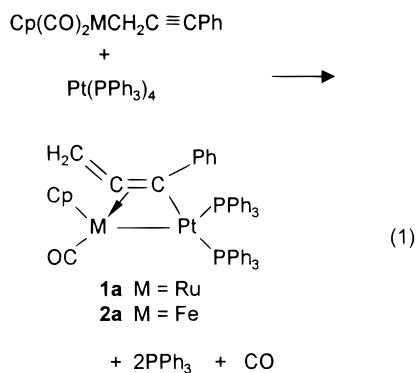
Results and Discussion

Reactions of Mononuclear Metal η^1 -Propargyl and η^1 -Allenyl Complexes with Pt(PPh₃)₄ and Pt(PPh₃)₂C₂H₄. The propargyl complexes Cp(CO)₂-

Table 1. Crystal Data, Data Collection, and Structure Refinement Parameters for Complexes **1b**, **3**, **6a**, and **8**

	1b	3	6a	8
formula	C ₄₅ H ₃₈ OP ₂ PtRu	C ₃₄ H ₂₇ O ₂ P ₂ PtRu	C ₃₇ H ₂₇ FeO ₅ P ₂ PtRu	C ₅₄ H ₄₂ FeO ₄ P ₂ PtRu
fw	952.89	794.71	934.59	1168.87
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
<i>a</i> (Å)	11.210(2)	11.186(3)	8.433(1)	16.724(4)
<i>b</i> (Å)	12.726(3)	11.992(3)	33.608(8)	13.636(3)
<i>c</i> (Å)	13.984(2)	13.551(3)	12.181(2)	20.264(4)
α (deg)	101.90(2)	100.74(2)		
β (deg)	101.74(2)	108.78(2)	99.62(2)	96.84(2)
γ (deg)	99.43(2)	112.03(2)		
<i>V</i> (Å ³)	1866.6(6)	1494.4(6)	3403.8(15)	4588.6(18)
ρ_{calc} (g cm ⁻³)	1.70	1.77	1.82	1.692
<i>Z</i>	2	2	4	4
cryst size (mm)	0.31 × 0.33 × 0.48	0.18 × 0.20 × 0.30	0.36 × 0.38 × 0.40	0.12 × 0.32 × 0.36
μ (cm ⁻¹)	44.56	54.80	52.74	37.82
temp (K)	298	298	298	298
<i>T</i> _{max} / <i>T</i> _{min}	1.628	2.564	2.286	1.294
2 θ scan range (deg)	4–52	4–50	4–52	4–42
data collected <i>h,k,l</i>	±14, ±16, ±18	±14, ±15, ±17	±11, ±42, ±16	±17, ±14, ±21
no. of reflens collected	7677	5609	7161	5381
no. of indep reflens	7357	5278	6703	4928
<i>R</i> _{merge} (%)	3.16	1.57	2.88	3.57
reflens	6125	4390	4212	3116
<i>F</i> _o ≥ 5 σ (<i>F</i> _o)				
<i>R</i> (<i>F</i>) (%)	3.49	3.85	4.63	5.11
<i>R</i> (<i>wF</i>) (%)	3.65	4.11	4.69	4.86
(Δ/σ) _{max}	0.011	0.19	0.103	0.25
<i>N</i> _o / <i>N</i> _v	16.2	14.4	11.5	6.44
GOF	1.020	0.90	1.198	1.140

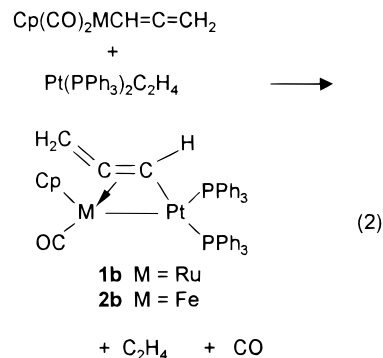
MCH₂C≡CPh react with Pt(PPh₃)₄ in THF at reflux over 2–9 h to afford the binuclear mixed-metal μ -allenyls (PPh₃)₂Pt(μ - η^1 : $\eta^2_{\alpha,\beta}$ -C(Ph)=C=CH₂)M(CO)Cp (M = Ru (**1a**), Fe (**2a**)) as yellow and orange solids in 56 and 80% yields, respectively (eq 1). The low isolated yield



of pure **1a** resulted from the difficulty of removal of the PPh₃ generated in the reaction by repeated crystallization. Chromatographic purification could not be employed since **1a** reacts with the support material.²⁰ These problems are avoided by using Pt(PPh₃)₂C₂H₄ in place of Pt(PPh₃)₄. The reaction of Cp(CO)₂RuCH₂C≡CPh with Pt(PPh₃)₂C₂H₄ under comparable conditions furnished **1a** in 87% yield; however, it required a longer time (20 h) for completion.

The η^1 -allenyls Cp(CO)₂MCH=C=CH₂ react with Pt(PPh₃)₂C₂H₄ in THF or hexane under much milder conditions than does Cp(CO)₂RuCH₂C≡CPh to generate

analogous products, (PPh₃)₂Pt(μ - η^1 : $\eta^2_{\alpha,\beta}$ -CH=C=CH₂)M(CO)Cp (M = Ru (**1b**), Fe (**2b**)), as yellow and orange solids, respectively (eq 2). Typically, these reactions

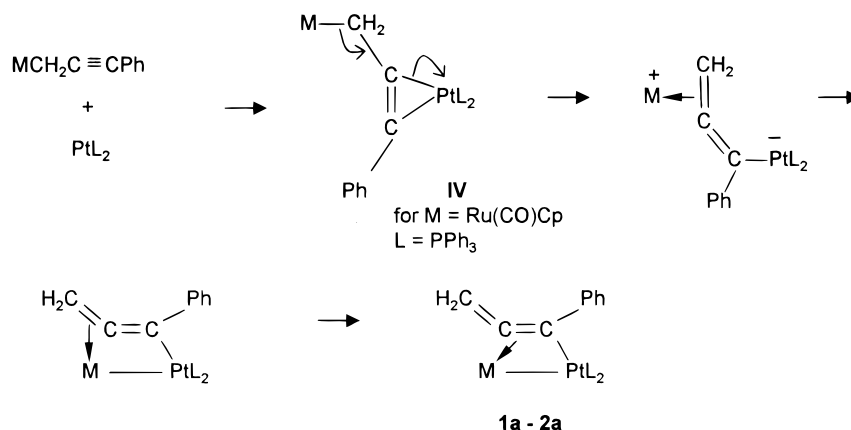


were commenced at −78 °C and continued with warming to room temperature until completion, and the yields of the binuclear products ranged from 60 to 87%.

Previous studies in this laboratory of reactions of metal propargyl complexes with metal carbonyls have resulted in the preparation of binuclear and trinuclear metal complexes of type **I** and **II**, respectively, as well as related products with various hydrocarbyl ligands.^{3,4,12} The synthesis of **1a–2a** by use of Pt(PPh₃)₄ or Pt(PPh₃)₂C₂H₄ represents the first successful application of this general methodology to binuclear metal μ - η^1 : η^2 -allenyl complexes. Furthermore, the products **1a** and **2a** are the first examples of mixed-metal μ -allenyl complexes of this structural type. The formation of **I** and **II** has been rationalized by a mechanism involving initial ligation of the metal propargylic C≡C to a coordinatively unsaturated metal in the reacting carbonyl.^{3,4} A suitable adaptation of this mechanism, shown

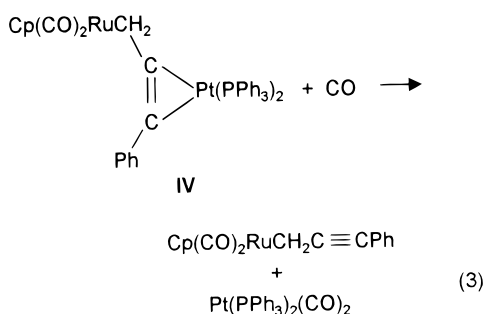
(20) Shuchart, C. E.; Willis, R. R.; Haggerty, B. S.; Rheingold, A. L.; Wojcicki, A. *Inorg. Chim. Acta*, in press.

Scheme 1



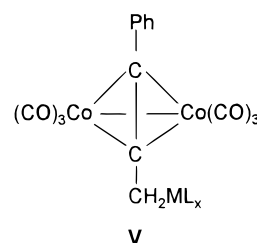
in Scheme 1, is proposed for the reactions of $\text{Cp}(\text{CO})_2\text{MCH}_2\text{C}\equiv\text{CPh}$ ($\text{M} = \text{Ru}, \text{Fe}$) with $\text{Pt}(\text{PPh}_3)_4$ and $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$.

