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Synthesis and reactivity of heterobinuclear complexes of ruthenium-platinum and iron-platinum

Willis, Richard Ronald, Ph.D.
The Ohio State University, 1992

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SYNTHESIS AND REACTIVITY OF 
HETEROBINUCLEAR COMPLEXES OF RUTHENIUM-PLATINUM
AND IRON-PLATINUM

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree of Doctor of Philosophy in the Graduate School of
The Ohio State University

By

Richard Ronald Willis

The Ohio State University
1992

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Approved by
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Dedicated to my wife and family
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<td>Me</td>
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<tr>
<td>Cy</td>
<td>cyclohexyl</td>
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NUMBERING OF COMPOUNDS

1  Cp(NO)₂CrCH₂C=Ph
2  (CO)₃Fe(μ-η²,η²-PhC=C=CH₂)Fe(CO)NO
3  (PhC=CH₂)₂
4  (CO)₆Fe₂[PhC=C(C₂H₄)C=Ph]
5  Cp(CO)₂FeCH₂C=Ph
6  (CO)₃Fe[μ-η⁴-C(O)C(Ph)=C(Fe(CO)₂Cp)=CH₂]
7  Cp(PPh₃)₂RuCH₂C=Ph
8  Cp(PPh₃)₂Ru[C=C(Ph)C(O)N(SO₂C₆H₄Me)C₄H₆]
9  Cp(CO)(PPh₃)RuCH₂C=Ph
10 Cp(CO)₂W-(μ-η²,η¹-CH₂=C(Ph)=C=CH₂)Pt(PPh₃)₂
11 TSI cycloadduct of Cp(CO)₂RuCH=CH₂
12 MeC₆H₄S(O)₂OCH₂C=Ph
13 Cp(CO)₂RuCH₂C=Ph
14a Cp(CO)Ru-(μ-η²,η¹-CH₂=C(Ph)=C=CH₂)Pt(PPh₃)₂
14b Cp(CO)Fe-(μ-η²,η¹-CH₂=C(Ph)=C=CH₂)Pt(PPh₃)₂
15a Cp(CO)Ru-(μ-η²,η¹-CH₂=C(H)=C=CH₂)Pt(PPh₃)₂
15b Cp(CO)Fe-(μ-η²,η¹-CH₂=C(H)=C=CH₂)Pt(PPh₃)₂
16a Cp(CO)Ru-(μ-η²,η¹-CH₂=C(Ph)=C=CH₂)Pt(PPh₃)(CO)
16b Cp(CO)Fe-(μ-η²,η¹-CH₂=C(Ph)=C=CH₂)Pt(PPh₃)(CO)
17 Cp(CO)Ru-(μ-η²,η²,η¹-CH₂=C(Ph)=C=CH₂)Pt(PPh₃)(CO)
C17 Cp(CO)Ru-(μ-η²,η²,η¹-CH₂=C(Ph)=C=CH₂)Pt(PPh₃)(CO)
18  Pt₂Fe (structure uncertain)
19a  Cp(CO)Ru-(μ-η²,η²,η¹-CH₂=CH₂=CH=CH₂)Ru(CO)₃Pt(PPh₃)(CO)
19b  Cp(CO)Fe-(μ-η²,η²,η¹-CH₂=CH₂=CH=CH₂)Ru(CO)₃Pt(PPh₃)(CO)
20a  Cp(CO)Ru-(μ-η²,η²,η¹-CH₂=CH₂=CH=CH₂)Ru(CO)₃Pt(PPh₃)(CO)
20b  Cp(CO)Fe-(μ-η²,η²,η¹-CH₂=CH₂=CH=CH₂)Ru(CO)₃Pt(PPh₃)(CO)
21a  Cp(CO)Ru-(μ-η²,η²,η¹-CH₂=CH₂=CH=CH₂)Ru(CO)₃Pt(PPh₃)(CO)
21b  Cp(CO)Fe-(μ-η²,η²,η¹-CH₂=CH₂=CH=CH₂)Ru(CO)₃Pt(PPh₃)(CO)
22  Cp(CO)₂RuC(Ph)=C=CH₂
23  Cp(CO)₂Ru[C=CH₂C(O)N(SO₂C₆H₄Me)C(Ph)]
24  Cp(CO)Ru-(μ-η²,η¹-CH₂=CH₂=CH=CH₂)Pt(PPh₃)₂
25a  Cp(CO)Ru-(μ-η²,η¹-CH₂=CH₂=CH=CH₂)Pt(PPh₃)₂
25b  Cp(CO)Ru-(μ-η²,η¹-CH₂=CH₂=CH=CH₂)Pt(PPh₃)₂
25c  Cp(CO)Ru-(μ-η²,η¹-CH₂=CH₂=CH=CH₂)Pt(PPh₃)(t-BuNC)
26  25a with Fe₂(CO)₉ product (structure uncertain)
27  Protonated 15a (structure uncertain)
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28b  Analogue of 28a from reaction of 15a with TSI
29a  Cp(CO)Ru[μ-η²,η¹-(C=CH₂=CH₂=CH=CH₂)N(SO₂C₆H₄Me)C(O)CH₂]Pt(PPh₃)₂
29b  Analogue of 29a from reaction of 15a with TSI
29c  Analogue of 29a from reaction of 25a with TSI
29d  Analogue of 29a from reaction of 25b with TSI
29e  Analogue of 29a from reaction of 25c with TSI
30  [Cp(CO)Ru-(μ-η²,η²,η¹-CH₂=CH₂=CH=CH₂)Au(PPh₃)Pt(PPh₃)₂]⁺
31  Analogue of 30 from reaction of 14a with [AuPPh₃]⁺
32  Cp(CO)Ru-(μ-H)(μ-C(H)(O)(CH₃))Pt(PPh₃)₂
33  [Cp(CO)(THF)Ru-(μ-C(H)(O)(CH₃))Pt(PPh₃)₂]⁺
INTRODUCTION

A. Heteronuclear Metal Complexes

The ability of transition metals to coordinate ligands is one of the most important concepts in inorganic chemistry, and the chemical transformations of ligands activated by coordination is fundamental to the fields of organometallic and coordination chemistry. Industrial catalysis is concerned with the chemical transformations of basic feedstocks or other simple molecules into useful compounds that are difficult to prepare on a large scale without the assistance of a catalyst. In the design of catalytic processes and systems, economic and environmental concerns are of the highest priority. A catalytic process that results in a high yield of a pure, desired product is considered to be a feasible one and placed into large-scale production only if the monetary cost, the risk of ecological damage and the risk of human injury is low. Therefore, the selection of the materials for the catalytic species, as a part of the overall design process, must be accomplished in a careful manner, and with great attention to detail. One type of species that has received significant attention by a number of research groups\(^1\) as having the potential to be a catalytically useful material has been the mixed-metal, or heteronuclear metal compound.

Heterobinuclear metal complexes and small heteronuclear metal
clusters have shown high catalytic activity and product selectivity in alcohol homologation, carbon monoxide hydrogenation, and other applications. One key to the successful use of heteronuclear metal complexes in homogeneous catalysis is the synergism evoked by the presence of two different metals with different coordination environments held in close proximity to one another. In heterogeneous catalysis, heteronuclear complexes have been shown to be useful precursors of highly dispersed metal crystallites adsorbed on support surfaces. As an example of the enhanced reactivity by heteronuclear metal complexes possessing a polar metal-metal bond, consider the hypothetical process of carbon monoxide activation. In the activation of carbon monoxide, it is proposed that interaction of the carbon monoxide oxygen atom with the early transition metal (M_E) and of the carbon atom with the late transition metal (M_L) causes the activation of the otherwise extremely inert carbon-oxygen bond towards hydrogenation or another catalytically important process.

Typical early-late heterobinuclear metal complexes have been prepared by various methodologies, but only three of the more general ones will be discussed presently. These include condensation, or small molecule elimination (Eq. 1), bridge-assisted neutral ligand substitution (Eq. 2), anionic ligand substitution (Eq. 3), and a combination of these methods (Eq. 4).
These methods represent the most common approaches taken towards the synthesis of heterobinuclear metal complexes. However, the complexes prepared in Eqs. 1 - 4 and other early-late mixed-metal complexes are often less stable than heterobinuclear metal species composed of two late transition metal fragments. Also, notice that the existence of a metal-metal bond is highly doubtful in two cases (in Eqs. 2 and 4). Thus it is often advantageous to first attempt the synthesis of stable heterobinuclear metal complexes.
complexes of two late transition metals via methodology that can later be adapted towards the preparation of early-late complexes, as shown by Casey and Bullock\textsuperscript{11b} (Eqs. 5 and 6). Although the method had to be altered significantly in order to be suitable for the preparation of

\[
\begin{align*}
\text{(CO)}_3\text{Mo}^- + \text{(CO)}_4\text{Mn} \xrightarrow{\text{Br}} \text{(CO)}_3\text{Mo}^- \text{Mn} \text{(CO)}_4
\end{align*}
\]

(Eq. 5)

the early-late zirconium-iron complex, the proven methodology of Eq. 5 was directly responsible for the eventual synthesis of the stable, analogous, zirconium-iron complex (Eq. 6). In the meantime, new complexes (such as the molybdenum-manganese complex in Eq. 5) were prepared, and the advancement of our understanding of heteronuclear metal chemistry was enhanced. Therefore one eventual application of the research directed towards the preparation of heterobinuclear metal complexes composed of two late transition metals, as well as the work described herein, may be to prepare early-late mixed-metal complexes via thoroughly established methodology.
Of particular interest to the field of heterogenous catalysis are heterobi- and trinuclear metal complexes and clusters that are bridged by hydrocarbyl ligands. These compounds serve as models for the catalytic intermediates of many processes such as hydrogenation and olefin metathesis. The number of such compounds is quite high, but several examples will suffice as an illustration of the methodology involved in the preparation of those complexes most closely associated to the work herein.

Heterobinuclear metal complexes without bridging hydrocarbyl ligands can be readily converted to such complexes via addition of an unsaturated molecule, such as phenylacetylene (Eq. 7). This simple ligand substitution reaction and subtle rearrangement have resulted in the formation of a heterobimetallic dimetallatetrahedrane. In this example, the two carbon atoms of the acetylene triple bond are interacting strongly with each metal, resulting in the weakening (lengthening) of the former triple bond. Such bond weakening through coordination could have an application in alkyne metathesis or some other related catalytic process where initial weakening of an acetylenic bond is necessary for further reaction to occur.

Another simple preparation of a heterobimetallic dimetallatetrahedrane is by replacement of one of the Co(CO)₃ units of the homobinuclear Co₂(CO)₆(μ-(CF₃)(C₂(CF₃)) with an isolobal fragment (Eq. 7).
such as Cp(CO)$_2$Mo. Interestingly, analogous complexes have been prepared by several research groups$^{16}$ including Wojicki$^{17}$ and co-workers, by a much different and less-well understood method (Eq. 9). Studies toward an understanding of the mechanism of this reaction have shown that (a) the proton derives from the protic acid, and (b) the reaction
proceeds via an intramolecular pathway.

The nuclearity of previously prepared heterobinuclear
dimetallatetrahedrane-containing complexes can be increased rather
easily as well. For example, Fe$_2$(CO)$_9$, a compound known to dissociate
into reactive mononuclear Fe(CO)$_x$ fragments in solution, reacted with
several heterobinuclear metal complexes to form two heterotrinuclear
clusters that differ from one another only in arrangement of the metal
fragments$^{18}$ (Eq. 10). These clusters serve well as examples of
heterogeneous catalyst systems where the different metals of a particular
surface interact individually with various parts of an attached
hydrocarbyl fragment. Such interactions tend to activate the hydrocarbyl
fragment toward further reaction in the catalytic cycle. For example, if
the interaction of two separate metal atoms with each carbon atom of a
bridging acetylene molecule is strong enough, the carbon-carbon bond
could be ruptured to

\[
\begin{array}{c}
R \\
C \\
M ---- M' \\
\end{array} \rightarrow \begin{array}{c}
R' \\
C \\
M ---- M' \\
\end{array}
\]

form two carbyne-type species (Eq. 11) capable of further desired (or
possibly undesired) reactivity.

The use of transition metal compounds possessing unsaturated
ligands to form heterobinuclear (and higher nuclearity) metal complexes
via interaction with electron-poor, unsaturated metal-containing species
is the most convenient method of preparation of bridging hydrocarbyls.
The transition metal compounds possessing unsaturated ligands are often referred to as molecular templates. Such templates, via utilization of the electron-rich part of the ligand, are responsible for the initial interaction with the unsaturated metal fragment. Once coordinated, the transition metal of the original template molecule is presently in close proximity to the newly coordinated metal, and the facile formation of a metal-metal bond is enhanced. The simplest example of the template concept is illustrated by the reaction of an osmium-alkyne complex (template) with cobalt, rhodium, and iridium-containing complexes (Eq. 12) that readily lose a carbon monoxide ligand (to become unsaturated) when exposed to the appropriate wavelength of ultraviolet light or to more strenuous thermal conditions.

Multiple bonds between transition metals and ligands, such as in the phenylethenyldiene (Eq. 13), the vinylcarbene (Eq. 14), and the carbyne (Eq. 15) examples below serve as templates in a simple sense owing to the rather uncomplicated products formed in a straightforward manner.
manner. In each case a bridging alkylidene or alkylidyne ligand is formed in addition to a heteronuclear metal-metal bond. These examples serve as an illustration of the different types of structure and bonding that can occur between two different fragments linked by a simple bridging hydrocarbyl ligand and a heteronuclear metal-metal bond.

\[ \text{mer-}(\text{CO})_3(\text{dppe})W=C=C(\text{Ph})H + (\text{PET}_3)_2\text{Pt}(\text{H})(\text{acetone})^+ \]  \hspace{1cm} \text{(13)}

\[ (\text{CO})_5W=C \quad (\text{CO})_6W \quad \text{Fe}(\text{CO})_3 \]

Of course the unsaturation of the template molecule need not directly involve the transition metal, as exemplified by the reaction of a transition metal acetylide complex with \( \text{Fe}_2(\text{CO})_9 \). Note that the formation of the trinuclear product in Eq. 16 was facilitated by the loss of
both carbonyl ligands from the acetylide-bearing metal, as well as by the replacement of several carbonyl ligands of Fe$_2$(CO)$_9$ by the triple bond of the acetylide ligand to form a metallatetrahedrane.

![Chemical structure](image)

A more complicated and richer reaction chemistry between an unsaturated hydrocarbyl ligand and Fe$_2$(CO)$_9$ was observed by Wojcicki and co-workers$^{24}$ (Eq. 17) as well as by Liu and co-workers$^{25}$ (Eq. 18)

![Chemical structure](image)

$M = Mo, W$; $R = Ph, Me, p$-tolyl
using transition metal propargyl complexes as templates. In organic chemistry, facile interconversion between propargyl and allenyl isomers is common, and thus the bridging allenyl ligands derived from propargyl ligands in the products of Eqs. 17 and 18 were not unexpected. However, owing to the diversity of bridging allenyl (Wojcicki group) and other (Liu group) products obtained, as well as to the potential of the bridging ligand to rearrange to form additional products, further examination of this ligand type was warranted.

Hetero- and homobis- and trinuclear metal complexes containing bridging allenyl ligands have been prepared by several other research groups through various means. For example, the research groups of Seyferth²⁷ (Eq. 19a) and Mathieu²⁸ (Eq. 19b), in separate experiments, reacted homobinuclear anionic metal complexes with propargyl halides to produce neutral, bridging allenyl ligand-containing compounds. In each case, an $S_N2'$ mechanism, where the binuclear anion attacked at the CR' carbon, was used to explain the formation of the bridging allenyl ligands.
(a) \[ \text{(CO)}_3\text{Fe} \xrightarrow{X\text{CR}_2\text{C}=\text{CR}'} \text{(CO)}_3\text{Fe} + \text{SR}'' \]

\[ R = \text{H, Me} \]
\[ R' = \text{H, Et} \]
\[ R'' = \text{Et, CMe}_3 \]

(b) \[ \text{(CO)}_3\text{Fe} \xrightarrow{\text{ClCH}_2\text{C}=\text{CH}} \]

The addition of a methylene group to a bridging acetylide ligand\(^\text{29}\) (Eq. 20), or of a proton to a bridging acetylenic alkylidene
ligand\textsuperscript{30} (Eq. 21) resulted in the formation of three additional \( \mu \)-allenyl complexes.

![Chemical structure](image)

\[
\text{Eq. 21}
\]

It has also been shown that \( \mu \)-allenyl complexes can be prepared through the simple rearrangement of other bridging hydrocarbyl ligands by the replacement of a metal fragment coupled with a ligand rearrangement\textsuperscript{31} (Eq. 22), loss of a ligand via thermolysis\textsuperscript{32} (Eq. 23), or by a two-electron reduction\textsuperscript{33} (Eq. 24).

![Chemical structure](image)

\[
\text{Eq. 22}
\]

\[
\text{Eq. 23}
\]
The synthesis of the bi- and trinuclear \( \mu \)-allenyl complexes in Eqs. 19 - 24 exemplify the ease of formation of such species via somewhat general approaches. Only one of the reactions involved the formation of a heteronuclear metal-metal bond, however, which is a common feature of many reaction products in our group. Owing to our interest in heteronuclear metal-metal bonds as well as bridging allenyl ligands, the approach taken in our group (and to a limited extent in the Liu group) is a general one leading to the formation of complexes possessing a newly-formed metal-metal bond in addition to a bridging allenyl ligand.

It has been shown (Eqs. 17 and 18) that the mononuclear transition metal propargyl and allenyl complexes show a tendency to react with appropriate unsaturated metal fragments to form stable bi- and trinuclear compounds. As a means of further examining such chemistry, this document is concerned with (a) the preparation and reactivity of new mononuclear propargyl complexes (templates) and especially with (b) the reactions of well-known and thoroughly studied mononuclear propargyl species with different types of unsaturated metal-containing species (substrates). Therefore the background of a chosen new source of unsaturated metal-containing species should be examined briefly.
B. Platinum(0) Reagents as Substrates for the Formation of Heteronuclear Metal-Metal Bonds

Oxidative addition reactions have been extensively studied\textsuperscript{34} as a means of forming platinum-carbon bonds. Of particular interest to this study was the reaction carried out by Collman and co-workers\textsuperscript{35} which resulted in the preparation of mononuclear metal σ-allenyl species (Eq. 25a). Indeed, recently Wojcicki and co-workers\textsuperscript{36} prepared a mononuclear metal σ-phenylpropargyl complex (Eq. 25b) based upon this methodology.

(a)

\[
\text{Pt(PPh}_3\text{)}_4 + \begin{array}{c}
\text{HC} &= \text{CR}^1\text{R}^2\text{X} \\
\text{H} &= \text{C} &= \text{C} &= \text{CR}^1 \\
\text{X} &= \text{C} &= \text{C} &= \text{CR}^2
\end{array} \rightarrow \\
\begin{array}{c}
\text{Pt} \\
\text{Pt} \\
\text{Pt}
\end{array} + \\
\begin{array}{c}
\text{Pt} \\
\text{Pt} \\
\text{Pt}
\end{array} \\
\text{Pt} \\
\text{Pt} \\
\text{Pt}

(25)

(b)

\[
(\text{PPh}_3)_2\text{PtC}_2\text{H}_4 + \text{XCH}_2\text{C} &= \text{CPh} \rightarrow \\
\text{X} &= \text{Pt} &= \text{PPh}_3 \\
\text{PPh}_3 &= \text{CH}_2\text{C} &= \text{CPh}
\]

Owing to the ease of product formation, it was postulated that a polar metal-halogen bond should also be able to oxidatively add to a platinum(0) center. As expected, main group and transition metal halide complexes oxidatively add to platinum, as observed by Pidcock\textsuperscript{37}(Eq. 26a) and Clark\textsuperscript{38}(Eq. 26b), but in the case of the trimethyltin chloride, a tin-carbon bond added to the platinum rather than the tin-chloride bond. It is believed
(a) (PPh₃)₂PtC₂H₄ + Me₃SnCl

(b) (PPh₃)₂PtC₂H₄ + Cp(CO)₂FeCl

that the mode of reaction is probably determined by kinetic rather than thermodynamic factors, but no information beyond this explanation was provided to rationalize the course of reaction in Eq. 26a. The reaction in Eq. 26b is a good example of formation of a heterobinuclear complex by the oxidative addition of a transition metal-halide (Fe-Cl) bond to a platinum(0) center.

In a related reaction (Eq. 27) carried out by Stang and co-workers, a carbon-hydrogen bond of the ethylene initially bound to platinum was activated, and a heteronuclear iridium-platinum complex bridged by a σ-π-vinyl ligand as well as a hydride ligand was formed. This
reaction demonstrates the ease with which heteronuclear metal-metal bond formation can occur with platinum, especially when accompanied by a carbon-hydrogen activation process coupled with oxidative addition. It has been shown that heteronuclear metal-metal bonds can be prepared from reaction of platinum(0) reagents with polar metal-substituent bonds. Another method for the preparation of heteronuclear metal-metal bonds, as mentioned above, was proposed to occur if the active metals were held in close proximity to one another via interaction of some other part of the template molecule with the platinum(0) reagent. In other words, the proper choice of attendant ligand is critical because an appropriate interaction between the ligand and the platinum will fix the two metal-containing molecules in space such that the formation of a metal-metal bond between both metals bound to the same ligand is feasible.

Of course a ligand can be used as a template source that is not carbon- or unsaturation-based. For example, electron rich nitride, or in the case below (Eq. 28), a phosphide ligand can draw two metals in close proximity to one another via a nucleophilic interaction with the electrophilic, unsaturated metal center. Powell and co-workers reacted a ruthenium

\[
\text{Cp(CO)_2Ru} \rightarrow \text{PR}_2 + \text{(PPh}_3)_2\text{PtC}_2\text{H}_4 \rightarrow \text{Ru–Pt(PPh}_3)_2
\]
phosphide-containing compound with a platinum(0) reagent to obtain a heterobinuclear complex bridged only by the \( \mu \)-phosphido ligand. This product is directly analogous to the ruthenium-platinum heterobinuclear complexes prepared by the author except that instead of an \( \eta^2,\eta^1 \)-phosphido ligand, the heteronuclear metal-metal bond is bridged by an \( \eta^2,\eta^1 \)-allenyl ligand (vide infra).

In 1980 Stone\textsuperscript{41} used the template approach to prepare heterobinuclear metal complexes involving platinum from the reaction of a Fischer carbene complex with a platinum reagent (Eq. 29a), and more recently Geoffroy\textsuperscript{42} reported a metal carbene as a reaction intermediate to explain the interesting result of the reaction shown in Eq. 29b. Both reactions involve interaction between the unsaturation of the carbene and the platinum center to form the heterobinuclear species bridged by an alkylidene ligand. Since 1980, the Stone research group and others have continued to exploit the carbene and

(a) \[
\text{(CO)}_5\text{Mn} = \text{C} \quad \text{OR} \quad \text{Pt}(0) \quad \text{(CO)}_5\text{Mn} \quad \text{PtL}_2
\]

(b) \[
\text{(CO)}_4\text{Fe} \quad \text{Fe} \quad \text{(CO)}_4 \quad \text{H}_2 \quad \text{[(CO)}_4\text{Fe} = \text{CH}_2] \quad \text{Pt}(0) \quad \text{(CO)}_4\text{Fe} \quad \text{PtL}_2
\]
carbyne ligands as electron-rich sources of unsaturation available for reaction with electrophilic metal species such as platinum(0) reagents.

In a similar fashion, the σ-acetylide ligand has been used to effect the formation of metal-metal heteronuclear bonds involving platinum, as for example, recently reported by Beck\textsuperscript{43} (Eq. 30). The resultant product contains one heteronuclear metal-metal bond bridged by the σ-π-interaction

\[
\begin{align*}
(CO)_5\text{Re}-C&\equiv C-\text{Re}(CO)_5 \\
+ (PPh_3)_2\text{PtC}_2\text{H}_4
\end{align*}
\]

of the acetylide ligand. Another interesting feature of the product of Eq. 30 is the carbonyl/phosphine exchange between the rhenium and platinum atoms. Later, related products formed as a result of such exchanges will be discussed.

In summary, it has been observed that early-late, as well as late-late binuclear mixed-metal complexes have an important role in industrial hetero- and homogeneous catalysis applications. In particular, complexes containing bridging hydrocarbyl, and more specifically, bridging allenyl ligands have been prepared and these serve well as models for reaction intermediates and surface interactions in catalytic processes. Owing to the ease with which platinum(0) reagents can oxidatively add to many different types of polar bonds, including metal halide bonds, the introduction of this catalytically active metal into hydrocarbyl-bridged
complexes has been effected as well. The production of heteronuclear allenyl-bridged, platinum-containing complexes, via reaction of transition metal propargyl and allenyl compounds (serving as templates) with platinum(0) reagents, as yet unreported, is the focus of the research described herein.

C. Statement of General Research Goals

The chemistry of transition metal propargyls \( L_nMCH_2C=CR \) and mononuclear allenyls \( L_nMCH=C=CH_2 \) is of particular interest in the Wojcicki group. Most recently, our focus has been on the growing number of heterobinuclear and homo- and heterotrinuclear metal bridging-allenyl complexes prepared by utilizing the propargyl or allenyl ligand as a template. Further elaboration of this idea is clearly warranted as there remains a general lack of a systematic synthetic approach to these types of compounds.

The synthetic approach taken in our research group has been to treat transition metal propargyl complexes with carefully chosen reactive transition metal substrates. The objective of the research discussed in this document was to expand the understanding of this chemistry by focusing on the reaction between different types of transition metal propargyl compounds (i.e., different metals as well as different ancillary ligands on the metal) with different types of substrates. As a result, one may then be able to predict the reactivity of different propargyl compounds with similar substrates, as well as the reactivity of different substrates with similar propargyl complexes. This may ultimately lead to a highly desired...
systematic synthetic scheme which will enable one to prepare bi- and trinuclear complexes of many different combinations and connectivities. Therefore, as introduced in the previous two sections, the major focus of this research has been on expanding the chemistry of heteronuclear complex formation by incorporation of platinum into the product molecules. Further, an inseparable goal was to study the reactivity of such heteronuclear products with electrophilic, nucleophilic, and unsaturated transition metal carbonyl-containing reagents. These studies by the author were proceeded by the preparation and subsequent reactivity of new transition metal propargyl complexes, and on the reactivity of some unsaturated substrates with known transition metal propargyl complexes.
EXPERIMENTAL

Characterization of Compounds

**Infrared Spectroscopy (IR):** Solution IR spectra were obtained on a Perkin-Elmer Model 283B spectrophotometer utilizing NaCl (0.2 mm) or KBr (0.1 mm) cells of various pathlengths. Calibration was against the characteristic 1583 cm\(^{-1}\) absorption of polystyrene. All numbers listed here correspond to carbonyl (\(v_{\text{CO}}\)) stretches unless otherwise noted.

**Nuclear Magnetic Resonance Spectroscopy (NMR):** Routine spectra were recorded by the author on either a Bruker AM-200, AM-250, or AC-300 NMR spectrometer. These included \(^1\text{H}, \, ^{31}\text{P}, \, \text{coupled and decoupled} \, ^{13}\text{C}, \) and high- and low-temperature NMR spectra. Dr. Charles Cottrell recorded the 2D spectra on a Bruker AM-500 instrument. Special assistance was obtained from Mr. Carl Engleman. Typical samples were dissolved in deuterated solvent under an argon atmosphere in 5 mm NMR tubes. Residual proton signal of the deuterated solvent was used for calibration. All chemical shift values are given in parts per million (\(\delta, \, \text{ppm}\)) and spin-spin coupling values, denoted by \(J\), are given in Hertz (Hz). In most cases, phenyl carbon atoms are not included in \(^{13}\text{C}\) NMR data given here.
**Mass Spectrometry (MS):** Mass spectra were recorded by either Mr. David Chang (FAB) or Mr. C. R. Weisenberger (EI) on a Kratos MS-30 or a VG70-250S spectrometer.

