

Table I. Electronic Absorption and ^{13}C NMR Spectroscopic Data for *cis*- and *trans*-Rh(en) $_2$ (NH $_3$)(H $_2$ O) $^{3+}$

complex	λ_{max} , nm	ϵ_{max} , M $^{-1}$ cm $^{-1}$	δ^a
<i>trans</i> -Rh(en) $_2$ (NH $_3$)(H $_2$ O) $^{3+}$	303	167	45.63
<i>cis</i> -Rh(en) $_2$ (NH $_3$)(H $_2$ O) $^{3+}$	309	227	47.68, 46.39, 45.99, 45.03 b

a Chemical shifts reported vs. Me $_4$ Si with dioxane (67.40 ppm) as an internal reference. b Reference 8.

controls and photolyses at 25 °C—were run for the corresponding length of time.

Spectroscopy. The photolysis and dark control solutions were analyzed both by electronic spectroscopy and by proton-decoupled ^{13}C NMR spectroscopy. Electronic spectroscopy utilized a Cary Model 14 UV-vis-near-IR spectrophotometer, and NMR experiments were run in 1/1 (v/v) D $_2$ O/H $_2$ O on a Varian XL-100 equipped with a Nicolet TT-100 data system operating at a frequency of 25.2 MHz. NMR procedures and data treatment have been described previously. 7 Table I reports the electronic absorption and ^{13}C NMR spectroscopic results on *cis*- and *trans*-Rh(en) $_2$ (NH $_3$)(H $_2$ O) $^{3+}$.

Results and Discussion

Figure 1 contains proton-decoupled ^{13}C NMR spectra of solutions of *cis*-Rh(en) $_2$ (NH $_3$)(H $_2$ O) $^{3+}$ which were (a) thermostated at 25 or 50 °C and kept in the dark for 5 h or (b) irradiated at 25 or 50 °C for 5 h. All spectra display the four peaks which correspond to the *cis*-Rh(en) $_2$ (NH $_3$)(H $_2$ O) $^{3+}$, whereas only the spectrum of the 50 °C photolysis solutions shows a significant peak at 45.63 ppm representing the *trans* isomer. Photoisomerization also occurred when *trans*-Rh(en) $_2$ (NH $_3$)(H $_2$ O) $^{3+}$ was irradiated at 50 °C. However, under the photolysis conditions at 50 °C (8 h for *trans* and 5 h for *cis*), *cis* \rightarrow *trans* photoisomerization was more pronounced than *trans* \rightarrow *cis* photoisomerization. This is not surprising since the respective extinction coefficients of the *cis* and *trans* isomers at the 313-nm irradiation wavelength are 225 and 150 M $^{-1}$ cm $^{-1}$, and photoaquation quantum yields for loss of X in the RhA $_4$ X $_2^+$ systems (A $_4$ = (NH $_3$) $_4^3$, (en) $_2^2$; X = Cl, Br) are generally larger for the *cis* isomer.

The fact that the *cis* complexes generally have greater substitutional quantum yields yet are predicted to have greater M-X bond energies in the excited states 9 suggests that six-coordinate excited-state lifetimes are longer for the *cis* complexes. If this same trend is observed for the five-coordinate, triplet fragments, i.e., X basal longer lived than X apical, we would expect the majority of product under extensive photolysis conditions to be the *trans* isomer, even if the free energies of X basal and X apical are approximately equal.

Trans \rightarrow *cis* and *cis* \rightarrow *trans* photoisomerizations are predicted for Rh(en) $_2$ (NH $_3$)(H $_2$ O) $^{3+}$ by the model for five-coordinate excited-state rearrangement 1,5 and are observed in this study. The experiment also demonstrates that the photochemistry of a complex may be modified by a change in temperature. These results confirm the model proposed initially by Vanquickenborne and Ceulemans 1 and also show that the stereochemical course of a d 6 substitution reaction can be driven and controlled by light, heat, or the combination of the two.

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Registry No. *trans*-Rh(en) $_2$ (NH $_3$)(H $_2$ O) $^{3+}$, 15337-82-3; *cis*-Rh(en) $_2$ (NH $_3$)(H $_2$ O) $^{3+}$, 70223-45-9.