To gain insight into the mechanism of formation of **1a**, a solution of $\text{Cp}(\text{CO})_2\text{RuCH}_2\text{C}\equiv\text{CPh}$ and $\text{Pt}(\text{PPh}_3)_2\text{-C}_2\text{H}_4$ in $\text{THF-}d_8$ at ambient temperature was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. After ca. 1 h, two new signals were observed at δ 27.4 (d, $J_{\text{PP}} = 37.2$ Hz, $J_{\text{PtP}} = 3350$ Hz) and 26.9 ($J_{\text{PP}} = 37.2$ Hz, $J_{\text{PtP}} = 3440$ Hz). A ^1H NMR spectrum of this solution showed that a doublet has grown in at δ 2.83 ($J_{\text{PH}} = 8.5$ Hz, $J_{\text{PtH}} = 54.4$ Hz). On prolonged storage (>18 h) or on warming the solution, the observed intermediate (**IV**) substantially converted to **1a** and some **3**. Attempts at isolation of **IV** also resulted in the formation of **1a**. Passing CO through a solution containing **IV** afforded $\text{Cp}(\text{CO})_2\text{-RuCH}_2\text{C}\equiv\text{CPh}$ and $\text{Pt}(\text{PPh}_3)_2(\text{CO})_2$ (eq 3), which were characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. No η^1 -allenyl $\text{Cp}(\text{CO})_2\text{RuC}(\text{Ph})=\text{C}=\text{CH}_2$ was observed.



The foregoing NMR data and the behavior of **IV** toward CO suggest that this intermediate has the structure presented in eq 3. Accordingly, the appearance of two $^{31}\text{P}\{^1\text{H}\}$ NMR signals as doublets with similar chemical shifts and comparable values of J_{PtP} is consistent with the presence of a $\text{Pt}(\text{PPh}_3)_2$ fragment bonded to an unsymmetrically substituted alkyne. The position of the ^1H CH_2 resonance at δ 2.83 is also compatible with such a structure. Although we could not find any examples of complexes containing a metal η^1 -propargyl group that is η^2 bonded through its $\text{C}\equiv\text{C}$ to another, single metal, stable compounds are known^{18,21} (cf. **V**) where such bonding occurs to both metal atoms of $\text{Co}_2(\text{CO})_6$. In **V** ($\text{ML}_x = \text{Cp}(\text{CO})_2\text{Fe}, \text{Cp}(\text{CO})_2\text{Ru}, \text{Cp-}$

$(\text{CO})_3\text{Mo}, \text{Cp}(\text{CO})_3\text{W}, (\text{CO})_5\text{Mn}$), the ^1H CH_2 resonance is observed in the region δ 3.55–2.19. The reaction of



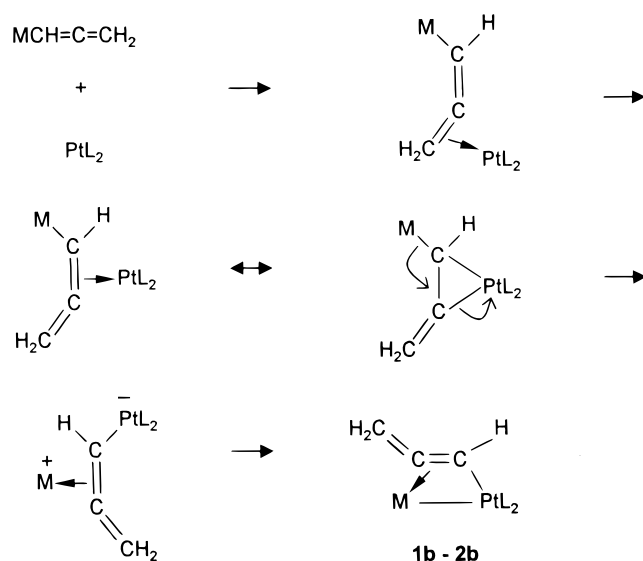
IV with CO is similar to the carbonylation of $\text{Pt}(\text{PPh}_3)_2\text{-C}_2\text{H}_4$ ($\text{PhC}\equiv\text{CPh}$), which affords $\text{Pt}(\text{PPh}_3)_2(\text{CO})_2$ and $\text{PhC}\equiv\text{CPh}$. However, it differs from the carbonylation of **1a**, which produces the η^1 -allenyl $\text{Cp}(\text{CO})_2\text{RuC}(\text{Ph})=\text{C}=\text{CH}_2$, in addition to $\text{Pt}(\text{PPh}_3)_2(\text{CO})_2$ (vide infra). Thus, it appears that **IV** contains an intact $\text{Cp}(\text{CO})_2\text{RuCH}_2\text{C}\equiv\text{CPh}$ fragment rather than a metal allenyl group bonded to $\text{Pt}(\text{PPh}_3)_2$.

The reactions in eq 2 represent the first examples of synthesis of any type of binuclear or polynuclear metal μ -allenyl complexes by treatment of metal η^1 -allenyls with metal carbonyls or related precursors of coordinatively unsaturated reactive ML_x species. The previously reported² reaction of $\text{Cp}(\text{CO})_2\text{RuCH}=\text{C}=\text{CH}_2$ with $\text{Fe}_2(\text{CO})_9$ afforded several mixed-metal trinuclear and tetranuclear organometallics, but no metal μ -allenyls. A reasonable mechanism for the reactions of $\text{Cp}(\text{CO})_2\text{-MCH}=\text{C}=\text{CH}_2$ ($\text{M} = \text{Ru}, \text{Fe}$) with platinum(0) complexes, which is similar to that for the corresponding reactions of $\text{Cp}(\text{CO})_2\text{MCH}_2\text{C}\equiv\text{CPh}$, appears in Scheme 2.

The proposed initial coordination of the terminal $\text{C}=\text{C}$ of $\text{Cp}(\text{CO})_2\text{MCH}=\text{C}=\text{CH}_2$ to $\text{Pt}(\text{PPh}_3)_2$ is preceded by a spectroscopically inferred similar mode of ligation of $\text{Cp}(\text{CO})_2\text{RuCH}=\text{C}=\text{CH}_2$ to iron carbonyl.² This μ - η^1 : $\eta^2_{\alpha,\beta}$ -allenyl species would then likely isomerize to a μ - η^1 : $\eta^2_{\alpha,\beta}$ counterpart, since rearrangement from μ - $\eta^1(\text{M})$: $\eta^2(\text{Pt})\text{-CH}=\text{C}=\text{CH}_2$ to μ - $\eta^1(\text{Pt})$: $\eta^2(\text{M})\text{-CH}=\text{C}=\text{CH}_2$ is best considered to occur from the latter. An alternative mechanistic possibility involving isomerization of $\text{Cp}(\text{CO})_2\text{MCH}=\text{C}=\text{CH}_2$ to $\text{Cp}(\text{CO})_2\text{MCH}_2\text{C}\equiv\text{CH}$ followed by a pathway presented in Scheme 1 seems unlikely, since the propargyls were found to react significantly more slowly than the η^1 -allenyls. No intermediates were detected in the reaction of $\text{Cp}(\text{CO})_2\text{RuCH}=\text{C}=\text{CH}_2$ with $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$ at ambient temperature.

(21) Wido, T. M.; Young, G. H.; Wojcicki, A.; Calligaris, M.; Nardin, G. *Organometallics* **1988**, 7, 452.

Scheme 2



Characterization of Heterobinuclear Metal μ - η^1 : $\eta^2_{\alpha,\beta}$ -Allenyl Complexes. The new heterobinuclear metal complexes **1a,b** and **2a,b** were characterized by IR and NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$) spectroscopy, FAB mass spectrometry, and chemical analysis. All four complexes yielded excellent C and H analysis and showed parent ion peaks in their mass spectra.

The IR spectrum of each complex shows a single ν -(CO) absorption at $1912\text{--}1896\text{ cm}^{-1}$; this absorption occurs at a lower frequency ($13\text{--}16\text{ cm}^{-1}$) for the PtFe complexes than for their PtRu counterparts. The presence of a carbonyl ligand is also evident in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra: the PtFe complexes show a signal at $\delta\ 220.4\text{--}220.2$, whereas the PtRu complexes resonate at $\delta\ 206.9\text{--}206.6$, all with platinum-195 satellites.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** and **2** are entirely consistent with the presence of a μ - η^1 : $\eta^2_{\alpha,\beta}$ -allenyl ligand that is η^1 bonded to Pt and η^2 bonded to Ru or Fe. Accordingly, the methine ^1H resonance of **1b** and **2b** occurs at $\delta\ 6.61$ ($^2J_{\text{PtH}} = 33.0\text{ Hz}$) and 7.03 ($^2J_{\text{PtH}} = 36.8\text{ Hz}$), respectively. In the homobinuclear metal complexes $\text{Fe}_2(\text{CO})_6(\mu\text{-SBu-}\delta)(\mu\text{-}\eta^1$: $\eta^2_{\alpha,\beta}\text{-CH=C=CH}_2)^9$ and $\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-}\eta^1$: $\eta^2_{\alpha,\beta}\text{-CH=C=CH}_2)^{10}$ the respective $=\text{CH}$ signals are observed at $\delta\ 8.7$ and 7.39 . The $=\text{CH}_2$ protons of **1** and **2** are inequivalent ($\delta\ 5.44\text{--}5.26$ and $4.89\text{--}4.66$) and show geminal coupling ($^2J_{\text{HH}} = 1.0\text{--}2.5\text{ Hz}$) as well as coupling to platinum-195 ($^4J_{\text{PtH}} = 10.0\text{--}19.7\text{ Hz}$). In contrast, the methylene protons of the homobinuclear $\text{Fe}_2(\text{CO})_6(\mu\text{-SBu-}\delta)(\mu\text{-}\eta^1$: $\eta^2_{\alpha,\beta}\text{-CH=C=CH}_2)^9$ and $\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-}\eta^1$: $\eta^2_{\alpha,\beta}\text{-CH=C=CH}_2)^{10}$ are equivalent at ambient temperature owing to fluxional behavior. A "windshield-wiper" type motion of the allenyl ligand was proposed to account for this fluxionality. Such an interchange pathway is entirely reasonable for homobinuclear complexes with identical ligand environments (except for the μ - η^1 : $\eta^2_{\alpha,\beta}$ -allenyl) at the two metals, since it leads to no net change in structure. However, for **1** and **2**, μ - η^1 (Pt): η^2 (Ru or Fe)-allenyl and μ - η^1 (Ru or Fe): η^2 (Pt)-allenyl attachments would be involved, and therefore an analogous mechanism may not be favorable. We find that complex **1a** does not exhibit fluxional behavior even at $100\text{ }^\circ\text{C}$ in toluene solution.