**Elemental Analyses (EA):** All elemental analyses (C and H only) were carried out by M-H-W Laboratories, Phoenix, Arizona.

**X-Ray Crystallography:** Crystal structures were obtained by Professor Arnold Rheingold and Brian Haggerty at the University of Delaware, by Professor Mario Calligaris and coworkers at the Universita di Trieste, Italy, or by Dr. Judith Gallucci at the Ohio State University.

**Materials**

Solvents were distilled under an argon atmosphere, and dried as follows: tetrahydrofuran (THF) and benzene from potassium/benzophenone, hexane and heptane from potassium, diethyl ether from sodium/potassium alloy (NaK$_{2.8}$) or n-butyl Grignard, dichloromethane (methylene chloride) from P$_4$O$_{10}$, and toluene from sodium.

All reagents below were used as received unless otherwise noted. The following chemicals were purchased from Aldrich Chemical Company, Milwaukee, Wisconsin: ethylene bromide, zinc chloride, Florisil (magnesium silicates), mercuric chloride, propargyl chloride, toluenesulfonyl isocyanate (TSI, distilled on high-vacuum line at 110°C), trimethylamine N-oxide (TMNO, sublimed from the dihydrate), tetracyanoethylene (TCNE, sublimed), triethylphosphine,
trimethylphosphite, triphenylphosphine, toluenesulfonyl chloride, diphenylacetylene, sulfur, selenium, n-butyl lithium (1.6 or 10 M solutions in hexane), cyclohexylamine (distilled from P₄O₁₀), diethylamine, diphenylmethylene malononitrile, furanoritrile, chlorosulfonyl isocyanate, trifluoroacetic acid, trifluoroacetic acid-d, sodium tetraphenylborate, dimethyl sulfate, dimethylacetylenedicarboxylate (DMAD), methyl-2-butynoate, phenylacetylene, triethylxonium hexafluorophosphate, silver triflate, t-butyl isocyanide, AIBN (2,2'-azobis(2-methylpropionitrile)), nitrosobenzene, benzoquinone, tropylium hexafluorophosphate. The following were obtained from Strem Chemical, Newburyport, Massachusetts: iron pentacarbonyl, dicobalt octacarbonyl (recrystallized at low temperature under carbon monoxide), tungsten hexacarbonyl, 1,3-(diphenylphosphino) propane (dppp). The following was obtained from Alfa Chemical, Ward Hill, Massachusetts: sublimed magnesium. The following was purchased from Cambridge Isotopes, Woburn, Massachusetts: all deuterated solvents. Johnson-Matthey provided ruthenium- and rhodium trichlorides via their loan program.

All of the following were prepared by published procedures or slight variations thereof: CpCr(NO)₂Cl, Fe₂(CO)₉, HOCH₂CsCPh, BrCH₂C≡CPh, [Cp(CO)₂Fe]₂, NaK₂, Cp(PPh₃)₂RuCl, Cp(CO)₃WCH₂CsCPh, [Rh(COD)Cl]₂, Rh₄(CO)₁₂, CpRh(CO)₂, Cp₂Rh₂(CO)₃, (PPh₃)₂PtC₂H₄, (CO)₅MnCH₂C≡CPh, ClCH₂C≡CPh, Pt(PPh₃)₄, Ru₃(CO)₁₂, methylsulfonyl sulfonamide.
Reactions

Most compounds discussed here are air-sensitive in solution, but are significantly more stable as solids. Exceptions will be noted elsewhere.

Reactions were carried out by use of standard Schlenk techniques or a Vacuum Atmospheres drybox under an argon atmosphere with freshly distilled solvents. The Schlenk line included a horizontal column of powdered P$_4$O$_{10}$ for drying and a column outfitted with an oxygen scavenger (BASF copper catalyst regenerated with 5% H$_2$ in N$_2$ at 160°C for 24 hours).

Reactions were monitored by either direct spectroscopic examination of reaction solution (solution IR or $^{31}$P NMR utilizing a D$_2$O-filled insert that fits into normal 5 mm NMR tubes) or by examination ($^1$H or $^{31}$P NMR) of an aliquot of reaction solution that had been stripped of its solvent in vacuo and replaced with an appropriate deuterated solvent.

Chromatography was performed on Grade III alumina under an argon atmosphere, unless noted otherwise. The alumina (from Aldrich) was deactivated by the addition of 6% H$_2$O in small increments by weight to material that had been heated at 130°C for 16 hours. Silica and Florisil were generally used as received from Aldrich, although exposure of older samples of Florisil to high vacuum for several hours was used for activation.

Melting points were obtained in unsealed capillary tubes using a Meltemp apparatus and are uncorrected. Decomposition points are approximate.
A. Studies Toward the Preparation and Reactivity of New Mononuclear Propargyl Complexes

1) Chromium Propargyl Complex Chemistry

Preparation of $\text{PhC}=\text{CCH}_2\text{MgBr}$

This reagent can be prepared in high yield only if the newly formed Grignard reagent is removed from the reaction system as it is formed so that it is not exposed to propargyl bromide. The following so-called Grignard Machine (graciously loaned to the author by Professor Emeritus Melvin Newman) reduces the possibility of forming a coupled diacetylene product.

As can be seen in Figure 1 "the apparatus is so designed that solvent (ether) may be distilled from a flask into a condenser above the magnesium-packed tube. The condensed ether runs down through the magnesium and runs by gravity back to the original pot, the return line being of such a height that the magnesium turnings are always covered with ether." The phenyl propargyl bromide is added dropwise at the top of the condenser.

The surface of the magnesium was activated just prior to reaction with ethylene bromide. A given quantity (usually between 1 and 10 mmole) of phenyl propargyl bromide and 0.5 mL of ethylene bromide was dissolved in 20 mL of ether and added slowly to the magnesium column via an addition funnel at the top of the condenser. After addition was complete, the reaction solution was refluxed for an additional 3 hours. The light
Figure 1. The Grignard Machine
yellow solution was then ready for use as below. In several cases the reaction was determined to be essentially quantitative by a simple titration with standardized HCl and was considered as such in reactions below.

**Preparation of \((\text{PhC}=\text{CCH}_2)_2\text{Zn}\)**

A 10 mmole quantity of the Grignard reagent prepared as above was added slowly to a stirred suspension of 5 mmole (0.73 g) of \(\text{ZnCl}_2\) in ether (50 mL). The reaction was complete within an hour at room temperature. Solvent was removed from the reaction solution under reduced pressure to yield a yellow gummy solid. The solid was washed with hexane (2 x 10 mL) to try to remove impurities, but the compound remained gummy despite these efforts.

\(^1\text{H NMR (CDCl}_3\) δ 7.32 (m, 5 H, Ph), 2.07 (s, 2 H, CH\(_2\)).

\(^{13}\text{C(\text{H}) NMR (CDCl}_3\) δ 131.6, 128.8, 128.5, 126.9 (Ph), 93.6 and 78.7 (C≡C), 25.5 (CH\(_2\)).

**Preparation of \(\text{Cp(NO)}_2\text{CrCH}_2\text{C}=\text{CPh (I)}\)**

The 10 mmole solution of the zinc reagent prepared above was added over the course of one hour, to a stirred solution of \(\text{Cp(NO)}_2\text{CrCl (2.1 g, 10 mmole)}\) in THF (100 mL) at -78°C. After the stirred solution had warmed slowly to room temperature over 18 hours, solvent was removed in vacuo. The resulting brown tar was then extracted consecutively with hexane (3 x 100 mL) and 5% ether in hexane (2 x 50 mL), and the combined extracts were stripped of solvent in vacuo. Chromatography of the residue on Grade III alumina (initial eluent hexane) with 1% diethyl ether in
hexane gave a yellow band of product. Removal of solvent in vacuo yielded 1.2 g (4 mmole, 40%) of gold leaflets of 1.

$^{13}$C($^1$H) NMR (CDCl$_3$) $\delta$ 130.9, 128.1, 126.2, 126.0 (Ph), 100.8, 85.0 (C=), 100.5 (Cp), 0.68 (CH$_2$).

**Reaction of Cp(CO)$_2$CrCH$_2$C≡CPh (1) with Fe$_2$(CO)$_9$**

To a stirred solution of Cp(NO)$_2$CrCH$_2$C≡CPh (0.20 g, 0.69 mmol) in hexane (45 mL) was added Fe$_2$(CO)$_9$ (0.50 g, 1.4 mmol) as a solid, at room temperature. The ensuing reaction was complete in one hour, as determined by the disappearance of the IR $v_{\text{N=O}}$ absorptions at 1789 and 1688 cm$^{-1}$ of Cp(NO)$_2$CrCH$_2$C≡CPh. The resulting red-brown solution was freed of the solvent under vacuum to give a red tar. This residue was dissolved in CH$_2$Cl$_2$ (0.5 mL), and the solution was introduced onto a 2 x 75 cm column of silica gel (TLC grade) packed in hexane. Slow elution with hexane gave a large red band, which was collected and concentrated to give (CO)$_3$Fe($\mu$-$\eta^2$;-$\eta^3$-PhC≡C=CH$_2$)Fe(CO)$_2$(NO) (2) as a red oil (0.095 g, 35% yield). Complex (2) sublimes onto a coldfinger at -78°C under reduced pressure (ca. 0.1 torr).

IR (cyclohexane) $v_{\text{C=O}}$ 2065 (s), 2031 (vs), 2009 (vs), 1931 (w); $v_{\text{N=O}}$ 1778 (vs).

$^1$H NMR (CD$_2$Cl$_2$) $\delta$ 7.57, 7.52, 7.33, 7.32 (4 s, 5 H, Ph), 4.58, 4.29 (2 d, 2$J = 0.7$, 2 H, =CH$_2$).

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) $\delta$ 211.4, 210.4 (Fe(CO)$_2$NO), 209.6 (br, Fe(CO)$_3$), 138.1, 130.6, 129.3, 128.6 (Ph), 111.8 (=C=), 80.5 (=CPh), 70.5 (=CH$_2$).

$^{13}$C NMR (CD$_2$Cl$_2$) $\delta$ 70.5 (t, $^1J_{\text{CH}} = 169$, =CH$_2$).
EI MS (relative intensity) 396.900 (exact M⁺, 4.4; calcd for C_{14}H_{7}Fe_{2}NO_{6} 396.897), 369 (M⁺ - CO, 46), 341 (M⁺ - 2CO, 40), 313 (M⁺ - 3CO, 41), 283 (M⁺ - 3CO - NO, 17), 227 (M⁺ - 5CO - NO, 36), 115 (CH₂C≡CPh⁺, 100).

Continued elution with hexane gave an orange band, which was collected and evaporated to dryness to afford known CpCr(CO)₂(NO)₆ as an orange solid, identified by its characteristic ¹H NMR (δ 5.08, 5 H, Cp) and IR (ν_C=O 2028 (s), 1959 (s) and ν_N=O 1719 (s)) spectra.

2) Reaction of Cp(CO)₂FeCH₂C≡CPh (5) with Fe₂(CO)₉

Preparation of (PhC≡CCH₂)₂ (3)

A solution of 13 mmole of BrMgCH₂C≡CPh (as determined by titration in the usual manner) in diethyl ether (50 mL) prepared in the Grignard machine was added quickly to 13 mmole (1.8 mL) of BrCH₂C≡CPh dissolved in 50 mL of diethyl ether. After stirring at room temperature for 16 hours, the reaction solution was freed of solvent in vacuo to yield about 5 mL of a viscous yellow oil. The oil was chromatographed on a silica gel column (2 x 20 cm) initially packed in hexane. Elution with 50:1 hexane/diethyl ether gave a nearly colorless solid (2.3 g, 77% yield) upon removal of solvent under reduced pressure.

¹H NMR (CDCl₃) δ 7.4-7.1 (m, 5 H, Ph), 2.75 (s, 2 H, CH₂).

¹³C{¹H} NMR (CDCl₃) δ 131.6, 128.2, 127.8, 123.7 (Ph), 88.3, 81.6 (C≡C), 19.8 (CH₂).

EI MS (relative intensity) 229 (M⁺ - 1, 31.0), 215 (M⁺ - 1 - CH₂, 17.1), 115 (CH₂C≡CPh⁺, 100).
Reaction of (PhC≡CCH₂)₂ (3) with Fe₂(CO)₉

A suspension of Fe₂(CO)₉ (1.1 g, 3.0 mmol) in a hexane solution (30 mL) of (PhC≡CCH₂)₂ (0.71 g, 3.1 mmol) was heated at reflux for 15 minutes. The reaction mixture was cooled to room temperature and filtered, and the filtrate was concentrated under vacuum to a red oil. Crystallization of the oil from 1:1 pentane/CH₂Cl₂ provided (CO)₆Fe₂[PhC≡C(C₂H₄)C≡Ph] (4) as light yellow air-stable crystals (1.4 g, 92% yield), mp 162°C.

¹H NMR Data for CH₂ protons (not reported by G.H. Young⁶⁷):
δ 3.32, 2.76 (2 dd, 2J = 13.6, 3J (vicinal) = 3.0).

Preparation of Cp(CO)₂FeCH₂C≡CPh (5)

This is a much higher-yield procedure than that from the literature.⁶⁸ In the drybox under argon, [Cp(CO)₂Fe]₂ (4.0 g, 11 mmol) was dissolved in THF (200 mL) to give a purple solution. A 2-fold excess of sodium-potassium alloy was added to this solution by pipet, and the resulting suspension was vigorously stirred at room temperature for 24 hours. A mixture of fine black precipitate and a light yellow solution was obtained. The mixture was filtered first through a course sintered-glass frit (B porosity), and then through a fine frit (D porosity) to separate the fine black precipitate. (Caution: when removed from the drybox the frits may ignite spontaneously; used frits and unreacted Na/K alloy should be treated with methanol.) The solution containing [Cp(CO)₂Fe]⁺ was removed from the drybox, cooled to -78°C, and PhC≡CCH₂Cl (2.0 mL, 20 mmol) was added dropwise via syringe over 10 minutes with stirring. The solution darkened, and a white precipitate formed within 15 minutes.
After the solution warmed to room temperature, the solvent was removed under reduced pressure, and the brown residue was extracted with hexane (2 x 100 mL, 1 x 50 mL). The dark yellow extracts were combined and filtered through a D-frit. Concentration of the solution induced the precipitation of a yellow, crystalline product. The liquid (ca. 10 mL) was removed by cannula, and the solid was dried under vacuum to give 5 (5.1 g) in 79% yield.

**Reaction of Cp(CO)\_2FeCH\_2C≡CPh (5) with Fe\_2(CO)\_9**

To a stirred solution of 5 (0.85 g, 2.9 mmol) in pentane was added Fe\_2(CO)\_9 (1.1 g, 2.9 mmol) as a solid, at room temperature. The resulting suspension was stirred for 40 hours, during which time the reaction mixture turned dark green and then orange. Stirring was discontinued at that point, and the mixture was allowed to settle. The orange solution was decanted by cannula from a brown precipitate and set aside for future workup.

The brown precipitate was dissolved in THF (50 mL), and the solution was filtered through a plug of Florisil (2 x 5 cm) on a sintered glass frit (D porosity). The filtrate was concentrated to 5 mL, and the precipitated solid was recrystallized from hexane (10 mL) at room temperature to give yellow crystals (0.15 g, 11% yield) of (CO)\_3Fe[\eta\^4-C(O)C(Ph)-C(Fe(CO)\_2Cp-CH\_2)] (6).

The orange solution was evaporated to dryness under vacuum to afford a brown residue, which was dissolved in CH\_2Cl\_2 (4 mL) and introduced onto a 2 x 10 cm column of Florisil (60-100 mesh) packed in hexane. Elution with 15:1 hexane/THF gave a purple band, which was
collected and evaporated to dryness to afford \( \text{[Cp(CO)}_2\text{Fe]}_2 \) (0.104 g, 10%), identified by comparison of its IR and \(^1\text{H} \) NMR spectra with the literature values.\(^{21}\) Elution with 3:1 hexane/THF gave an orange band, which was collected and freed of solvent to yield additional 6 (0.26 g, 19%; combined yield of 6, 0.41 g, 30%), mp 81°C dec.

3) Preparation and Reactivity of \( \text{Cp(PPh}_3\text{)}_2\text{RuCH}_2\text{C}≡\text{CPh} \) (7)

Preparation of \( \text{Cp(PPh}_3\text{)}_2\text{RuCH}_2\text{C}≡\text{CPh} \) (7)

Sublimed magnesium (1.0 g, 41 mmol) in 100 mL of diethyl ether was treated with a trace amount of HgCl\(_2\) (approx. 5 mg), and the clear mixture was gently warmed with a heat gun until it became cloudy (ca. 10 seconds). It was then cooled to 0°C and treated dropwise, via syringe, with PhC≡CCH\(_2\)Cl (1.0 mL, \( d = 1.5 \) g/mL, 10 mmol) over 5 minutes. The resulting solution was allowed to warm (1 hour) and was stirred at room temperature for 10 hours. After settling, it was added dropwise, by cannula, over 15 minutes to 100 mL of a toluene solution of \( \text{Cp(PPh}_3\text{)}_2\text{RuCl} \) (1.0 g, 1.4 mmol) at -78°C. The mixture was allowed to warm to room temperature in 6 hours, and solvent was removed from the orange solution under vacuum to leave an orange-red gummy residue. The residue was extracted with toluene (2 x 50 mL), and the extracts were filtered and concentrated to approximately 10 mL. Addition of 50 mL of hexane induced the precipitation of a light orange solid. The solid was collected on a frit and washed with hexane (10 mL) to yield 0.96 g (85%) of \( \text{Cp(PPh}_3\text{)}_2\text{RuCH}_2\text{C}≡\text{CPh} \) (7), mp 150°C dec.
$^{1}$H NMR (CDCl$_3$) $\delta$ 7.7-7.1 (m, 35 H, Ph), 4.31 (s, 5 H, Cp), 1.95 (t, $^{3}J_{PH} = 12.1$, 2 H, CH$_2$).

$^{13}$C NMR (CDCl$_3$) $\delta$ 139.7, 135.1, 133.6, 131.9, 130.1, 129.0, 126.5, 125.9 (8m, Ph), 123.5 (t, $^{3}J_{CH} = 7.6$, $\equiv$CPh), 109.1 (t, $^{2}J_{CH} = 2.0$, $\equiv$CCH$_2$), 84.9 (dm, Cp), -22.5 (tt, $^{1}J_{CH} = 135$, $^{2}J_{CP} = 11.8$, CH$_2$).

$^{31}$P($^{1}$H) NMR (CDCl$_3$) $\delta$ 50.1 (s).

Anal. Calcd. for C$_{50}$H$_{42}$P$_2$Ru: C, 74.29; H, 5.34; Found: C, 74.52; H, 5.25%.

Reaction of Cp(PPh$_3$)$_2$RuCH$_2$C=CPPh (7) with $p$-MeC$_6$H$_4$SO$_2$N=C=O (TSI)

A solution of the propargyl complex 7 (0.10 g, 0.12 mmol) in CH$_2$Cl$_2$ (10 mL) was treated with an excess of TSI (0.22 mL, d = 1.3 g/mL, 1.5 mmol) dropwise over 5 minutes at room temperature. The solution changed color from orange to green during the addition. Solvent and excess TSI were then removed under vacuum and by washing with hexane (5 mL), respectively, to give a green solid, which was purified by chromatography on alumina with CH$_2$Cl$_2$ as eluent, yield 0.085 g (71%) of the cycloaddition product 8.

IR (CH$_2$Cl$_2$) 1740.

$^{1}$H NMR (CDCl$_3$) $\delta$ 8.0-6.9 (m, 7 Ph and C$_6$H$_4$), 4.12 (s, 5 H, Cp), 3.48 (s, br, 2 H, CH$_2$), 2.42 (s, 3 H, Me).

$^{13}$C($^{1}$H) NMR (CDCl$_3$) $\delta$ 194.2 (m, CO), 167.6 (s, $^{2}J_{PC} = 3.5$, CRu), 142.7 (s, CPh), 136-126 (m, Ph and C$_6$H$_4$), 84.4 (s, Cp), 38.7 (s, CH$_2$), 21.5 (s, Me).

$^{31}$P($^{1}$H) NMR (CDCl$_3$) $\delta$ 47.5 (s).
Mass spectrum (FAB), $^{102}$Ru isotope, 1004 (M$^+$ + H), 741 (M$^+$ - PPh$_3$), 691 (Cp(PPh$_3$)$_2$Ru$^+$), 429 (Cp(PPh$_3$)Ru$^+$).

**Reaction of Cp(PPh$_3$)$_2$RuCH$_2$C=CHPh (7) with Co$_2$(CO)$_8$**

Freshly recrystallized Co$_2$(CO)$_8$ (0.11 g, 0.32 mmol) was added with stirring to a solution of the propargyl complex (0.25 g, 0.31 mmol) in THF (40 mL) at room temperature, and the solution darkened immediately. A 2-mL aliquot was withdrawn and evaporated to dryness, and the residue was examined by NMR spectroscopy as a CDCl$_3$ solution ($^1$H NMR $\delta$ 7.7-6.7 (m, Ph), 4.88 (s, br, Cp), 3.46 (br, CH$_2$)). $^{31}$P($^1$H) NMR $\delta$ 41.0 (s.).

Chromatography of the reaction mixture on a column of alumina (20 x 3 cm) with hexane as eluent afforded (CO)$_3$Co($\mu$-$\eta^2$-PhC=CMe)Co(CO)$_3$ (0.061 g, 49% yield) after solvent removal from a red band.

**Reaction of Cp(PPh$_3$)$_2$RuCH$_2$C=CPh (7) with Fe$_2$(CO)$_9$**

A stirred solution of Cp(PPh$_3$)$_2$RuCH$_2$C=CPh (0.75 g, 0.93 mmol) in THF (35 mL) was charged with Fe$_2$(CO)$_9$ (0.73 g, 2.0 mmol), as a solid at room temperature. After 2 hours of stirring, the solvent was removed under reduced pressure and the resulting red residue was dissolved in CH$_2$Cl$_2$ and chromatographed on an alumina column (3 x 30 cm). Elution with CH$_2$Cl$_2$ yielded a yellow band that gave 0.12 g (23% yield) of Cp(PPh$_3$)(CO)RuCH$_2$C=CPh (9) as an orange solid upon solvent removal in vacuo.

IR (THF) 1916.

$^1$H NMR (CDCl$_3$) $\delta$ 7.5 (m, 20 H, Ph), 4.91 (s, 5 H, Cp), 2.55 (s, 2 H, CH$_2$).
$^{13}$C\{H\} NMR (CDCl$_3$) δ 217.8 (Ru-CO), 170.0, 149.9 (C≡C), 135-125 (Ph), 90.6 (Cp), 15.2 (CH$_2$).

$^{31}$P\{H\} NMR δ 41.0 (s).

**Reaction of Cp(PPh$_3)_2$RuCH$_2$C≡CPh (7) with W(CO)$_5$THF**

A solution of W(CO)$_6$ (0.11 g, 0.30 mmol) in THF (50 mL) at room temperature was charged with trimethylamine-N-oxide (TMNO) (0.067 g, 0.60 mmol) as a solid with stirring. After 2 hours, an IR spectrum showed that at least 60% of the W(CO)$_6$ had been converted to W(CO)$_5$THF (new ν$_{C=O}$ stretches at 2067 (w), 2010 (m), 1928 (vs), and 1897 (s) cm$^{-1}$). The reaction solution was then cooled to 0° C, and Cp(PPh$_3)_2$RuCH$_2$C≡CPh (0.20 g, 0.24 mmol) was added as a solid. The solution was heated at reflux temperature for 24 hours before solvent removal in vacuo. The red residue was dissolved in CH$_2$Cl$_2$ (2 mL) and placed upon a column of alumina (2 x 20 cm) packed in hexane. Elution with a solution of 1:1 hexane/diethyl ether gave a yellow band which yielded 0.021 g of a yellow solid of Cp(CO)(PPh$_3$)RuCl$_5^{0a}$ (identified by a characteristic ν$_{C=O}$ absorption at 1958 cm$^{-1}$ and by a $^1$H NMR signal for the Cp protons at δ 4.61) which apparently formed from reaction with CH$_2$Cl$_2$. No other product was isolated from this column.

4) **Reactions of Cp(CO)$_3$WCH$_2$C≡CPh with Rhodium and Platinum**

**Containing Reagents**

Reaction of Cp(CO)$_3$WCH$_2$C≡CPh with [Rh(COD)Cl]$_2$
To a solution of Cp(CO)₃WCH₂C≡CPh (0.48 g, 1.1 mmol) in hexane (45 mL) at room temperature was added [Rh(COD)Cl]₂ (0.49 g, 0.50 mmol) as a solid. No reaction to form new products was observed via examination of solution by IR after 6 hours at reflux temperature. Upon cooling the solution to room temperature, solvent was removed under reduced pressure, and THF (45 mL) was added to dissolve the residue. After the solution had been stirred for 36 hours at room temperature, an IR spectrum taken of the reaction solution showed complete loss of νC≡C at 2190 cm⁻¹. However, a clean product was not obtained either by chromatography (decomposition) or by recrystallization.

**Reaction of Cp(CO)₃WCH₂C≡CPh with Rh₄(CO)₁₂**

A solution of Cp(CO)₃WCH₂C≡CPh (0.20 g, 0.44 mmol) in hexane (50 mL) at room temperature was charged with 0.40 g (0.53 mmol) of Rh₄(CO)₁₂ as a solid. After the solution had been stirred for 24 hours at room temperature, an IR spectrum showed loss of the tungsten propargyl νC=O stretches at 2021 (m) and 1945 (s) cm⁻¹ and the appearance of two new stretches at 1937 (s) and 1818 (w). No change was noted in the Rh₄(CO)₁₂ νC=O stretches, however. Solvent was removed under vacuum, and the purple residue was dissolved in CH₂Cl₂ (2 mL) and placed on a column (2 x 20 cm) of alumina packed in hexane. Elution with diethyl ether gave a large purple band that yielded 0.056 g of a brown solid upon solvent removal in vacuo.

IR (THF) 2062 (s), 1993 (vs).

¹H NMR (CDCl₃) δ 7.5-7.2 (m, 5 H, Ph), 5.19 (s, 5 H, Cp), 3.25 (d, J = 2.2, 1 H of CH₂?), 2.65 (s, 1 H of CH₂). NOTE: Spectrum not clean.
Owing to low yields and product instability, this system was not examined further.

**Reaction of Cp(CO)$_3$WCH$_2$C≡CPh with CpRh(CO)$_2$**

A solution of Cp(CO)$_3$WCH$_2$C≡CPh (0.10 g, 0.22 mmol) in hexane (45 mL) was treated with 0.1 mL (0.20 g, d = 2.0 g/mL, 0.90 mmol) of CpRh(CO)$_2$ and heated at reflux temperature for 2 hours. Since no apparent reaction was observed via IR spectroscopy, the reaction solution was subjected to irradiation from a high-pressure Hg-vapor lamp (Hanovia) for 3 hours. The reaction solution darkened from yellow to orange and a yellow solid was also observed. The reaction mixture was then subjected to a Schlenk-filtration, and solvent was removed from the filtrate in vacuo. Both the solid and the residue from the filtrate were analyzed by NMR, and both showed a myriad of signals/products. Typical chromatography of the yellow solid yielded only a small amount (0.020 g) of a pink solid that was not present before chromatography, as ascertained by a comparison of its $^1$H NMR spectrum to the reaction solution spectrum taken before chromatography.

**Reaction of Cp(CO)$_3$WCH$_2$C≡CPh with Cp$_2$Rh$_2$(CO)$_3$**

A solution of Cp(CO)$_3$WCH$_2$C≡CPh (0.11 g, 0.24 mmol) and Cp$_2$Rh$_2$(CO)$_3$ (0.10 g, 0.24 mmol) in hexane (45 mL) was heated at reflux temperature for 48 hours. Upon cooling to room temperature, solvent was removed under reduced pressure to yield a red tar. The tar was dissolved in CH$_2$Cl$_2$ (2 mL) and loaded onto a column (2 x 20 cm) of alumina packed in hexane. Elution with hexane yielded a small amount of CpRh(CO)$_2$ as a
yellow band that disappeared (evaporated) upon removal of solvent in vacuo. Elution with 1.0% diethyl ether in hexane gave three bands: an orange band and a pink band that yielded multiple unidentified products upon solvent removal in vacuo, and a yellow band that gave 0.015 g of a yellow solid upon solvent removal under reduced pressure.