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Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

Synthesis and Characterization of Cp $_2$ Rh $_2$ (NO) $_2$ and Cp $_3$ Rh $_3$ (NO) $_2$

P. A. Dimas, R. J. Lawson, and J. R. Shapley*

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Relatively few bi- or polynuclear cyclopentadienylmetal nitrosyl compounds have been prepared. 1,2 The known binuclear compounds include Cp $_2$ M $_2$ (NO) $_2$ (Cp = η^5 -C $_5$ H $_5$; M = Fe, 3,4 Co 5,6), which contain bridging nitrosyls, and Cp $_2$ Cr $_2$ (NO) $_4$ 7,8 and Cp $_2$ (η^1 -C $_5$ H $_5$)Mn $_2$ (NO) $_3$ 9,10 which have both bridging and terminal nitrosyls. The two known trinuclear compounds are Cp $_3$ Mn $_3$ (NO) $_4$ 7,11 which has a face-bridging nitrosyl in addition to three edge-bridging ones, and Cp $_3$ Co $_3$ (NO) $_2$ 12 for which two face-bridging nitrosyls have been proposed. We wish to report the rhodium congeners of the known cobalt compounds, namely, Cp $_2$ Rh $_2$ (NO) $_2$ and Cp $_3$ Rh $_3$ (NO) $_2$.

Experimental Section

The preparation of Rh $_2$ (CO) $_4$ Cl $_2$ was adapted from the method of McCleverty and Wilkinson. 13 CpRh(CO) $_2$ was prepared by reaction of cyclopentadienylthallium in 40% excess with Rh $_2$ (CO) $_4$ Cl $_2$ in an ethereal suspension, followed by chromatography on a Florisil column eluted with pentane. Nitric oxide was generated by addition of aqueous acidic FeSO $_4$ to a NaNO $_2$ solution 14 and was dried by passage through silica gel at -78 °C. All solvents were used as received without further purification, except THF, which was distilled from Na/benzophenone prior to use. Infrared spectra were recorded on Perkin-Elmer 467 and 599 spectrophotometers and calibrated with cyclohexane (2138 cm $^{-1}$) and polystyrene. ^1H NMR spectra were recorded on a Varian EM-390 spectrophotometer. Microanalyses were performed by the School of Chemical Sciences analytical laboratory. Mass spectra were obtained on a Varian-MAT CH-5 spectrometer (electron impact) or a Varian 731 spectrometer (field desorption) by the School of Chemical Sciences mass spectroscopy laboratory.

Preparation of Cp $_2$ Rh $_2$ (NO) $_2$ and Cp $_3$ Rh $_3$ (NO) $_2$. In a nitrogen atmosphere [Rh(CO) $_2$ Cl] $_2$ (1.46 g, 3.75 mmol) was dissolved in 75 mL of THF. The solution was stirred while nitric oxide was slowly bubbled through for 2.5 h. The solution turned from orange to dark brown within the first 15 min of nitrosylation. The reaction vessel was flushed with N $_2$, and freshly sublimed CpTi (3.03 g, 11.3 mmol) was added. The reaction mixture was stirred for an additional 14 h and then filtered. The solid collected was set aside for further workup (see below). The filtrate was evaporated under reduced pressure and subjected to purification by column chromatography (silica gel/benzene). The only significant product was contained in a dark brown band. The solution was evaporated to give Cp $_2$ Rh $_2$ (NO) $_2$ as a brown solid (108 mg, 0.27 mmol, 7.3% yield). Slightly higher yields (ca. 9%) were obtained by prolonged nitrosylation (20 h). An analytical sample was crystallized from benzene/pentane. Anal. Calcd for C $_{10}$ H $_{10}$ N $_2$ O $_2$ Rh $_2$: C, 30.33; H, 2.55; N, 7.07. Found: C, 30.60; H, 2.60; N, 6.94. IR (ν_{NO}): 1565 (m), 1516 (s) cm $^{-1}$ (KBr); 1568 (m),

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1517 (s) cm^{-1} (CHCl_3). $^1\text{H NMR}$ (CDCl_3 , 28 °C): τ 4.86 (virtual t, $|^2J_{\text{Rh-H}} + ^3J_{\text{Rh-H}}| = 1.4 \text{ Hz}$).¹⁵ Mass spectrum, m/z (relative intensity): 396 (9) [M^+], 366 (0.2) [$\text{M}^+ - \text{NO}$], 335 (0.1) [$\text{M}^+ - \text{C}_5\text{H}_5$], 334 (0.9) [$\text{M}^+ - 2\text{NO} - \text{H}_2$], 306 (1) [$\text{C}_5\text{H}_4\text{Rh}_2^+$], 242 (3) [C_3Rh_2^+], 233 (100) [$(\text{C}_5\text{H}_5)_2\text{Rh}^+$], 218 (8) [Rh_2C^+], 207 (2) [Rh_2H^+], 168 (11) [$\text{C}_5\text{H}_5\text{Rh}^+$], 142 (2) [$\text{C}_3\text{H}_3\text{Rh}^+$], 103 (2) [Rh^+]. Mp: 135 °C dec.