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** and **2** μ -allenyl resonances were observed at $\delta\ 176.4\text{--}165.3$ ($=\text{C=}$), $149.8\text{--}149.1$ or $122.3\text{--}114.7$ ($=\text{CPh}$ or $=\text{CH}$, respectively), and $97.2\text{--}94.3$ ($=\text{CH}_2$). These chemical shifts are similar to those reported for $\text{Fe}_2(\text{CO})_6(\mu\text{-SBu-}\delta)(\mu\text{-}\eta^1$: $\eta^2_{\alpha,\beta}\text{-CH=C=CH}_2)^9$ and $\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-}\eta^1$: $\eta^2_{\alpha,\beta}\text{-CH=C=CH}_2)^{10}$ at $\delta\ 180.0\text{--}176.6$, $118.2\text{--}114.9$, and $96.2\text{--}93.4$, respectively. The $=\text{CH}$ carbon signals of **1b** and **2b** show a large $^1J_{\text{PtC}}$ of $715\text{--}725\text{ Hz}$ to indicate that the μ -allenyl is σ bonded to platinum, as well as two very different $^2J_{\text{PC}}$ values for trans-P,C ($80.2\text{--}84.7\text{ Hz}$) and cis-P,C ($\leq 4.5\text{ Hz}$). The magnitude of the coupling constant $^1J_{\text{CH}}$ (160 Hz) in the ^{13}C NMR spectrum of **1b** is consistent with sp^2 hybridization at this $=\text{CH}$ carbon. The $=\text{CH}_2$ resonances reveal carbon-13 coupling to one phosphorus ($^3J_{\text{PC}} = 2.3\text{--}3.5\text{ Hz}$) and to platinum-195 ($^2J_{\text{PtC}} = 32\text{--}42\text{ Hz}$). As for the $=\text{CH}$ above, $^1J_{\text{CH}}$ values of 160 Hz for both **1a** and **1b** indicate sp^2 hybridization at the $=\text{CH}_2$ carbon. The relative downfield position at $\delta\ 97.2\text{--}94.3$ of the $=\text{CH}_2$ ^{13}C resonance of **1** and **2** is consistent with the presence of uncoordinated $\text{C}_\beta=\text{C}_\gamma$ and points to a μ - η^1 : $\eta^2_{\alpha,\beta}$ -allenyl structure. For comparison, $\text{M}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-}\eta^1$: $\eta^2_{\beta,\gamma}\text{-C(Ph)=C=CH}_2)$ ($\text{M}_2 = \text{Ru}_2$ or Os_2) display $^{13}\text{C}=\text{CH}_2$ signals much farther upfield, at $\delta\ 1.0$ (Ru_2) and -3.3 (Os_2).^{8b}

The PPh_3 ligands are, as expected, inequivalent in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, giving rise to two signals in the range $\delta\ 30.9\text{--}21.5$ with a $^2J_{\text{PP}} = 1.0\text{--}4.3\text{ Hz}$ and characteristic $^1J_{\text{PtP}}$ values of $2766\text{--}2925$ and $3415\text{--}3689\text{ Hz}$. The signal with the smaller $^1J_{\text{PtP}}$ is assigned to the phosphorus trans to the allenyl C_α which belongs to the more labile phosphine.^{22,23} This feature will be addressed again in the context of structure and reactivity of **1** and **2**.

The characterization of **3**, prepared by treatment of **1a** with CO or with $\text{Fe}_2(\text{CO})_9$ (vide infra), is considered together with that of **1** and **2** because of the structural similarity of these complexes.²⁴ The IR spectrum of **3** shows two $\nu(\text{CO})$ absorptions at 2018 and 1947 cm^{-1} , and the presence of two carbonyls is also evident in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, which reveals resonances at $\delta\ 204.2$ (RuCO) and 193.2 (PtCO , $^2J_{\text{PC}} = 5.0\text{ Hz}$). The μ -allenyl ligand is η^1 : $\eta^2_{\alpha,\beta}$ bonded, as reflected by the slightly broadened (probably owing to unresolved geminal coupling) ^1H NMR signals of the CH_2 group at $\delta\ 5.60$ and 5.02 with the accompanying platinum-195 satellites ($^4J_{\text{PtH}} = 17.7$ and 14.4 Hz , respectively) and by the $^{13}\text{C}\{^1\text{H}\}$ NMR signals at $\delta\ 163.3$ ($=\text{C=}$), 148.2 ($=\text{CPh}$), and 98.4 ($=\text{CH}_2$), all very similar to those for **1a** and **2a**. There is only a single $^{31}\text{P}\{^1\text{H}\}$ resonance at $\delta\ 24.4$, with a $^1J_{\text{PtP}} = 3277\text{ Hz}$. The chemical composition of **3** was confirmed by elemental analysis and by the appearance of the parent ion peak in the FAB mass spectrum.

Single-crystal X-ray diffraction studies of **1b** and **3** were undertaken to provide precise structural details and possibly help rationalize different chemical reactivity of the two complexes (vide infra). Yellow crystals of

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(23) Willis, R. R.; Calligaris, M.; Faleschini, P.; Gallucci, J. C.; Wojcicki, A. *J. Organomet. Chem.* **2000**, 593/594, 465.

(24) Complex **3** was incorrectly reported as $(\text{PPh}_3)\text{Pt}(\mu\text{-}\eta^1$: $\eta^2\text{-C(Ph)=C=CH}_2)\text{Ru(CO)Cp}$ in review articles.^{1a,c}

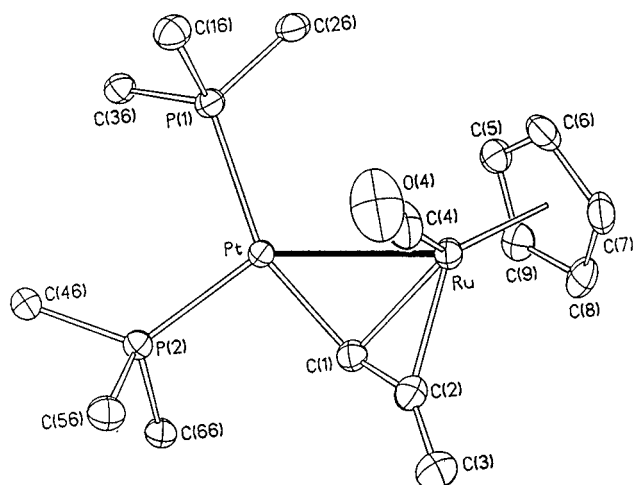


Figure 1. ORTEP diagram of **1b**. Only the ipso carbon atoms of the PPh₃ groups are shown, and the hydrogen atoms are omitted.

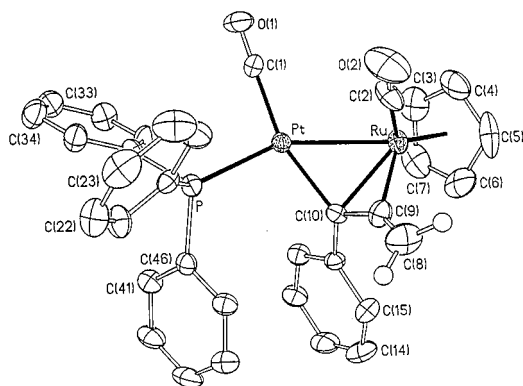


Figure 2. ORTEP diagram of **3**. Phenyl hydrogen atoms have been omitted.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1b**

Pt–Ru	2.718(1)	Ru–C(2)	2.098(7)
Pt–P(1)	2.302(2)	Ru–C(4)	1.838(6)
Pt–P(2)	2.255(2)	C(1)–C(2)	1.383(9)
Pt–C(1)	2.015(6)	C(2)–C(3)	1.308(10)
Ru–C(1)	2.116(6)	C(4)–O(4)	1.147(7)
Ru–Pt–P(1)	109.2(1)	Pt–Ru–C(4)	75.1(2)
P(1)–Pt–P(2)	107.4(1)	Pt–Ru–C(1)	47.3(2)
Ru–Pt–C(1)	50.5(2)	Ru–C(1)–C(2)	70.2(4)
P(2)–Pt–C(1)	94.6(2)	Pt–C(1)–C(2)	123.9(4)
P(1)–Pt–C(1)	156.8(2)	Ru–C(2)–C(3)	141.1(6)
Ru–Pt–P(2)	142.9(1)	Ru–C(2)–C(1)	71.5(4)
Pt–Ru–C(2)	76.3(2)	C(1)–C(2)–C(3)	147.3(7)
C(1)–Ru–C(4)	98.2(3)	Ru–C(4)–O(4)	176.3(7)
C(2)–Ru–C(4)	84.1(3)		

the two complexes were grown from dichloromethane/hexane at -5°C (**1b**) and room temperature (**3**). The respective molecular structures of **1b** and **3** are shown in Figures 1 and 2, whereas selected bond distances and angles are given in Tables 2 and 3. The two structures are remarkably similar. Both contain a μ -allenyl ligand that is η^1 bonded to Pt and η^2 attached, through the $C_\alpha=C_\beta$ bond, to Ru. The Pt–Ru bond distances of 2.718(1) Å in **1b** and 2.668(1) Å in **3** fall in the range of Pt–Ru bond lengths reported for a number of trinuclear and tetranuclear complexes.^{25–29} The μ -allenyl ligands