IR (CH$_2$Cl$_2$) 1969 (s), 1899 (m), 1880 (s).

$^1$H NMR (CDCl$_3$) $\delta$ 7.4-7.1 (m, Ph), 5.14 (s, Cp), 2.99 (s, CH$_2$).

**Reaction of Cp(CO)$_3$WCH$_2$C=CPH with (PPh$_3$)$_2$PtC$_2$H$_4$**

To a stirred solution of (PPh$_3$)$_2$PtC$_2$H$_4$ (0.71 g, 0.95 mmol) in ethylene-saturated THF (30 mL) at -78°C was added, over 5 minutes, an ethylene-saturated THF solution (10 mL) of Cp(CO)$_3$WCH$_2$C=CPH (0.40 g, 0.90 mmol). The initial yellow solution slowly darkened to red while warming to room temperature over 12 hours. A red tar was obtained upon evaporation of solvent under reduced pressure. The tar was dissolved in CH$_2$Cl$_2$ (2 mL) and introduced onto a Grade III alumina column initially packed in hexane. Elution with a solution of 1:1 hexane/diethyl ether removed a large yellow band resulting in 0.12 g of 10 (12% yield) upon solvent removal in vacuo.

IR (THF) 1913 (vs), 1801 (vs), 1703 (m).

$^1$H NMR (CD$_2$Cl$_2$) $\delta$ 7.7-7.0 (m, 35 H, Ph), 6.28 (d, $J_{HH} = 5$, $J_{PtH} = 15$, 1 H of CH$_2$), 6.10 (d, $J_{HH} = 5$, 1 H of CH$_2$), 4.96 (s, 5 H, Cp).

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) $\delta$ 158.7 (=C=), 139.6 (=CPH), 110.3 (d, $J_{PH} = 3$, =CH$_2$), 88.7 (Cp).

$^{31}$P($^1$H) NMR $\delta$ 28.7 (d, $J_{PP} = 4.9$, $J_{PtP} = 3157$), 18.9 (d, $J_{PP} = 4.9$, $J_{PtP} = 3796$).
Analysis was unsatisfactory.

5) Reactions of Other Propargyl and Allenyl Compounds

Reaction of (CO)\textsubscript{5}MnCH\textsubscript{2}C\equiv CPh with (PPh\textsubscript{3})\textsubscript{2}PtC\textsubscript{2}H\textsubscript{4}

A stirred solution of (CO)\textsubscript{5}MnCH\textsubscript{2}C\equiv CPh (0.14 g, 0.42 mmol) in THF (10 mL) at -20°C was treated with (PPh\textsubscript{3})\textsubscript{2}PtC\textsubscript{2}H\textsubscript{4} as a solid. After the solution warmed to 0°C over one hour, a 0.4 mL aliquot was withdrawn and examined directly by $^{31}$P NMR: $\delta$ 31.5 (s, $J_{\text{PP}} = 3208$). Attempts at the isolation of a solid were fruitless, as apparently the material decomposed at or near room temperature. Solvent removal under reduced pressure also caused product decomposition.

Reaction of Cp(CO)\textsubscript{2}FeCH\textsubscript{2}C\equiv CPh (5) with W(CO)\textsubscript{5}THF

A stirred solution of W(CO)\textsubscript{6} (0.43 g, 1.2 mmol) in THF (100 mL) at room temperature was treated with trimethylamine-N-oxide (TMNO) (0.27 g, 2.4 mmol) as a solid at once. After having been stirred for 1.5 hours, the solution darkened from yellow to brown, and an IR spectrum revealed that W(CO)\textsubscript{5}-THF (see page 36) was present in solution. Cp(CO)\textsubscript{2}FeCH\textsubscript{2}C\equiv CPh (0.30 g, 1.0 mmol) was added as a solid, and the solution was heated at reflux temperature for 9 hours. No reaction was observed via examination of the reaction solution by IR spectroscopy.

Reaction of Cp(CO)\textsubscript{2}FeCH\textsubscript{2}C\equiv CPh (5) with PPh\textsubscript{3}AuCl

An aliquot (0.2 mL) of a stirred solution of Cp(CO)\textsubscript{2}FeCH\textsubscript{2}C\equiv CPh (0.17 g, 0.57 mmol) and PPh\textsubscript{3}AuCl (0.31 g, 0.62 mmol) in THF (25 mL) at
room temperature was checked by solution IR spectroscopy after one hour. No reaction had occurred. Thus, the solution was cooled to -78°C and TlBF₄ (0.25 g, 0.62 mmol) was added as a solid at once. Upon warming to room temperature, the solution was filtered and solvent was removed from the filtrate under vacuum. Only a mixture of unidentifiable compounds was observed by ¹H NMR spectroscopy.

**Reaction of Cp(CO)₂RuCH₂C≡CPh (13) with excess PEt₃**

A stirred solution of Cp(CO)₂RuCH₂C≡CPh (0.17 g, 0.50 mmol) in THF (40 mL) at room temperature was treated dropwise with a 1.0 M solution (3.5 mL, excess) of PEt₃ in THF over 5 minutes. No reaction, including carbonyl insertion, was observed (by IR or NMR) even after 24 hours at reflux temperature. For example, the ¹H NMR spectrum revealed only the Ph (ca. 7.2, m, 5 H), Cp (5.27, s, 5 H), and CH₂ (2.17, s, 2 H) resonances for Cp(CO)₂RuCH₂C≡CPh.

**Reaction of Cp(CO)₂RuCH=CH₂ with p-MeC₆H₄S(O)₂N=C=O (TSI)**

A solution of Cp(CO)₂RuCH=CH₂ (0.15 g, 0.57 mmol) in THF (10 mL) at -78°C was treated with a slight excess of a standard 0.079 M TSI solution (8.0 mL, 0.63 mmol). After the solution warmed to room temperature over 2 hours, an aliquot was withdrawn and its solvent removed in vacuo. The red residue was then dissolved in CDCl₃ (0.5 mL) for ¹H NMR analysis (δ 7.4-6.9 (m, Ph), 6.60 (t, JHH = 2.0, CH), 4.25 (s, Cp), 2.85 (d, JHH = 2.0, CH₂), 2.56 (s, Me)).
Several attempts at recrystallization of residues remaining after solvent removal under reduced pressure were fruitless. A solid was never obtained.

**Reaction of Cp(CO)$_2$RuCH$_2$C≡CPh (13) with CpRh(C$_2$H$_4$)$_2$**

To a stirred solution of Cp(CO)$_2$RuCH$_2$C≡CPh (0.14 g, 0.43 mmol) in hexane (35 mL) at 0°C was charged 0.10 g (0.45 mmol) of CpRh(C$_2$H$_4$)$_2$ as a solid at once. The yellow solution was heated at reflux temperature for 24 hours. No reaction was evidenced by IR or NMR spectroscopies.

**Attempted Preparation of Cp(P(OMe)$_3$)$_2$RuCH$_2$C≡CPh**

A stirred solution of Cp(P(OMe)$_3$)$_2$RuCl in THF (150 mL) at -78°C was treated with a diethyl ether (40 mL) solution of 10 mmoles of ClMgCH$_2$C≡CPh, as prepared in the Grignard Machine. The clear yellow solution turned greenish and cloudy over a 6 hour warm-up to room temperature, followed by 12 hours at room temperature. Filtration of the solution followed by toluene (2 x 100 mL) extractions yielded only a complex mixture of products (by $^1$H NMR) upon solvent removal in vacuo.

6) Miscellaneous Preparations and Reactions

**Preparation of $p$-MeC$_6$H$_4$S(O)$_2$OCH$_2$C≡CPh (12)**

In the drybox, 21 g (0.38 mol) of KOH was pulverized with a mortar and pestle and charged to a small powder addition funnel. Meanwhile, outside the box (Schlenk-line), a solution of PhC≡CCH$_2$OH (5.0 g, 38 mmol) and $p$-MeC$_6$H$_4$S(O)$_2$Cl (8.7 g, 46 mmol) in diethyl ether (100 mL) was cooled
to -10°C with a MeOH/ice bath. With very vigorous stirring, the colorless solution was treated with the solid KOH, in small increments, over 45 minutes. No excess heat was observed during the addition. After stirring at -10°C for one hour, the precipitate-laiden (KCl) suspension was added to a 500 mL separatory funnel containing 100 mL of ice water. The aqueous layer was extracted with ether (2 x 50 mL) and the combined organics were dried over MgSO$_4$ for an hour. Solvent was removed under reduced pressure to yield 8.0 g (75%) of a fluffy colorless solid, 12.

$^1$H NMR (CDCl$_3$) $\delta$ 7.85 (m, 5 H, Ph), 7.28-7.05 (m, 4 H, C$_6$H$_4$), 4.96 (s, 2 H, CH$_2$), 2.39 (s, 3 H, Me).

$^{13}$C NMR (CDCl$_3$) $\delta$ 145.0 (m, C$_6$H$_4$ and Ph), 88.9 (s, PhC=C-), 80.6 (t, $J_{CH}$ = 8.0, PhC=C-), 58.6 (t, $J_{CH}$ = 156, CH$_2$), 21.5 (quartet, $J_{CH}$ = 127, Me).

EI MS (relative intensity) 286.0667 (exact M$,^+$, 5.2; calcd for C$_{16}$H$_{14}$O$_3$S: 286.0664), 115 (PhC=CCH$_2^+$, 100).

**Preparation of Cp(CO)$_2$RuCH$_2$C=CPH (13) from p-MeC$_6$H$_4$S(O)$_2$OCH$_2$C=CPH and [Cp(CO)$_2$Ru]$	ext{'}$**

A stirred solution of [Cp(CO)$_2$Ru]$^-$ in THF (200 mL) at -78°C was treated with 1 equivalent of the tosylate (1.8 g, 6.3 mmol) in 30 mL of THF. The mixture was allowed to warm to room temperature over 2 hours, and solvent was removed under vacuum to leave a brown gummy residue. The residue was extracted with hexane (2 x 100 mL, 2 x 50 mL), and the combined extracts were filtered and concentrated to 10 mL to yield 1.2 g (57%) of Cp(CO)$_2$RuCH$_2$C=CPH after decantation and drying under reduced pressure.
Preparation of \( p-\text{MeC}_6\text{H}_4\text{S(O)}_2\text{NH}_2 \)

A stirred solution of TSI (0.30 mL, 2.0 mmol) in benzene (10 mL) at room temperature was treated with 3 drops of water (excess). After stirring at room temperature for 2 hours, the colorless solid was collected on a frit, washed with hexane (2 x 10 mL) and dried under vacuum (0.30 g, 88% yield).

\(^1\)H NMR (CDCl\(_3\)) \( \delta \) 7.8-7.3 (m, 4 H, \( \text{C}_6\text{H}_4 \)), 4.92 (s, br, 2 H, NH\(_2\)), 2.43 (s, 3 H, Me).

\(^{13}\)C\(^{(1)}\)H NMR (CDCl\(_3\)) \( \delta \) 143.5, 129.6, 126.4, (\( \text{C}_6\text{H}_4 \)), 21.4 (s, Me).

EI MS (relative intensity) 171.0349 (exact M\(^+\), 34.0; calcd. for \( \text{C}_7\text{H}_9\text{NO}_2\text{S} \): 171.0354), 155 (M\(^+\) - NH\(_2\), 31.6), 91 (MeC\(_6\text{H}_4^+\), 100).

Anal Calcd. for \( \text{C}_7\text{H}_9\text{NO}_2\text{S} \): C, 49.10; H, 5.30; Found: C, 49.28; H, 5.25%.

Reaction of \( (\text{PPh}_3)_2\text{PtC}_2\text{H}_4 \) with \( p-\text{MeC}_6\text{H}_4\text{S(O)}_2\text{NH}_2 \)

A stirred solution of \( p-\text{MeC}_6\text{H}_4\text{S(O)}_2\text{NH}_2 \) (0.090 g, 0.53 mmol) in benzene (20 mL) at room temperature was charged with \( (\text{PPh}_3)_2\text{PtC}_2\text{H}_4 \) (0.40 g, 0.54 mmol) as a solid at once. The initial nearly colorless solution/suspension darkened to yellow over 1.5 hours. Solution volume was reduced to about 4 mL under vacuum, and the cloudy suspension was filtered. Solvent was removed from the filtrate under reduced pressure, and hexane (10 mL) was added while stirring the mixture vigorously. After 18 hours, a pink-orange solid (0.36 g, 76%) was collected on a frit and dried in vacuo.

\(^1\)H NMR (CDCl\(_3\)) \( \delta \) 8.0-7.0 (m, 6 Ph and \( \text{C}_6\text{H}_4 \)), 3.18 (s, br, 2 H, NH\(_2\)), 2.27 (s, 3 H, Me).
\(^{31}\)P\(^{1}\)H NMR (CDCl\(_3\)) \(\delta \) 8.0 (s, \(J_{\text{PtP}} = 3449\)).

FAB MS (rel. intensity) 890 (M\(^+\), (PPh\(_3\))\(_2\)Pt(p-MeC\(_6\)H\(_4\)S(O)\(_2\)NH\(_2\)), 100), 719 ((PPh\(_3\))\(_2\)Pt\(^+\), 60.3).

**Preparation of (PPh\(_3\))\(_2\)Pt(PhC≡CPh)**

A mixture of PhC≡CPh (0.060 g, 0.33 mmol) and (PPh\(_3\))\(_2\)PtC\(_2\)H\(_4\) (0.25 g, 0.33 mmol) was stirred in THF (15 mL) for 30 minutes before solvent was removed under reduced pressure.

\(^{13}\)C\(^{1}\)H NMR (CDCl\(_3\)) \(\delta \) 124.9 (m, C≡C).

**B. Reactions of Ruthenium and Iron Propargyl and Allenyl Complexes with Platinum(0) Reagents**

1) Reactions with (PPh\(_3\))\(_2\)PtC\(_2\)H\(_4\) and Pt(PPh\(_3\))\(_4\)

**Reaction of Cp(CO)\(_2\)RuCH\(_2\)C≡CPh (13) with Pt(PPh\(_3\))\(_4\)**

To a stirred solution of Cp(CO)\(_2\)RuCH\(_2\)C≡CPh (13) (0.55 g, 1.6 mmol) in THF (100 mL) at room temperature was added Pt(PPh\(_3\))\(_4\) (2.7 g, 2.2 mmol) as a solid. The orange solution was heated at reflux temperature for 9 hours, during which time the solution became deep red. After cooling to room temperature, the solution was concentrated \textit{in vacuo} to about 10 mL, and 20 mL of hexane was added with stirring. The red solution was cooled to -23°C for 12 hours and filtered to give a yellow solid of Cp(CO)Ru-(\(\mu-\eta^{2},\eta^{1}\)-CH\(_2\)=C=C(Ph))Pt(PPh\(_3\))\(_2\), 14a. Repeated concentration/recrystallization of the resultant mother liquors gave an overall 56% yield (0.93g) of 14a, mp 175°C dec.
IR (CH$_2$Cl$_2$) 1912.

$^1$H NMR (CDCl$_3$) $\delta$ 7.9-6.9 (m, 7 Ph) 5.43 (d, $J_{HH} = 2.2, J_{PH} = 17.8, 1$ H of CH$_2$), 4.89 (d, $J_{HH} = 2.2, J_{PH} = 13.5, 1$ H of CH$_2$), 4.26 (s, 5 H, Cp).

$^{13}$C($^1$H) NMR (CDCl$_3$) $\delta$ 206.6 (s, $J_{PtC} = 48$, Ru-CO), 165.3 (s, =C=), 149.1 (s, =C(Ph)), 97.2 (d, $J_{PC} = 2.3, J_{PtC} = 32$, =CH$_2$), 85.2 (s, Cp).

$^{13}$C NMR (CDCl$_3$) $\delta$ 97.2 (dt, $J_{PC} = 2.3, J_{CH} = 160, J_{PtC} = 32$, =CH$_2$).

$^{31}$P($^1$H) NMR (CDCl$_3$) $\delta$ 23.6 (d, $J_{PP} = 4.2, J_{PtP} = 2766$), 21.5 (d, $J_{PP} = 4.2, J_{PtP} = 3689$).

FAB MS $^{102}$Ru isotope, (relative intensity) 1029 (M$^+$, 4.3), 1001 (M$^+$ - CO, 21), 719 (Pt(PPh$_3$)$_2$+, 100).

Anal. Calcd. for C$_{51}$H$_{42}$O$_2$PtRu: C, 59.53; H, 4.11; Found: C, 59.58; H, 3.75%.

As an alternative to the above, a stirred solution of Cp(CO)$_2$RuCH$_2$C=CPPh (13) (0.11 g, 0.31 mmol) and (PPh$_3$)$_2$PtC$_2$H$_4$ (0.30 g 0.40 mmol) in ethylene-saturated THF (15 mL) was heated at reflux temperature for 20 hours. Work-up was as above, except that only one recrystallization was necessary owing to no free PPh$_3$ being present at the completion of the reaction.

Reaction of Cp(CO)$_2$FeCH$_2$C=CPPh (5) with Pt(PPh$_3$)$_4$

A solution of Cp(CO)$_2$FeCH$_2$C=CPPh (5) (0.25 g, 0.86 mmol) and Pt(PPh$_3$)$_4$ (1.3 g, 1.0 mmol) in THF (80 mL) was heated at reflux temperature for 2 hours before the orange solid Cp(CO)Fe-(µ-η$_2$-η$_1$-CH$_2$=C(Ph))Pt(PPh$_3$)$_2$ (14 b) was isolated as above (0.68 g, 80% yield), mp 160°C dec.

IR (CH$_2$Cl$_2$) 1896.
$^1$H NMR (CDCl$_3$) $\delta$ 7.7-6.9 (m, 7 Ph), 5.26 (d, $J_{HH} = 2.1$, $J_{PtH} = 19.7$, 1 H of CH$_2$), 4.83 (d, $J_{HH} = 2.1$, $J_{PtH} = 14.3$, 1 H of CH$_2$), 3.76 (s, 5 H, Cp).

$^{13}$C($^1$H) NMR (CDCl$_3$) $\delta$ 220.4 (d, $J_{PtC} = 8.0$, Fe-CO), 173.3 (s, =C=), 149.8 (s, =C(Ph)), 96.9 (d, $J_{PC} = 3.5$, $J_{PtC} = 36$, =CH$_2$), 82.6 (s, Cp).

$^{31}$P($^1$H) NMR (CDCl$_3$) $\delta$ 27.7 (d, $J_{PP} = 1.0$, $J_{PpP} = 3500$), 26.0 (d, $J_{PP} = 1.0$, $J_{PpP} = 2813$).

FAB MS (relative intensity) 984 (M$^+$, 1.7), 956 (M$^+$ - CO, 25.6), 840 (M$^+$ - (PhC=CH$_2$), 100).

Chemical analysis calculated for C$_{51}$H$_{42}$OP$_2$PtFe: C, 62.20; H, 4.40; Found: C, 62.41; H, 4.49%.

**Reaction of Cp(CO)$_2$RuCH=C=CH$_2$ with (PPh$_3$)$_2$PtC$_2$H$_4$**

To a stirred suspension of (PPh$_3$)$_2$PtC$_2$H$_4$ (1.6 g, 2.1 mmol) in hexane (40 mL) at -20°C was added a hexane solution (15 mL) of Cp(CO)$_2$RuCH=C=CH$_2$ (0.50 g, 1.9 mmol) via double-ended needle. The stirred yellow solution/white suspension was allowed to warm to room temperature over one hour. The reaction was complete in two hours at room temperature as determined by $^{31}$P($^1$H) NMR spectroscopy (vide infra) and as evidenced by a gradual change in color of the suspended particles from white to yellow. The yellow solid of Cp(CO)Ru(μ-η$_2$CO$^{1}$CH$_2$=C=C(H))Pt(PPh$_3$)$_2$ (15a) (1.6 g, 87% yield) was collected on a frit and washed with hexane (3 x 10 mL) and dried in vacuo, mp 160°C dec.

IR(CH$_2$Cl$_2$) 1912.

$^1$H NMR (CDCl$_3$) $\delta$ 8.0-7.2 (m, 6 Ph), 6.61 (m, $J_{PtP} = 33.0$, 1 H, C(H)), 5.44 (d, $J_{HH} = 2.5$, $J_{PtH} = 19.2$, 1 H of CH$_2$), 4.66 (d, $J_{HH} = 2.5$, $J_{PtH} = 15.0$, 1 H of CH$_2$), 4.52 (s, 5 H, Cp).
$^{13}$C($^1$H) NMR (CDCl$_3$): $\delta$ 206.9 (s, $J_{PC} = 38.4$, Ru-CO), 168.0 (s, =C=), 114.7 (d, $J_{PC} = 85.0$, $J_{PtC} = 725$, =C(H)), 95.6 (d, $J_{PC} = 3.1$, $J_{PtC} = 36.5$, =CH$_2$), 82.3 (s, Cp).

$^{13}$C NMR (CDCl$_3$): $\delta$ 95.6 (dt, $J_{CP} = 3.1$, $J_{CH} = 160$, $J_{PtC} = 36.5$, =CH$_2$).

$^{31}$P($^1$H) NMR (CDCl$_3$): $\delta$ 27.7 (d, $J_{PP} = 4.3$, $J_{PtP} = 2852$), 21.8 (d, $J_{PP} = 4.3$, $J_{PtP} = 3620$).

FAB MS: 102Ru isotope, (relative intensity) 953 (M$^+$, 7.7), 886 (M$^+$ - CO - C$_3$H$_3$, 8.0), 719 (Pt(PPh$_3$)$_2^+$, 76.0).

Anal. Calcd. for C$_{45}$H$_{38}$OP$_2$PtRu: C, 56.72; H, 3.99; Found: C, 56.74; H, 4.08%.

Alternatively, compound 15a could be prepared exactly as above in THF solution rather than hexane suspension, with identical results. If the reaction does not go to completion, a one hour reflux in hexane or THF serves to force the reaction to completion.

**Reaction of Cp(CO)$_2$FeCH=C=CH$_2$ with (PPh$_3$)$_2$PtC$_2$H$_4$**

To a stirred solution of Cp(CO)$_2$FeCH=C=CH$_2$ (0.33 g, 1.5 mmol) in THF (50 mL) at -15°C was added (PPh$_3$)$_2$PtC$_2$H$_4$ (1.0 g, 1.3 mmol) as a solid. The colorless solid dissolved in the yellow solution over 30 minutes. The orange solution warmed to room temperature during one hour. The solution was then concentrated to about 10 mL in vacuo, and 20 mL of hexane was added with vigorous stirring. After cooling at -23°C for 12 hours, orange Cp(CO)Fe-(μ-η$^2$=η$^1$-CH$_2$=C=C(H))Pt(PPh$_3$)$_2$ (15 b) (0.730 g, 62% yield) was collected on a frit, washed with hexane (2 x 20 mL), and dried in vacuo, mp 140°C dec.

IR (CH$_2$Cl$_2$) 1899.
$^1$H NMR (CDCl$_3$) δ 8.1-7.2 (m, 6 Ph), 7.03 (m, $J_{PtH} = 36.8$, 1 H, C(H)), 5.43 (d, $J_{HH} = 1.0$, $J_{PtH} = 10.0$, 1 H of CH$_2$), 4.67 (d, $J_{HH} = 1.0$, $J_{PtH} = 10.1$, 1 H of CH$_2$), 4.05 (s, 5 H, Cp).

$^{13}$C($^1$H) NMR (CDCl$_3$) δ 220.2 (d, $J_{PC} = 8.6$, $J_{PtC} = 84.6$, Fe-CO), 176.4 (s, =C=), 122.3 (dd, $J_{PC} = 80.2$, $J_{PtC} = 715$, C(H)), 94.3 (d, $J_{PC} = 2.9$, $J_{PtC} = 41.7$, =CH$_2$), 79.7 (s, Cp).

$^{31}$P($^1$H) NMR (CDCl$_3$) δ 30.9 (d, $J_{PP} = 1.0$, $J_{PtP} = 2925$), 27.7 (d, $J_{PP} = 1.0$, $J_{PtP} = 3415$).

FAB MS (relative intensity) 908 (M+, 2.6), 880 (M$^+$ - CO, 15.2), 840 (M$^+$ - CO - C$_3$H$_3$, 48.9), 719 (Pt(PPh$_3$)$_2^+$, 100).

Anal. Calcd. for C$_{45}$H$_{38}$OP$_2$PtFe: C, 59.55; H, 4.22; Found: C, 59.82; H, 4.21%.

2) Control Reactions with (PPh$_3$)$_2$Pt(CO)$_2$

**Reaction of (PPh$_3$)$_2$PtC$_2$H$_4$ with CO**

A THF (25 mL) solution of (PPh$_3$)$_2$PtC$_2$H$_4$ (0.68 g, 0.91 mmol) at room temperature was exposed to a carbon monoxide purge via a long needle through a pierceable septum in the reaction flask. Excess gas was vented through another shorter needle connected to a mineral oil bubbler. Immediately the solution changed from colorless to red. Solvent was removed under reduced pressure, and the red residue was treated with hexane (15 mL) for 36 hours to cause for the formation of a solid. The pink solid was collected on a frit. The $^{31}$P($^1$H) NMR (δ 7.7 ($J_{PtP} = 3232$) spectrum was identical to that obtained by Halpern et al.$^{70}$
Reaction of $\text{Cp(CO)}_2\text{RuCH}_2\text{C}=$CPh (13) with (PPh$_3)_2\text{Pt(CO)}_2$

A solution of $\text{Cp(CO)}_2\text{RuCH}_2\text{C}=$CPh (13) (0.10 g, 0.30 mmol) and
(PPh$_3)_2\text{Pt(CO)}_2$ (0.25 g, 0.32 mmol) in THF (25 mL) was heated at reflux temperature for 2 hours. After cooling to room temperature, solvent was evaporated in vacuo and recrystallization from 2:1 hexane/THF (15 mL) yielded 0.28 g (91%) of 14a.

Reaction of $\text{Cp(CO)}_2\text{FeCH}_2\text{C}=$CPh (5) with (PPh$_3)_2\text{Pt(CO)}_2$

A solution of $\text{Cp(CO)}_2\text{FeCH}_2\text{C}=$CPh (5) (0.093 g, 0.32 mmol) and
(PPh$_3)_2\text{Pt(CO)}_2$ (0.25 g, 0.32 mmol) in THF (25 mL) was heated at reflux temperature for 24 hours. Less than 10% conversion to 14b was noted by $^1\text{H}$ and $^{31}\text{P}(^1\text{H})$ NMR spectroscopy.

Reaction of $\text{Cp(CO)}_2\text{RuCH}=$C=CH$_2$ with (PPh$_3)_2\text{Pt(CO)}_2$

A solution of $\text{Cp(CO)}_2\text{RuCH}=$C=CH$_2$ (0.093 g, 0.30 mmol) and
(PPh$_3)_2\text{Pt(CO)}_2$ (0.25 g, 0.32 mmol) in THF (25 mL) was freed of solvent in vacuo after 2 hours of stirring at room temperature. Recrystallization of the residue from 2:1 hexane/THF yielded 0.26 g (91%) of 15a.

Reaction of $\text{Cp(CO)}_2\text{FeCH}=$C=CH$_2$ with (PPh$_3)_2\text{Pt(CO)}_2$

To a stirred solution of $\text{Cp(CO)}_2\text{FeCH}=$C=CH$_2$ (0.070 g, 0.32 mmol) in THF (25 mL) at room temperature was added (CO)$_2\text{Pt(PPh}_3)_2$ (0.250 g, 0.322 mmol) as a solid. The reaction was complete after stirring at room temperature for 2 hours, as ascertained by $^1\text{H}$ and $^{31}\text{P}(^1\text{H})$ NMR spectroscopy. Solvent was removed under reduced pressure, and the red
residue was subjected to recrystallization from 2:1 hexane/diethyl ether to give 0.26 g (90%) of 15 b.

