

Synthesis and Electrochemical Analysis of Several Triruthenium Alkyldiyne Carbonyl Clusters

JAMES T. MCFADDEN

Communicated by Dr. William Feighery

ABSTRACT: Metal-containing polymers and related materials have been the focus of much attention recently due to their potentially useful electronic, optical, and magnetic properties. We report here the synthesis and electrochemical analysis of several transition metal cluster compounds having the general formula $H_3Ru_3(\mu_3-CY)(CO)_{9-n}L_n$ ($n = 0, 3$; $L = PPh_3$) (1). Of particular interest are cluster derivatives in which the apical substituent, Y, is an organic π -system or a metal-containing fragment as these clusters are possible precursors to metal cluster-containing polymer systems. The synthesis of $H_3Ru_3(\mu_3-C-allyl)(CO)_9$ (2), $H_3Ru_3(\mu_3-C-allyl)(CO)_6(PPh_3)_3$, $H_3Ru_3(\mu_3-C-C_6H_4CH_3)(CO)_9$, $H_3Ru_3(\mu_3-C-C_6H_4CH_3)(CO)_6(PPh_3)_3$, $H_3Ru_3(\mu_3-C-C_6H_4CH_3-Mo(CO)_3)(CO)_9$ and $H_3Ru_3(\mu_3-C-C_6H_4CH_3-Mo(CO)_3)(CO)_6(PPh_3)_3$ is reported along with infrared spectral characterization and cyclic voltammetric analysis. In addition, we report on the attempted synthesis of the clusters $H_3Ru_3(\mu_3-C-indenyl)(CO)_9$, $H_3Ru_3(\mu_3-C-stilbenyl)(CO)_9$ and $H_3Ru_3(\mu_3-C-[Ru^{II}(bpy)_3])(CO)_9$.

Our increasingly technological world depends on the development of materials with improved properties, catalysts that are faster and more specific, polymers that conduct electricity, materials with unique optical and magnetic properties. In 1979, the synthesis of $H_3Ru_3(\mu_3-COMe)(CO)_9$ and other isostructural clusters were reported.¹ These clusters have the general formula $H_3M_3(\mu_3-CY)(CO)_9$, where $M = Fe, Ru$ or Os and $Y = alkyl, aryl$ or other substituent (Figure 1).² At present, our research efforts are concentrated on the ruthenium clusters of this series. Specifically, on clusters with the formula $H_3Ru_3(\mu_3-CY)(CO)_9$, where $Y = allyl, indene, stilbene, Ru^{II}(bpy)_3$, and other metal containing substituents. It is hoped that these clusters might be precursors to interesting polymeric or electronic materials. To determine if this is the case, we have also studied the electrochemical behavior of the allyl substituted clusters and tolyl substituted clusters which contain metal fragments.

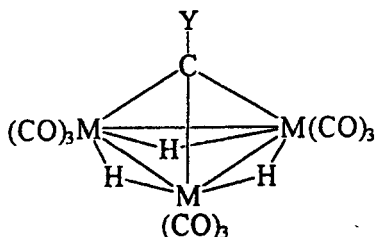


Figure 1

More specifically, we have concentrated on the behavior of the clusters $H_3Ru_3(\mu_3-C-C_6H_4CH_3-[Mo(CO)_3])(CO)_9$

JAMES MCFADDEN will receive a B.S. in Chemistry with minors in Mathematics and Biology in May 1999. McFadden has been doing research with Dr. William Feighery for a year and a half. This paper was written as a final report to the Student/Mentor Academic Research Team (SMART) program after receiving a summer research grant.

and $H_3Ru_3(\mu_3-C-C_6H_4CH_3-[Mo(CO)_3])(CO)_6(PPh_3)_3$. Due to the presence of a metallic ligand on the apical tolyl substituent we felt that these clusters would demonstrate interesting electrochemical characteristics.

We now report the synthesis of various tolyl and allyl derivatized clusters as well as the attempted synthesis of clusters with indene, stilbene and $Ru^{II}(bpy)_3$ ligands. With each reported synthesis is included the infrared spectrum analysis of the resulting product. For several of these reported clusters, the products were tested via cyclic voltammetry to produce an electrochemical analysis.