Table 3. Selected Bond Distances (Å) and Angles (deg) for **3**

Pt–Ru	2.668(1)	Ru–C(2)	1.844(12)
Pt–P	2.293(2)	C(10)–C(9)	1.402(9)
Pt–C(1)	1.882(10)	C(9)–C(8)	1.313(9)
Pt–C(10)	2.025(9)	C(10)–C(16)	1.507(11)
Ru–C(10)	2.162(9)	C(1)–O(1)	1.140(12)
Ru–C(9)	2.107(8)	C(2)–O(2)	1.155(15)
Ru–Pt–P	153.4(1)	Pt–Ru–C(10)	48.2(2)
Ru–Pt–C(1)	108.3(3)	Ru–C(10)–C(9)	68.7(5)
P–Pt–C(1)	97.8(3)	Pt–C(10)–C(9)	114.3(7)
Ru–Pt–C(10)	52.7(3)	Ru–C(9)–C(8)	138.5(9)
P–Pt–C(10)	101.7(3)	Ru–C(9)–C(10)	73.0(4)
C(1)–Pt–C(10)	160.1(4)	C(10)–C(9)–C(8)	148.5(10)
Pt–Ru–C(9)	73.7(3)	C(9)–C(10)–C(16)	121.0(8)
C(10)–Ru–C(2)	100.8(4)	Pt–C(1)–O(1)	175.7(8)
C(9)–Ru–C(2)	80.5(4)	Ru–C(2)–O(2)	176.1(10)
Pt–Ru–C(2)	77.8(3)		

$C(1)H=C(2)=C(3)H_2$ in **1b** and $C(10)(Ph)=C(9)=C(8)-H_2$ in **3** are characterized by the C(1)–C(2) and C(10)–C(9) distances of 1.383(9) and 1.402(9) Å, respectively, which are typical of the C=C bonds elongated by coordination to metal.¹ In contrast, the bond lengths C(2)–C(3) and C(9)–C(8), 1.308(10) and 1.313(9) Å, respectively, represent normal distances of free C=C. For comparison, in the homobinuclear metal complexes $Fe_2(CO)_6(\mu-SBu-t)(\mu-\eta^1:\eta^2_{\alpha,\beta}-CH=C=CH_2)^9$ and $Fe_2(CO)_6(\mu-PPh_2)(\mu-\eta^1:\eta^2_{\alpha,\beta}-CH=C=CH_2)^{10}$ the distances $C_\alpha-C_\beta$ are 1.365(3) and 1.363(9) Å, whereas the distances $C_\beta-C_\gamma$ are 1.317(3) and 1.335(9) Å, respectively. The allenyl bond angles C(1)–C(2)–C(3) in **1b** and C(10)–C(9)–C(8) in **3** measure, in the indicated order, $147.3(7)^\circ$ and $148.5(10)^\circ$. They are somewhat less obtuse than the bond angles $153.1(2)^\circ$ and $156.7(7)^\circ$ reported respectively for $Fe_2(CO)_6(\mu-SBu-t)(\mu-\eta^1:\eta^2_{\alpha,\beta}-CH=C=CH_2)^9$ and $Fe_2(CO)_6(\mu-PPh_2)(\mu-\eta^1:\eta^2_{\alpha,\beta}-CH=C=CH_2)^{10}$. However, the bond angles in all of the foregoing and other crystallographically characterized $\mu-\eta^1:\eta^2_{\alpha,\beta}$ -allenyl metal complexes^{8a,23,30} are considerably smaller than the corresponding bond angles in the $\mu-\eta^1:\eta^2_{\beta,\gamma}$ -allenyl complexes $Ru_2(CO)_6(\mu-PPh_2)(\mu-\eta^1:\eta^2_{\beta,\gamma}-C(Ph)=C=CH_2)$ ($172.3(3)^\circ$)^{8b} and its Os_2 analogue ($170.6(11)^\circ$).^{1c}

The two Pt–P bond distances in **1b** are unequal, with Pt–P(1) = 2.302(2) and Pt–P(2) = 2.255(2) Å. A slightly longer Pt–P bond distance for the phosphorus approximately trans to the bridging hydrocarbyl C_α (P(1)–Pt–C(1) = $156.8(2)^\circ$) compared to that approximately trans to Ru (Ru–Pt–P(2) = $142.9(1)^\circ$) has been also noted in other μ -allenyl and related complexes containing a $RuPt(PPh_3)_2$ fragment.^{23,31} Significantly, it is the PPh₃ trans to Ru (Ru–Pt–P = $153.4(1)^\circ$) that remains in the product complex **3** after carbonylation of **1a**. The other PPh₃ ligand of **1a**, trans to the allenyl C_α , undergoes substitution by CO.

Our final comments in this section concern $\eta^1:\eta^2_{\alpha,\beta}$ vs $\eta^1:\eta^2_{\beta,\gamma}$ bonding for binuclear metal μ -allenyl complexes.

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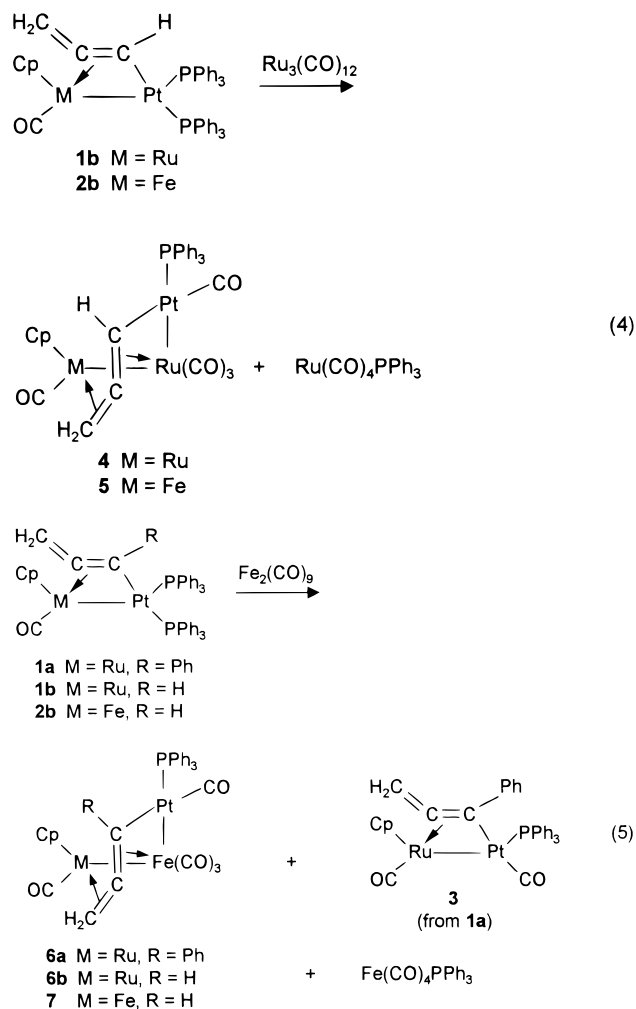
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With the exception of $M_2(CO)_6(\mu-PPh_2)(\mu-\eta^1:\eta^2_{\beta,\gamma}-C(Ph)=C=CH_2)$ ($M_2 = Ru_2$ or Os_2),^{8b} all of the structurally characterized compounds are of the type $\mu-\eta^1:\eta^2_{\alpha,\beta}$.^{1,10,23,30} It has been suggested¹⁰ that this structural preference for $Fe_2(CO)_6(\mu-PPh_2)(\mu-\eta^1:\eta^2_{\alpha,\beta}-CH=C=CH_2)$ may result from the relatively short M–M bond distance when M is a first-row transition metal. However, the present and another recent study²³ show that even the heavier metals Pt and Ru, with longer M–M bond distances, invariably afford binuclear $\mu-\eta^1:\eta^2_{\alpha,\beta}$ -allenyl complexes and do so irrespective of whether ambient or high temperatures are employed in their synthesis. Furthermore, the preparative methods used in this study would not be expected to result in a preference for either the internal or the terminal allenyl C=C bond coordination to metal in the product. Therefore, it appears that other factors must be involved in dictating the preference for $\mu-\eta^1:\eta^2_{\alpha,\beta}$ bonding, especially for the second- and third-row transition metals.