C. Reactions of Binuclear Complexes with Fe₂(CO)₉, Ru₃(CO)₁₂, and Carbon Monoxide

1) With Fe₂(CO)₉

Reaction of Cp(CO)Ru-(μ-η²,η¹-C₄H₂=C=C(Ph))Pt(PPh₃)₂ (14a) with Fe₂(CO)₉

To a stirred solution of 14a (1.1 g, 1.1 mmol) in THF (100 mL) at room temperature was added Fe₂(CO)₉ (0.52 g, 1.4 mmol) as a solid. The stirred suspension turned red over 36 hours. Solvent was removed in vacuo to yield a red tar which was dissolved in CH₂Cl₂ (2 mL), and the resulting solution was introduced onto a Grade III (6% H₂O) alumina column (20 x 2 cm) packed in hexane. Elution with a 4% solution of diethyl ether in hexane gave Cp(CO)Ru-(μ-η²,η¹-C₄H₂=C=C(Ph))Pt(PPh₃)(CO) (16a) (0.11 g, 13% yield) as a yellow solid upon solvent removal in vacuo, mp 160°C dec.

IR (CH₂Cl₂) 2018 (s), 1947 (s).

¹H NMR (CDCl₃) δ 8.2-7.3 (m, 4 Ph), 5.60 (s, Jₚₚ = 17.7, 1 H of CH₂), 5.02 (s, Jₚₚ = 14.3, 1 H of CH₂), 4.80 (s, 5 H, Cp).

¹³C¹H NMR (CDCl₃) δ 204.2 (s, Ru-CO), 193.2 (d, JₚC = 5.0, Pt-CO), 163.3 (d, JₚC = 5.0, =C=), 148.2 (s, =C(Ph)), 98.4 (s, =CH₂), 84.6 (s, Cp).

³¹P¹H NMR (CDCl₃) δ 24.4 (s, Jₚₚ = 3277).
FAB MS$^{102}$Ru isotope, (relative intensity) 795 (M+, 3.8), 767 (M+ - CO, 4.9), 739 (M+ - 2CO, 6.6).

Anal. Calcd. for C$_{34}$H$_{27}$O$_2$PPtRu: C, 51.39; H, 3.42; Found: C, 51.23; H, 3.37%.

Further elution with a 15% diethyl ether in hexane solution gave the heterotrinuclear Cp(CO)Ru-(μ-η$^2$,η$^2$,η$^1$-CH$_2$=C(C(Ph))Fe(CO)$_3$Pt(PPh$_3$)(CO) (17) (0.18 g, 17% yield) as an orange solid upon solvent removal in vacuo, mp 180°C dec.

IR (CH$_2$Cl$_2$) 2025 (s), 1996 (vs), 1954 (m).

$^1$H NMR (CDCl$_3$) δ 7.7-7.0 (m, 4 Ph), 4.82 (s, 5 H, Cp), 3.86 (d, $J_{HH}$ = 5.1, 1 H of CH$_2$), 2.82 (d, $J_{HH}$ = 5.1, $J_{PH}$ = 21.1, 1 H of CH$_2$).

$^{13}$C($^1$H) NMR (CDCl$_3$) δ 213.6 (d, $J_{PC}$ = 4.2, $J_{PtC}$ = 50.0, Fe-CO's), 203.5 (s, $J_{PtC}$ = 50.0, Ru-CO), 191.7 (d, $J_{PC}$ = 4.9, Pt-CO$^*$), 187.7 (d, $J_{PC}$ = 5.0, =C=*$), 152.2 (d, $J_{PC}$ = 2.7, -C(Ph)), 84.7 (s, Cp), 13.4 (s, =CH$_2$).

*Assignments arbitrary.

$^{13}$C NMR (CDCl$_3$) δ 133.4 (t, $J_{CH}$ = 156, =CH$_2$).

$^{31}$P($^1$H) NMR (CDCl$_3$) δ 27.7 (s, $J_{PtP}$ = 3074).

FAB MS$^{102}$Ru isotope, (relative intensity) 935 (M+, 5.7), 853 (M+ - 3CO, 10.4).

Anal. Calcd. for C$_{37}$H$_{27}$FeO$_5$PPtRu: C, 47.54; H, 2.89; Found: C, 47.71; H, 2.87%.

**Reaction of Cp(CO)Ru-(μ-η$^2$,η$^2$,η$^1$-CH$_2$=C(C(Ph))Fe(CO)$_3$Pt(PPh$_3$)(CO) (17) under UV Irradiation and Thermal Conditions**

A sample of 17 (0.050 g, 0.054 mmol) was dissolved in toluene-d$_8$ (0.5 mL) in an NMR tube and heated in an oil bath for 3 hours at 90°C. No
reaction was noted via $^1$H or $^{31}$P($^1$H) NMR spectroscopy. The room temperature solution was then exposed to light with a wavelength of 254 nm in a Rayonet apparatus (10 lamps) for 24 hours. A 1:1 mixture of 17/new product (C17) was obtained, as ascertained by $^1$H NMR spectroscopy.

Data for C17 (obtained from a solution containing a mixture of 17 and C17):

$^1$H NMR (toluene-$d_8$) $\delta$ 7.4-6.8 (m, 4 Ph), 4.85 (s, 5 H, Cp) 3.75 (d, $J_{HH} = 3.0$, $J_{PtP} = 9.0$), 1 H of CH$_2$), 3.61 (d, $J_{HH} = 3.0$, $J_{PtP} = 8.0$, 1 H of CH$_2$).

$^{31}$P($^1$H) NMR (toluene-$d_8$) $\delta$ 26.2 (s, $J_{PtP} = 3398$).

The photochemical reaction was repeated on a larger scale in THF solvent with the same result. That is, only about one half of the 17 was converted to C17. Chromatography on alumina gave only 17 as an isolable species, as no C17 was eluted from the column.

**Reaction of Cp(CO)Fe($\mu$-$\eta^2$,$\eta^1$-CH$_2$=C=C(Ph))Pt(PPh$_3$)$_2$ (14 b) with Fe$_2$(CO)$_9$**

A stirred solution of 14 b (0.45 g, 0.46 mmol) in THF (100 mL) at room temperature was treated with Fe$_2$(CO)$_9$ (0.20 g, 0.55 mmol) as a solid in one portion. After 3 hours at reflux temperature, the reaction mixture was freed of solvent in vacuo to yield a red tar. The tar was dissolved in CH$_2$Cl$_2$ (2 mL) and chromatographed on an alumina column (3 x 30 cm) packed in hexane. Elution with a solution of 25:1 hexane/diethyl ether developed a brown band that yielded 0.11 g (32% yield) of a brown solid, Cp(CO)Fe($\mu$-$\eta^2$,$\eta^1$-CH$_2$=C=C(Ph))Pt(PPh$_3$)(CO) (16 b).

IR (THF) 2014 (s), 1962 (s).
$^1$H NMR (CDCl$_3$) $\delta$ 7.7-7.0 (m, 4 Ph), 5.50 (d, $J_{HH} = 1.6$, $J_{PtH} = 20$, 1 H of CH$_2$), 4.99 (d, $J_{HH} = 1.6$, $J_{PtH} = 16$, 1 H of CH$_2$), 4.37 (s, 5 H, Cp).

$^{31}$P($^1$H) NMR (CDCl$_3$) $\delta$ 26.9 (s, $J_{PtP} = 3381$).

FAB MS and elemental analysis were unsatisfactory.

Further elution with 3:1 hexane/ether yielded a yellow band that gave a yellow compound (18) (0.077 g) upon solvent removal in vacuo.

IR (CH$_2$Cl$_2$) 2028 (s), 2000 (m), 1985 (vs), 1931 (s).

$^1$H NMR (CDCl$_3$) $\delta$ 7.9-6.9 (m, Ph), 2.05 (d, $J_{PH} = 3.6$, $J_{PtP} = 35$).

$^{13}$C($^1$H) NMR (CDCl$_3$) $\delta$ 217.5 (s, $J_{PtC} = 33$, Fe-CO's), 194.2 (C= ?), 163.2, 161.3, 148.6, (all singlets, ?), 86.5 (s, =CH$_2$).

$^{31}$P($^1$H) NMR (CDCl$_3$) $\delta$ 19.2 (d, $J_{PP} = 3.5$, $J_{PtP} = 3682$, $J_{Pt'-P} = 215$), 12.9 (d, $J_{PP} = 3.5$, $J_{PtP} = 3478$, $J_{Pt'-P} = 215$).

FAB MS was inconclusive.

X-ray fluorescence showed a 2:1 ratio of platinum to iron atoms in the compound. The spectrum was calibrated by use of a sample of known composition (1:1) of platinum and iron atoms, 14 b.

**Reaction of Cp(CO)Ru($\mu$-$\eta^2$,$\eta^1$-CH$_2$=C=C(H))Pt(PPh$_3$)$_2$ (15a) with Fe$_2$(CO)$_9$**

A stirred solution of 15a (0.90 g, 0.95 mmol) in THF (100 mL) at room temperature was treated with Fe$_2$(CO)$_9$ (0.36 g, 0.99 mmol) as a solid. The orange suspension slowly turned into a red solution over 16 hours of stirring. Solvent was removed in vacuo, and the red residue obtained was chromatographed as above. Elution with a 25% solution of diethyl ether in hexane gave Cp(CO)Ru($\mu$-$\eta^2$,$\eta^2$,$\eta^1$-CH$_2$=C=C(H))Fe(CO)$_3$Pt(PPh$_3$)(CO) (19a) (0.16 g, 20% yield) as a red solid upon solvent removal in vacuo, mp 176°C dec.
IR (CH₂Cl₂) 2027 (s), 1997 (vs), 1953 (s).

¹H NMR (CDCl₃) δ 7.90 (d, JₚH = 10.7, JₚₜH = 47.0, 1 H, C(H)), 7.8-7.2 (m, 3 Ph), 4.64 (s, 5 H, Cp), 3.54 (d, JₜH = 4.9, JₚₜH = 11.4, 1 H of CH₂), 2.65 (dd, JₜH = 4.9, JₚH = 1.1, JₚₜH = 19.2, 1 H of CH₂).

¹³C{¹H} NMR (CDCl₃) δ 214.5 (d, JₚₗC = 4.2, JₚₜₗC = 48, Fe-CO's), 203.7 (s, JₚₜₗC = 9.5, Ru-CO), 194.9 (d, JₚC = 2.5, =C=), 194.1 (d, JₚC = 4.9, JₚₗC 61.4, Pt-CO*), 135.5 (d, JₚₗC = 5.4, JₚₗC = 702, =C(H)), 85.1 (s, Cp), 13.8 (s, JₚₗC = 42.3, =CH₂). *Assignments arbitrary.

³¹P{¹H} NMR (CDCl₃) δ 28.3 (s, JₚₘₗP = 3092).

FAB MS ¹⁰²Ru isotope, (relative intensity) 859 (M⁺, 36.0), 831 (M⁺ - CO, 59.2), 803 (M⁺ - 2CO, 35.9) 775 (M⁺ - 4CO, 48.5), 747 (M⁺ - 5CO, 96.8).

Anal. Calcd. for C₃₁H₂₃FeO₅PPtRu: C, 43.37; H, 2.70; Found: C, 43.27; H, 2.73%.

**Reaction of Cp(CO)Fe(μ-η²,η¹-CH₂=C=C(H))Pt(PPh₃)₂ (15 b) with Fe₂(CO)₉**

To a stirred solution of 15b (0.34 g, 0.37 mmol) in THF (30 mL) at room temperature was added Fe₂(CO)₉ (0.15 g, 0.41 mmol) as a solid. The orange suspension turned deep red over 21 hours of stirring at room temperature. After solvent removal in vacuo, the red residue was chromatographed as above. Elution with a solution of 10% diethyl ether in hexane gave Cp(CO)Fe(μ-η²,η²-CH₂=C=C(H))Fe(CO)₃Pt(PPh₃)(CO) (19 b) (0.078 g, 26% yield) as a red solid upon solvent removal in vacuo, mp 110°C dec.

IR (CH₂Cl₂) 2024 (s), 1994 (vs), 1951 (m).

¹H NMR (CDCl₃) δ 8.04 (dt, JₚH = 10, JₚₗH = 1.2, JₚₗₜH = 48, 1 H, C(H)), 7.8-7.1 (m, 3 Ph), 4.20 (s, 5 H, Cp), 3.41 (dd, JₚₗH = 5.0, JₚₗₜH = 1.0,
$J_{PH} = 18.3$, 1 H of CH$_2$, 2.26 (dt, $J_{HH} = 4.6$, $J_{HH} = 1.0$, $J_{PH} = 25.0$, 1 H of CH$_2$).

$^{13}$C({}^1H) NMR (CDCl$_3$) δ 214.6 (s, $J_{PC} = 52$, Fe-CO's), 210.3 (s, $J_{PTC} = 13$, Fe-CO), 194.7 (s, Pt-CO*), 193.5 (d, $J_{PC} = 4.0$, =C=), 139.1 (d, $J_{PC} = 5.0$, - C(H)), 81.4 (s, Cp), 18.8 (s, $J_{PTC} = 46.0$, =CH$_2$). *Assignments arbitrary.

$^{31}$P({}^1H) NMR (CDCl$_3$) δ 28.5 (s, $J_{PTP} = 3062$).

FAB MS (relative intensity) 813 (M+, 4.9), 785 (M$^+$ - CO, 21.4), 729 (M$^+$ - 3CO, 72.8), 701 (M$^+$ - 4CO, 73.1), 673 (M$^+$ - 5CO, 100).

Anal. Calcd. for C$_{31}$H$_{23}$O$_5$Fe$_2$PtP: C, 45.78; H, 2.85; Found: C, 44.64; H, 3.06%.

2) With Ru$_3$(CO)$_{12}$

**Reaction of Cp(CO)Ru-($\mu$-$\eta^2$,{$\eta^1$}-CH$_2$=C=C(Ph))Pt(PPh$_3$)$_2$ (14a) with Ru$_3$(CO)$_{12}$**

A stirred solution of 14a (0.20 g, 0.19 mmol) in THF (25 mL) at room temperature was treated with solid Ru$_3$(CO)$_{12}$ (0.15 g, 0.23 mmol) in one portion. After 15 hours of stirring of this solution, the solvent was removed under reduced pressure to give a red gummy residue. The residue was dissolved in CH$_2$Cl$_2$ (1.5 mL) and loaded onto a column of alumina (3 x 20 cm) packed in hexane. Elution with 25:1 hexane/diethyl ether gave an orange band which upon solvent removal in vacuo yielded 16a (0.062 g, 41% yield) as a yellow solid. Elution with 8:1 hexane/diethyl ether yielded a pink band which gave a red solid of Cp(CO)Ru-($\mu$-$\eta^2$,{$\eta^2$},{$\eta^1$}-CH$_2$=C=C(Ph))Ru(CO)$_3$Pt(PPh$_3$)(CO) (20a) (0.047 g, 26% yield) upon removal of solvent under vacuum: mp 90° C dec.
IR (THF) 2064 (w), 2036 (s), 2007 (vs), 1996 (vs), 1971 (vs), 1932 (m).

$^1$H NMR (CDCl$_3$) $\delta$ 7.7-7.0 (m, 4 Ph), 4.82 (s, 5 H, Cp), 3.63 (d, $J_{HH} = 5.5$, $J_{PH} = 29$, 1 H of CH$_2$), 2.52 (d, $J_{HH} = 5.5$, $J_{PPH} = 35$, 1 H of CH$_2$).

$^{13}$C($^1$H) NMR (CDCl$_3$) $\delta$ 200.0 (Ru-CO's), 184.5 (=C=), 147.4 (=C(Ph)), 135-125 (Ph), 83.5 (Cp), 22.1 (=CH$_2$).

$^{31}$P($^1$H) NMR (CDCl$_3$) $\delta$ 26.2 (s, $J_{PP} = 3000$).

**Reaction of Cp(CO)Fe(μ-η$_2^2$,η$_1$-CH$_2$=C=C(Ph))Pt(PPh$_3$)$_2$ (14 b) with Ru$_3$(CO)$_2$**

To a stirred solution of 14 b (0.20 g, 0.20 mmol) at room temperature in THF (20 mL) was added solid Ru$_3$(CO)$_2$ (0.18 g, 0.28 mmol) in one portion. As no reaction was evidenced by $^{31}$P NMR spectroscopy at room temperature, the red solution was heated at reflux temperature for 3 hours. After the solution cooled to room temperature, the reaction solvent was removed under reduced pressure to yield a dark red tar. The tar was dissolved in CH$_2$Cl$_2$ (2 mL) and placed on a column of alumina (3 x 20 mL) packed in hexane. Elution with a solution of 10:1 hexane/diethyl ether yielded a red band from which 0.017 g (11 % yield) of Cp(CO)Fe(μ-η$_2^2$,η$_1$-CH$_2$=C=C(Ph))Ru(CO)$_3$Pt(PPh$_3$)(CO) (20 b) was obtained as a red solid after solvent removal under reduced pressure.

IR (THF) 2068 (m), 2035 (vs), 2020 (sh), 2004 (vs), 1970 (m), 1960 (w).

$^1$H NMR (CDCl$_3$) $\delta$ 7.5-7.0 (m, 4 Ph), 4.31 (s, 5 H, Cp), 3.39 (d, $J_{HH} = 5.5$, $J_{PH} = 25$, 1 H of CH$_2$), 2.02 (d, $J_{HH} = 5.5$, $J_{PPH} = 30$, 1 H of CH$_2$).

$^{31}$P($^1$H) NMR (CDCl$_3$) $\delta$ 24.7 (s, $J_{PP} = 2964$).
Reaction of \( \text{Cp(CO)Ru-} \{ \mu-\eta^2, \eta^1 \text{CH}_2=\text{C} = \text{C(H)} \} \text{Pt(PPh}_3)_2 \) (15a) with Ru\(_3\)(CO)\(_{12}\)

To a stirred solution of 15a (0.41 g, 0.43 mmol) in THF (30 mL) at -78°C was added Ru\(_3\)(CO)\(_{12}\) (0.32 g, 0.50 mmol) as a solid. The orange suspension was allowed to warm to room temperature over 4 hours, and the resulting red solution was stirred at ambient temperature for 12 hours. Solvent was removed in vacuo, and the red residue was chromatographed as above. Elution with a solution of 25% diethyl ether in hexane gave \( \text{Cp(CO)Ru-} \{ \mu-\eta^2, \eta^2, \eta^1 \text{CH}_2=\text{C} = \text{C(H)} \} \text{Ru(CO)}_3 \text{Pt(PPh}_3)_3 \)(CO) (21a) (0.085 g, 22% yield) as a red solid upon solvent removal in vacuo, mp 107°C dec.

IR (CH\(_2\)Cl\(_2\)) 2038 (s), 2015 (m), 2000 (w), 1971 (s).

\(^1\)H NMR (CDCl\(_3\)) \( \delta \) 7.9-7.0 (m, 3 Ph), 4.96 (s, 5 H, Cp), 2.66 (s, br, 1 H of CH\(_2\)), 2.32 (m, 1 H of CH\(_2\)) [C(H) buried in phenyl region].

\(^{13}\)C\(^{(1}\)H\) NMR (CDCl\(_3\)) \( \delta \) 201.1 (s, Ru-CO's), 200.7 (s, Ru-CO), 199.9 (s, Pt-CO*), 196.9 (s, =C=*), 166.6 (d, \( J_{PC} = 4.0 \), C(H)), 89.4 (s, Cp), 44.4 (s, =CH\(_2\)). *Assignments arbitrary.

\(^{31}\)P\(^{(1}\)H\) NMR (CDCl\(_3\)) \( \delta \) 25.0 (s, \( J_{PP} = 2840 \)).

FAB MS \(^{102}\)Ru isotope, (relative intensity) 905 (M\(^+\), 1.0), 977 (M\(^+\) - CO, 3.6), 849 (M\(^+\) - 2CO, 2.3), 821 (M\(^+\) - 3CO, 5.5), 793 (M\(^+\) - 4CO, 2.7), 765 (M\(^+\) - 5CO, 5.5), 420 (M\(^+\) - Pt(PPh\(_3\))(CO), 100).

Reaction of \( \text{Cp(CO)Fe-} \{ \mu-\eta^2, \eta^1 \text{CH}_2=\text{C} = \text{C(H)} \} \text{Pt(PPh}_3)_2 \) (15 b) with Ru\(_3\)(CO)\(_{12}\)

A suspension of 15 b (0.30 g, 0.33 mmol) and Ru\(_3\)(CO)\(_{12}\) (0.22 g, 0.34 mmol) in hexane was heated at reflux temperature for 1 hour, during
which time a red solution/suspension was formed. While hot, the material was filtered through a pad of Celite, and solvent was removed from the red solution in vacuo to yield a red tar. The tar was dissolved in CH₂Cl₂ (3 mL) and added to a short Grade III alumina column (10 x 5 cm) packed in hexane. Rapid elution with hexane removed unwanted impurities as an orange band. Further rapid elution with THF yielded a red band. Compound Cp(CO)Fe-(μ-η²,η²,η¹-
CH₂=C=C(Ph))Ru(CO)₃Pt(PPh₃)(CO) (21 b) (0.095 g, 34% yield) was purified by recrystallization from THF/hexane, mp 97°C dec.

IR (CH₂Cl₂) 2036 (s), 2010 (vs), 1994 (m), 1970 (m).

¹H NMR (CDCl₃) δ 8.1-7.4 (m, 3 Ph), 7.21 (d, JₚH = 10.0, Jₚₚ = 50.0, 1 H, C(H)), 4.49 (s, 5 H, Cp), 2.75 (s, br, 1 H of CH₂), 2.34 (d, JₜH = 4.0, Jₜₚ = 20.0, 1 H of CH₂).

¹³C{¹H} NMR (CDCl₃) δ 216.1 (s, Jₚₚₚ = 53.0, Fe-CO), 208.0 (s, br, Ru-CO's) 199.7 (s, Pt-CO*), 196.7 (s, =C=), 167.4 (d, Jₚₚ = 4.0, C(H)), 86.1 (s, Cp), 44.9 (s, =CH₂). *Assignments arbitrary.

³¹P{¹H} NMR (CDCl₃) δ 24.1 (s, Jₚₚ = 2854).

FAB MS ¹⁰²Ru isotope, (relative intensity) 859 (M⁺, 35.6), 831 (M⁺ - CO, 59.2), 803 (M⁺ - 2CO, 35.9), 775 (M⁺ - 3CO, 48.5), 747 (M⁺ - 4CO, 98.7), 719 (M⁺ - 5CO, 100).

Anal. Calcd. for C₃₁H₂₃FeO₅PₙₚₚRu: C, 43.37; H, 2.70; Found: C, 43.35; H, 3.08%.

3) With Carbon Monoxide

Reaction of Cp(CO)Fe(μ-η²,η¹-CH₂=C=C(Ph))Pt(PPh₃)₂ (14b) with CO
A solution of 14 b (0.050 g, 0.051 mmol) in CD₂Cl₂ (0.50 mL) was prepared in a screw-cap NMR tube equipped with a pierceable septum. Carbon monoxide was then bubbled gently through the solution via a long needle through the septum. Excess gas was vented through another shorter needle connected to a mineral oil bubbler. After 18 hours of CO bubbling, 16 b and PPh₃ were observed as major reaction products by ³¹P{¹H} NMR. Only about 50% of starting 14 b was converted to Cp(CO)₂FeCH₂C≡CPh and (PPh₃)₂Pt(CO)₂. After exposure of the reaction solution, in an analogous manner, to argon for 18 hours, no new 14 b was observed in either ¹H or ³¹P NMR spectra. Instead, the relative intensities for the resonances of the products observed in a ratio of 2:2:1, were Cp(CO)₂FeCH₂C≡CPh, 16b, and Pt(PPh₃)₄, respectively. Other minor signals were observed in the spectra as well.

**Reaction of Cp(CO)Ru(μ-η²,η¹-CH₂=C≡C(Η))Pt(PPh₃)₂ (15a) with CO**

A solution of 15a (0.050 g, 0.053 mmol) in CD₂Cl₂ (0.50 mL) was prepared in a screw-cap NMR tube equipped with a pierceable septum. Carbon monoxide was bubbled through a needle in the septum, as above, for 3 hours. At this time, a ³¹P{¹H} NMR spectrum revealed complete loss of starting 15a and the appearance of a large broad signal at δ 7.5 ppm (s, Jₚₜₚ = 3275) as the major platinum-containing species [(PPh₃)₂Pt(CO)₂]⁷⁰. A ¹H NMR spectrum revealed replacement of resonances for 15a by those for Cp(CO)₂RuCH=C=CH₂ (esp. important signals: 5.37 (t, J_HH = 6.4, =CH), 5.28 (s, Cp), and 3.99 (d, J_HH = 6.4, =CH₂)).⁵⁸ Carbon monoxide was replaced by argon, and after 2 hours, ³¹P{¹H} and ¹H NMR spectra revealed nearly complete reverse reaction to starting 15a. This process
could be repeated two additional times (in each direction) without significant (25%) decomposition to intractable solid materials.

**Reaction of Cp(CO)Fe(μ-η^2,η^1-CH_2=C=C(H))Pt(PPh_3)_2 (15 b) with CO**

A solution of 15 b (0.050 g, 0.055 mmol) in CD_2Cl_2 (0.50 mL) was prepared in a screw-cap NMR tube equipped with a pierceable septum. The tube was then exposed to carbon monoxide, as above. Again, a ^31P(^1H) NMR spectrum showed complete loss of 15b signals and growth of the resonance for (PPh_3)_2Pt(CO)_2. A ^1H NMR spectrum revealed replacement of signals of 15b for those of Cp(CO)_2FeCH=C=CH_2 (5.23 (t, J_HH = 6.0, CH), 4.90 (s, Cp), 4.11 (d, J_HH = 6.0, -CH_2))^{51}. Bubbling of argon through the solution for 2 hours caused the reaction to completely reverse, as above, as did also simple removal of solvent under reduced pressure followed by addition of fresh CD_2Cl_2 (under argon).

**Prolonged Reaction of Cp(CO)Ru(μ-η^2,η^1-CH_2=C=C(Ph))Pt(PPh_3)_2 (14a) with Carbon Monoxide**

A screw-cap NMR tube outfitted with a pierceable septum was charged with 14a (0.035 g, 0.034 mmol) and C_6D_6 (0.6 mL). Carbon monoxide was bubbled through the solution as above. After 8 hours, a ^31P(^1H) NMR spectrum showed complete replacement of 14a signals by those of (PPh_3)_2Pt(CO)_2 (major) and 16a (very minor). A ^1H NMR spectrum was consistent with the presence of a phenylallenyl complex, 22:

^1H NMR (C_6D_6) δ 7.8-6.9 (m, 5 H, Ph), 4.49 (s, 5 H, Cp), 4.28 (s, 2 H, CH_2).
Replacement of carbon monoxide with argon converted the above back to original 14a. The process could be repeated once, in both directions, without significant loss of material owing to decomposition (noted by the precipitation of intractable solid material).

**Reaction of Cp(CO)Ru(μ-η²,η¹-CH₂=C=C(Ph))Pt(PPh₃)₂ (14a) with Carbon Monoxide, followed by Fe₂(CO)₉**

A stirred solution of 14a (0.10 g, 0.097 mmol) in THF (5 mL) at room temperature was subjected to a purge of carbon monoxide via a needle through a pierceable septum. Excess gas was vented through the Schlenk flask sidearm to a mineral oil bubbler. After 18 hours, Fe₂(CO)₉ (0.050 g, 0.14 mmol) was added as a solid at once. The solution/suspension was stirred under carbon monoxide for 3 hours, and then placed under an argon atmosphere, as above. Two hours later, an aliquot (0.5 mL) of reaction solution was depleted of solvent in vacuo and redissolved in CDCl₃ (0.5 mL) for NMR analysis. **H and 3¹P{¹H} NMR spectra indicated the presence of Cp(CO)₂RuC(Ph)=C=CH₂, (PPh₃)₂PtFe₂(CO)₈,⁷¹ Fe(CO)₄PPh₃,⁷² and a small amount of 16a. No iron- and ruthenium-containing binuclear or trinuclear complexes previously prepared by Shuchart⁵⁸ were detected by **H NMR spectroscopy.