EXPERIMENTAL SECTION

General

$H_3Ru_3(\mu_3-COMe)(CO)_9$ and $H_3Ru_3(\mu_3-CBr)(CO)_9$ were prepared by literature methods.^{1,2} Chemicals were used as received without further purification. Solvents were used as received except where noted; THF was distilled over Na/benzophenone, methylene chloride was distilled over P_2O_5 , and cyclohexane from $CaCl_2$. Infrared spectra were recorded in cyclohexane solution on a Perkin-Elmer series 1600 FTIR.

$H_3Ru_3(\mu_3-C-allyl)(CO)_9$

Into a 50-mL, three-necked flask equipped with reflux condenser, nitrogen gas inlet and stirbar was placed $H_3Ru_3(\mu_3-CBr)(CO)_9$ (100.9 mg), nitrogen saturated methylene chloride (7 mL) and allyltrimethylsilane (1 mL).⁴ To this was added silver tetrafluoroborate (150 mg) in methylene chloride (3 mL) via cannula transfer. The resulting solution was allowed to stir at reflux temperature for 2 hours. The solution was then filtered over silica gel and dried via rotary evaporator. The dried orange-brown product was purified on silica gel eluting with cyclohexane and methylene chloride (3:1). Extraction of the top band by methylene chloride yielded $H_3Ru_3(\mu_3-C-allyl)(CO)_9$ (54.4 mg, 57.3% yield).

$H_3Ru_3(\mu_3-C-allyl)(CO)_6(PPh_3)_3$

Into a 50-mL, three-necked flask equipped with reflux condenser, nitrogen gas inlet and stirbar was placed $H_3Ru_3(\mu_3-$

C-allyl)(CO)₉ (27.2 mg), nitrogen saturated methylene chloride (20 mL) and triphenylphosphine (79.1 mg). This was allowed to stir overnight under a blanket of nitrogen. The product was then dried and the reaction was repeated with additional methylene chloride (20 mL) and triphenylphosphine (79.1 mg). The resulting solution was again allowed to stir overnight at room temperature, and then was dried a second time. To the flask was added another 20 mL of methylene chloride and 79.1 mg triphenylphosphine. This solution was allowed to stir for 5 minutes at room temperature and then for 1 hour at reflux temperature under a blanket of nitrogen. The product was dried and purified by preparative thin-layer chromatography on silica gel eluting with cyclohexane and methylene chloride (3:1). Extraction of the third band by methylene chloride yielded the product H₃Ru₃(μ₃-C-allyl)(CO)₆(PPh₃)₃.

H₃Ru₃(μ₃-C-C₆H₄CH₃)(CO)₉

Into a 100-mL, 3-necked flask equipped with stirbar, nitrogen gas inlet and pressure-equalizing dropping funnel was placed AlCl₃ (300.0 mg) and methylene chloride (25 mL). Then a solution of H₃Ru₃(μ₃-COMe)(CO)₉ (116.5 mg) in toluene (15 mL) was added dropwise.³ After stirring for 55 minutes under a blanket of nitrogen, the resulting solution was dried under low-pressure vacuum to produce the yellow solid H₃Ru₃(μ₃-C-C₆H₄CH₃)(CO)₉ (48.6 mg, 38.3% yield).

H₃Ru₃(μ₃-C-C₆H₄CH₃)(CO)₆(PPh₃)₃

Into a 50-mL 3-necked flask equipped with stirbar and reflux condenser was placed triphenylphosphine (40.0 mg) in dry methylene chloride (17.5 mL). 24.3 mg H₃Ru₃(μ₃-C-C₆H₄CH₃)(CO)₉ in 2.5 mL dry methylene chloride was added, and nitrogen gas was bubbled through for 15 minutes prior to stirring overnight at reflux temperature. The resulting reddish-brown solution was dried under rotary evaporation and purified by preparative thin-layer chromatography on silica gel, eluting with cyclohexane and methylene chloride (3:1). Extraction of the sixth band by methylene chloride yielded the product H₃Ru₃(μ₃-C-C₆H₄CH₃)(CO)₆(PPh₃)₃ (54.2 mg, moist).