One of those factors may be metal-to-(η^2 -allenyl) π -bonding, which is expected to have an effect on M–M bond distance. Metal-to-($C_\beta=C_\gamma$) π -interaction will lead to $C_\alpha-C_\beta-C_\gamma$ bending, which in turn will enhance separation between the metal atoms. For the heavier metals, which engage more extensively in π -bonding than their lighter counterparts, M-to-M separation may thus become too large for a bonding interaction to occur. As a result, the metal will prefer interaction with $C_\alpha=C_\beta$, which positions it within bonding distance of the other metal. Interestingly, in the complex $Ru_2(CO)_6(\mu-PPh_2)(\mu-\eta^1:\eta^2_{\beta,\gamma}-C(Ph)=C=CH_2)$, the bond distance Ru–Ru = 2.860(1) Å and the bond angle $C_\alpha-C_\beta-C_\gamma = 172.3(3)^\circ$;^{8b} this is to be compared with Ru–Ru = 2.7863(8) Å (av) and $C_\alpha-C_\beta-C_\gamma = 143.7(4)^\circ$ (av) in $Ru_2(CO)_6(\mu-PPh_2)(\mu-\eta^1:\eta^2_{\alpha,\beta}-C(Ph)=C=CH_2)$.^{8a} The near linearity of the $C_\alpha-C_\beta-C_\gamma$ fragment in the former may result as a compromise between strength of the Ru-to-($C_\beta=C_\gamma$) π -interaction and a Ru–Ru bond distance needed to effect $\mu-\eta^1:\eta^2_{\beta,\gamma}$ -allenyl ligation.

Reactions of Heterobinuclear Metal $\mu-\eta^1:\eta^2_{\alpha,\beta}$ -Allenyl Complexes with Ruthenium and Iron Carbonyls. The reactions of **1** and **2** with an excess of $Ru_3(CO)_{12}$ (eq 4) or $Fe_2(CO)_9$ (eq 5) were generally conducted in THF at room temperature. The orange solutions of the reactants gradually darkened to red, and complete reaction was observed within 16–36 h by 1H and $^{31}P\{^1H\}$ NMR spectroscopy. The reaction of **2b** with $Ru_3(CO)_{12}$ was also carried out in hexane at reflux and reached completion in 1 h. All of the products were isolated after column chromatography on alumina of the crude reaction mixtures.

The principal products of these reactions are the heterotrimetallic $\mu_3-\eta^1:\eta^2:\eta^2$ -allenyl complexes $(PPh_3)(CO)Pt(\mu_3-\eta^1:\eta^2:\eta^2-C(R)=C=CH_2)M'(CO)_3M(CO)Cp$ ($M' = M = Ru$, $R = H$ (**4**); $M' = Ru$, $M = Fe$, $R = H$ (**5**); $M' = Fe$, $M = Ru$, $R = Ph$ (**6a**); $M' = Fe$, $M = Ru$, $R = H$ (**6b**); $M' = M = Fe$, $R = H$ (**7**)), which were isolated as red or orange (**6b**) solids in 17–34% yield. The reaction of **1a** with $Fe_2(CO)_9$ afforded, in addition to **6a**, the heterobimetallic $\mu-\eta^1:\eta^2_{\alpha,\beta}$ -allenyl complex **3** in 12% yield. Another major side product encountered in the synthesis of **4–7** was $M'(CO)_4PPh_3$ ($M' = Ru$ or Fe). These secondary products were readily separated from **4–7** by column chromatography. The formation of M' -



$(CO)_4PPh_3$ may be ascribed to fragmentation of $Ru_3(CO)_{12}$ and $Fe_2(CO)_9$ to mononuclear carbonyl species and reaction of the latter with the PPh_3 released by the $Pt(PPh_3)_2$ fragment of **1** and **2** during its conversion to the $Pt(CO)PPh_3$ in **3–7**. This fragmentation to generate labile metal carbonyls also accounts for the ready availability of free CO required for the substitution at platinum.

The surprising aspect of the formation of **4–7** according to eqs 4 and 5 concerns connectivity of the two C=C bonds of the μ -allenyl to $M'(CO)_3$ and $M(CO)Cp$. It had been expected that the free $C_\beta=C_\gamma$ bond of **1** and **2** would coordinate to the incipient $M'(CO)_3$, while the $C_\alpha=C_\beta$ bond would remain attached to $M(CO)Cp$. The observed opposite coordination selectivity suggests that the reactive site in **1** and **2** is not $C_\beta=C_\gamma$. Instead, the simplest mechanistic scenario would appear to entail insertion of $M'(CO)_3$ into the $Pt-M(CO)Cp$ bond and displacement of $M(CO)Cp$ from $C_\alpha=C_\beta$ to $C_\beta=C_\gamma$. The reason for this preference is not obvious, since the alternative $Pt-M-M'$ bond sequence would also lead to a stable electronic arrangement at each metal. The substitution of CO for PPh_3 at $Pt(PPh_3)_2$ probably occurs in the final stages of the reaction, as evidenced by a virtual lack of reactivity toward $Fe_2(CO)_9$ of the $Pt(CO)-PPh_3$ -containing complex **3**.

Characterization of Heterotrinuclear Metal $\mu_3-\eta^1:\eta^2:\eta^2$ -Allenyl Complexes. The chemical composition of complexes **4–7** was established by elemental analysis

and FAB mass spectrometry, which showed the parent ions and fragments resulting from loss of CO. Considerable information concerning the structure of **4–7** was obtained from the IR and ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, although these data did not unequivocally resolve the questions of μ -allenyl–metal and metal–metal connectivity. For that reason, an X-ray analysis of **6a** was undertaken. The other heterotrinnuclear metal μ -allenyls are assigned structures similar to that of **6a** on the basis of their spectroscopic similarities. Salient spectroscopic properties will be examined first.

The IR spectra of **4–7** in the $\nu(\text{CO})$ region exhibit three or four bands at $2038\text{--}1951\text{ cm}^{-1}$ due to terminal carbonyl ligands. The presence of CO at each of the three metal centers is unambiguously indicated by the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, which show signals of the FeCO at δ 216.1–210.3, RuCO at δ 208.0–200.7, and PtCO at δ 199.9–191.7. Separate resonances were observed for the CO's bonded to the two Ru and the two Fe atoms in **4** and **7**, respectively, with those of the $\text{M}(\text{CO})_3$ carbonyls in all of **4–7** being broadened by fluxionality. No platinum-195 satellites could be detected for the PtCO signals owing to the low intensity of these resonances.

The positions of the resonances of the allenyl hydrogen and carbon atoms reflect coordination to metal of both C=C bonds. Accordingly, the $=\text{CH}_2$ protons give rise to two signals in the range δ 3.86–2.26 with the geminal coupling constant $^2J_{\text{HH}} = 4.0\text{--}5.0\text{ Hz}$ and platinum-195 satellites ($^4J_{\text{PtH}} \leq 25.0\text{ Hz}$). The positions of these signals are considerably upfield from those of the binuclear $\mu\text{-}\eta^1\text{:}\eta^2\alpha,\beta$ -allenyl precursors (δ 5.44–5.26 and 4.89–4.66). Such an upfield shift is typical for $=\text{CH}_2$ protons upon coordination of the $\text{C}=\text{CH}_2$ to metal.³² The methine proton in **4**, **5**, **6b**, and **7** resonates at δ 8.04–7.21 and shows coupling to ^{195}Pt (47–50 Hz), ^{31}P (10–11 Hz), and, in some cases, CH_2 protons ($\leq 1.1\text{ Hz}$). The allenyl carbon atoms of **4–7** display $^{13}\text{C}\{^1\text{H}\}$ NMR signals at δ 196.9–187.7 ($=\text{C}=\text{}$), 167.4–135.5 ($=\text{CH}$ or $=\text{CPh}$), and 44.9–13.4 ($=\text{CH}_2$), with irregularly observed coupling to ^{31}P ($J_{\text{PC}} \leq 5.4\text{ Hz}$) and ^{195}Pt ($^1J_{\text{PtC}} \approx 700\text{ Hz}$, $^2J_{\text{PtC}} \approx 60\text{ Hz}$, $^3J_{\text{PtC}} = 46\text{ Hz}$). As noted for the $=\text{CH}_2$ protons, the $=\text{CH}_2$ carbon resonance occurs at a considerably higher field for **4–7** than for the precursor **1** or **2** to suggest coordination of the $\text{C}_\beta=\text{C}_\gamma$ to metal. It is also noteworthy that the $^1J_{\text{CH}}$ of 156 Hz for the $=\text{CH}_2$ of **6a** is slightly less than that of the parent complex **1a** or of **1b** (both $^1J_{\text{CH}} = 160\text{ Hz}$) to indicate a lower s character of the carbon bond to hydrogen upon ligation. Furthermore, the chemical shifts of the allenyl carbon atoms in **4–7** are very similar to those reported for the structurally analogous triangular metal $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2$ -allenyl complexes **III**.^{1b,c}

Orange crystals of **6a** for an X-ray diffraction study were obtained from dichloromethane/hexane. The molecular structure together with the atom-numbering scheme is shown in Figure 3, whereas selected bond distances and angles are given in Table 4. Molecules of **6a** are comprised of the $\text{Pt}(\text{CO})\text{PPh}_3$, $\text{Fe}(\text{CO})_3$, and $\text{Ru}(\text{CO})\text{Cp}$ fragments that are Pt–Fe–Ru bonded in an open trimetallic array. The metal–metal bonds are supported by a $\mu\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2$ -allenyl ligand. The Pt–Fe–