**Reaction of Cp(CO)₂RuC(Ph)=C=CH₂ (22) with p-MeC₆H₄S(O)₂N=C=O (TSI)**

A solution of 14a (0.10 g, 0.097 mmol) in toluene (10 mL) at room temperature was treated with carbon monoxide (as per prolonged reaction, page 61) for 18 hours to insure complete conversion to
Cp(CO)$_2$RuC(Ph)=C=CH$_2$ and (PPh$_3$)$_2$Pt(CO)$_2$ (confirmed by D$_2$O-insert $^{31}$P($^1$H) NMR spectroscopy on a 0.4 mL aliquot of reaction solution). The reaction solution was placed under argon and immediately cooled to -78°C. Meanwhile, a standard toluene solution of TSI (0.079 M) had been prepared in the drybox. Two equivalents (2.5 mL, 0.20 mmol) of the standard TSI solution was added via syringe, over 5 minutes, to the cooled reaction solution. The resulting solution was allowed to warm to room temperature over one hour, and a colorless precipitate was noted. A $^{31}$P($^1$H) NMR spectrum of the solid (CDCl$_3$ as solvent) revealed a singlet at δ 5.10 ppm ($J_{ptp} = 3698$), indicating a mononuclear platinum-containing species. A 1:1 mixture of Cp(CO)$_2$RuC(Ph)=C=CH$_2$ and an allenyl-derived cycloaddition product was observed in a $^1$H NMR spectrum:

$^1$H NMR (CDCl$_3$) δ

22. 5.28 (s, 5 H, Cp), 4.14 (s, 2 H, =CH$_2$).

23. 5.00 (s, 5 H, Cp), 3.16 (s, 2 H, -CH$_2$) [δ 2.54 in C$_6$D$_6$].

The reaction solution was filtered (this removed most of the colorless mononuclear platinum-containing adduct). Solvent was then removed under reduced pressure and hexane (10 mL) was added to the red residue. An orange powder was isolated by filtration after the mixture was allowed to stir for 18 hours. A small portion of this solid was submitted for FAB mass spectrometry.

FAB MS $^{102}$Ru isotope, (rel. intensity) 339 (M$^+$ + 1 (Cp(CO)$_2$RuC(Ph)=C=CH$_2$), 20.6), 311 (M$^+$ + 1 - CO, 7.8), 283 (M$^+$ + 1 - 2CO, 21.9). Note: This is a significantly different fragmentation pattern than that for Cp(CO)$_2$RuCH=C=CH$_2$. No satisfactory mass spectral data for the cycloaddition adduct was obtained.
The orange powder was dissolved in CH$_2$Cl$_2$ (0.75 mL) and loaded onto a column (1 x 10 cm) of alumina packed in hexane. Neither product was removed from the column, even when CH$_2$Cl$_2$ was used as eluent.

**Reaction of Cp(CO)$_2$RuC(Ph)=C=CH$_2$ (22) with Diphenylacetylene (PhC=CPh)**

A stirred solution of 14a (0.10 g, 0.097 mmol) in benzene (10 mL) at room temperature was treated with carbon monoxide, as above, for 16 hours. Meanwhile, a benzene (5 mL) solution of PhC=CPh (0.020 g, 0.11 mmol) was prepared. The acetylene solution was added to the solution of the mononuclear Ru- and Pt-containing species over 5 minutes. NMR spectra ($^1$H and $^{31}$P($^1$H)) taken after 3 hours showed essentially signals for (PPh$_3$)$_2$Pt(PhC=CPh) and Cp(CO)$_2$RuC(Ph)=C=CH$_2$ only, so solvent was removed in vacuo to yield a red tar. The tar was dissolved in CD$_2$Cl$_2$ (0.5 mL) to obtain $^{13}$C($^1$H) NMR data for both products simultaneously.

**Cp(CO)$_2$RuC(Ph)=C=CH$_2$:**

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) $\delta$ 206.6 (s, =C=), 200.4 (s, Ru-CO's), 89.2 (s, Cp), 68.1 (s, =C(Ph)), 61.8 (s, =CH$_2$).

**(PPh$_3$)$_2$Pt(PhC=CPh):**

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) $\delta$ 139.1-128 (Ph), 124.9 (s, br, C=C).

**Reaction of Cp(CO)$_2$RuCH$_2$C=Ph (13) with (PPh$_3$)$_2$PtC$_2$H$_4$, then CO**

A stirred solution of Cp(CO)$_2$RuCH$_2$C=Ph (13) (0.14 g, 0.42 mmol) in ethylene-saturated THF (25 mL) at room temperature was treated with (PPh$_3$)$_2$PtC$_2$H$_4$ (0.33 g, 0.44 mmol) as a solid in one portion. After the solution was stirred for one hour, a 2 mL aliquot was removed, freed of
solvent in vacuo, and dissolved in CDCl₃ (0.5 mL) for NMR analysis. At this time the intermediate I from Scheme 3 (page 129) was the major product in the ¹H and ³¹P(¹H) NMR spectra. The reaction solution was then subjected to carbon monoxide purge via a needle through a septum, and the excess gases were vented via another needle through the septum connected to a mineral oil bubbler. After one hour of carbon monoxide purge, another aliquot was withdrawn and treated as above for ¹H and ³¹P(¹H) NMR analysis. The intermediate I had converted back quantitatively to Cp(CO)₂RuCH₂C≡CPh (13) and (PPh₃)₂Pt(CO)₂. No signals for Cp(CO)₂RuC(Ph)=C=CH₂ (22) were observed.

**Reaction of Cp(CO)Ru(μ-η²,η¹CH₂=C=C(Ph))Pt(PPh₃)(CO) (16a) with CO and Reverse of this Reaction**

A solution of 16a (0.030 g) in C₆D₆ (0.5 mL) in an NMR tube equipped with a septum was purged with carbon monoxide for 6 hours at room temperature. Excess gases were vented via another needle through the septum. ¹H and ³¹P(¹H) NMR spectral data showed the formation of (PPh₃)₂Pt(CO)₂ and Cp(CO)₂RuC(Ph)=C=CH₂ (22) in about a 1:1:1 ratio to 16a. Resonances for other compounds, probably mononuclear Pt-containing species, were also observed. Replacement of the carbon monoxide atmosphere for argon (for 18 hours) resulted in the formation of a small amount of 14a. The other Pt-containing species (³¹P(¹H) NMR around δ 5 ppm) did not react with Cp(CO)₂RuC(Ph)=C=CH₂ to revert back to 16a.

**Reaction of Cp(CO)Ru(μ-η²,η¹CH₂=C=C(Ph))Pt(PPh₃)(CO) (16a) with PPh₃**
A solution of 16a (0.13 g, 0.16 mmol) and PPh₃ (0.050 g, 0.19 mmol) in toluene (40 mL) was heated at 100°C for 18 hours. An IR spectrum showed that the reaction was nearly complete (owing to the loss of the \( \nu_{C=O} \) absorption bands at 2018 and 1947 cm\(^{-1} \) and replacement with one at 1912 cm\(^{-1} \)), so solvent was removed under reduced pressure. The entire red residue was then dissolved in CDCl₃ (0.6 mL) for NMR analysis.\(^{31}P(\text{H})\) and \(^{1}H\) NMR spectra showed complete conversion of 16a to 14a. Very minor decomposition was also noted in the NMR spectra.

D. General Reactions of Binuclear Compounds

1) With Nucleophiles

**Reaction of Cp(CO)Ru(\( \mu-\eta^2,\eta^1-\text{CH}_2=\text{C}(:\text{C(Ph)})\))Pt(PPh₃)₂ (14a) with \( p\)-MeC₆H₄S(O)₂NH₂**

A stirred solution of 14a (0.15 g, 0.15 mmol) in benzene (20 mL) at room temperature was treated with \( p\)-MeC₆H₄S(O)₂NH₂ (0.030 g, 0.18 mmol) as a solid at once. No reaction was observed via \(^{31}P\) and \(^{1}H\) NMR spectroscopy at room (24 hours) or reflux (2 hours) temperature.

**Reaction of Cp(CO)Ru(\( \mu-\eta^2,\eta^1-\text{CH}_2=\text{C}(:\text{C(H)})\))Pt(PPh₃)₂ (15a) with Diethylamine (HNEt₂)**

To a stirred solution of 15a (0.20 g, 0.21 mmol) in THF (30 mL) at -78°C was charged HNEt₂ (0.050 mL, \( d = 0.71\) g/mL, 0.49 mmol) dropwise
over 2 minutes. No reaction was noted (via $^1$H NMR) spectroscopy at -78°C, room temperature or reflux temperature (one hour).

**Reaction of Cp(CO)Ru(μ-η²,η¹-CH$_2$=C≡C(Ph))Pt(PPh$_3$)$_2$ (15a) with Cyclohexylamine**

A stirred solution of 15a (0.20 g, 0.21 mmol) in THF (20 mL) at room temperature was treated dropwise, over 5 minutes, with 0.10 mL (d = 0.82 g/mL, 1.0 mmol) of cyclohexylamine. No reaction was noted (via $^1$H NMR spectroscopy) after 24 hours at room temperature followed by 4 hours at reflux temperature.

**Reaction of Cp(CO)$_2$RuCH$_2$C≡CPh with Pt(PPh$_3$)$_4$, then with Sulfur**

A solution of Cp(CO)$_2$RuCH$_2$C≡CPh (13) (0.26 g, 0.77 mmol) in THF (85 mL) at room temperature was treated with Pt(PPh$_3$)$_4$ (1.2 g, 0.77 mmol) as a solid and then heated at reflux temperature for 9 hours. After the solution cooled to room temperature, sulfur (0.050 g, 1.5 mmol) was added as a solid to react with excess triphenylphosphine. A $^{31}$P($^1$H) NMR spectrum confirmed that only PPh$_3$S and 14a were present in the reaction solution. Addition of more sulfur (0.050 g, 1.5 mmol) as a solid caused decomposition to intractable materials after another 24 hours of stirring at room temperature.

**Reaction of Cp(CO)Ru(μ-η²,η¹-CH$_2$=C≡C(Ph))Pt(PPh$_3$)$_2$ (14a) with Selenium**

A solution of 14a (0.15 g, 0.15 mmol) at room temperature in THF (50 mL) was treated with selenium (0.030 g, 0.38 mmol) as a solid. No reaction
was noted by $^{31}$P($^1$H) NMR after 24 hours at room temperature. Heating at reflux temperature for one hour caused for decomposition as in the preceding reaction.

**Reaction of Cp(CO)Ru($\mu$-$\eta^2$-$\eta^1$-CH$_2$=C=CH)Pt(PPh$_3$)$_2$ (15a) with n-BuLi**

A stirred solution of 15a (0.20 g, 0.21 mmol) in THF (15 mL) at -78°C was treated dropwise with 0.33 mL of a 1.6 M hexane solution of n-BuLi (0.53 mmol) over 5 minutes. After this solution warmed to room temperature over 5 hours, a D$_2$O-insert $^{31}$P($^1$H) NMR spectrum showed a 1:1 mixture of 15a and a new product:

$^{31}$P($^1$H) NMR (D$_2$O) $\delta$ 28.0 (d, $J_{PP} = 4.0$, $J_{PtP} = 2698$), 24.3 (d, $J_{PP} = 4.0$, $J_{PtP} = 3716$).

The reaction could not be driven to completion by utilizing reflux temperature or a gross excess of n-BuLi, nor could the new product be isolated without decomposition after removal of solvent under reduced pressure.

**Reaction of Cp(CO)Ru($\mu$-$\eta^2$-$\eta^1$-CH$_2$=C=CH)Pt(PPh$_3$)$_2$ (15a) with KOH**

An aliquot (1.18 mL) of a standard solution (0.178 M) of KOH (0.012 g, 0.21 mmol, from the drybox) in deoxygenated H$_2$O (10 mL) was added dropwise to a stirred solution of 15a (0.20 g, 0.21 mmol) at -78°C in THF (8 mL). No reaction was noted (via D$_2$O insert $^{31}$P($^1$H) NMR) even after heating the solution at reflux temperature for 18 hours.

**Reaction of Cp(CO)Ru($\mu$-$\eta^2$-$\eta^1$-CH$_2$=C=CH)Pt(PPh$_3$)$_2$ (15a) with PEt$_3$**
A stirred solution of 15a (0.10 g, 0.11 mmol) in THF (20 mL) at -78°C was treated with PEt₃ (0.050 mL, 0.34 mmol) dropwise for one minute. The solution was allowed to warm to room temperature over 6 hours, and solvent was freed under vacuum. A small portion (2.0 mL) of THF was added to the orange residue, and the resulting orange solution/suspended white solid was passed through a plug of Celite with the assistance of an additional portion (8 mL) of THF. Volume of the filtrate was then reduced to about 2 mL, and hexane (10 mL) was carefully layered on top of the orange THF solution. After slow diffusion of the two solvents at 0°C for 24 hours, a yellow solid of Cp(CO)Ru-(μ-η²,η¹-CH₂=CH=C(H))Pt(PET₃)₂ (24, 0.062 g, 85% yield) was isolated.

IR (CH₂Cl₂) 1892.

¹H NMR (CDCl₃) δ 6.42 (m, Jₚ₅H = 31, 1 H, CH), 5.41 (m, Jₚ₅H = 20, 1 H of CH₂), 5.00 (s, 5 H, Cp), 4.70 (m, Jₚ₅H = 13, 1 H of CH₂), 2.1-0.75 (several multiplets, PCH₂CH₃).

³¹P(¹H) NMR (CDCl₃) δ 23.9 (s, br, Jₚ₃P = 3681), 12.4 (s, br, Jₚ₃P = 2733).

FAB MS ¹⁰²Ru isotope, (relative intensity) 665 (M⁺, 6.1), 547 (M⁺ - PEt₃, 6.0), 429 (M⁺ - 2PEt₃, 12.1).

Reaction of Cp(CO)Ru(μ-η²,η¹-CH₂=CH=C(Ph))Pt(PPh₃)₂ (14a) with 1,3-(Diphenylphosphino)propane (dppp)

A stirred solution of 14a (0.22 g, 0.21 mmol) in THF (15 mL) at -78°C was treated dropwise (via Hamilton syringe) over 10 minutes with a solution of dppp (0.068 g, 0.21 mmol) in THF (5 mL). After the solution warmed (6 hours) while being stirred at room temperature for 18 hours,
solvent was removed under reduced pressure. The orange residue was then dissolved in freshly distilled THF (2 mL), treated with hexane (7 mL) while being stirred vigorously, and placed in the freezer for 18 hours. A yellow solid of Cp(CO)Ru-(μ-η^2,η^1-CH_2=CH=C(Ph))Pt(dppp), 25a (0.077 g, 40% yield) was collected on a frit.

IR (CH_2Cl_2) ν_{C=O} 1901 (s); ν_{C≡C} 1712 (m).

^1H NMR (C_6D_6) δ 7.7-7.1 (m, 5 Ph), 6.12 (d, J_{HH} = 2.2, J_{Ph} = 24, 1 H of CH_2), 5.56 (d, J_{HH} = 2.2, J_{Ph} = 15, 1 H of CH_2), 4.46 (s, 5 H, Cp).

^31P{^1H} NMR (C_6D_6) δ 4.0 (d, J_{PP} = 22.5, J_{PPh_3} = 2526), -1.1 (d, J_{PP} = 22.5, J_{PPh_3} = 3427).

FAB MS 102Ru isotope, (rel. intensity) 918 (M^+ + H, 31.3), 890 (M^+ + H - CO, 3.7), 607 (Pt(dppe)^+, 9.2).

**Reaction of Cp(CO)Ru(μ-η^2,η^1-CH_2=CH=C(H))Pt(PPh_3)_2 (15a) with 1,3-(Diphenylphosphino)propane (dppe)**

To a stirred solution of 15a (0.28 g, 0.29 mmol) in THF (15.0 mL) at -78°C was added a THF (5 mL) solution of dppe (0.12 g, 0.29 mmol) dropwise over 3 minutes. The solution was allowed to warm to room temperature over 6 hours, and solvent was removed under reduced pressure. The yellow residue was dissolved in THF (3.0 mL), treated with hexane (7.0 mL), and placed in the freezer for 18 hours. The yellow solid of Cp(CO)Ru-(μ-η^2,η^1-CH_2=CH=C(H))Pt(dppe), 25b (0.12 g, 49% yield) was collected on a frit, mp = 165°C dec.

IR (CH_3CN) ν_{C=O} 1902 (s); ν_{C≡C} 1714 (m).
$^1$H NMR (CDCl$_3$) δ 7.7-7.0 (m, 4 Ph), 6.70 (s, br, $J_{\text{PtH}} = 37$, 1 H, CH), 5.59 (s, br, $J_{\text{PtH}} = 27$, 1 H of CH$_2$), 4.77 (s, br, $J_{\text{PtH}} = 18$, 1 H of CH$_2$), 4.58 (s, 5 H, Cp).

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) δ 206.5 (s, Ru-CO), 168.9 (s, =C=), 112.4 (d, $J_{\text{PC}} = 85$, $J_{\text{PtC}} = 722$, =CH), 94.5 (s, =CH$_2$), 82.3 (s, Cp), 27.2, 20.6 (CH$_2$ of dppp).

$^{31}$P($^1$H) NMR (CD$_2$Cl$_2$) δ 5.4 (d, $J_{\text{PP}} = 20$, $J_{\text{PtP}} = 2564$), 1.5 (d, $J_{\text{PP}} = 20$, $J_{\text{PtP}} = 3406$).

FAB MS $^{102}$Ru isotope, (rel. intensity) 841 (M$^+$, 19.2), 813 (M$^+$ - CO, 3.7), 607 (Pt(dppp)$^+$, 10.3).

Anal. Calcd. for C$_{36}$H$_{34}$O$_2$PtRu: C, 51.43; H, 4.08; Found: C, 51.66; H, 4.26%.

**Reaction of Cp(CO)Ru(μ-η$^2$;η$^1$-CH$_2$=C=C(Ph))Pt(PPh$_3$)$_2$ (14a) with t-BuNC**

A stirred orange-red solution of 14a (0.20 g, 0.19 mmol) in THF (10 mL) at -78°C was treated with t-BuNC (0.10 mL, 0.89 mmol) dropwise over 5 minutes. The solution immediately turned yellow, although the reaction was not complete, as ascertained by NMR spectroscopy, until the solution had warmed to room temperature over 8 hours followed by 8 additional hours. Solvent was removed under reduced pressure, and the yellow residue was washed with 4:1 hexane/THF (5 mL) to cause the formation of a yellow precipitate of Cp(CO)Ru(μ-η$^2$;η$^1$-CH$_2$=C=C(Ph))Pt(PPh$_3$)(t-BuNC), 25c (0.12 g, 67% yield), mp, 98°C.

IR (CH$_2$Cl$_2$) 1901.
$^1$H NMR \((\text{CDCl}_3)\) $\delta$ 7.8-6.7 (m, 4 Ph), 5.62 (s, $J_{\text{PtP}} = 17$, 1 H of CH$_2$), 4.98 (s, $J_{\text{PtH}} = 13$, 1 H of CH$_2$), 4.74 (s, 5 H, Cp), 1.29 (s, 9 H, Me's of t-Bu);

$\text{(C}_6\text{D}_6)\) $\delta$ 7.7, 7.5, 7.4, 7.0-6.8 (m, 4 Ph), 6.06 (s, $J_{\text{PtH}} = 17$, 1 H of CH$_2$), 5.57 (s, $J_{\text{PtH}} = 13$, 1 H of CH$_2$), 4.82 (s, 5 H, Cp), 0.87 (s, 9 H, Me's of t-Bu).

$^{13}\text{C}$($^1$H) NMR \((\text{CD}_2\text{Cl}_2)\) $\delta$ 205.0 (s, $J_{\text{PtC}} = 50.4$, Ru-CO), 166.5 (s, =C=), 150.1 (s, =C(Ph)), 97.0 (s, $J_{\text{PtC}} = 32.2$, =CH$_2$), 84.1 (s, Cp), 29.9 (s, Me's of t-Bu). Possibilities: 143.8 (s, br, Ru-C=N) and 57.0 (s, quaternary carbon of t-Bu).

$^{31}\text{P}$($^1$H) NMR \((\text{CDCl}_3)\) $\delta$ 25.6 (s, $J_{\text{PtP}} = 3544$).

FAB MS $^{102}$Ru isotope, (relative intensity), 850 (M$^+$, 68.0), 767 (M$^+$ - t-BuNC, 9.4), 540 (Pt(PPh$_3$)(t-BuNC)$^+$, 18.9).

Anal. Calcd. for C$_{38}$H$_{36}$NOPtRu: C, 53.71; H, 4.27; Found: C, 54.01; H, 4.51%.

**Reaction of Cp(CO)Ru-(μ-$\eta^2,\eta^1$-CH$_2$=C=C(Ph))Pt(dpdp) (25a) with Carbon Monoxide**

A solution of 25a (0.040 g, 0.044 mmol) in C$_6$D$_6$ (0.6 mL) was purged with carbon monoxide as described earlier (page 59). No reaction was noted via $^1$H NMR spectroscopy, even after four days at 70°C.

**Reaction of Cp(CO)Ru-(μ-$\eta^2,\eta^1$-CH$_2$=C=C(Ph))Pt(dpdp) (25b) with Fe$_2$(CO)$_9$**

A stirred solution of 25b (0.14 g, 0.17 mmol) in THF (25 mL) at room temperature was treated with Fe$_2$(CO)$_9$ (0.065 g, 0.18 mmol) as a solid in one portion. The resulting suspension was heated at reflux temperature
for 1 hour, filtered through a plug of Celite upon cooling to room
temperature, and freed of solvent under reduced pressure. The red
residue was dissolved in CH$_2$Cl$_2$ (1 mL) and placed upon a column of
alumina (2 x 10 cm) packed in hexane. Elution with a solution of 1:1
hexane/diethyl ether gave a yellow band that yielded 0.025 g of a yellow
solid (26) upon solvent removal in vacuo.

IR (THF) 2014 (s), 1978 (vs), 1963 (s), 1912 (vs), 1792 (vw).

$^1$H NMR (CDCl$_3$) $\delta$ 8.0-7.1 (m, Ph), 6.73 (br, 1 H, CH), 5.43 (br, 2 H,
CH$_2$), 4.90 (s, 5 H, Cp), 3.0-1.5 (several signals for P-CH$_2$-CH$_2$-CH$_2$-P
protons).

$^{31}$P{${^1}$H} NMR (CDCl$_3$) $\delta$ 10.4 (d, $J_{PP} = 21$, $J_{PtP} = 2604$), 2.5 (d, $J_{PP} =
21$, $J_{PtP} = 3280$).

FAB MS $^{102}$Ru isotope, (relative intensity) 1009 (M$^+$, 14.0), 981 (M$^+$ -
CO, 4.0), 953 (M$^+$ - 2CO, 3.1), 925 (M$^+$ - 3CO, 22.4), 897 (M$^+$ - 4CO, 91.1), 869
(M$^+$ - 5CO, 36.2), 702 (FePt(dppp)C$_3$H$_3$+$^+$, 23.3), 646 (Pt(dppp)C$_3$H$_3$+$^+$, 100).

**Reaction of Cp(CO)Ru-(μ-η$_2$tyl)-CH$_2$=C=C(H))Pt(dppp) (25b) with t-BuNC**

A stirred solution of 25b (0.20 g, 0.24 mmol) in THF (10 mL) at -78°C
was treated with three drops of t-BuNC. No reaction was observed at -78°
or room temperature (3 hours), and only slight decomposition was noted
by $^1$H and $^{31}$P{$^1$H} NMR spectroscopy after 18 hours at reflux temperature.

**NMR Tube Reaction of Cp(CO)Ru-(μ-η$_2$tyl)-CH$_2$=C=C(H))Pt(dppp) (25b)
with Carbon Monoxide**

A solution of 25b (0.025 g, 0.030 mmol) in C$_6$D$_6$ (0.5 mL) at room
temperature was purged with carbon monoxide for 3 hours as described
previously. No reaction was observed by $^1$H and $^{31}$P($^1$H) NMR spectroscopy. The reaction tube was then heated at 70°C for 48 hours (under carbon monoxide atmosphere), and only 25b and uncharacterizable material were observed by $^1$H and $^{31}$P NMR.

2) With Electrophiles

Reaction of Cp(CO)Ru($\mu$-$\eta^2$,H$^{1}$-CH$_2$=C=$\eta$1-CH$_2$=C(Ph))Pt(PPh$_3$)$_2$ (14a) with (Ph)$_2$C=C(CN)$_2$

To a stirred solution of 14a (0.20 g, 0.19 mmol) in benzene (9 mL) at room temperature was added a benzene (3 mL) solution of (CN)$_2$C=CPh$_2$ (0.21 mL, d = 1.0 g/mL, 0.92 mmol) in one portion. After stirring at reflux temperature for two hours, an aliquot of reaction solution was withdrawn, freed of solvent under reduced pressure, and examined by $^1$H and $^{31}$P($^1$H) NMR spectroscopy. No reaction was noted.

Reaction of Cp(CO)Ru($\mu$-$\eta^2$,H$^{1}$-CH$_2$=C=$\eta$1-CH$_2$=C(H))Pt(PPh$_3$)$_2$ (15a) with (MeO)$_2$SO$_2$

A stirred solution of 15a (0.20 g, 0.21 mmol) in THF (10 mL) at -78°C was treated with 0.045 mL (d = 1.3 g/mL, 0.47 mmol) of (MeO)$_2$SO$_2$ in one portion. Again, no reaction was noted even after 24 hours at reflux temperature.

Reaction of Cp(CO)Ru($\mu$-$\eta^2$,H$^{1}$-CH$_2$=C=$\eta$1-CH$_2$=C(H))Pt(PPh$_3$)$_2$ (15a) with $\text{H}_2$

A stirred solution of 15a (0.23 g, 0.24 mmol) in THF at room temperature was purged with $\text{H}_2$ gas via a needle through a septum
(excess gases were vented through the sidearm of the Schlenk flask connected to a mineral oil bubbler via flexible tubing) for 1 hour. No reaction was noted via $^1$H and $^{31}$P($^1$H) NMR spectroscopy. The vessel was then heated at reflux temperature while stirring under an atmosphere of H$_2$ for 2 hours, but again no reaction was noted when monitored by NMR spectroscopy.

**Reaction of Cp(CO)Ru($\mu$-η$^2$,$\eta^1$-CH$_2$=C(H))Pt(PPh$_3$)$_2$ (15a) with Et$_3$O$^+PF_6^-$**

A stirred solution of 15a (0.20 g, 0.21 mmol) in dichloromethane (20 mL) at -78°C was treated with a CH$_2$Cl$_2$ (10 mL) solution of EtO$_3^+PF_6^-$ (0.068 g, 0.31 mmol) dropwise over 3 minutes. After the solution was allowed to warm to room temperature over 6 hours, an aliquot of reaction solution was removed, freed of solvent in vacuo, and analyzed by $^1$H and $^{31}$P($^1$H) NMR spectroscopy in the usual fashion. Only a myriad of signals owing to a complex mixture of products was observed in the spectra.

**Reaction of Cp(CO)Ru($\mu$-η$^2$,$\eta^1$-CH$_2$=C(Ph))Pt(PPh$_3$)$_2$ (14a) with ClSO$_2$N=C=O**

To a stirred solution of 14a (0.16 g, 0.16 mmol) in THF (10 mL) at -78°C was added 0.060 mL (d = 1.6 g/mL, 0.68 mmol) of ClSO$_2$N=C=O dropwise over one minute. While stirring for one hour, the solution color changed from orange to dark red. The reaction solution was allowed to warm to room temperature over 6 hours and was stirred for 12 hours. The cloudy brown solution was filtered, and solvent was removed in vacuo from the brown-orange filtrate to yield a brown tar. Attempted purification of the tar by recrystalization or by chromatography resulted in
decomposition only. The product(s) appears to be quite sensitive to air and CDCl₃.