H₃Ru₃(μ₃-C-C₆H₄CH₃-Mo(CO)₃)(CO)₉

To an evacuated schlenk flask equipped with nitrogen inlet, stirbar and pressure-equalizing dropping funnel was added Mo(CO)₃(CH₃CN)₃ (22.3 mg) in dry tetrahydrofuran (10 mL). This system was then submerged into a -60°C cryobath, and to the flask was added H₃Ru₃(μ₃-C-C₆H₄CH₃)(CO)₉ (24.3 mg) in tetrahydrofuran (10 mL) from the dropping funnel. The resulting solution was stirred at -60°C for 30 minutes and then at room temperature for 30 minutes. The product was dried under low-pressure vacuum leaving behind reddish-brown, solid H₃Ru₃(μ₃-C-C₆H₄CH₃-Mo(CO)₃)(CO)₉.

H₃Ru₃(μ₃-C-C₆H₄CH₃-Mo(CO)₃)(CO)₆(PPh₃)₃

22.3 mg Mo(CO)₃(CH₃CN)₃ in 10 mL dry tetrahydrofuran was added to an evacuated schlenk flask equipped with nitrogen inlet, stirbar and pressure-equalizing dropping funnel.

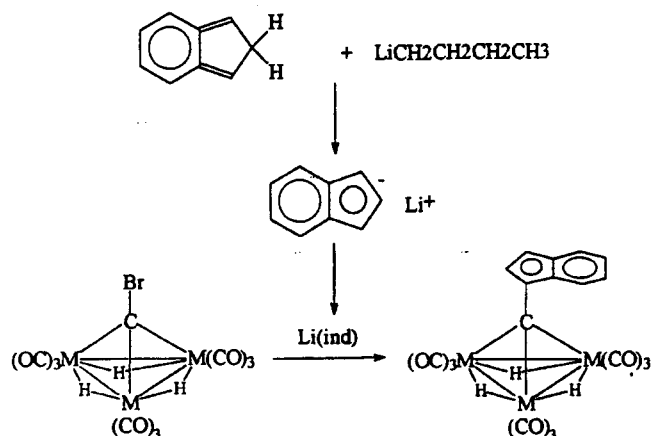
This system was then submerged into a -60°C cryobath, and H₃Ru₃(μ₃-C-C₆H₄CH₃)(CO)₆(PPh₃)₃ (54.2 mg) in tetrahydrofuran (10 mL) was added from the dropping funnel. The resulting solution was stirred at -60°C for 30 minutes and then at room temperature for 30 minutes. The product was dried under low-pressure vacuum leaving behind solid, orange H₃Ru₃(μ₃-C-C₆H₄CH₃-Mo(CO)₃)(CO)₆(PPh₃)₃.

H₃Ru₃(μ₃-C-indyl)(CO)₉

1 mL indene, 104 mg aluminum trichloride, and 10 mL methylene chloride were placed into a 50-mL schlenk flask equipped with stirbar, nitrogen gas inlet, and pressure-equalizing dropping funnel. (AlCl₃ reacts upon addition to a solution of indene in CH₂Cl₂ to form a red product releasing gas and heat.) A solution of H₃Ru₃(μ₃-COMe)(CO)₉ (20.6 mg) in methylene chloride (10 mL) was added dropwise, and the resulting solution was allowed to stir for 15 minutes under a blanket of nitrogen. The solution was then poured into 50 mL of HCl (10%) and the organic layer was separated and the aqueous portion was rinsed with CH₂Cl₂. The organic layers were combined, dried over magnesium sulfate, and filtered. The resulting solution was dried by means of rotary evaporation, leaving behind a yellow solid.

Lithium indenide

Into a nitrogen blanketed, 100-mL schlenk flask was placed dry tetrahydrofuran (40 mL) which was cooled to -60°C in a cryobath. 2 mL indene and 12 mL 1.6 M butyl lithium were added to the cooled flask, and the resulting yellow solution was allowed to react for 30 minutes. The solution was then heated to room temperature to allow the product butane to escape leaving behind lithium indenide. (Scheme 1).