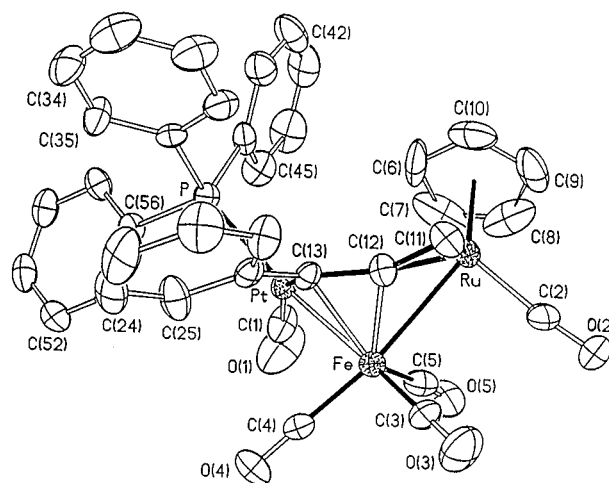


Figure 3. ORTEP diagram of **6a**. The hydrogen atoms have been omitted.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **6a**

Pt–Fe	2.528(2)	Fe–C(12)	1.981(10)
Ru–Fe	2.761(2)	Fe–C(13)	2.116(10)
Pt–P	2.291(3)	Ru–C(2)	1.832(13)
Pt–C(1)	1.874(12)	Ru–C(11)	2.214(9)
Pt–C(13)	2.022(9)	Ru–C(12)	2.116(9)
Fe–C(3)	1.752(12)	C(11)–C(12)	1.431(13)
Fe–C(4)	1.792(12)	C(12)–C(13)	1.362(13)
Fe–C(5)	1.767(12)		
Pt–Fe–Ru	84.1(1)	Pt–C(13)–C(12)	114.2(6)
Fe–Pt–P	158.4(1)	Pt–C(13)–C(26)	124.5(6)
C(1)–Pt–C(13)	158.0(5)	Ru–C(12)–C(13)	129.1(7)
Fe–Pt–C(1)	104.4(4)	C(13)–C(12)–C(11)	149.7(9)
Fe–Pt–C(13)	54.0(3)	Pt–C(1)–O(1)	175.5(12)
P–Pt–C(1)	97.3(4)	Ru–C(2)–O(2)	175.0(10)
P–Pt–C(13)	104.4(3)	Fe–C(5)–O(5)	173.5(9)

Ru bond angle is $84.1(1)^\circ$, nearly a right angle, and large enough so as not to allow for a bonding interaction between Pt and Ru (Pt–Ru separation = 3.55 Å , ca. $0.7\text{--}0.9\text{ Å}$ longer than a Pt–Ru single bond²⁹). The Pt–Fe bond length of $2.528(2)\text{ Å}$ is somewhat shorter than that found in $(\text{CO})_3\text{Fe}(\mu\text{-CO})(\mu\text{-dppm})\text{PtBr}_2$ ($2.6474(4)\text{ Å}$, dppm = bis(diphenylphosphino)methane),³³ $(\text{CO})_3\text{-(SiPh}_3\text{)Fe}(\mu\text{-PPh}_2)\text{Pt}(\text{CO})\text{PPh}_3$ ($2.620(1)\text{ Å}$),³⁴ and a number of other platinum–iron complexes.²⁹ The Ru–Fe single bond distance of $2.761(2)\text{ Å}$ falls in the range of Ru–Fe distances observed in binuclear and trinuclear ruthenium–iron μ -allenyl and related complexes ($2.62\text{--}2.79\text{ Å}$).^{2,4} The μ -allenyl ligand is η^1 bonded to Pt (Pt–C(13) = $2.022(9)\text{ Å}$) and η^2 bonded through each of the internal C(12)=C(13) and the terminal C(11)=C(12) double bond to Fe (Fe–C(13) = $2.116(10)\text{ Å}$, Fe–C(12) = $1.981(10)\text{ Å}$) and Ru (Ru–C(12) = $2.116(9)\text{ Å}$, Ru–C(11) = $2.214(9)\text{ Å}$), respectively. These distances are comparable to the M–C bond distances associated with μ -allenyl groups in related compounds.^{2,4,8,10,30} Both C(12)=C(13) ($1.362(13)\text{ Å}$) and C(11)=C(12) ($1.431(13)\text{ Å}$) are elongated by coordination to metal from free C=C bonds in metal η^1 -allenyl complexes.^{35–37} Carbon–

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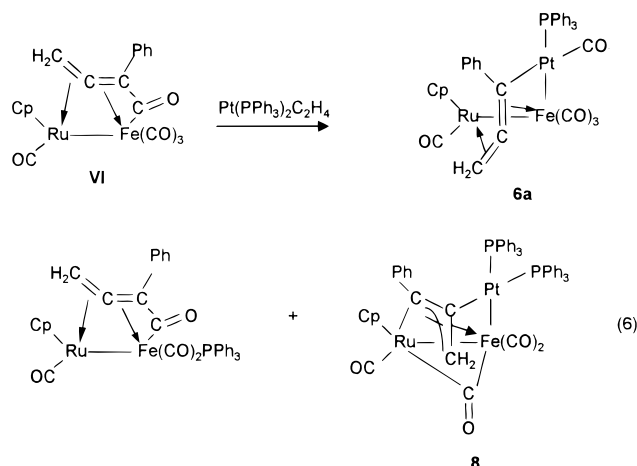
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carbon bond lengthening of a similar magnitude has been noted for triangular metal μ - η^1 : η^2 : η^2 -allenyl complexes, with $C_\beta=C_\gamma$ generally being longer than $C_\alpha=C_\beta$.^{1b,c} The angle C(13)–C(12)–C(11) of **6a** (149.7(9)°) is in the range observed for closed trinuclear metal μ -allenyls **II** (127–152°).^{1b,c}

Complexes **4–7** are representative of 48-electron open trinuclear metal clusters.³⁸ Such clusters are known for PtM₂ (e.g., M = Mn, Fe, Co); however, they adopt linear or close to linear structure, with Pt bonded to both M atoms.^{38–40} Triangular, Pt-containing clusters also have been reported.^{29,38} We attempted to convert **6a** to a closed trimetallic cluster by thermolysis and photolysis, however without much success. No reaction was observed when **6a** in THF was heated at 60 °C for 24 h. Photolysis with 254 nm lamps resulted in ca. 50% consumption of **6a** accompanied by loss of CO to form a product that showed two CH₂ proton resonances at δ 3.75 ($J_{\text{HH}} = 3.0$, $J_{\text{PtH}} = 9.0$ Hz) and 3.61 ($J_{\text{HH}} = 3.0$, $J_{\text{PtH}} = 8.0$ Hz) and a $^{31}\text{P}\{^1\text{H}\}$ NMR signal at δ 26.2 ($^1J_{\text{PtP}} = 3398$ Hz). However, this product could not be isolated pure because of instability in solution and toward column chromatography.

Reaction of $(\text{CO})_3\text{Fe}(\mu\text{-}\eta^3\text{:}\eta^2\text{-C(O)C(Ph)=C=CH}_2\text{)-Ru(CO)Cp}$ (VI) with $\text{Pt(PPh}_3)_2\text{C}_2\text{H}_4$ and Characterization of a Heterotrinuclear Metal Product, $(\text{PPh}_3)_2\text{Pt}(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^3\text{-C(Ph)CCH}_2\text{)Ru(CO)Cp}(\mu_2\text{-CO})\text{Fe(CO)}_2$ (8**).** Since the reactions of **1** and **2** with iron and ruthenium carbonyls lead to insertion of the $\text{Fe}(\text{CO})_3$ and $\text{Ru}(\text{CO})_3$ fragments into the Pt–Ru and Pt–Fe bonds, it was of interest to ascertain whether reaction of a similar binuclear RuFe complex with $\text{Pt(PPh}_3)_2\text{C}_2\text{H}_4$ would result in the formation of a Ru–Pt–Fe bonded product. The μ -allenylcarbonyl $(\text{CO})_3\text{Fe}(\mu\text{-}\eta^3\text{:}\eta^2\text{-C(O)C(Ph)=C=CH}_2\text{)Ru(CO)Cp}$ (**VI**) was selected for this experiment, as analogous binuclear RuFe μ -allenyls are not known. Although both C=C bonds are ligated to metal in **VI**, this feature was not expected to impede reactivity. The reactions of **1** and **2** with $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ suggest that a free C=C bond of μ -allenyl does not initiate the formation of trimetallic products.

Stirring a THF solution of equimolar amounts of **VI** and $\text{Pt(PPh}_3)_2\text{C}_2\text{H}_4$ first at 0 °C and then at room temperature afforded a mixture of three products (eq 6), which were separated by column chromatography and isolated in the indicated yields: orange **6a** (25%), known⁴ red-orange $(\text{PPh}_3)(\text{CO})_2\text{Fe}(\mu\text{-}\eta^3\text{:}\eta^2\text{-C(O)C(Ph)=C=CH}_2\text{)Ru(CO)Cp}$ (19%), and red $(\text{PPh}_3)_2\text{Pt}(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^3\text{-C(Ph)CCH}_2\text{)Ru(CO)Cp}(\mu_2\text{-CO})\text{Fe(CO)}_2$ (**8**) (19%). Monitoring the reaction solution by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy resulted in the detection of an intermediate with signals at δ 25.4 ($^1J_{\text{PtP}} = 3877$ Hz) and 22.3 ($^1J_{\text{PtP}} = 2866$ Hz). These values of $^1J_{\text{PtP}}$ would be consistent with the presence of Ru or Fe and a hydrocarbyl group in the positions trans to the respective PPh_3 ligands at platinum.^{22,23} The intermediate decomposed to the aforementioned three products.