The filtered solid described above was extracted with dichloromethane (500 mL). The resulting yellow solution was reduced in volume to less than 30 mL and then placed in a freezer at -15 °C. Subsequently, a fine dark precipitate of $\text{Cp}_3\text{Rh}_3(\text{NO})_2$ was collected by filtration (43.5 mg, 0.23 mmol, 3% yield). Alternatively, the yellow solution described above was evaporated under reduced pressure and the resulting solid recrystallized from ethanol to afford the product as a brown powder. A similar reaction involving 24 h of nitrosylation provided the compound in 9% yield. Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2\text{Rh}_3$: C, 31.94; H, 2.68; N, 4.96. Found: C, 31.94; H, 2.66; N, 4.97. IR (ν_{NO}): 1392 cm^{-1} (KBr); 1360 cm^{-1} (CHCl_3). $^1\text{H NMR}$ (CDCl_3 , 28 °C): τ 4.68 (s). Mass spectrum, m/z (relative intensity): 564 (10) [M^+], 534 (8) [$\text{M}^+ - \text{NO}$], 502 (6) [$\text{M}^+ - 2\text{NO} - \text{H}_2$], 500 (6) [$\text{M}^+ - 2\text{NO} - 2\text{H}_2$], 295 (36) [$\text{C}_7\text{H}_7\text{Rh}_2^+$], 260 (6) [$\text{C}_4\text{H}_6\text{Rh}_2^+$], 254 (10) [C_4Rh_2^+], 245 (20) [$\text{C}_3\text{H}_3\text{Rh}_2^+$], 233 (100) [$(\text{C}_5\text{H}_5)\text{Rh}^+$], 181 (80) [$\text{C}_5\text{H}_6\text{Rh}^+$], 168 (41) [$\text{C}_5\text{H}_5\text{Rh}^+$], 105 (32) [H_3Rh^+]. Mp: 250 °C dec.

Reaction of $\text{CpRh}(\text{CO})_2$ with NO. Isolation of $\text{Cp}_2\text{Rh}_2(\text{NO})(\text{NO}_2)$. A solution of $\text{CpRh}(\text{CO})_2$ (136 mg, 0.61 mmol) in 30 mL of dichloromethane was flushed thoroughly with nitrogen. Bubbling a stream of nitric oxide through this solution for several hours did not initiate a reaction. When air (6.0 cm^3) was injected with a syringe through a septum, the solution turned deep red within 15 s, and a red precipitate was formed. The solvent was removed under reduced pressure and the residue was separated by TLC (pentane/dichloromethane). Four major bands were observed: (1) yellow $\text{CpRh}(\text{CO})_2$ (73 mg, 0.33 mmol, 54% recovery); (2) brown $\text{Cp}_2\text{Rh}_2(\text{NO})_2$ (4.3 mg, 0.01 mmol, 7% conversion); (3) a red band; (4) a green band (1.9 mg). The red band was identified as $\text{Cp}_2\text{Rh}_2(\text{NO})(\text{NO}_2)$ (0.5 mg, 0.001 mmol, 1% conversion). IR (ν_{NO}): 1532 cm^{-1} (KBr). $^1\text{H NMR}$ (CDCl_3 , 28 °C): τ 4.70 (5 H, d, $^2J_{\text{Rh-H}} = 0.95 \text{ Hz}$), 4.72 (5 H, d, $^2J_{\text{Rh-H}} = 0.95 \text{ Hz}$). Mass spectrum (field desorption), m/z : 412 [M^+]. The green band contained a mixture of $\text{Cp}_3\text{Rh}_3(\text{NO})_2$ and $\text{C}_3\text{-Cp}_3\text{Rh}_3(\text{CO})_3$,¹⁶ (ratio ca. 1:5), which we were unable to separate by TLC.