Scheme 1

H₃Ru₃(μ₃-C-indyl)(CO)₉

To a 50-mL schlenk flask equipped with stirbar and nitrogen gas inlet was added H₃Ru₃(μ₃-CBr)(CO)₉ (91 mg) in tetrahydrofuran (40 mL).⁴ This system was cooled in a -60°C cryobath for 3 minutes prior to the addition of lithium indenide (5.5 mL). The solution was allowed to react for 15 minutes at -60°C and for 30 minutes at room temperature.

Triruthenium Clusters

Table 1. Infrared Stretching Frequency Data

compound	v-CO (in cyclohexane), 2150-1800 cm ⁻¹ a
H ₃ Ru ₃ (μ ₃ -C-allyl)(CO) ₉ , Figure 1	2078 vs, 2031 vs, 2014 vs, 1992 vw, 1977 vw
H ₃ Ru ₃ (μ ₃ -C-allyl)(CO) ₆ (PPh ₃) ₃ , Figure 2	2036 m, 2014 m, 1966 m
H ₃ Ru ₃ (μ ₃ -C-C ₆ H ₄ CH ₃)(CO) ₉	2106 vw, 2079 vs, 2066 m, 2034 vs, 2018 s
H ₃ Ru ₃ (μ ₃ -C-C ₆ H ₄ CH ₃)(CO) ₆ (PPh ₃) ₃	2038 s, 2017 s, 1969 s
H ₃ Ru ₃ (μ ₃ -C-C ₆ H ₄ CH ₃ -Mo(CO) ₃)(CO) ₉	2079 vs, 2034 vs, 2018 m, 1988 vs, 1969 vw, 1951 w, 1926 vw, 1907 vw
H ₃ Ru ₃ (μ ₃ -C-C ₆ H ₄ CH ₃ -Mo(CO) ₃)(CO) ₆ (PPh ₃) ₃	2038 m, 2018 m, 1988 vs, 1970 m, 1951 s, 1926w, 1908 vw
Mo(CO) ₃ (CH ₃ CN) ₃	2023 vw, 1951 vw
H ₃ Ru ₃ (μ ₃ -C-indyl)(CO) ₉ , Friedel-Crafts Reaction	2078 m, 2034 w, 2017 vw
H ₃ Ru ₃ (μ ₃ -C-indyl)(CO) ₉ , halide substitution	2086 vs, 2066 w, 2040 vs, 2027 s, 2000 vw
H ₃ Ru ₃ (μ ₃ -C-stilbyl)(CO) ₉	2079 m, 2056 vw, 2034 m, 2019 w
H ₃ Ru ₃ (μ ₃ -C-[Ru ^{II} (bpy) ₃])(CO) ₉	2079 s, 2070 m, 2055 w, 2031 vs, 2018 m, 2002 w

a. Stretching frequencies in **bold** type are the major stretches for that compound.

Methanol (2 mL) was then added and the resulting solution was dried using rotary evaporation.

H₃Ru₃(μ₃-C-stilbyl)(CO)₉

90.0 mg AlCl₃ in 10 mL methylene chloride were added to a 50-mL, 3-necked flask equipped with stirbar, nitrogen gas inlet, and pressure-equalizing dropping funnel. A solution of stilbene (50.6 mg), H₃Ru₃(μ₃-COMe)(CO)₉ (20.0 mg) and methylene chloride (10 mL) was added dropwise,³ and the resulting solution turned deep purple and was allowed to stir for 15 minutes under a blanket of nitrogen. After 15 minutes the solution was poured into 50 mL of HCl (10%). The organic layer was separated and the aqueous portion was rinsed twice with 10 mL of CH₂Cl₂. The organic layers were combined, dried over magnesium sulfate, and filtered. The resulting solution was dried by rotary evaporation.