**Reaction of Cp(CO)Ru(μ-η²,η¹-CH₂=C=CH)Pt(PPh₃)₂ (14a) with Fumaronitrile (NCCH=CHCN)**

A stirred solution of 14a (0.15 g, 0.15 mmol) in benzene (10 ml) at room temperature was charged with 0.025 g (0.32 mmol) of fumaronitrile as a solid in one portion. No reaction was noted after three hours (via NMR), so the reaction solution was heated at reflux temperature for two hours before an aliquot (0.5 mL) was withdrawn and freed of solvent under reduced pressure. The ³¹P(¹H) NMR spectrum revealed a signal at δ 22.9 (s, Jpₚₚ = 3707), and the ¹H NMR gave a doublet at δ 2.45 (JₚH = 5.8, JₚH = 60) corresponding to about a 2:3 ratio of (PPh₃)₂Pt(CNCH=CHCN) to 14a. A total of 24 hours at reflux temperature resulted in the 75% conversion of 14a to (PPh₃)₂Pt(CNCH=CHCN), Cp(CO)₂RuC(Ph)=C=CH₂ (22) (see pages 61 and 62), and other unidentifiable compounds.

**Note:** Spectroscopic properties of the proposed (PPh₃)₂Pt(CNCH=CHCN) prepared here match well with those from the literature.

**Reaction of Cp(CO)Ru(μ-η²,η¹-CH₂=C=H)Pt(PPh₃)₂ (15a) with Dimethylacetylenedicarboxylate (DMAD)**

A stirred solution of 15a (0.22 g, 0.23 mmol) in THF (7 mL) at -78°C was treated dropwise over 15 minutes with 1.5 mL (0.24 mmol) of a previously prepared standard (0.163 M) solution of DMAD in THF. After warming to room temperature (8 hours) and stirring for 12 hours, an aliquot was withdrawn and freed of solvent under reduced pressure for
NMR analysis. A $^{31}$P($^1$H) NMR spectrum revealed only (PPh$_3$)$_2$Pt(DMAD) (as determined by comparison of spectral data to those in the literature 73). A $^1$H NMR spectrum showed the presence of a variety of products, the only characterizable ones being (PPh$_3$)$_2$Pt(DMAD) and Cp(CO)$_2$RuCH=C=CH$_2$.

Data for (PPh$_3$)$_2$Pt(DMAD):

$^1$H NMR (CDCl$_3$) $\delta$ 8.0-7.3 (m, Ph), 3.31 (s, $J_{PtH} = 702$, Me's of DMAD).

$^{31}$P($^1$H) NMR (CDCl$_3$) $\delta$ 23.3 (s, $J_{PtP} = 3729$).

Reaction of Cp(CO)Ru($\mu$-$\eta^2$,$\eta^1$-CH$_2$=C=C(H))Pt(PPh$_3$)$_2$ (15a) with Methyl-2-butynoate (MeC=CCO$_2$Me)

To a stirred solution of 15a (0.15 g, 0.16 mmol) in THF (5 mL) at -78°C was added 1.7 mL (0.17 mmol) of a standard (0.10 M) solution of MeC=CCO$_2$Me in THF dropwise over 15 minutes. After the solution warmed to room temperature over 8 hours and was stirred for 8 hours, an aliquot was withdrawn and freed of solvent under vacuum for NMR analysis. Meanwhile, another equivalent of MeC=CCO$_2$Me was added (at room temperature) and the solution was stirred at room temperature for 6 additional hours. In both instances, NMR spectral results were the same: Only one half of the original 15a was consumed (based upon comparison of relative intensities of $^1$H and $^{31}$P NMR signals) to form (PPh$_3$)$_2$Pt(MeC=CCO$_2$Me)$_73$ and Cp(CO)$_2$RuCH=C=CH$_2$, among other, uncharacterized materials.

Data for (PPh$_3$)$_2$Pt(MeC=CCO$_2$Me):

$^1$H NMR (CDCl$_3$) $\delta$ 7.9-6.9 (m, 6 Ph), 3.30 (s, 3 H, Me of carboxylate), 1.98 (d, $J_{PH} = 8.1$, $J_{PtH} = 36.0$, 3 H, CMe).
Reaction of $\text{Cp(CO)Ru(}\mu\eta^2,\eta^1\text{-CH}_2=\text{C}=\text{C}(\text{H}))\text{Pt(PPh}_3\text{)}_2$ (15a) with Phenylacetylene ($\text{PhC}=\text{CH}$)

To a stirred solution of 15a (0.10 g, 0.11 mmol) in THF (10 mL) at -78°C was added, dropwise over 5 minutes, 1.2 mL (0.11 mmol) of a standard (0.091 M) solution of PhC=CH in THF. After allowing the reaction solution to warm to room temperature over 6 hours, an aliquot of solution was removed, freed of solvent in vacuo, and analyzed by $^1\text{H}$ and $^{31}\text{P}({^1\text{H}})$ NMR spectroscopy. The spectra revealed that about half of the starting 15a had been consumed to form Pt(PPh$_3$)$_4$, Cp(CO)$_2$RuCH=CH$_2$, and a small amount of (PPh$_3$)$_2$Pt(PhC=CH)$_3$ among other, unidentifiable products. Addition of another equivalent of the standard PhC=CH solution did not drive the reaction further. Instead, over 48 hours, the reaction appeared to reverse somewhat to a possible equilibrium situation, involving 15a, (PPh$_3$)$_2$Pt(PhC=CH), and Cp(CO)$_2$RuCH=CH$_2$. See Results and Discussion for details.

Data for (PPh$_3$)$_2$Pt(PhC=CH):

$^1\text{H}$ NMR (CDCl$_3$) $\delta$ 7.7-6.9 (m, Ph).

$^{31}\text{P}({^1\text{H}})$ NMR (CDCl$_3$) $\delta$ 29.6 (d, $J_{PP}$ = 34, $J_{PtP}$ = 3539), 25.3 (d, $J_{PP}$ = 34, $J_{PtP}$ = 3453).
A stirred solution of 15a (0.10 g, 0.11 mmol) in THF (10 mL) at room temperature was treated with PhC=CHPh (0.030 g, 0.14 mmol) in one portion as a solid. After 2 hours of stirring, an aliquot (1.2 mL) was removed and freed of solvent in vacuo for NMR analysis. Only about one half of the starting 15a had been consumed (based upon relative intensities of appropriate signals) to form (PPh₃)₂Pt(PhC≡CH₇₃ Pt(PPh₃)₄, and Cp(CO)₂RuCH=CH₂. After 48 hours, the reaction had reversed only slightly to reach an equilibrium situation, as in the reaction of 15a with PhC≡CH.

Data for (PPh₃)₂Pt(PhC≡CH):

1H NMR (CDCl₃) δ 7.5-7.1 (m, Ph).

31P{1H} NMR (CDCl₃) δ 26.2 (s, Jₚₚ = 3448).

Reaction of (PPh₃)₂Pt(PhC≡CH) with a slight excess of Cp(CO)₂RuCH=CH₂

A stirred solution of Cp(CO)₂RuCH=CH₂ (0.063 g, 0.24 mmol) in THF (10 mL) at room temperature was treated with (PPh₃)₂Pt(PhC≡CH) (0.15 g, 0.17 mmol) as a solid. After stirring for 2 hours, an aliquot was removed and freed of solvent in vacuo. The residue was dissolved in CDCl₃ (0.5 mL), and ¹H and ³¹P{¹H} NMR spectra were obtained. The ³¹P{¹H} NMR spectrum revealed complete loss of (PPh₃)₂Pt(PhC≡CH) and the formation of 15a. The ¹H NMR spectrum revealed essentially only the presence of 15a and the excess Cp(CO)₂RuCH=CH₂. Another spectrum taken after 5 days showed that a very small amount of (PPh₃)₂Pt(PhC≡CH) had reformed, however.
Reaction of Cp(CO)Ru(μ-η²,η¹-CH₂=C=C(H))Pt(PPh₃)₂ (15a) with CF₃COOH

A solution of 15a (0.20 g, 0.21 mmol) in CH₂Cl₂ (9 mL) was treated with 1.35 mL of a 0.16 M (0.22 mmol) solution of CF₃COOH in CH₂Cl₂, dropwise, over 5 minutes, at -78°C. No color change (orange solution) was noted. Reaction was complete within 1.5 hours at -78°C, as ascertained by D₂O-insert ³¹P{¹H} NMR spectroscopy. Slow warming to room temperature over the course of 4 hours and solvent removal in vacuo yielded a yellow oil. Hexane (10 mL) was added with vigorous stirring to result in the formation of a yellow solid (27) which was collected on a frit and dried in vacuo.

IR (CH₂Cl₂) 2024 (m), 1974 (s).

¹H NMR (CD₂Cl₂) δ 8.0-7.0 (m, 6 Ph), 6.10 (m, 1 H), 6.03 (dd, J_HH = 2.3, J_HH = 7.2, 1 H), 4.98 (s, 5 H, Cp), 3.84 (m, 1 H), 2.28 (m, 1 H).

¹³C{¹H} NMR (CD₂Cl₂) δ 199.7 (s, Ru-CO), 199.3 (s), 160.1 (m), 136.1-126.2 (Ph), 124.7 (s, J_PtC = 30.0), 99.1 (d, J_PC = 32.0, J_PtC = 120), 62.5 (d, J_PC = 31, J_PtC = 130), 89.6 (s, Cp).

³¹P{¹H} NMR (CD₂Cl₂) δ 15.1 (d, J_PP = 7.0, J_PtP = 4078), 14.1 (d, J_PP = 7.0, J_PtP = 3946).

Anal. Calcd. for C₄₈H₃₉F₃O₄P₂PtRu: C, 52.65; H, 3.59; Found: C, 52.94; H, 4.06%.

Metathesis of Product from Reaction of 15a with CF₃COOH

The yellow CF₃COO⁻ salt of above was dissolved in methanol (5 mL), and an equimolar amount of NaBPh₄ dissolved in methanol (5 mL) was added via cannula. An off-white precipitate of the tetraphenylborate salt was obtained and collected on a frit in typical yields of 60%. Spectral
properties were essentially identical to those above, although the
tetraphenylborate salt was less soluble in organic solvents than the
trifluoroacetate salt.

IR (CH$_2$Cl$_2$) 2017 (s), 1962 (s).

$^1$H NMR (CD$_2$Cl$_2$) $\delta$ 8.0-6.9 (m, 6 Ph), 6.42 (m, 1 H), 6.15 (m, 1 H),
5.19 (s, 5 H, Cp), 3.94 (m, 1 H), 2.40 (m, 1 H).

$^{31}$P($^1$H) NMR (CD$_2$Cl$_2$) $\delta$ 15.1 (d, $J_{PP} = 6.0, J_{P_{Pt}} = 4324$), 14.9 (d, $J_{PP} = 6.0, J_{P_{Pt}} = 4015$).

Reaction of Cp(CO)Ru($\mu$-$\eta^2$-$\eta^1$-CH$_2$=C=C(CH$_3$))Pt(PPh$_3$)$_2$ (15a) with ClCH$_2$COOH

A stirred solution of 15a (0.12 g, 0.13 mmol) in THF (5 mL) at -78°C was treated with 2.0 mL (0.13 mmol) of a standard (0.064 M) solution of ClCH$_2$CO$_2$H in THF dropwise over 5 minutes. Upon warming the solution to room temperature over 4 hours, only signals for unreacted 15a and several signals corresponding to an unidentified material were observed by D$_2$O-insert $^{31}$P($^1$H) NMR spectroscopy.

Reaction of Cp(CO)Ru($\mu$-$\eta^2$-$\eta^1$-CH$_2$=C=C(CH$_3$))Pt(PPh$_3$)$_2$ (15a) with Tetracyanoethylene (TCNE)

To a solution of 15a (0.20 g, 0.21 mmol) in dichloromethane (10 mL) at -78°C was charged 0.030 g (0.23 mmol) of TCNE as a solid with stirring. After one hour, a D$_2$O-insert $^{31}$P($^1$H) NMR spectrum showed signals of two distinguishable products along with a host of other signals:

$^{31}$P($^1$H) NMR (D$_2$O):

Product One: $\delta$ 14.5 (s, $J_{P_{Pt}} = 3748, (PPh$_3$)$_2$Pt(TCNE)).
Product Two: δ 26.6 (d, J_{PP} = 7.0, J_{PtP} = 2891), 19.7 (d, J_{PP} = 7.0, J_{PtP} = 3248).

When the reaction solution was allowed to warm to room temperature, complete decomposition occurred of all products except Product One.

**Reaction of Cp(CO)Ru(μ-η^{2},η^{1}-CH_{2}=C=C(Ph))Pt(PPh_{3})_{2} (14a) with Toluenesulfonyl isocyanate (TSI)**

A stirred solution of 14a (0.15 g, 0.15 mmol) in toluene (6.0 mL) at -78°C was treated with 3.0 mL (0.24 mmol) of a standard (0.079 M) solution of TSI in toluene. The resulting solution warmed to room temperature over 8 hours and was stirred for 10 additional hours. The solution was clear red initially, but a yellow solid in orange solution was observed at the end of the reaction. This solid (28a, 0.10 g, 54% yield) was collected on a frit.

IR (CH_{2}Cl_{2}) 1924 (s), 1670 (s).

^{1}H NMR (CDCl_{3}) δ 12.1 (s, 1 H, NH), 8.1-6.8 (m, 7 Ph), 5.96 (s, J_{PtH} = 10, 1 H, CH), 4.48 (s, 5 H, Cp), 2.43 (s, 3 H, Me).

^{13}C(^{1}H) NMR (CDCl_{3}) δ 201.9 (Ru-CO), 178.1 (-N(H)=C=O), 164.5 (=C=), 146.2 (C(PH)), 108.4 (CH), 86.6 (Cp), 21.5 (Me).

^{31}P(^{1}H) NMR (CDCl_{3}) δ 21.6 (d, J_{PP} = 11, J_{PtP} = 2789), 20.9 (d, J_{PP} = 11, J_{PtP} = 3923).

FAB MS^{102}Ru isotope, (relative intensity) 1226 (M^{+}, 16.3), 1998 (M^{+} - CO, 9.8), 1070 (M^{+} - 156, 31.4), 964 (M^{+} - PPh_{3}, 21.6), 719 (PtPPh_{3})^{2+}, 100).

Anal. Calcd. for C_{59}H_{49}NO_{4}P_{2}PtRuS: C, 57.79; H, 4.03; Found: C, 57.64; H, 4.12%.
A small amount of another product, nearly pure 29a, could be obtained by extracting the residue left after solvent removal from the filtrate under reduced pressure with 3:1 hexane/toluene (3 x 9 mL).

IR (CH\textsubscript{2}Cl\textsubscript{2}) 1899 (s), 1724 (s).

\textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}) \(\delta\) 8.5-6.5 (m, 7 Ph), 4.84 (s, 5 H, Cp), 3.71 (d, \(J_{HH} = 21.3\), \(J_{PP} = 17.2\), 1 H of CH\textsubscript{2}), 2.72 (dt, \(J_{HH} = 21.5\), \(J_{PH} = 14.5\), 1 H of CH\textsubscript{2}), 1.88 (s, 3 H, Me).

\textsuperscript{13}C{\textsuperscript{\textsuperscript{1}}H} NMR (C\textsubscript{6}D\textsubscript{6}) \(\delta\) 206.2 (Ru-CO), 174.5 (d, \(J_{PC} = 8.5\), \(J_{PP} = 120\), =C-Pt), 153.1 (s, -NC(Ph)), 151.5 (N=C=O ?), 86.3 (s, Cp), 52.5 (s, \(J_{PtC} = 54.7\), CH\textsubscript{2}), 20.6 (s, Me).

\textsuperscript{31}P{\textsuperscript{\textsuperscript{1}}H} NMR (C\textsubscript{6}D\textsubscript{6}) \(\delta\) 22.7 (d, \(J_{PP} = 11.3\), \(J_{PP} = 2643\)), 16.3 (d, \(J_{PP} = 11.3\), \(J_{PP} = 3621\)).

FAB MS \textsuperscript{102}Ru isotope, (relative intensity) 1226 (M\textsuperscript{+}, 25.4), 719 (Pt(PPh\textsubscript{3})\textsubscript{2}\textsuperscript{+}, 100).

Anal. Calcd. for C\textsubscript{57}H\textsubscript{49}N\textsubscript{6}O\textsubscript{4}P\textsubscript{2}PtRuS: C, 57.79; H, 4.03; Found: C, 57.88; H, 4.43%.

If compound 29a is left in CD\textsubscript{2}Cl\textsubscript{2} solution over 18 hours at ambient temperature, another product is detected by \textsuperscript{31}P{\textsuperscript{\textsuperscript{1}}H} NMR: \(\delta\) 21.4 (d, \(J_{PP} = 12.8\), \(J_{PP} = 2455\)) and 19.3 (d, \(J_{PP} = 12.8\), \(J_{PP} = 4452\)). Unfortunately, an attempt to repeat this isomerization on a preparatory scale was unsuccessful.

\textbf{Reaction of \textit{Cp(CO)Ru(\mu-\eta^2,\eta^1-CH\textsubscript{2}=C=C(H))Pt(PPh\textsubscript{3})\textsubscript{2} (15a) with p-MeC\textsubscript{6}H\textsubscript{4}S(O)\textsubscript{2}N=C=O (TSI) }

The reaction of 15a with TSI was carried out under 5 different sets of conditions. The standard TSI solutions used in this work were prepared
in the drybox by utilizing the appropriate dry solvent and were 0.079 M. Fresh standard solutions were prepared for each individual reaction. All results, as reported here, are based upon \(^1\)H and \(^{31}\)P\(^{(1)}\)H NMR spectral data obtained on residues from solvent removal under reduced pressure from aliquots of reaction solution. These residues were then dissolved in appropriate deuterated solvents. Ratios of products are based upon comparison of integrated Cp resonances (\(^1\)H NMR) and/or relative intensities of \(^{31}\)P\(^{(1)}\)H NMR resonances.

**Intermediate X:**
\(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 8.2-6.8 (m, Ph), 5.15 (d, \(J_{PH} = 20, 1\) H, CH), 4.41 (s, Cp), 3.25 (d, \(J_{HH} = 19.5, 1\) H of CH\(_2\)), 2.85 (d, br, \(J_{HH} = 19.5, 1\) H of CH\(_2\)).
\(^{31}\)P\(^{(1)}\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 62.0 (d, \(J_{PP} = 15.2, J_{PtP} = 137, Ru-PPh_3\)), 17.0 (d, \(J_{PP} = 15.2, J_{PtP} = 2711, Pt-PPh_3\)).

**Intermediate Y:**
\(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 4.76 (s, Cp).
\(^{31}\)P\(^{(1)}\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 33.6 (d, \(J_{PP} = 3.6, J_{PtP} = 2912\)), 16.2 (d, \(J_{PP} = 3.6, J_{PtP} = 3230\)).

**Complex 28b:**
\(^1\)H NMR (CDCl\(_3\)) \(\delta\) 12.4 (s, 1 H, NH), 8.0-7.1 (m, 6 Ph), 5.91 (s, 1 H, CH), 3.94 (s, 5 H, Cp).
\(^{31}\)P\(^{(1)}\)H NMR (CDCl\(_3\)) \(\delta\) 25.4 (d, \(J_{PP} = 5.3, J_{PtP} = 2791\)), 18.4 (d, \(J_{PP} = 5.3, J_{PtP} = 3538\)).

**Complex 29b:**
\(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 8.5-6.5 (m, Ph), 4.75 (s, Cp), 3.50 (d, \(J_{HH} = 22.2, J_{PtH} = 11.7, 1\) H of CH\(_2\)), 3.15 (dt, \(J_{HH} = 22.2, J_{PH} = 6.1, 1\) H of CH\(_2\)).
\[ ^{31}P(1H) \text{ NMR} (C_6D_6) \delta 26.3 (d, J_{PP} = 9.6, J_{PtP} = 2889), 20.7 (d, J_{PP} = 9.6, J_{PtP} = 3804). \]

Mononuclear Pt-containing Complexes: \(^{31}P(1H)\) NMR resonances around \(\delta 5\) ppm.

Mononuclear Ru-containing Complexes: \(^{31}P(1H)\) NMR resonances around \(\delta 45\) ppm.

Experiment 1

A stirred solution of 15a (0.20 g, 0.21 mole) in benzene (10 mL) at room temperature was treated with 0.050 mL (d = 1.3 g/mL, 0.33 mmol) TSI. After 20 hours, a brown-red solution with a finely divided solid was observed. A 1 mL aliquot was removed and freed of solvent in vacuo for NMR. The major products were 28b and mononuclear Ru and Pt-containing compounds in a relative ratio of 1:1:1 based upon signal intensities as described above. A minor product (about 1/3 as abundant as 28b) was 29b. The ratio of reaction products did not change after another 24 hours of stirring at room temperature.

Experiment 2

A stirred solution of 15a (0.15 g, 0.16 mmol) in benzene (5.0 mL) at room temperature was treated with 2.0 mL (0.16 mmol) of the standard TSI solution in benzene. An aliquot (0.5 mL) was removed for NMR spectroscopic analysis after 6 hours at room temperature. About one-third of the original 15a was still present, with the following species present in decreasing amounts: Y, X, 28b, 29b, mononuclear Pt and Ru species. After an additional 15 hours, NMR spectra showed a slight increase in the
amount of X, slight decrease in 15a and Y, and a large increase in 28b. Another 1.0 mL portion of the standard TSI solution was added at room temperature, and spectral data were taken again after 2 hours. 15a and Y were now gone, X and 29b were about the same as previously, and 28b was the major product. After another 4 hours, the X converted almost entirely to mononuclear ruthenium- and platinum-containing compounds.

Experiment 3

A stirred solution of 15a (0.15 g, 0.16 mmol) in toluene (7.0 mL) at -78°C was treated with 2 mL of the standard TSI solution in toluene dropwise, over 5 minutes. After the solution warmed slowly to about 0°C, only about 1/3 of 15a had reacted, and Y was the other major compound visible in the spectra. All other products were seen in only trace amounts. The reaction solution was then cooled again to -78°C, and another 1.0 mL of standard TSI solution was added dropwise over 5 minutes. The solution was allowed to warm to room temperature over 6 hours, and then was maintained for 12 hours at this temperature. Spectral data revealed four products, in the following decreasing amounts: Y, X, 28b, 29b. Typical chromatography on residue left after solvent removal under reduced pressure gave X, Y, 28b and platinum and ruthenium mononuclear compounds in a single narrow band. That is, the compounds could not be separated by chromatography.

Experiment 4

This experiment was exactly the same as Experiment 3, except that the reaction solution was allowed to warm to room temperature more
quickly (over 3 hours) and the first spectra were not recorded for another 1.5 hours of stirring at room temperature. Data at this point showed the following products in the indicated ratio: Y: 15a: X; 3:2:1. After 18 more hours at room temperature, only a slight decrease in the amount of 15a was noted.

**Experiment 5**

This experiment was identical to Experiment 4 except that 4 mL of the standard TSI solution was added instead of 2 mL, at -78°C. After the 3 hour warm-up to room temperature, the products 28b, 29b, and Y were present in the ratio 2:2:1. After 3 more hours at room temperature, only a 1:1 mixture of 28b and 29b was noted.

**Reaction of Cp(CO)Ru-μ-η²,η¹-CH₂=C=C(Ph))Pt(dppe) (25a) with p-MeC₆H₄S(Ο)₂N=C=O (TSI)**

A stirred solution of 25a (0.27 g, 0.29 mmol) in benzene (10 mL) at room temperature was treated with TSI (0.075 mL) dropwise over one minute. After 15 hours, solvent was freed under vacuum, and the orange residue was thoroughly washed with hexane (2 x 15 mL) to yield a yellow powder (29c) (0.17 g, 53% yield).

IR (CH₂Cl₂) 1894 (s), 1708 (m).

$^1$H NMR (CDCl₃) δ 8.0-6.8 (m, 5 Ph), 4.55 (s, 5 H, Cp), 3.41 (d, $J_{PH} = 23$, $J_{PtP} = 21$, 1 H of CH₂), 2.82 (m, 1 H of CH₂).

$^{31}$P($^1$H) NMR (CDCl₃) δ 0.47 (d, $J_{PP} = 26.5$, $J_{PtP} = 2362$), -6.6 (d, $J_{PP} = 26.5$, $J_{PtP} = 3468$).
FAB MS $^{102}$Ru isotope, (rel. intensity) 1114 ($M^+$, 24.2), 1086 ($M^+$ - CO), 20.3), 607 (Pt(dpdp)$^+$, 61.6).

**Reaction of Cp(CO)Ru-($\mu$-$\eta^2$-$\eta^1$-CH$_2$=C=C(H))Pt(dpdp) (25b) with TSI**

A solution of 25b (0.025 g) in C$_6$D$_6$ in an NMR tube equipped with a septum was charged with one drop of TSI (excess) and checked by $^1$H and $^{31}$P($^1$H) NMR spectroscopy after one hour. A product (29d) spectroscopically analogous to 29a was observed as the major product, but both the $^1$H and $^{31}$P($^1$H) NMR spectra contained a myriad of impurities. Other reactions involving TSI showed more promise, thus this reaction was not repeated on a preparatory scale.

$^1$H NMR (C$_6$D$_6$) $\delta$ 8.2-6.7 (m, 4 Ph), 4.47 (s, 5 H, Cp), 3.31 (m, 1 H of CH$_2$), 3.07 (m, 1 H of CH$_2$).

$^{31}$P($^1$H) NMR (C$_6$D$_6$) $\delta$ 2.2 (d, $J_{PP}$ = 24, $J_{PtP}$ = 2549), -4.0 (d, br, $J_{PP}$ = 24, $J_{PtP}$ = 3250).

**Reaction of Cp(CO)Ru-($\mu$-$\eta^2$-$\eta^1$-CH$_2$=C=C(Ph))Pt(PPh$_3$)(t-BuNC) (25c) with TSI**

A stirred solution of 25c (0.10 g, 0.12 mmol) in toluene (7.0 mL) at -78°C was treated with 3.0 mL (0.24 mmol) of a standard (0.079 M) solution of TSI in toluene dropwise over 5 minutes. The solution then allowed to warm to room temperature over 6 hours and was stirred for 12 additional hours. Solution volume was reduced to about 1 mL under reduced pressure and hexane (10 mL) was added with vigorous stirring to cause the precipitation of a yellow powder (29e, 0.075 g, 60% yield).

IR (CH$_2$Cl$_2$) 1908 (s), 1714 (m).
$^1$H NMR (C$_6$D$_6$) $\delta$ 8.3-6.5 (m, 4 Ph), 5.38 (s, 5 H, Cp), 3.66 (dd, $J_{HH} = 21.6$, $J_{PH} = 1.8$, $J_{PtH} = 50$, 1 H of CH$_2$), 3.29 (dd, $J_{HH} = 21.6$, $J_{PH} = 6.6$, 1 H of CH$_2$).

$^{13}$C($^1$H) NMR (C$_6$D$_6$) $\delta$ 203.1 (s, Ru-CO), 167.7 (s, =C-Pt), 141.1 (-NC(Ph)), 85.3 (s, Cp), 52.7 (s, CH$_2$), 21.1 (s, Me).

$^{31}$P($^1$H) NMR (C$_6$D$_6$) $\delta$ 14.6 (s, $J_{PtP} = 3538$).

FAB MS $^{102}$Ru isotope, (relative intensity) 1047 (M$^+$, 14.0), 1019 (M$^+$ - CO, 9.3), 850 (M$^+$ - TSI, 100).

Anal. Calcd. for C$_{46}$H$_{43}$N$_2$O$_4$PPtRuS: C, 52.77; H, 4.14; Found: C, 52.51; H, 4.27%.