Changing the volume of air injected into the reaction vessel appeared to affect the yields of all the products proportionately. However, when pure oxygen was used instead of air or when the solution was exposed to the atmosphere for more than 5 min, extensive decomposition occurred. Likewise, if multiple aliquots of air were injected into a sample of $\text{CpRh}(\text{CO})_2$ with concomitant nitrosylation, complete conversion to products could not be obtained without extensive formation of an insoluble red precipitate.

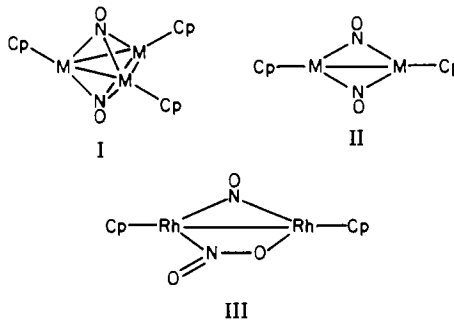
Pyrolysis of $\text{Cp}_2\text{Rh}_2(\text{NO})_2$. $\text{Cp}_2\text{Rh}_2(\text{NO})_2$ (61 mg) was dissolved in xylenes (20 mL) and heated under a nitrogen atmosphere for 24 h. The $^1\text{H NMR}$ spectrum of the resulting solution indicated clean conversion to $\text{Cp}_3\text{Rh}_3(\text{NO})_2$, which was subsequently isolated in quantitative yield.

Results and Discussion

The reaction of $\text{CpCo}(\text{CO})_2$ with nitric oxide to give $\text{Cp}_2\text{Co}_2(\text{NO})_2$ has been reported to occur very rapidly at room temperature.⁵ We were surprised to find that an analogous reaction with $\text{CpRh}(\text{CO})_2$ takes place rapidly only upon addition of small amounts of air. Under these circumstances the reaction does produce $\text{Cp}_2\text{Rh}_2(\text{NO})_2$, but much of the rhodium is lost to an intractable red precipitate. Small amounts of $\text{Cp}_3\text{Rh}_3(\text{CO})_3$, $\text{Cp}_3\text{Rh}_3(\text{NO})_2$, and $\text{Cp}_2\text{Rh}_2(\text{NO})(\text{NO}_2)$ also are formed. An alternative procedure was attempted, involving treatment of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ with nitric oxide (presumably generating $[\text{Rh}(\text{NO})_2\text{C}]_x$ ^{17,18}) and then with cyclopentadienylthallium. This procedure provided reproducible but low yields of $\text{Cp}_2\text{Rh}_2(\text{NO})_2$ and $\text{Cp}_3\text{Rh}_3(\text{NO})_2$.

The electron-impact mass spectra of $\text{Cp}_2\text{Rh}_2(\text{NO})_2$ and $\text{Cp}_3\text{Rh}_3(\text{NO})_2$ show significant molecular ions together with ions derived by loss of NO ligands and fragmentation of the cyclopentadienyl rings. The largest peaks, by far, in the mass spectra of these two rhodium compounds are due to the Cp_2Rh^+ ion. Similar fragmentation patterns have been observed for $[\text{CpM}(\text{NO})]_2$ ($\text{M} = \text{Fe}, ^3\text{Co}^5$), for $\text{Cp}_3\text{Co}_3(\text{NO})_2$,¹² and to a lesser extent for $\text{Cp}_2\text{Rh}_2(\text{CO})_2(\mu\text{-CH}_2)$.¹⁹ Cp_2M_2^+ , CpM^+ , $\text{C}_3\text{H}_3\text{M}^+$, and CpMNO^+ fragments are commonly encountered in the mass spectra of these cyclopentadienyliron, -cobalt, and -rhodium compounds.