Complex **8** was characterized by elemental analysis, FAB mass spectrometry, and IR and NMR spectroscopy. Its structure was determined by an X-ray diffraction analysis. The ^1H NMR spectrum shows a doublet resonance at δ 3.05 ($^2J_{\text{HH}} = 4.9$, $^3J_{\text{PtH}} = 44.3$ Hz), which is assigned to one of the inequivalent protons of CH₂. The signal of the second proton could not be located. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, resonances are observed of a bridging CO (δ 248.9),⁴¹ FeCO's (δ 214.3), and a RuCO (δ 205.8). The signals at δ 182.3, 156.4, and 69.8 are assigned to C_β , C_α , and C_γ , respectively, of a new C₃ hydrocarbyl ligand.^{23,31} However, the nature of this ligand and its connectivity to metals are not apparent from these data. No platinum-195 satellites could be observed in the spectrum owing to the limited solubility of **8**. The two $^{31}\text{P}\{^1\text{H}\}$ resonances at δ 24.1 ($^1J_{\text{PtP}} = 4053$ Hz) and 22.2 ($^1J_{\text{PtP}} = 2819$ Hz) point, as in the case of the reaction intermediate, to the presence of a hydrocarbyl carbon and Ru or Fe at the Pt center.

Because the foregoing data left an incomplete structural picture of **8**, an X-ray diffraction study was carried out on a crystal obtained from chloroform/hexane at –23 °C. The molecular structure is shown in Figure 4, and selected bond distances and angles are furnished in Table 5. Molecules of **8** may be described as open, Pt–Fe–Ru (angle = 125.9(1)°) bonded clusters containing an η^3 -allyl ligand (C(5)C(6)C(7)) attached to iron. The $\text{Pt(PPh}_3)_2$ group is connected essentially symmetrically to the central carbon C(6) (Pt–C(6)–C(5) = 114.6(11)°, Pt–C(6)–C(7) = 111.4(11)°), whereas the Ru(CO)Cp fragment is an anti substituent at the terminal CPh (C(7)). The C–C bond distances of the η^3 -allyl ligand are unequal (C(5)–C(6) = 1.341(23) Å, C(6)–C(7) = 1.433(19) Å), and the angle C(5)–C(6)–C(7) is normal (120.9(13)°). The two Pt–P bond lengths are different, with Pt–P(1) (2.299(4) Å) > Pt–P(2) (2.258(4) Å), as expected for phosphines trans to a hydrocarbyl carbon and a metal, respectively.^{22,23} The Pt–Fe bond distance of 2.696(2) Å is normal (cf. discussion of the structure of **6a**). The Ru–Fe bond length (2.639(3) Å) is also unexceptional and may be compared with that of 2.742–(2) Å in **VI**.⁴ The former bond is supported by an unsymmetrically bridging carbonyl C(3)O(3) (Fe–C(3) = 1.918(16) Å, Ru–C(3) = 2.125(17) Å; Fe–C(3)–O(3) = 147.7(14)°, Ru–C(3)–O(3) = 131.0(13)°).

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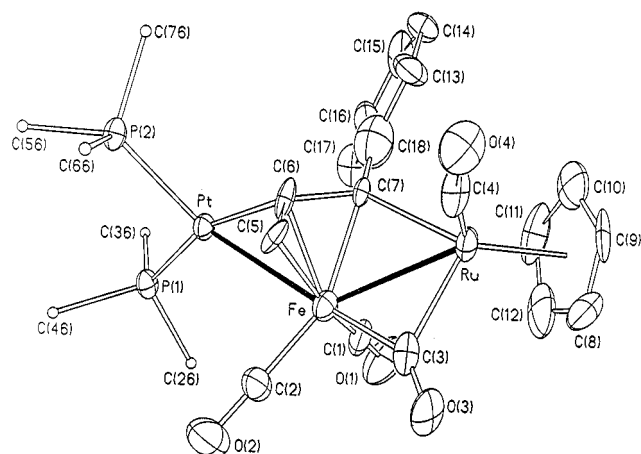
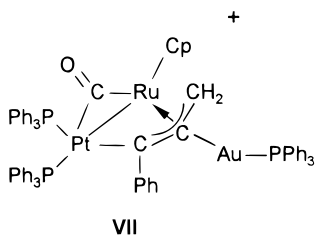


Figure 4. ORTEP diagram of **8**. Only the ipso carbon atoms of the PPh₃ groups are shown, and the hydrogen atoms are omitted.

Table 5. Selected Bond Distances (Å) and Angles (deg) for **8**

Pt–Fe	2.696(2)	Fe–C(5)	2.141(16)
Ru–Fe	2.639(3)	Fe–C(6)	1.965(16)
Pt–P(1)	2.299(4)	Fe–C(7)	2.037(14)
Pt–P(2)	2.258(4)	Ru–C(3)	2.125(17)
Pt–C(6)	2.062(15)	Ru–C(4)	1.849(17)
Fe–C(1)	1.824(18)	Ru–C(7)	2.102(13)
Fe–C(2)	1.748(18)	C(5)–C(6)	1.341(23)
Fe–C(3)	1.918(16)	C(6)–C(7)	1.433(19)
Pt–Fe–Ru	125.9(1)	Pt–C(6)–C(5)	114.6(11)
Fe–Pt–P(2)	138.6(1)	Pt–C(6)–C(7)	111.4(11)
P(1)–Pt–C(6)	161.9(4)	Ru–C(7)–C(6)	122.0(10)
Fe–Pt–P(1)	115.8(1)	Ru–C(3)–O(3)	131.0(13)
Fe–Pt–C(6)	46.4(4)	Ru–C(4)–O(4)	168.1(14)
P(1)–Pt–P(2)	101.9(1)	Fe–C(1)–O(1)	174.0(15)
P(2)–Pt–C(6)	96.0(4)	Fe–C(2)–O(2)	178.3(18)
Fe–Ru–C(4)	103.5(5)	Fe–C(3)–O(3)	147.7(14)
C(3)–Ru–C(4)	93.1(7)	C(5)–C(6)–C(7)	120.9(13)
C(3)–Ru–C(7)	93.4(6)	C(6)–C(7)–C(18)	122.4(12)
C(5)–Fe–C(7)	70.5(6)		

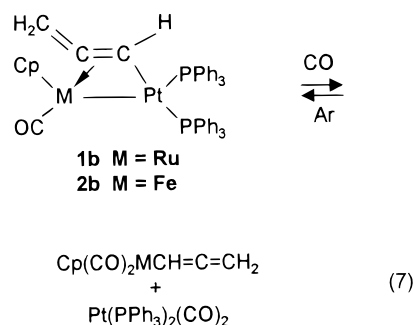
Overall, the structure of cluster **8** has features that are similar to those of the RuPtAu complex [(PPh₃)₂Pt-(μ₂-CO)RuCpAu(PPh₃)₂(μ₃-η¹:η³:η¹-CH₂CCPh)]⁺ **VII**,



except that the latter contains only one M–M bond. However, the formation of **8**, compared with that of **VII** from **1a** and [Au(PPh₃)]⁺, involves a more extensive rearrangement of the metal framework around the C₃ hydrocarbyl ligand. In contrast to the formation of **8**, the conversion of **VI** to **6a**, also by the reaction in eq 6, occurs with only one major structural change, viz., replacement of the acyl CO by PtL₂.

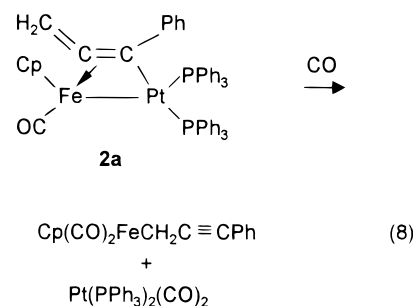
Reactions of Heterobinuclear Metal μ-η¹:η²_{α,β}-Allenyl Complexes with CO and of Mononuclear Metal η¹-Propargyl and η¹-Allenyl Complexes with Pt(PPh₃)₂(CO)₂. The formation of **3** by replacement of one PPh₃ ligand with CO upon treatment of **1a** with Fe₂(CO)₉ (cf. eq 5) prompted us to examine carbonylation

reactions of **1** and **2**. We find that **1b** and **2b** readily react according to eq 7 when CO is passed through their solutions in CD₂Cl₂ at room temperature.



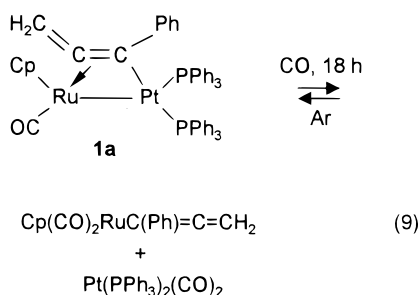
In ca. 3 h, ³¹P{¹H} NMR spectra showed complete disappearance of **1b** and **2b** and formation of Pt(PPh₃)₂(CO)₂,¹⁷ while ¹H NMR spectra demonstrated the presence of Cp(CO)₂MCH=C=CH₂ (M = Ru, Fe). Carbon monoxide was then replaced with Ar, and after 2 h complete regeneration of **1b** and **2b** was noted. This cycle can be repeated at least two more times without observation of any significant decomposition.