H₃Ru₃(μ₃-C-[Ru^{II}(bpy)₃])(CO)₉

180.0 mg AlCl₃ in 10 mL methylene chloride were added to a 50-mL, 3-necked flask equipped with stirbar, nitrogen gas inlet, and pressure-equalizing dropping funnel. A solution of

Ru^{II}(bpy)₃ (21.8 mg), H₃Ru₃(μ₃-COMe)(CO)₉ (21.7 mg) and methylene chloride (10 mL) was added dropwise,³ and the resulting solution was allowed to stir for 30 minutes under a blanket of nitrogen. After 30 minutes, 50 mL of HCl (10%) was added and the organic layer was separated and the aqueous portion was rinsed twice with 20 mL of CH₂Cl₂. The organic layers were combined, dried over magnesium sulfate, and filtered. The resulting solution was dried by means of rotary evaporation.

ELECTROCHEMISTRY

All electrochemical measurements were performed using a BAS 100 B/W electrochemical workstation. Cyclic voltammetric experiments were made using dry methylene chloride as solvent, and 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte, and at a scan rate of 100 mV/sec. The working electrode was a 3 mm Pt disk while the auxiliary electrode was a Pt wire. A silver wire was used as a pseudo-reference electrode, and all measurements are reported relative to the ferrocene/ferrocenium couple (E⁰ = 0.00 V) which was added after each run. The concentration of analyte was approximately 1 x 10⁻³ M and compensation was made for solution resistance.

Table 2 Cyclic Voltammetry Data

compound	E ¹ _{1/2} , (E ¹ _{pa})	E ² _{pa}
H ₃ Ru ₃ (μ ₃ -C-allyl)(CO) ₉	(849 mV)	
H ₃ Ru ₃ (μ ₃ -C-allyl)(CO) ₆ (PPh ₃) ₃	59 mV, (506.5 mV)	
H ₃ Ru ₃ (μ ₃ -C-C ₆ H ₄ CH ₃)(CO) ₉	(849 mV)	
H ₃ Ru ₃ (μ ₃ -C-C ₆ H ₄ CH ₃)(CO) ₆ (PPh ₃) ₃	59 mV, (506.5 mV)	
H ₃ Ru ₃ (μ ₃ -C-C ₆ H ₄ CH ₃ -Mo(CO) ₃)(CO) ₉ , first analysis	(-226, 127, 424, 711 mV)	-33 mV
H ₃ Ru ₃ (μ ₃ -C-C ₆ H ₄ CH ₃ -Mo(CO) ₃)(CO) ₉ , second analysis (after 15 min)	(-226, 168, 665, 1028 mV)	-33 mV
H ₃ Ru ₃ (μ ₃ -C-C ₆ H ₄ CH ₃ -Mo(CO) ₃)(CO) ₆ (PPh ₃) ₃	(1109.5 mV)	