The $^1\text{H NMR}$ spectra of $\text{Cp}_2\text{Rh}_2(\text{NO})_2$ and $\text{Cp}_3\text{Rh}_3(\text{NO})_2$ indicate equivalent cyclopentadienyl rings in each molecule. The single, low-energy nitrosyl stretching IR band observed for $\text{Cp}_3\text{Rh}_3(\text{NO})_2$ is consistent with axially symmetric structure I, which is the same as that proposed for $\text{Cp}_3\text{Co}_3(\text{NO})_2$.¹² Two



nitrosyl bands are observed for $\text{Cp}_2\text{Rh}_2(\text{NO})_2$ both in solution and as a solid. Closely similar values were reported for $\text{Cp}_2\text{Co}_2(\text{NO})_2$.⁵ A single-crystal X-ray diffraction study⁶ of $\text{Cp}_2\text{Co}_2(\text{NO})_2$ showed a planar, symmetrical $\text{Co}_2(\mu\text{-NO})_2$ core (II). Since such a centrosymmetric structure should show only one nitrosyl stretching frequency, Byers and Dahl²⁰ have recently suggested that a second crystalline form with a bent $\text{Co}_2(\text{NO})_2$ core exists. An X-ray study of $\text{Cp}_2\text{Rh}_2(\text{NO})_2$ would be a useful comparison, but, unfortunately, we have been unable to grow suitable single crystals.

The $^1\text{H NMR}$ spectrum of $\text{Cp}_2\text{Rh}_2(\text{NO})(\text{NO}_2)$ indicates nonequivalent cyclopentadienyl rings, and the IR spectrum contains a bridging nitrosyl band at 1523 cm^{-1} . These data and the 18-electron rule lead us to propose structure II, containing a bridging nitro ligand.

The mechanism of the reaction of $\text{CpRh}(\text{CO})_2$ with NO in the presence of air is not clear, although the expected role for NO_2 is consistent with the production of $\text{Cp}_2\text{Rh}_2(\text{NO})(\text{NO}_2)$. Attempts to interconvert $\text{Cp}_2\text{Rh}_2(\text{NO})(\text{NO}_2)$ and $\text{Cp}_2\text{Rh}_2(\text{NO})_2$ have been unsuccessful. Nitrosylation of $\text{Cp}_2\text{Rh}_2(\text{NO})_2$ and admission of air resulted in total decomposition. Oxidation of $\text{Cp}_2\text{Rh}_2(\text{NO})_2$ also was attempted with trimethylamine oxide, oxygen, and hydrogen peroxide. The first two reagents afforded no reaction, and the last resulted in decomposition. Removal of oxygen from $\text{Cp}_2\text{Rh}_2(\text{NO})(\text{NO}_2)$ with $\text{P}(\text{C}_6\text{H}_{11})_3$ also failed.

The pyrolysis of $\text{Cp}_2\text{Rh}_2(\text{NO})_2$ to afford $\text{Cp}_3\text{Rh}_3(\text{NO})_2$ in high yield is in accord with the reactivity of $\text{Cp}_2\text{Co}_2(\text{NO})_2$.¹⁰ In the case of the cobalt compounds conversion was achieved by heating $\text{Cp}_2\text{Co}_2(\text{NO})_2$ in THF at 50 °C for 7 days. $\text{Cp}_2\text{Rh}_2(\text{NO})_2$ is stable under these conditions, and refluxing xylene is needed for clean conversion. Both metal-metal and metal-nitrosyl bonds should be stronger for rhodium relative to cobalt, consistent with the harsher conditions required.

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Registry No. $\text{Cp}_2\text{Rh}_2(\text{NO})_2$, 67426-08-8; $\text{Cp}_3\text{Rh}_3(\text{NO})_2$, 75495-01-1; $\text{Cp}_2\text{Rh}_2(\text{NO})(\text{NO}_2)$, 75365-54-7; $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, 14523-22-9; $\text{CpRh}(\text{CO})_2$, 12192-97-1; $\text{Cp}_3\text{Rh}_3(\text{CO})_3$, 12148-54-8.

Contribution from the Department of Chemistry, Eastern Illinois University, Charleston, Illinois 61920, and SRI International, Menlo Park, California 94025

Mixed-Metal Carbonyl Complexes of Cr, Mo, and W Containing Bridging $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$

R. L. Keiter,*^{1a} S. L. Kaiser,^{1a} N. P. Hansen,^{1a} J. W. Brodack,^{1a} and L. W. Cary^{1b}

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Numerous carbonyl complexes of Cr, Mo, and W are known which contain $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, L-L, as a chelating ligand. Less common are those in which L-L serves as a bridging ligand, particularly between atoms of two different metals.^{2,3} Our recent successes in the syntheses of complexes containing L-L as a monodentate ligand (e.g., $(\text{OC})_5\text{WL-L}$ and $(\text{OC})_4\text{W(L-L)}_2$) by base and free-radical catalyzed addition reactions prompted us to explore these approaches as avenues to mixed-metal L-L-bridged complexes.⁴

Experimental Section

Physical Measurements. ³¹P NMR and infrared spectra were obtained from chloroform solutions as described elsewhere.⁴ Chemical shifts downfield from H_3PO_4 are measured as positive. Microanalyses were obtained from Galbraith Laboratories, Knoxville, Tenn.