Reactions of **1a** and **2a** proceed much less readily than those of **1b** and **2b**. Thus, bubbling CO through a solution of **2a** in CD₂Cl₂ at room temperature afforded only ca. 50% conversion to Cp(CO)₂FeCH₂C≡CPh and Pt(PPh₃)₂(CO)₂ after 18 h (eq 8). Replacement of CO



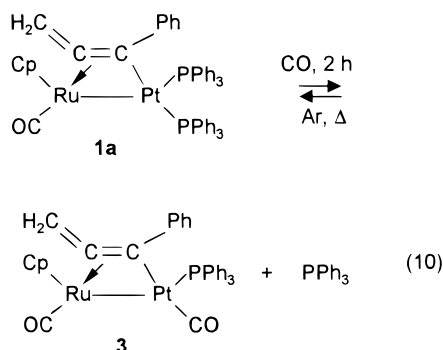
with Ar at this point had no effect on the relative amounts of **2a** and Cp(CO)₂FeCH₂C≡CPh in solution, even after 18 h. The only change observed by NMR was conversion of Pt(PPh₃)₂(CO)₂ to Pt(PPh₃)_x¹³ (and presumably also Pt and CO).

When a CD₂Cl₂ solution of **1a** was similarly treated with CO for 18 h, Cp(CO)₂RuC(Ph)=C=CH₂ and Pt(PPh₃)₂(CO)₂ were formed (eq 9). The characterization



of the former product was described elsewhere.²³ No corresponding η¹-propargyl, Cp(CO)₂RuCH₂C≡CPh, was detected. The reaction can be reversed by passage of Ar through the solution. However, if the reaction of **1a** with

CO is conducted for only 2 h, complex **3** and PPh_3 are observed as products in high yield by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy (eq 10). The reverse of this substitu-



tion reaction requires heating in toluene at 100 °C for 18 h under Ar. Treatment of **3** with CO at room temperature for 18 h resulted in the formation of $\text{Cp}(\text{CO})_2\text{RuC}(\text{Ph})=\text{C}=\text{CH}_2$, a small amount of $\text{Pt}(\text{PPh}_3)_2(\text{CO})_2$, and other mononuclear Pt-containing species. Passage of Ar through this reaction mixture produced some **1a**, but no detectable **3**.

Several aspects of the aforementioned reactions invite further comments. That the CO-induced fragmentation of **1b** and **2b** proceeds much more rapidly than that of **1a** and **2a** appears to be influenced by two factors: (i) the substituent at the allenyl C_α (H or Ph) and (ii) the nature of the organometallic product (η^1 -allenyl or η^1 -propargyl). That the $\mu\text{-CH}=\text{C}=\text{CH}_2$ complexes react faster than their $\mu\text{-C}(\text{Ph})=\text{C}=\text{CH}_2$ counterparts has also been observed for similar fragmentations of **1a** and **1b** induced by fumaronitrile and several alkynes.²³ This reactivity order may be attributed to the expected stronger $\text{M}-(\eta^2\text{-C}(\text{R})=\text{C})$ interaction in **1a** and **2a** than in **1b** and **2b** caused by the electron-withdrawing $\text{R} = \text{Ph}$ group. However, steric effects associated with the Ph substituent may also be a contributing factor. The slower formation of $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$ from **2a** than of the appropriate η^1 -allenyl complexes from **1a,b** and **2b** may be ascribed to the apparent requirement of migration of Fe from $\text{C}_\alpha=\text{C}_\beta$ to $\text{C}_\beta=\text{C}_\gamma$ to afford the η^1 -propargyl product (cf Scheme 2). However, it is not clear why **1a** yields $\text{Cp}(\text{CO})_2\text{RuC}(\text{Ph})=\text{C}=\text{CH}_2$, and **2a** furnishes $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$ upon reaction with CO. Both $\text{Cp}(\text{CO})_2\text{RuCH}_2\text{C}\equiv\text{CPh}$ and $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$ are stable compounds, but $\text{Cp}(\text{CO})_2\text{FeC}(\text{Ph})=\text{C}=\text{CH}_2$, unlike $\text{Cp}(\text{CO})_2\text{RuC}(\text{Ph})=\text{C}=\text{CH}_2$, has not been reported.

The reverse of the reactions in eqs 7–9 also proceeds much more rapidly for the Ru and Fe η^1 -allenyls than for the η^1 -propargyl $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$. These and related reactions were also investigated on a synthetic scale by use of equimolar amounts of the η^1 -allenyl or η^1 -propargyl complex and $\text{Pt}(\text{PPh}_3)_2(\text{CO})_2$. With $\text{Cp}(\text{CO})_2\text{MCH}=\text{C}=\text{CH}_2$ ($\text{M} = \text{Ru}, \text{Fe}$) in THF at room temperature, the reaction was over in 2 h, and excellent isolated yields (87–90%) of **1b** and **2b** were obtained. With $\text{Cp}(\text{CO})_2\text{RuCH}_2\text{C}\equiv\text{CPh}$, the reaction required reflux temperature of THF and reached completion in 2

h to afford 92% isolated **1a**. In sharp contrast, heating $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$ and $\text{Pt}(\text{PPh}_3)_2(\text{CO})_2$ in THF at reflux for 24 h gave only 10% conversion to **2a** (in situ ^1H NMR characterization).

The foregoing reactions of $\text{Cp}(\text{CO})_2\text{MCH}=\text{C}=\text{CH}_2$ and $\text{Cp}(\text{CO})_2\text{MCH}_2\text{C}\equiv\text{CPh}$ ($\text{M} = \text{Ru}, \text{Fe}$) with $\text{Pt}(\text{PPh}_3)_2(\text{CO})_2$ may be compared with analogous reactions involving other Pt(0) complexes, including $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$ and $\text{Pt}(\text{PPh}_3)_4$. The latter also proceed at ambient temperature for the η^1 -allenyls, but require higher temperatures for the η^1 -propargyls. The difference in reactivity may be due to the more extensive rearrangements required for the propargyls compared to the allenyls, as proposed in the reaction mechanisms depicted in Schemes 1 and 2.

Conclusions

This study has demonstrated that reactions of metal η^1 -propargyls with zerovalent metal compounds can be used for synthesis of heterobinuclear metal $\mu\text{-}\eta^1\text{:}\eta^2_{\alpha,\beta}$ -allenyl complexes (**III**). Previously reported products of such reactions include $\mu\text{-}\eta^3\text{:}\eta^2$ -allenyl/propargyl (**I**) and $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2$ -allenyl (**II**) complexes.^{3,4} We have now found that treatment of $\text{Cp}(\text{CO})_2\text{MCH}_2\text{C}\equiv\text{CPh}$ ($\text{M} = \text{Ru}, \text{Fe}$) with $\text{Pt}(\text{PPh}_3)_4$ or $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$ affords $(\text{PPh}_3)_2\text{Pt}(\mu\text{-}\eta^1\text{:}\eta^2_{\alpha,\beta}\text{-C}(\text{Ph})=\text{C}=\text{CH}_2)\text{M}(\text{CO})\text{Cp}$ (**1a**, **2a**). The η^1 -allenyls $\text{Cp}(\text{CO})_2\text{MCH}=\text{C}=\text{CH}_2$ ($\text{M} = \text{Ru}, \text{Fe}$) react with $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$ analogously, and significantly faster than the η^1 -propargyls, to yield $(\text{PPh}_3)_2\text{Pt}(\mu\text{-}\eta^1\text{:}\eta^2_{\alpha,\beta}\text{-CH}=\text{C}=\text{CH}_2)\text{M}(\text{CO})\text{Cp}$ (**1b**, **2b**) (eqs 1, 2). The new heterobinuclear metal complexes show two types of chemical behavior that are unprecedented for metal μ -allenyls. First, they serve as precursors of open trinuclear metal μ_3 -allenyl products, $(\text{PPh}_3)(\text{CO})\text{Pt}(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-C}(\text{R})=\text{C}=\text{CH}_2)\text{M}'(\text{CO})_3\text{M}(\text{CO})\text{Cp}$ ($\text{M}, \text{M}' = \text{Ru}, \text{Fe}$, **4–7**), which are obtained upon reaction of **1** and **2** with $\text{Ru}_3(\text{CO})_{12}$ or $\text{Fe}_2(\text{CO})_9$ (eqs 4, 5). These reactions proceed by insertion of $\text{M}'(\text{CO})_3$ into the $\text{Pt-M}(\text{CO})\text{Cp}$ bond rather than by coordination to $\text{M}'(\text{CO})_3$ of the free $\text{C}_\beta=\text{C}_\gamma$ bond of the μ -allenyl ligand. Second, **1** and **2** display unusual propensity to fragmentation into mononuclear metal complexes upon reaction with CO. Accordingly, $\text{Cp}(\text{CO})_2\text{MCH}=\text{C}=\text{CH}_2$ ($\text{M} = \text{Ru}, \text{Fe}$), $\text{Cp}(\text{CO})_2\text{RuC}(\text{Ph})=\text{C}=\text{CH}_2$, and $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$, as well as $\text{Pt}(\text{PPh}_3)_2(\text{CO})_2$, are obtained by carbonylation of the appropriate **1** and **2** (eqs 7–9). These reactions are readily reversed by passage of Ar at ambient temperature into solution of the η^1 -allenyl products, but not of the η^1 -propargyl product.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles for **1a**, **3**, **6a**, and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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