1. This is data for the first couple or first irreversible oxidation wave.
2. This is data for the second oxidation.

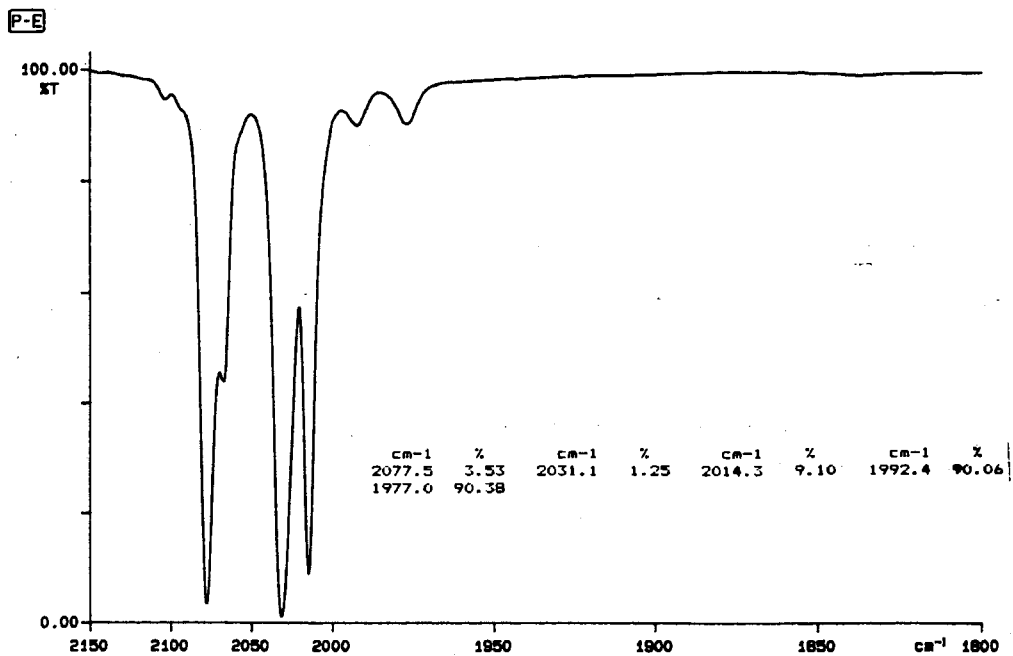


Figure 2. ν-CO IR spectrum of H₃Ru₃(μ₃-C-allyl)(CO)₉.

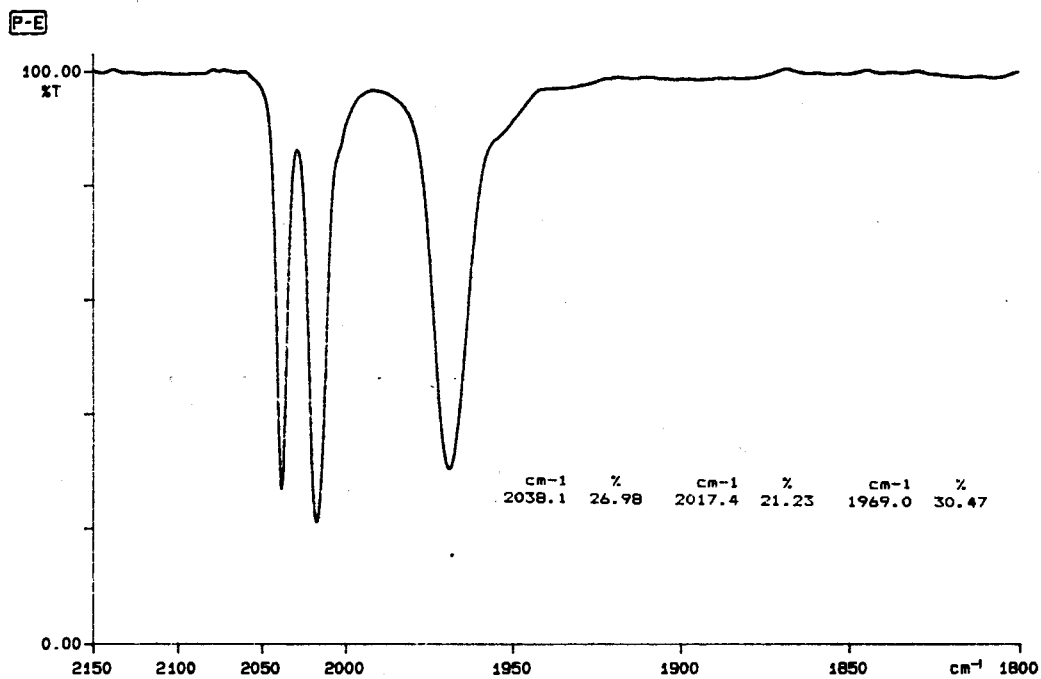


Figure 3. ν-CO IR spectrum of H₃Ru₃(μ₃-C-tolyl)(CO)₆(PPh₃)₃.