Materials. Diphenylvinylphosphine, diphenylphosphine, and the metal carbonyls were purchased from Pressure Chemical Co. and used without further purification. All reactions were carried out under a nitrogen atmosphere.

$(\text{OC})_5\text{WPPh}_2\text{CH}=\text{CH}_2$ and $(\text{OC})_5\text{WPPh}_2\text{H}$ were prepared as described previously.⁴ $(\text{OC})_5\text{CrPPh}_2\text{CH}=\text{CH}_2$ (38.2%) and $(\text{OC})_5\text{WPPh}_2\text{H}$ (95%)^{5,6} were prepared by the indirect method of Strohmeier.⁴ $(\text{OC})_5\text{MoPPh}_2\text{CH}=\text{CH}_2$ (97%) and $(\text{OC})_5\text{MoPPh}_2\text{H}$ (73%)^{5,6} were prepared from the thermal reaction of phosphine and $\text{Mo}(\text{CO})_6$ in 1,2-dimethoxyethane.⁷

$(\text{OC})_5\text{CrPPh}_2\text{CH}=\text{CH}_2$: mp 58–59 °C; IR 1985 (B_1), 2067 ($\text{A}_1^{(2)}$), 1943 ($\text{E} + \text{A}_1^{(1)}$); ³¹P NMR δ 47.4.

Anal. Calcd for $\text{C}_{19}\text{H}_{13}\text{O}_5\text{PCr}$: C, 56.45; H, 3.24; P, 7.66. Found: C, 56.33; H, 3.31; P, 7.72.

$(\text{OC})_5\text{MoPPh}_2\text{CH}=\text{CH}_2$: mp 57–58 °C; IR 1991 (B_1), 2074 ($\text{A}_1^{(2)}$), 1949 ($\text{E} + \text{A}_1^{(1)}$); ³¹P NMR δ 29.3.

Anal. Calcd for $\text{C}_{19}\text{H}_{13}\text{O}_5\text{PMo}$: C, 50.91; H, 2.92; P, 6.91. Found: C, 50.87; H, 3.07; P, 7.06.

$(\text{OC})_5\text{CrPPh}_2\text{H}$: mp 60–61 °C (lit.⁴ mp 55–65 °C); ³¹P NMR δ 32.9.

$(\text{OC})_5\text{MoPPh}_2\text{H}$: mp 74–75.5 °C (lit.⁴ mp 73–75 °C); ³¹P NMR δ 6.7.

Base-Catalyzed Reactions of $(\text{OC})_5\text{MPPh}_2\text{H}$ with $(\text{OC})_5\text{M'PPh}_2\text{CH}=\text{CH}_2$ ($\text{M} = \text{Cr, Mo, W}$). The same experimental procedure was used to prepare each of the six dimetallic complexes. The procedure will be illustrated for the molybdenum-tungsten complex. To a solution of $(\text{OC})_5\text{WPPh}_2\text{H}$ (4.22 mmol) in dry THF (80 ml) were added $(\text{OC})_5\text{MoPPh}_2\text{CH}=\text{CH}_2$ (4.22 mmol) and potassium *tert*-butoxide (0.08 g). The solution was heated under reflux for 1 h, cooled, and stripped of solvent; the resulting residue was crystallized from a $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ mixture to give $(\text{OC})_5\text{MoPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{W}(\text{CO})_5$ in 88% yield.

$(\text{OC})_5\text{MoPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{W}(\text{CO})_5$: mp 195–198 °C dec; IR 1986 (B_1), 2074 ($\text{A}_1^{(2)}$), 1948 ($\text{E} + \text{A}_1^{(1)}$); ³¹P NMR δ_{MoP} 31.6 (² J_{PP} = 35.5 Hz), δ_{WP} 12.9 (² J_{PP} = 35.5, J_{WP} = 241.6 Hz).

Anal. Calcd for $\text{C}_{36}\text{H}_{24}\text{O}_{10}\text{P}_2\text{MoW}$: C, 45.12; H, 2.52; P, 6.46. Found: C, 44.99; H, 2.62; P, 6.76.