**Reaction of Cp(CO)Fe-(\mu-\eta^2,\eta^1$-$CH_2=C=C(Ph))Pt(PPh$_3$)$_2$ (14b) with TSI**

A stirred solution of 14b (0.15 g, 0.15 mmol) in toluene (7.0 mL) at -78°C was treated with 2.0 mL (0.16 mmol) of a standard (0.079 M) solution of TSI in toluene dropwise over 5 minutes. Only decomposition to a complex mixture of products was noted by the examination of reaction solution aliquots (0.4 mL) by ($D_2$O-insert) $^{31}$P($^1$H) NMR spectroscopy.

**Reaction of Cp(CO)Ru-(\mu-\eta^2,\eta^1$-$CH_2=C=C(Ph))Pt(PPh$_3$)$_2$ (14a) with Methylsulfonyl Sulfonamide (Me-S(O)$_2$N=S=O)**

A stirred solution of 14a (0.17 g, 0.17 mmol) in toluene (7.0 mL) at -78°C was treated with 1.2 mL (0.17 mmol) of a standard (0.14 M) solution of methylsulfonyl sulfonamide in toluene. No reaction was noted by $^{31}$P($^1$H) or $^1$H NMR spectroscopy after warming the solution to room temperature over 6 hours. Likewise, no reaction was noted after another equivalent of the standard solution was added followed by an additional 24
hours of stirring at ambient temperature. Heating the solution at 60°C for 4 hours resulted in very slow decomposition of the original 14a.

Reaction of Cp(CO)Ru(μ-η²,η¹-CH₂=C=C(H))Pt(PPh₃)₂ (15a) with PPh₃AuSO₃CF₃

To a stirred solution of PPh₃AuCl (0.11 g, 0.22 mmol) in THF (5 mL) at room temperature was charged AgSO₃CF₃ (0.055 g, 0.21 mmol) as a solid in one portion. The flask was covered with aluminum foil, and after 2 hours the dark solid (AgCl) was filtered away through a pad of Celite. An additional portion of THF (10 mL) was used to wash the filter pad. This solution of gold reagent (approx. 15 mL) was added to a stirred solution of 15a (0.20 g, 0.21 mmol) in THF (10 mL) at -78°C dropwise over 8 minutes. The resulting solution appeared lighter yellow in color (probably dilution) than the original solution of 15a and was clear at this point. After warming to room temperature (one hour) and stirring for an hour, a cloudy mixture was noted. Solvent was removed from the suspension under reduced pressure, and the gummy tan residue was washed with diethyl ether (10 mL) to give a tan solid (0.15 g, 46% yield) of 30, mp >200°C.

IR (CH₂Cl₂) 1899.

1H NMR (CDCl₃) δ 8.55 (m, 1 H, CH), 7.8-7.1 (m, 9 Ph), 4.81 (s, 5 H, Cp), 3.71 (d, Jₚₜ = 4.0, 1 H of CH₂), 2.21 (d, Jₚₜ = 9.0, 1 H of CH₂).

13C{¹H} NMR (CD₂Cl₂) δ 209.0 (Ru-CO), 161.3 (d, Jₚₜ = 73.9, =C=), 120.8 (d, Jₚₜ = 112, C(H)), 90.1 (s, =CH₂), 85.1 (s, Cp).

3¹P{¹H} NMR (CDCl₃) δ 39.5 (d, Jₚₚ = 13, Au-PPh₃), 26.5 (t, Jₚₚ = 13, Jₚₚ = 2600), 20.5 (d, Jₚₚ = 13, Jₚₚ = 4471).
FAB MS $^{102}$Ru isotope, (relative intensity) 1412 (M$^+$ (cation only), 18.2), 1150 (M$^+$ - PPh$_3$, 28.1), 719 (Pt(PPh$_3$)$_2^+$, 100).

**Reaction of Cp(CO)Ru($\mu$-$\eta^2$,$\eta^1$-CH$_2$=C=C(Ph))Pt(PPh$_3$)$_2$ (14a) with PPh$_3$AuSO$_3$CF$_3$**

A stirred solution of PPh$_3$AuCl (0.050 g, 0.10 mmol) in THF (3 mL) at room temperature in an aluminum foil-covered flask was treated with AgSO$_2$CF$_3$ (0.026 g, 0.10 mmol) as a solid in one portion. After the solution had been stirred at room temperature for 1.5 hours, the AgCl was filtered away via a Celite plug. The filter plug was washed with an additional 8.0 mL of THF to give 11 mL of solution, which was added, over 5 minutes, to a stirred THF (5.0 mL) solution of 14a (0.11 g, 0.11 mmol) at -78°C. The combined solution warmed to room temperature over 2 hours and was stirred for an additional 12 hours before hexane (10 mL) was added to induce precipitation of a solid. The greenish-yellow solid (0.090 g, 55% yield) was collected on a frit, washed with 10 mL of 2:1 hexane/THF and dried in vacuo, mp $>$ 200°C.

IR (CH$_2$Cl$_2$) 1895.

$^1$H NMR (CDCl$_3$) $\delta$ 8.0-7.1 (m, 10 Ph), 4.86 (s, 5 H, Cp), 3.76 (d, $J_{PH}$ = 4.0, 1 H of CH$_2$), 2.51 (d, $J_{PH}$ = 8.0, 1 H of CH$_2$).

$^{31}$P($^1$H) NMR (CDCl$_3$) $\delta$ 39.3 (d, $J_{PP}$ = 15.6), 23.2 (dd, $J_{PP}$ = 15.6, $J_{PP}$ = 11.4, $J_{PtP}$ = 2535), 14.3 (d, $J_{PP}$ = 11.4, $J_{PtP}$ = 4651).

FAB MS $^{102}$Ru isotope, (relative intensity) 1488 (M$^+$ (cation only), 56.2), 1226 (M$^+$ - PPh$_3$, 85.3), 719 (Pt(PPh$_3$)$_2^+$, 100).

Anal. Calcd. for C$_{70}$H$_{57}$AuF$_3$O$_4$P$_3$PtRuS: C, 51.35; H, 3.51; Found: C, 51.26; H, 3.69%.
3) Studies Toward Elucidation of the Mechanism of Formation of
\(\text{Cp(CO)Ru-(\mu-H)(\mu-C(H)(C(O)CH_3))P(t(PPh_3)_2}\ (32)\)

The formation of 32 was examined in many different ways, most of which are described below. All results, as reported below, are based upon
\(\text{^1H and } \text{^31P}[^1H] \text{NMR spectral data obtained by the dissolution in appropriate deuterated solvents of residues left after the removal of solvent under reduced pressure from aliquots of reaction solutions. All reactions were with 15a as reagent.}

Data for 32:76

\(\text{^1H NMR (CD}_2\text{Cl}_2) \delta 7.49-7.12 (m, 6 \text{ Ph}), 6.23 (d, J_{PH} = 6.7, J_{PtH} = 11.8, 1 \text{ H}, \text{ CH}), 4.41 (s, 5 \text{ H}, \text{ Cp}), 1.44 (s, \text{ br, 3 H}, \text{ CH}_3), -8.57 (dd, J_{PH} = 21.1, J_{PH} = 78.0, J_{PtH} = 587, 1 \text{ H}, \mu-\text{H})\).

\(\text{^31P}[^1H] \text{NMR (CD}_2\text{Cl}_2) \delta 21.5 (d, J_{PP} = 13.2, J_{PtP} = 4321), 16.0 (d, J_{PP} = 13.2, J_{PtP} = 2268)\).

**Reaction of 15a in Wet Chloroform**

A stirred solution of 15a (0.10 g, 0.11 mmol) in water-saturated chloroform (approx. 6 drops of H_2O in 5 mL CHCl_3) was heated at reflux temperature for 24 hours. No reaction to form 32 was noted by \(^1\text{H NMR spectroscopy as only resonances for 15a were observed.}

**Reaction with Activated Neutral Alumina in Diethyl Ether or THF**

In the drybox, a stirred solution of 15a (0.10 g, 0.11 mmol) in diethyl ether or THF (10 mL) was treated with 1.0 g of activated alumina. No reaction was noted by NMR even after 24 hours. The 15a in solution was
adsorbed onto the alumina by removal of solvent under reduced pressure. Extractions of the yellow solid on a frit with ether (3 x 5 mL) and CH$_2$Cl$_2$ (2 x 5 mL) recovered 0.040 g of 15a.

**Reaction with Deactivated Neutral Alumina in Diethyl Ether or THF**

A procedure directly analogous to that above was carried out except with deactivated (6% H$_2$O or D$_2$O) alumina instead of activated (essentially no H$_2$O or D$_2$O). The result was the same as with activated alumina, viz., no reaction.

**Reaction with Silica in THF**

A stirred solution of 15a (0.20 g, 0.21 mmol) in THF (15 mL) at room temperature was treated with 3 grams of silica. After 18 hours of stirring, the reaction solution was freed of solvent in vacuo to yield yellow-colored silica. Extractions with CH$_2$Cl$_2$ (2 x 10 mL) recovered only 15a as a characterizable species.

**Reaction with Deactivated Alumina in CH$_2$Cl$_2$ or CHCl$_3$**

A stirred solution of 15a (0.10 g, 0.11 mmol) in CH$_2$Cl$_2$ (10 mL) at room temperature was treated with 1.5 g of deactivated alumina. After stirring the mixture for 2 hours, solvent was removed in vacuo. Extractions of the bright-yellow solid on a frit with CH$_2$Cl$_2$ (3 x 5 mL) yielded 0.050 g (0.052 mmol) of 32, a sample of which was examined by $^1$H NMR.

**Reaction with Silica or Florisil in CH$_2$Cl$_2$**
In an analogous manner, a CH$_2$Cl$_2$ (10 mL) solution of 15a (0.20 g, 0.21 mmol) was treated with either silica or Florisil. Extractions with CH$_2$Cl$_2$ (as above) yielded only 32, determined by $^1$H NMR spectroscopy on an isolated sample.

**Reaction with Partially Deactivated Basic, Neutral, or Acidic Alumina**

A stirred solution of 15a (0.10 g, 0.11 mmol) in CHCl$_3$ (10 mL) at room temperature was treated with one gram of an activated alumina. No reaction was noted in any of the three cases after 3 hours, as determined by $^1$H NMR spectroscopy. A small quantity (0.010 mL) of water was added to each reaction solution in one portion to "deactivate" the alumina somewhat. The reactions were then monitored as often as required to determine the length of time for the reaction to become essentially complete. **Result:** Acidic, 1 hour; Neutral, 12 hours; Basic, 24 hours.

**Reaction with Activated (Neutral) Deuterated Alumina**

A stirred solution of 15a (0.10 g, 0.11 mmol) in diethyl ether (10 mL) at room temperature was treated with 1.0 g of the title alumina in the drybox. No reaction was observed after 24 hours, and no incorporation of deuterium into 15a was evident as ascertained by $^1$H NMR spectroscopy.

**Reaction with Deactivated (Neutral) Deuterated Alumina**

A stirred solution of 15a (0.10 g, 0.11 mmol) in CH$_2$Cl$_2$ (10 mL) at room temperature was treated with 4.5 g of the title alumina (6% D$_2$O, Grade III). After 12 hours, $^1$H and $^{31}$P($^1$H) NMR spectral data indicated that some deuterium incorporation had occurred because the resonances
in the $^{31}$P($^1$H) NMR spectrum were multiplets rather than the typical doublets. A sample of residue left after solvent removal in vacuo was dissolved in CH$_2$Cl$_2$ (0.5 mL) and examined by 2D NMR spectroscopy.

**Reaction of Deactivated (Neutral) Deuterated Alumina in CDC$_3$**

This reaction was carried out exactly as directly above except that CDC$_3$ (7.0 mL) was used as solvent for the reaction, and THF was used as 2D NMR spectroscopy solvent.

**Reaction with Popowa Sand in "Wet" CH$_2$Cl$_2$**

A stirred solution of 15a (0.10 g, 0.11 mmol) in CH$_2$Cl$_2$ (10 mL) saturated with H$_2$O at room temperature was treated with 3 grams of Popowa sand (very fine particles). No reaction, except partial decomposition, was noted by $^1$H NMR spectroscopy after 24 hours.

**Reaction with Cr$_2$O$_3$**

A stirred solution of 15a (0.13 g, 0.14 mmol) in 3:1 THF/CHCl$_3$ (20 mL) at room temperature was treated with dry, powdery Cr$_2$O$_3$ (0.60 g) as a solid in one portion. Removal of solvent from an aliquot of reaction solution (0.5 mL) and examination of the residue dissolved in CDC$_3$ (0.5 mL) by $^1$H and $^{31}$P($^1$H) NMR spectroscopy showed no reaction after 3 hours. Solvent was removed under reduced pressure and replaced by CHCl$_3$ (15 mL) and five drops of water. No reaction was observed (monitored as above) even after 36 hours.
**Reaction with Alumina in Presence of 2,2'-Azobis(2-methylpropionitrile) (AIBN)**

A stirred THF (20 mL) solution of 15a (0.15 g, 0.16 mmol) in the presence of Grade III alumina (1 gram) was charged with AIBN (0.010 g) in one portion as a solid. Again, no reaction was observed as monitored by $^1\text{H}$ and $^{31}\text{P}(^1\text{H})$ NMR spectroscopy as above.

**Reaction with Alumina in Presence of Nitrosobenzene (or Benzoquinone)**

A Schlenk flask was charged with 15a (0.10 g, 0.11 mmol), 1 gram of Grade III alumina, and nitrosobenzene (0.010 g). The vessel was evacuated and filled with argon. CHCl$_3$ (10 mL) was then added while the reaction contents were stirred vigorously at room temperature. After 2 hours, removal of solvent from an aliquot (0.5 mL) of reaction solution in vacuo, followed by dissolution in CDCl$_3$ and examination of $^1\text{H}$ and $^{31}\text{P}(^1\text{H})$ NMR spectra, showed no reaction! Substitution of benzoquinone for nitrosobenzene (another experiment) produced the same result—no reaction.

**Reactions of Cp(CO)Ru-(μ-H)(μ-C(H)(C(O)CH$_3$))Pt(PPh$_3$)$_2$ (32)**

**Reaction of Cp(CO)Ru-(μ-H)(μ-C(H)(C(O)CH$_3$))Pt(PPh$_3$)$_2$ (32) with KOH**

A stirred ethanol (5 mL) solution of 32 (0.050 g, 0.052 mmol) at -78°C was treated dropwise over 5 minutes with 0.42 mL (0.053 mmol) of a standard (0.13 M) solution of KOH in ethanol. After warming to (8 hours) and stirring at room temperature (12 hours), the solution was filtered and freed of solvent under reduced pressure. The entire residue was then
dissolved in CD$_2$Cl$_2$ for NMR analysis. No reaction was observed via $^1$H NMR spectroscopy.

**Reaction of Cp(CO)Ru-(μ-H)(μ-C(H)(C(O)CH$_3$)Pt(PPh$_3$)$_2$ (32) with C$_7$H$_7^+PF_6^-$**

A stirred solution of 32 (0.10 g, 0.10 mmol) in THF (10 mL) was charged with C$_7$H$_7^+PF_6^-$ (0.025 g, 0.11 mmol) as a solid in one portion. After an 8 hour warmup to room temperature, followed by 12 hours of additional stirring, an aliquot (0.5 mL) freed of solvent in vacuo and dissolved in CDCl$_3$ was examined by $^1$H and $^{31}$P($^1$H) NMR spectroscopy and revealed nearly complete reaction. Hexane (10 mL) was added to induce precipitation of product (33), which was isolated by decantation (0.114 g, 71% yield) as an orange tar.

IR (THF) 1920 (s), 1771 (s).

$^1$H NMR (CD$_2$Cl$_2$) $\delta$ 7.74 (d, $J_{PH} = 4.0$, $J_{PtH} = 23$, 1 H, CH), 7.3-7.0 (m, 6 Ph), 4.87 (s, 5 H, Cp), 1.57 (s, 3 H, Me).

(acetone-d$_6$) $\delta$ 8.05 (d, $J_{PH} = 4.0$, $J_{PtH} = 23$, 1 H, CH), 7.7-7.1 (m, 6 Ph) 4.88 (s, 5 H, Cp), 1.62 (s, 3 H, Me).

$^{13}$C($^1$H) NMR (CD$_2$Cl$_2$) $\delta$ 193.6 (s, Ru-CO), 177.7 (s, Me-CO-C) 140-129 (m, Ph), 85.8 (s, Cp), 25.9 (d, $J_{PC} = 3.0$, Me) No signal was observed for CH.

$^{31}$P($^1$H) NMR (acetone-d$_6$) $\delta$ 25.2 (d, $J_{PP} = 21$, $J_{PtP} = 2776$), 15.9 (d, $J_{PP} = 21$, $J_{PtP} = 4325$).

FAB mass spectrum and elemental analyses were inconclusive.
RESULTS AND DISCUSSION

A. Studies Toward the Preparation of New Transition Metal Propargyl Compounds and Heteronuclear Complexes

1) Preparation of Complexes Containing Negative Phenylpropargyl Species and Chromium Propargyl Chemistry

Transition-metal propargyl and allenyl complexes are generally prepared via reaction of a negatively-charged transition metal complex

\[ [M'] + XCH_2C≡CR \rightarrow [M]-CH_2C≡CR + X^- \] (31)

[M]' with a propargyl halide (X) (Eq. 31). Usually, when R = H, an SN2' mechanism leads to the formation of an allenyl species, except in certain cases, such as when utilizing Cp(CO)_3W^- as the transition-metal anion. In general, the reaction in the opposite sense, that is, of a transition metal halide complex with a negatively polarized propargyl

\[ [M]-X + CH_2C≡CR \rightarrow [M]-CH_2C≡CR + X^- \] (32)

species is much less common (Eq. 32). The major reason for this is the ease of preparation of a transition metal anion complex vs. the difficulty in preparing compounds containing the negatively polarized propargyl.
group. This difficulty was essentially overcome by using the so-called Grignard Machine loaned to us by Professor Emeritus Melvin Newman. This apparatus (Figure 1, page 27) was designed to eliminate the coupling reaction of the newly-formed Grignard anion with the propargyl halide. In the words of (then) Master's candidate, D. C. Rowland, "the apparatus is so designed that solvent (ether) may be distilled from a flask into a condenser above the magnesium-packed tube. The condensed ether runs down through the magnesium and runs by gravity back to the original pot, the return line being of such a height that magnesium turnings are always covered with ether." The phenylpropargyl bromide is added dropwise at the top of the condenser, and the newly formed Grignard is pushed through the magnesium turnings by the ether flow before the next drop of phenylpropargyl bromide is released. Thus, coupling of the bromide and the Grignard to form a diacetylene product is essentially eliminated. The reaction was virtually quantitative, as well, as evidenced by simple titration with standardized HCl on aliquots of reaction solution.\(^66\)

The yield reported for the reaction of the following chromium halide with phenylpropargyl Grignard (Eq. 33) was low (26%)\(^68\) when the

\[
\text{Cp(NO)}_2\text{CrCl} + X\text{MgCH}_2\text{C}=\text{CPh} \longrightarrow \text{Cp(NO)}_2\text{CrCH}_2\text{C}=\text{CPh} \quad (33)
\]

Grignard reagent was not prepared in the Grignard Machine. Thus, optimization of the yield of \(\text{Cp(NO)}_2\text{CrCH}_2\text{C}=\text{CPh} \) (1) was an early goal. Unfortunately, it was discovered that the yield was low not necessarily
because of a low abundance of fresh Grignard reagent, but because the Grignard was too reactive towards the \( \text{Cp(NO)}_2\text{CrCl} \) compound.

For this reason the negative phenylpropargyl was made less reactive by treating the Grignard with \( \text{ZnCl}_2 \) (Eq. 34). Spectroscopic data for \( \text{Zn(CH}_2\text{C}=\text{CPh})_2 \) include only \( ^1\text{H} \) and \( ^{13}\text{C}\{^1\text{H}\} \) NMR data owing to the instability of \( \text{Zn(CH}_2\text{C}=\text{CPh})_2 \) in the solid state. The \( ^1\text{H} \) NMR spectrum shows the typical multiplets around \( \delta \) 7.3 ppm for the phenyl proton resonances, as well as a singlet at \( \delta \) 2.07 ppm for the methylene protons. The \( ^{13}\text{C}\{^1\text{H}\} \) NMR spectrum has typical phenyl signals as well as resonances for the acetylenic carbon atoms at \( \delta \) 93.6 and 78.7 ppm. The methylene carbon signal occurs at \( \delta \) 25.5 ppm. The acetylenic carbon resonances are quite typical for a mononuclear propargyl complex\(^80\) (see Table 2), as is the methylene proton resonance. The \( \text{CH}_2 \) carbon resonance is somewhat downfield from those of other transition metal propargyl compounds,\(^24,68,76,81\) indicating a small contribution of \( sp^2 \) hybridization at this carbon atom.

The preparation of compound 1 from \( \text{Zn(CH}_2\text{C}=\text{CPh})_2 \) is then straightforward and the yield is increased to 40\% (Eq. 35). Previously unreported \( ^{13}\text{C}\{^1\text{H}\} \) NMR spectroscopic data for 1 include typical phenyl (\( \delta \) 130.9, 128.1, 126.2, 126.0), acetylenic (\( \delta \) 100.8, 85.0), and cyclopentadienyl (\( \delta \) 100.8, 85.0).
resonances. The CH$_2$ carbon signal at $\delta$ 0.68 ppm is also normal. Since the yield of the reaction to prepare 1 was increased, it was now possible to make a large enough quantity of 1 to study its reactivity with Fe$_2$(CO)$_9$. It was of interest to compare such reactivity of 1 to that of the isoelectronic and isostructural species, Cp(CO)$_2$FeCH$_2$C=CPH.

Reaction of 1 with Fe$_2$(CO)$_9$ in hexane at room temperature is complete within one hour (Eq. 36) and affords after workup (CO)$_3$Fe(μ-η$^2$,η$^3$-PhC=C=CH$_2$)Fe(CO)$_2$NO (2) and CpCr(CO)$_2$NO (identified by a comparison of obtained spectroscopic properties to those from the literature$^{65}$). Complex 2 was isolated in 35% yield as a red oil that is air sensitive both as a neat sample and in solution. It is the first example of a binuclear iron compound with a μ-η$^2$,η$^3$-allenyl ligand. Other heterobinuclear metal-μ-η$^2$,η$^3$-allenyl complexes have been obtained by reaction of Cp(CO)$_3$MCH$_2$C=CPH (M = Mo,W) with Fe$_2$(CO)$_9$$^{24b,c}$ (see Table 1 (a) and Eq. 17); however, the reaction in Eq. 6 represents the only known case of complete transfer of the propargyl group as the corresponding allenyl ligand from a transition-metal propargyl complex to a metal-containing substrate. The additional heterobinuclear complexes in Table 1

$$\begin{align*}
\text{Cp(NO)}_2\text{CrCH}_2\text{C}=\text{CPh} \\
1 + \text{Fe}_2(\text{CO})_9 \\
\text{1. Hexane, RT, 1 hr.} \\
\text{2. Chromatography on silica gel} \\
\text{2} \quad \text{(36)} \\
\text{Cp(CO)}_2\text{Cr(NO)}
\end{align*}$$
Table 1. Comparison of $^{13}$C NMR data$^a$ between $\mu$-$\eta^2,\eta^3$-binuclear and $\eta^3$-mononuclear allenyl complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\equiv C =$</th>
<th>C(R)</th>
<th>CH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(C$_\beta$)</td>
<td>(C$_\alpha$)</td>
<td>(C$_\gamma$)</td>
</tr>
<tr>
<td>(CO)$_3$Fe-$\mu$-$\eta^2,\eta^3$-PhC=$\equiv$CH$_2$Fe(CO)$_2$NO (2)</td>
<td>111.8</td>
<td>80.5</td>
<td>70.5 (169)</td>
</tr>
<tr>
<td>L(CO)$_2$M-$\mu$-$\eta^2,\eta^3$-CH$_2$=$\equiv$C=CR)Fe(CO)$_3$ (a)$^{24}$</td>
<td>120.1 - 92.1</td>
<td>93.1 - 80.0</td>
<td>70.5 - 67.2</td>
</tr>
<tr>
<td>M= W, Mo; L= Cp, Cp'; R= p-tolyl, Ph, Me</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L(CO)$_2$Co-$\mu$-$\eta^2,\eta^3$-CH$_2$=$\equiv$C=CR)Fe(CO)$_3$ (b)$^{31}$</td>
<td>122.4 - 121.0</td>
<td>92.1 - 87.4</td>
<td>69.2 - 66.1</td>
</tr>
<tr>
<td>L= CO, PPh$_3$; R= Me, CH$_2$OH</td>
<td></td>
<td></td>
<td>(166)</td>
</tr>
<tr>
<td>Cp$_2$(Me)Zr($\eta^3$-CPh=$\equiv$CH$_2$)(c)$^{82}$</td>
<td>120.5</td>
<td>114.1</td>
<td>55.5 (167)</td>
</tr>
<tr>
<td>[Cp$_2$(Et)Zr($\eta^3$-CR=$\equiv$CCH$_2$)] (d)$^{83}$</td>
<td>168.6</td>
<td>141.6</td>
<td>75.3</td>
</tr>
</tbody>
</table>

$^a$At 25°C, in CDCl$_3$ (a, b), CD$_2$Cl$_2$ (c), $d_8$-THF (d), or C$_6$D$_6$ (e).

$^b$R = Cp(Et)Zr-
(b), as mentioned briefly in the Introduction, were prepared (by Osella and coworkers\textsuperscript{31}) via a two-step process from the reaction of a dicobalt hexacarbonyl bridging-acetylene complex with Fe(CO)\textsubscript{5}, followed by replacement of a carbonyl ligand with triphenylphosphine. The similarity in the data for the analogous complexes, a and b, is readily apparent.

The data for the other three types of complexes (shown below) in Table 1 are for mononuclear $\eta^3$ and $\eta^2$ (3-electron-donating) species that have recently appeared in the literature.\textsuperscript{82,83} These complexes have similar $^{13}$C NMR and other spectroscopic properties to those of the binuclear $\mu$-$\eta^2,\eta^3$ allenyl complexes. The other two complexes shown (e and f)\textsuperscript{84,85} are mononuclear $\eta^2$ complexes that are related to c and d only.
in that they are mononuclear allenyl complexes in which this ligand is also 3-electron-donating. Spectroscopic and chemical properties for e and f differ significantly from those of c and d.

The characterization of 2 is facilitated by the similarity of its $^{13}\text{C}^{[\text{H}]}$ as well as its $^1\text{H}$ NMR spectra to those of previously synthesized and, where applicable, structurally elucidated heteronuclear metal-$\mu$-$\eta^2,\eta^3$ allenyl complexes. As can be seen in Table 1, the chemical shifts for the resonances assigned to the allenyl carbons ($\delta$ 111.8 (=C=), 80.5 (=CPh), 70.5 (CH$_2$)) correspond closely with reported values for the analogous carbon atoms (and protons as well) of a, b and to the mononuclear $\eta^3$-allenyl, c. The values of the coupling constants ($^1J_{\text{CH}}$) of the CH$_2$ group for 2, a, b, and c are in the narrow range of 166 to 169 Hz., and are indicative of sp$^2$ hybridization at this carbon. The presence of the NO ligand on 2 was confirmed by a strong absorption (1778 cm$^{-1}$) in the diagnostic region of the IR spectrum. Further discussion concerning a possible mechanistic pathway for the course of reaction will accompany the discussion of the reaction of Cp(CO)$_2$FeCH$_2$C≡CPh with Fe$_2$(CO)$_9$.

2) The Reaction of Cp(CO)$_2$FeCH$_2$C≡CPh with Fe$_2$(CO)$_9$

Early investigations of the reaction of Cp(NO)$_2$CrCH$_2$C≡CPh (1) (and also of Cp(CO)$_2$FeCH$_2$C≡CPh) with Fe$_2$(CO)$_9$ showed the presence of a minor product (4) that did not contain a cyclopentadienyl (Cp) resonance, as evidenced by its $^1\text{H}$ NMR spectrum. Close inspection of the $^1\text{H}$ NMR spectrum of 1 (and of Cp(CO)$_2$FeCH$_2$C≡CPh) showed the presence of an extraneous resonance at $\delta$ 2.75. This turned out to be the resonance for the
CH₂ protons of (PhC≡CH₂)₂ (3), a common by-product formed from the coupling of phenylpropargyl groups in the syntheses of 1 and Cp(CO)₂FeCH₂C≡CPh. Careful purification of 1 (by chromatography) and Cp(CO)₂FeCH₂C≡CPh (by crystallization) removed the impurity of 3, and when the reactions of the two metal propargyls with Fe₂(CO)₉ were repeated, 4 was no longer obtained.