Triruthenium Clusters

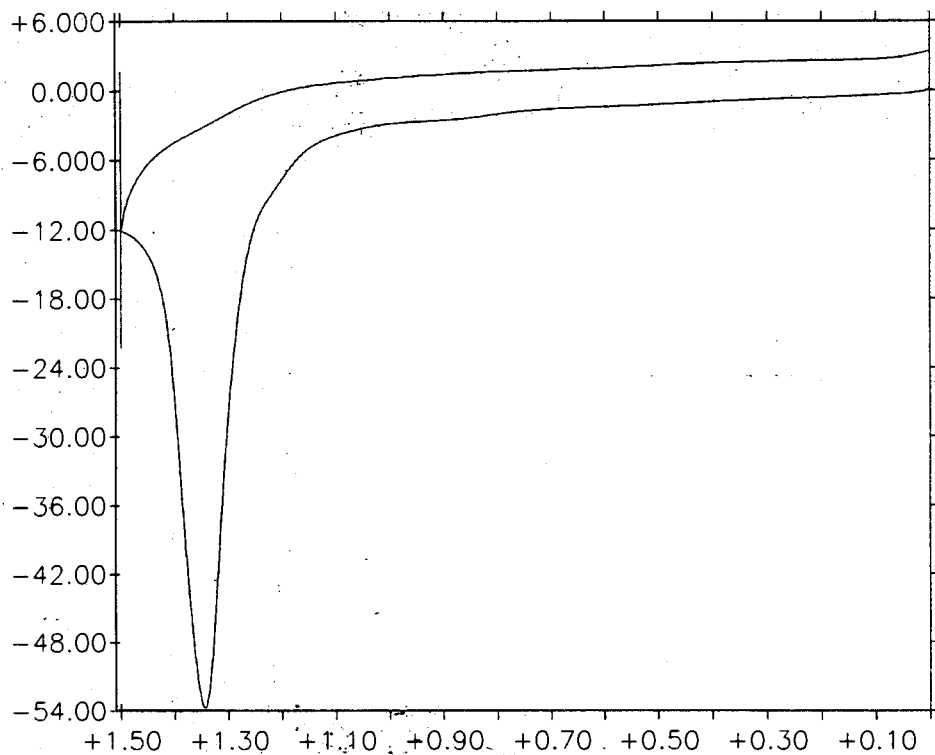


Figure 4. Cyclic Voltammogram of $\text{H}_3\text{Ru}_3(\mu_3\text{-C-allyl})(\text{CO})_9$.

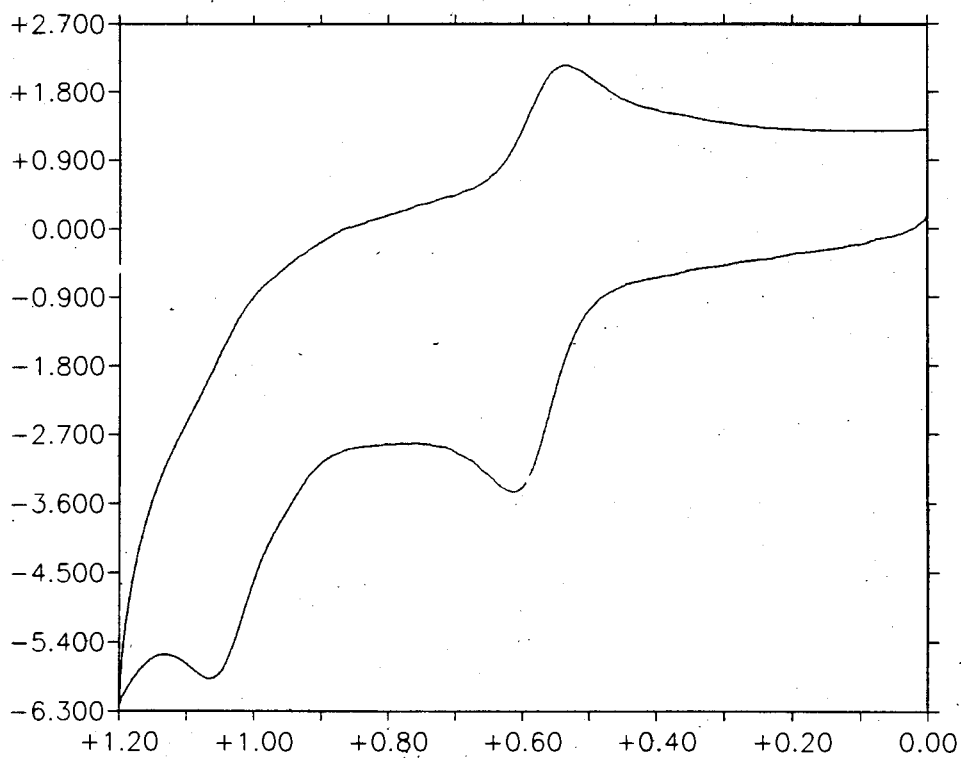


Figure 5. Cyclic Voltammogram of $\text{H}_3\text{Ru}_3(\mu_3\text{-C-tolyl})(\text{CO})_6(\text{PPh}_3)_3$.