$(\text{OC})_5\text{MoPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{Cr}(\text{CO})_5$: mp 190–191 °C dec; IR 1987 (B_1), 2075, 2065 ($\text{A}_1^{(2)}$), 1950 ($\text{E} + \text{A}_1^{(1)}$); ³¹P NMR δ_{MoP} 31.8 (² J_{PP} = 32.4 Hz), δ_{CrP} 51.1 (² J_{PP} = 32.4 Hz).

$(\text{OC})_5\text{MoPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{Mo}(\text{CO})_5$: mp 198–200 °C dec (lit.³ 192–194 °C); IR 1992 (B_1), 2075 ($\text{A}_1^{(2)}$), 1954 ($\text{E} + \text{A}_1^{(1)}$); ³¹P NMR δ_{P} 31.7.

$(\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{Cr}(\text{CO})_5$: mp 205–208 °C dec; IR 1986 (B_1), 2067, 2077 ($\text{A}_1^{(2)}$), 1944 ($\text{E} + \text{A}_1^{(1)}$); ³¹P NMR δ_{WP} 13.0 (² J_{PP} = 32.2, J_{WP} = 241.5 Hz), δ_{CrP} 50.9 (² J_{PP} = 32.2 Hz).

Anal. Calcd for $\text{C}_{36}\text{H}_{24}\text{O}_{10}\text{P}_2\text{CrW}$: C, 47.29; H, 2.65; P, 6.78. Found: C, 46.93; H, 2.78; P, 6.85.

$(\text{OC})_5\text{WPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{W}(\text{CO})_5$: mp 217–218 °C dec;² IR 1984 (B_1), 2073 ($\text{A}_1^{(2)}$), 1943 ($\text{E} + \text{A}_1^{(1)}$); ³¹P NMR δ_{WP} 12.7 (m, ABX pattern, ² J_{PP} = 36.6 Hz, J_{WP} = 241.6 Hz).

$(\text{OC})_5\text{CrPPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2\text{Cr}(\text{CO})_5$: mp 192–193 °C dec (lit.³ 200–201 °C); IR 1986 (B_1), 2065 ($\text{A}_1^{(2)}$), 1945 ($\text{E} + \text{A}_1^{(1)}$); ³¹P NMR δ_{P} 51.1.

Results and Discussion

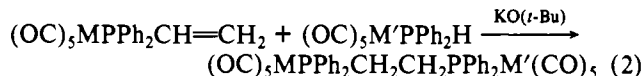
There are six possible $(\text{OC})_5\text{ML-LM}'(\text{CO})_5$ complexes of Cr, Mo, and W, three homometallic ($\text{M} = \text{M}'$) and three heterometallic ($\text{M} \neq \text{M}'$). Of these only the homometallic complexes have been previously reported.^{2,3}

Substitution reactions provide a straightforward method of synthesis for the homometallic species. For example, L-L displaces Y from $(\text{OC})_5\text{MY}$ under mild conditions (eq 1)^{2,8}

$$2(\text{OC})_5\text{MY} + \text{L-L} \rightarrow (\text{OC})_5\text{ML-LM}'(\text{CO})_5 + 2\text{Y} \quad (1)$$


The mixed-metal complexes, however, cannot be obtained directly in good yield from such reactions because of competitive formation of the more symmetrical ($\text{M} = \text{M}'$) products. The $\text{M} \neq \text{M}'$ complexes could be prepared by isolating $(\text{OC})_5\text{ML-L}$, a complex containing L-L as a monodentate ligand, and allowing it to react with $(\text{OC})_5\text{M'Y}$.

We have now shown that the isolation of the intermediate "dangling" ligand complex may be avoided entirely by using starting materials which all contain coordinated phosphines (eq 2). The reactants are easily synthesized, and the six



dimetallic combinations of Cr, Mo, and W are obtained in good yield when the reaction is carried out in the presence of catalytic amounts of potassium *tert*-butoxide.⁹ Either combination of reactants gives the desired product. For example, the synthesis of $(\text{OC})_5\text{CrL-LW}(\text{CO})_5$ proceeds equally well

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(9) The free-radical catalyst AIBN does not appear to be useful in these reactions. Reactions with this catalyst led to the formation of blue decomposition products, and only starting materials were isolated.

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