RESULTS

In general, the infrared spectra of clusters having the general formula $H_3Ru_3(\mu_3-CY)(CO)_9$ and $H_3Ru_3(\mu_3-CY)(CO)_6(PPh_3)_3$ are very characteristic, containing three strong bands in the CO stretching region. The data for the clusters reported here is given in Table 1. The infrared spectra for the clusters $H_3Ru_3(\mu_3-C-allyl)(CO)_9$ and $H_3Ru_3(\mu_3-C-tolyl)(CO)_6(PPh_3)_3$ are shown for reference in figures 2 and 3, respectively.

In addition to their infrared spectra analysis, each of the allyl and tolyl clusters were analyzed electrochemically by cyclic voltammetry. Electrochemical data is summarized in Table 2. (N.B. The values are referenced to the ferrocene/ferrocene couple at $E_{1/2} = 0$ V.) The voltammograms for the clusters $H_3Ru_3(\mu_3-C-allyl)(CO)_9$ and $H_3Ru_3(\mu_3-C-tolyl)(CO)_6(PPh_3)_3$ are shown for reference in figures 4 and 5, respectively.

DISCUSSION

The clusters $H_3Ru_3(\mu_3-C-allyl)(CO)_9$, $H_3Ru_3(\mu_3-C-allyl)(CO)_6(PPh_3)_3$, $H_3Ru_3(\mu_3-C-C_6H_4CH_3)(CO)_9$, $H_3Ru_3(\mu_3-C-C_6H_4CH_3)(CO)_6(PPh_3)_3$, $H_3Ru_3(\mu_3-C-C_6H_4CH_3-Mo(CO)_3)(CO)_9$ and $H_3Ru_3(\mu_3-C-C_6H_4CH_3-Mo(CO)_3)(CO)_6(PPh_3)_3$ were synthesized and then analyzed by both infrared spectra and cyclic voltammetry. A reversible couple for the clusters $H_3Ru_3(\mu_3-C-allyl)(CO)_6(PPh_3)_3$ and

$H_3Ru_3(\mu_3-C-C_6H_4CH_3)(CO)_6(PPh_3)_3$ are expected due to the electron donating abilities of the phosphine groups. The attachment of the molybdenum half sandwiches created an unusual and unexpected result in the cyclic voltammetry (c.v.). Since the c.v. for the oxidation of the cluster $H_3Ru_3(\mu_3-C-C_6H_4CH_3-Mo(CO)_3)(CO)_9$ altered over time it is likely that certain components of the cluster decomposed upon oxidation.

In the analysis of the clusters $H_3Ru_3(\mu_3-C-indyl)(CO)_9$, $H_3Ru_3(\mu_3-C-stilbyl)(CO)_9$ and $H_3Ru_3(\mu_3-C-[Ru^{II}(bpy)_3])(CO)_9$ the IR spectra suggest that the clusters were in fact synthesized. Without H-NMR analysis, however, it is difficult to be certain if the compounds were synthesized. All of these newly formed clusters must be further analyzed by various methods of characterizations, but there is a promising assurance that the clusters were, in fact, formed in most cases. The next step in the research is to find other similar clusters and compare them to the ones we have already synthesized. Furthermore, we are interested in improving several of the syntheses themselves to optimize time, effort, and yield.

REFERENCES:

- (1) J. B. Keister, M. W. Payne and M. J. Muscatella, *Organometallics* 1983, 2, 219.
- (2) J. B. Keister and T. L. Horling, *Inorg. Chem.* 1980, 19, 2304.
- (3) J. B. Keister, *Polyhedron* 1988, 7, 847.