In order to prepare 4 in higher yields, larger quantities of 3 were required. Authentic compound 3 was prepared and isolated quite easily, as described in the Experimental, and ¹H NMR, ¹³C(¹H) NMR, and EI mass spectra were obtained for the product. The acetylenic (δ 88.3 and 81.6) and CH₂ carbon (δ 19.8) chemical shifts were quite typical, as was that of the methylene protons (δ 2.75). The phenylpropargyl radical-cation was the base peak in the mass spectrum, although the (M - 1)⁺ was also observed at relatively high intensity.

The ferrole compound (4) was obtained nearly quantitatively in 15 minutes at refluxing hexane temperature (Eq. 37). Since most spectroscopic properties of 4 have already been reported,²⁴a only the incorrectly reported ¹H NMR data will be given here. The salient features
of the spectrum of 4 are two doublets of doublets, comprising an AA'BB'
spectrum, at δ 3.32 and 2.76; the $^{2}J_{HH}$ (geminal) coupling is 13.6 Hz and the
$^{3}J_{HH}$ (vicinal) coupling is 1.6 Hz. These resonances are assigned to the
$C_2H_4$ protons of the four-membered ring.

Unlike in the case of the preparation of 1, Cp(CO)$_2$FeCH$_2$C≡CPh (5)
can be prepared rather easily from the Cp(CO)$_2$Fe$^-$ anion and

$$[\text{Cp(CO)}_2\text{Fe}]^- + \text{ClCH}_2\text{C}≡\text{CPh} \rightarrow \text{Cp(CO)}_2\text{FeCH}_2\text{C}≡\text{CPh} \quad (38)$$

ClCH$_2$C≡CPh (Eq. 38). A new procedure, based upon that of Shuchart,$^{76}$
and modified somewhat to avoid the use of filter paper (see Experimental
Section) for the removal of unreacted NaK$_{2.8}$, was developed to prepare 5
in very high yield (79%).

The reaction of pure 5 with Fe$_2$(CO)$_9$ was shown to produce only

$$\text{(CO)}_3\text{Fe}[\mu-\eta^1\text{-C(O)(C(Ph)≡C(Fe(CO)}_2\text{Cp})≡CH}_2] \quad (39)$$

(CO)$_3$Fe[$\mu-\eta^4\text{-C(O)(C(Ph)≡C(Fe(CO)}_2\text{Cp})≡CH}_2] \quad (39)$. This $\mu^3$-allyl-$\eta^1$-carbonyl complex has been completely characterized,
including structurally, and will not be discussed in this context. However,
Scheme 1. Possible pathway for reaction of 5 with \( \text{Fe}_2(\text{CO})_9 \).

\[
\text{Cp(CO)}_2\text{FeCH}_2\text{C}≡\text{CPh} + "\text{Fe(CO)}_4" \rightarrow \text{Cp(CO)}_2\text{FeCH}_2
\]

\[
\text{Fe(CO)}_3
\]

mechanistic considerations are in order because the course of reaction followed in Eq. 39 will be compared to other reactions later.
A suggested mechanism, based on that given for the reactions of metal-propargyl complexes with various neutral electrophiles\textsuperscript{88,89} is set out in Scheme 1. It is proposed that the reaction proceeds by nucleophilic attack of the propargylic C≡C on a coordinatively unsaturated Fe(CO)\textsubscript{4} species to give a binuclear iron-acetylene complex. This complex (g) rearranges to a dipolar metal-\(\eta^2\)-allene zwitterion bearing an Fe(CO)\textsubscript{3} group as the negative terminus (h). Intermediate h then collapses by

\textbf{Scheme 2.} Possible pathway for reaction of 1 with Fe\textsubscript{2}(CO)\textsubscript{9}. 

\[
\begin{align*}
\text{Cp(NO)}\textsubscript{2}CrCH\textsubscript{2}C≡CPh & \quad + \quad "\text{Fe(CO)}_x" \\
1 & \quad \rightarrow \\
& \quad (x = 3 \text{ or } 4) \\
\text{Cp(NO)}\textsubscript{2}Cr-CH\textsubscript{2}C≡CPh & \quad + \quad \text{Dissociation} \\
& \quad + \quad \text{.....} \\
\text{Cp(NO)}\textsubscript{2}CrNO & \quad + \quad 2
\end{align*}
\]
attack of the Fe(CO)$_3$ at the coordinated allene to give j. Intermediate j is directly analogous to the [3+2] cycloaddition products obtained in the reaction of transition metal propargyl complexes with reagents such as $p$-toluenesulfonyl isocyanate.$^{68}$

On the other hand, the reaction to form 2, where the propargyl group is completely transferred to another transition metal as an allenyl ligand, probably commences in an analogous fashion, except without carbon monoxide insertion, to the corresponding binuclear metal-$\eta^2$-allene-$\eta^1$-yl species (h') (Scheme 2). Intermediate h' might then be expected to display low stability with respect to chromium-$\eta^2$-allene bond dissociation, since [CpCr(NO)$_2$]$^+$ has been shown to behave as a hard acid toward 2-electron donor ligands.$^{90}$ Dissociation of this weak $\pi$-bond could then lead to the observed formation of 2 and CpCr(CO)$_2$(NO).

3) Preparation and Reactivity of Cp(PPh$_3$)$_2$RuCH$_2$C≡CPh

The preparation of Cp(PPh$_3$)$_2$RuCH$_2$C≡CPh (7) from the corresponding ruthenium chloride and phenylpropargyl Grignard (Eq. 40) was not as straightforward as it appears. For example, owing to the
inherent stability of a ruthenium-bromine bond vs. a ruthenium-carbon bond, the phenylpropargyl Grignard reagent had to be prepared in the absence of any bromine or bromide source. Thus, the magnesium of the Grignard Machine, which is activated by the addition of ethylene bromide, could not be used to prepare the Grignard reagent for Eq. 40 (Otherwise, no 7 was prepared from reaction of \( \text{PhC}=\text{CCH}_2\text{MgBr} \) with \( \text{Cp(PPh}_3\text{)}_2\text{RuCl} \). Instead, only \( \text{Cp(PPh}_3\text{)}_2\text{RuBr} \) was observed). A new procedure was devised that eliminated all sources of bromide ion. This process utilized \( \text{HgCl}_2 \) as the magnesium "activator", and only \( \text{ClCH}_2\text{C}=\text{CPh} \) was used as the phenylpropargyl halide source. Yields of 100% by NMR (87% isolated) could then be attained of 7.

Compound 7 was fully characterized spectroscopically. The \( ^1\text{H} \) NMR spectrum showed the typical multiplets in the phenyl region, a singlet resonance for the Cp protons at \( \delta 4.31 \), and a triplet \( (^{3}J_{\text{PH}} = 12.1) \) at \( \delta 1.95 \) for the methylene protons. The \( ^{13}\text{C} \) NMR spectrum (Figure 2) revealed signals for the acetylenic carbons as two triplets \( \delta 123.5 \) \( (J_{\text{CP}} = 7.6) \) and \( \delta 109.1 \) \( (J_{\text{CP}} = 2.0) \), a doublet of multiplets at \( \delta 84.9 \) for the Cp, and a triplet of triplets \( (^{1}J_{\text{CH}} = 135, ^{2}J_{\text{PC}} = 11.8) \) at \( \delta -22.5 \) for the \( \text{CH}_2 \) carbon atom. The triphenylphosphine phosphorus atoms are shown to be equivalent in the \( ^{31}\text{P}(^1\text{H}) \) NMR spectrum, which shows a single resonance at \( \delta 50.1 \). Purity of 7 is noted by the good elemental analysis.

Recently, in addition to compound 7, numerous mononuclear propargyl and allenyl complexes have been prepared and examined spectroscopically, and several of these have been examined structurally as well. Owing to this flurry of activity, a careful examination of some of these new data and how it relates to bi- and trinuclear complexes to be
Figure 2. $^{13}$C NMR Spectrum of Cp(PPh$_3$)$_2$CH$_2$C≡CPh (7).
discussed later is appropriate. Specifically, an examination of $^{13}$C NMR spectroscopic data can allow one to correlate structure to chemical shift, and even to a limited degree, to reactivity of these mononuclear complexes. This theme of correlation between $^{13}$C NMR data and structure will be touched upon several times in this document. The pairs of compounds to be discussed are shown here:

\begin{align*}
\text{Cp(CO)$_2$RuCH$_2$C=CPh} & \quad \text{Cp(CO)$_2$WCH$_2$C=CH} \\
\text{Cp(CO)$_2$RuCH=C=CH} & \quad \text{Cp(CO)$_2$WCH=C=CH} \\
(PPh$_3$)$_2$BrPtCH$_2$C=CPh & \\
(PMe$_3$)$_3$Pt(C)(Ph)=C=CH$^+$
\end{align*}

The foregoing $\eta^1$-propargyl and $\eta^1$-allenyl complexes serve as a good starting point for a discussion of $^{13}$C NMR spectroscopic data. The most diagnostic feature of an $\eta^1$-propargyl complex is the chemical shift of the CH$_2$ carbon atom, which usually occurs at negative $\delta$ values relative to TMS. In Table 2, the CH$_2$ carbon atoms of the propargyl complexes resonate at $\delta$ -5.5 to -33.3 ppm. The other two propargylic carbons resonate in the typical chemical shift range for acetylenic carbon atoms (ca. $\delta$ 120 - 60 ppm) as shown in Table 2.

On the other hand, the most diagnostic feature of the $\eta^1$-allenyl complexes is the central carbon resonance at around $\delta$ 210 to 200 ppm. In general, the chemical shift for the CH$_2$ carbon is diagnostic as well (ca. $\delta$ 60 to 70), but the $^{13}$C NMR resonance for the central carbon atom is
usually the spectroscopic feature that alerts the reader to the type of complex under discussion. It is this spectroscopic feature of the phenylallenyl complex \((\text{PMe}_3)_3\text{PtC(Ph)C}=\text{CH}_2^+\), for example, that enabled the characterization of it structurally as an allenyl rather than a propargyl species.

As mentioned in the Introduction, the reaction chemistry of \(\eta^1\)-mononuclear propargyl and allenyl complexes is diverse and

**Table 2.** A comparison of \(^{13}\text{C}\) NMR data for mononuclear \(\eta^1\)-propargyl and allenyl complexes, in CDCl\(_3\) or CD\(_2\)Cl\(_2\) at 25°C (\(^1J_{\text{CH}}\) in Hz).

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\beta) or (=\text{CCH}_2)</th>
<th>C(R)</th>
<th>CH(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cp(CO)}_2\text{RuCH}_2\text{C} = \text{CPh}\text{76})</td>
<td>81.6</td>
<td>101.2</td>
<td>-26.4 (143)</td>
</tr>
<tr>
<td>(\text{Cp(CO)}_2\text{RuCH} = \text{C} = \text{CH}_2\text{76})</td>
<td>206.1</td>
<td>58.4 (166)</td>
<td>63.1 (167)</td>
</tr>
<tr>
<td>(\text{Cp(CO)}_3\text{WCH}_2\text{C} = \text{CH}_2\text{92})</td>
<td>92.0</td>
<td>68.4</td>
<td>-33.3</td>
</tr>
<tr>
<td>(\text{Cp(CO)}_3\text{WCH} = \text{C} = \text{CH}_2\text{92})</td>
<td>209.1</td>
<td>48.6</td>
<td>62.2</td>
</tr>
<tr>
<td>((\text{PPh}_3)_2\text{BrPtCH}_2\text{C} = \text{CPh}\text{93})</td>
<td>81.7</td>
<td>95.7</td>
<td>-5.5 (140)</td>
</tr>
<tr>
<td>((\text{PMe}_3)_3\text{PtC(Ph)} = \text{C} = \text{CH}_2^+)</td>
<td>202.4</td>
<td>101.6</td>
<td>69.9 (167)</td>
</tr>
</tbody>
</table>
extensive. An example of the diversity of the reaction chemistry of \( \text{Cp(CO)}_2\text{RuCH}_2\text{C}\equiv\text{CPh} \) is shown in Eq. 41. Owing to the rich chemistry of \( \text{Cp(CO)}_2\text{RuCH}_2\text{C}\equiv\text{CPh} \) observed by Shuchart\(^{76} \) (Eq. 41), reactions of 7 with several substrates were investigated to determine the effect that replacement of the two carbonyl ligands in \( \text{Cp(CO)}_2\text{RuCH}_2\text{C}\equiv\text{CPh} \) with triphenylphosphine would have on reactivity. Owing to the more electron-releasing phosphines on ruthenium, and hence a more electron-rich ruthenium atom of 7, it was observed that 7 reacts with electrophiles much more rapidly than does \( \text{Cp(CO)}_2\text{RuCH}_2\text{C}\equiv\text{CPh} \); however, its
reactions tend to be complicated by dissociation of PPh$_3$, and products are generally less stable and more difficult to purify than those derived from Cp(CO)$_2$RuCH$_2$C≡CPh. However, some useful information was gleaned from investigation of the reactivity of 7.

Compound 7 reacts rapidly with p-toluenesulfonyl isocyanate (TSI) to afford the [3+2] cycloaddition adduct 8 (Eq. 42). Qualitatively, this reaction proceeds at least as fast as that of (CO)$_4$(PPh$_3$)MnCH$_2$C≡CPh with TSI,

\[
\text{Cp(PPh$_3$)$_2$RuCH$_2$C≡CPh} \quad 7
\]
\[
+ \quad \text{Tosyl-N=C=O} \quad \text{(TSI)}
\]

which is more than 75 times faster than the corresponding reaction of TSI with Cp(CO)$_2$RuCH$_2$C≡CPh.$^{68}$ The green solid 8 was characterized by IR and NMR spectroscopy and mass spectrometry. The IR spectrum shows a lactam ν$_{C=O}$ band at 1740 cm$^{-1}$, and the $^{13}$C($^1$H) NMR spectrum displays resonances of the ring carbons at δ 194.2 (CO), 167.6 (CRu), 142.7 (CPh), and 38.7 (CH$_2$) ppm. These values are in good agreement with those reported for other [3+2] cycloadducts of metal-propargyl compounds and organic isocyanates and related species.$^{68,94}$ The $^1$H NMR spectrum shows a singlet at δ 3.48 ppm for the methylene protons, and the FAB mass spectrum adds further support to the proposed formulation. The fragmentation pattern involves ions that derive from loss of PPh$_3$ and the lactam ring by the molecular ion.
Compound 7 also reacted very rapidly with \( \text{Co}_2(\text{CO})_8 \) (Eq. 43).

\[
7 + \text{Co}_2(\text{CO})_8 \rightarrow \begin{array}{c}
\text{CH}_2\text{Ru(PPPh}_3\text{)}_2\text{Cp} \\
\text{Me}
\end{array}
\text{workup} (\text{H}^+) \begin{array}{c}
\text{(CO)}_3\text{Co} \\
\text{Ph}
\end{array} \begin{array}{c}
\text{Co(CO)}_3 \\
\text{Ph}
\end{array}
\]

The \( ^{31}\text{P}[^{1}\text{H}] \) and \( ^{1}\text{H} \) NMR spectra of the reaction solution suggested the presence of a trinuclear \( \text{Co}_2\text{Ru} \) complex structurally analogous to those observed by Young,\(^{16a}\) et al., except that the \( \text{Cp(CO)}_3\text{M} \) \((\text{M} = \text{Mo}, \text{W})\) group is replaced here by \( \text{Cp(PPPh}_3\text{)}_2\text{Ru} \). Unfortunately, the product decomposed during purification by chromatography, and only \( \text{(CO)}_3\text{Co(μ-η}^2-\text{PhC=}\text{CMe})\text{Co(CO)}_3 \)^{16a} could be isolated after workup.

Reaction of 7 with \( \text{Fe}_2(\text{CO})_9 \) in THF at room temperature proceeds differently from the corresponding reaction of \( \text{Cp(CO)}_2\text{RuCH}_2\text{C}=\text{CPh} \).\(^{76}\) No heteronuclear metal complexes were observed, and only products of exchange of CO and PPPh\(_3\) were apparently obtained (Eq. 44). These products are \( \text{Fe(CO)}_4\text{PPPh}_3 \)^{95} and \( \text{Cp(CO)(PPPh}_3\text{)RuCH}_2\text{C}=\text{CPh} \) (9). The new ruthenium propargyl complex was formulated on the basis of spectroscopic data, which include an IR \( \nu_{C=O} \) band at 1916 cm\(^{-1} \) (in THF), \(^{1}\text{H} \) NMR signals at \( δ \) 4.92 (Cp) and 2.55 (br, CH\(_2\)) ppm, and \(^{13}\text{C}[^{1}\text{H}] \) NMR resonances at \( δ \) 217.8 (CO), 169.2 (=CPh), 150.5 (=CCH\(_2\)), 90.6 (Cp), and 15.2 (CH\(_2\)) ppm, and a \( ^{31}\text{P}[^{1}\text{H}] \) NMR resonance at \( δ \) 41.0 ppm (all in CDCl\(_3\)).

Compound 9 was also prepared from reaction of 7 with carbon monoxide. The reaction in Eq. 44 is directly analogous to the reaction of
Cp(PPh\textsubscript{3})\textsubscript{2}RuCl with Fe\textsubscript{2}(CO)\textsubscript{9}, which leads to formation of Fe(CO)\textsubscript{4}PPh\textsubscript{3} and Cp(CO)(PPh\textsubscript{3})RuCl.\textsuperscript{50} Also, the reaction of 7 with W(CO)\textsubscript{5}-THF gave carbon monoxide for triphenylphosphine exchange as well. Thus, owing to the propensity of 7 to undergo facile CO substitution, no further reactions of this propargyl complex with metal carbonyls were investigated.

4) Reactions of Cp(CO)\textsubscript{3}WCH\textsubscript{2}C≡CPh with Rhodium and Platinum Reagents

Complexes containing rhodium have been shown during the past two decades to display high catalytic activity.\textsuperscript{3,4} Therefore, the introduction of this metal into a heterobi- or trimetallic system, where synergistic or other interactions may enhance catalytic properties, is highly desirable. Thus, a series of Rh-containing species were prepared and used in reactions with Cp(CO)\textsubscript{3}WCH\textsubscript{2}C≡CPh or other transition-metal propargyls. The reagents are shown in Eq. 45.

Unfortunately, none of the reagents in Eq. 45 yielded any stable, isolable products. Treatment of Cp(CO)\textsubscript{3}WCH\textsubscript{2}C≡CPh with the COD-containing dimer gave no reaction in inert solvent, or decomposition in THF. Rh\textsubscript{4}(CO)\textsubscript{12} as a reagent yielded an impure product (even after
chromatography), whose $^1$H NMR spectrum showed a Cp resonance at $\delta$ 5.19 ppm and two doublets ($J_{HH} = 2.2$) at $\delta$ 3.25 and 2.65 ppm, and whose IR spectrum revealed only two $\nu_{C=O}$ stretches, at 2062 and 1993 cm$^{-1}$.

The CpRh(CO)$_2$ reagent was shown to be rather inert under thermal conditions, so a photochemical reaction, utilizing a high-pressure Hg-vapor lamp (Hanovia), with Cp(CO)$_3$WCH$_2$C=CPh was carried out. Again, no discernible new products were obtained. The somewhat less inert Cp$_2$Rh$_2$(CO)$_3$ was treated with Cp(CO)$_3$WCH$_2$C=CPh in hexane at reflux temperature for two days. A very small amount of a yellow solid was obtained from chromatography of the reaction solution. Its IR (1969 (s), 1899 (m), 1880 (s) cm$^{-1}$) and $^1$H NMR (7.4-7.1 (m, Ph), 5.14 (s, Cp), 2.99 (s, CH$_2$)) spectra indicate that this product contains only W or Rh because just one Cp resonance was observed.

The reaction of Cp(CO)$_3$WCH$_2$C=CPh with (PPh$_3$)$_2$PtC$_2$H$_4$ (Eq. 46) was more interesting. The initially ethylene-saturated THF
reaction solution was not homogeneous after warming to room
temperature, so chromatography was carried out to purify 10. Compound
10 was characterized spectroscopically. Its IR spectrum (1913 (vs), 1801
(vs), 1703 (w)), and specifically the lowest energy carbonyl stretching
frequency, indicates the possibility of an inserted carbonyl between the
platinum and the C(Ph)-carbon atom, but this is not borne out in the FAB
mass spectrum. The $^{31}\text{P}[^1\text{H}]$ NMR data ($\delta$ 28.7 (d, $J_{pp} = 4.9$, $J_{ptp} = 3157$),
18.9 (d, $J_{pp} = 4.9$, $J_{ptp} = 3796$) is indicative of two inequivalent phosphorus
atoms on the same platinum atom. The two inequivalent CH$_2$ proton ($\delta$
6.28 and 6.10) signals coupled to one another by 5.0 Hz., fall in the range
typical of olefinic protons, suggesting that the remote carbon-carbon $\pi$-
bond of the $\mu$-allenyl group is not involved in bonding to a transition metal.
If the remote $\pi$-bond were involved in bonding to tungsten, one would
expect the terminal carbon atom to have more methylene rather than
olefin character, thus giving an upfield shift in the $^1\text{H}$ NMR resonances.
This phenomenon will surface again later in the discussion concerning
ruthenium- and platinum-containing binuclear complexes. The $^{13}\text{C}[^1\text{H}]$
NMR spectrum shows a typical chemical shift for the central (=C=) allenyl
carbon ($\delta$ 158.7), indicating a large departure from linearity about this
atom, a normal signal for the C(Ph)-carbon ($\delta$ 139.6), and a slightly more
downfield than usual signal for the CH$_2$ carbon atom at $\delta$ 110.3 ppm. This
slightly downfield chemical shift is consistent with the downfield shift of the CH$_2$ protons in the $^1$H NMR spectrum.

5) Reactions of Other Metal Propargyl and Allenyl Compounds

In order to introduce manganese into a heteronuclear metal compound, the reaction of (CO)$_5$MnCH$_2$C≡CPh with (PPh$_3$)$_2$PtC$_2$H$_4$ (Eq. 47) was carried out at -20°C to 0°C in THF. A $^{31}$P($^1$H) NMR spectrum taken at 0°C of the reaction solution revealed only the presence of the intermediate of possible structure shown in Eq. 47 ($\delta$ 31.5 (s, br, $J_{\text{Pt-P}} = 3208$)). Attempts at isolation

$$\text{(CO)}_5\text{MnCH}_2\text{C=CH}_2 + \text{Pt(PPh}_3\text{)}_2\text{C}_2\text{H}_4 \rightarrow \text{(CO)}_5\text{MnCH}_2\text{C=CH}_2\text{Pt(PPh}_3\text{)}_2$$

upon warming to room temperature were fruitless, however.

Two exploratory reactions of Cp(CO)$_2$FeCH$_2$C≡CPh (5) were carried out. In the first, no reaction was observed when 5 was treated with W(CO)$_5$·THF, even at elevated temperature for a long reaction time (in THF at reflux temperature for 9 hours). In contrast, the reaction of 5 with PPh$_3$Au$^+$ resulted in decomposition and/or formation of unstable and intractable material. While the former result was as expected (vide supra, page 117), the latter was not predicted. However, this result was still useful because it implied that reaction of PPh$_3$Au$^+$ with a somewhat less
nucleophilic reagent (such as the binuclear complexes discussed below) may proceed at such a rate as to be controlled by low temperature. This was indeed shown to be the case (page 237).

To ascertain whether carbon monoxide insertion could occur with Cp(CO)$_2$RuCH$_2$C≡CPh, the ruthenium propargyl was treated with

$$\text{Cp(CO)}_2\text{RuCH}_2\text{C≡CPh} + \text{PEt}_3 \xrightarrow{\Delta, \text{THF}} \text{No Reaction}$$

excess triethylphosphine (Eq. 48) in THF at reflux temperature for 24 hours. No reaction was observed. In fact, the only transition-metal propargyl species shown to insert carbon monoxide to date is the one prepared by Ungvary and Wojcicki, PPh$_3$(CO)$_3$CoCH$_2$C≡CR (R = Me, Ph, CH$_2$Cl).$^{81}$

In another exploratory reaction, Cp(CO)$_2$RuCH$_2$C≡CPh was treated with CpRh(C$_2$H$_4$)$_2$ in hexane at reflux temperature for 24 hours. Surprisingly, the acetylenic triple bond of the ruthenium propargyl complex did not displace an ethylene molecule from CpRh(C$_2$H$_4$)$_2$. Since it is well known$^{76}$ that the triple bond of Cp(CO)$_2$RuCH$_2$C≡CPh reacts quite readily with unsaturated metal fragments, the reaction must not have occurred because the rhodium center did not lose an ethylene molecule under the conditions here (69°C for 24 hours). This was rather discouraging because Shore and co-workers$^{98}$ observed loss of carbon monoxide from CpRh(CO)$_2$ at only slightly more forcing reaction conditions (110°C for 24 hours).
Another intriguing reaction is the one between 
\( \text{Cp(CO)}_2\text{RuCH}=\text{C}=\text{CH}_2 \) and toluenesulfonl isocyanate (TSI, Eq. 49). It was 

\[
\text{Cp(CO)}_2\text{RuCH}=\text{C}=\text{CH}_2 + p-\text{MeC}_6\text{H}_4\text{S(O)}_2\text{-N}=\text{C}=\text{O}
\]

\[
\text{Cp}_\text{RuC}_\text{N-tosyl} \quad (\text{tosyl} = \text{C}_6\text{H}_4\text{S(O)}_2^-) \quad 11
\]

shown by Rosenblum and co-workers\(^9\) that the iron analogue of the ruthenium allenyl complex, \( \text{Cp(CO)}_2\text{FeCH}=\text{C}=\text{CH}_2 \), reacts with TSI cleanly to produce the iron counterpart of 11. Compound 11 itself, on the other hand, proved to be too unstable to isolate as a solid. The only evidence for 11 is provided by a \(^1\text{H}\) NMR spectrum. The triplet \((J_{HH} = 2.0)\) for the CH proton at \( \delta 6.60 \text{ ppm} \) and the doublet \((J_{HH} = 2.0)\) for the CH\(_2\) protons at \( \delta 2.85 \text{ ppm} \) compare very well to the values reported by Rosenblum for the iron analogue \((\delta 6.29 \text{ (t, } J_{HH} = 2.0, 1 \text{ H, CH}), \text{ and } 2.94 \text{ (d, } J_{HH} = 2.0, 2 \text{ H, CH}))\). Removal of solvent from 11 under reduced pressure causes irreversible degradation of the yellow solution to a gummy red tar. Thus, no other spectroscopic properties could to be obtained for 11. However, it is clear, based upon the chemical shift of the CH\(_2\) protons \((2.85 \text{ ppm})\), that 11 is an allenyl-derived TSI cycloaddition product. Recall that typical CH\(_2\) chemical shift values for propargyl-derived TSI cycloaddition complexes fall in the range \( \delta 3.5-5.0 \text{ ppm} \).
6) Miscellaneous Reactions

In an effort to prepare \(\text{Cp(CO)}_2\text{RuCH}_2\text{C}≡\text{CPh}\) in a slightly different way, the phenylpropargyl tosylate (12) was generated as per Eq. 50.46

\[ p\text{-MeC}_6\text{H}_4\text{S(O)}_2\text{Cl} + \text{HOCH}_2\text{C}≡\text{CPh} \rightarrow \mu\text{-MeC}_6\text{H}_4\text{S(O)}_2\text{O-CH}_2\text{C}≡\text{CPh} \]

previous syntheses of transition-metal propargyl complexes involved the use of liquid propargyl halides. One advantage of a solid reagent over a liquid one is that solids are often easier to handle experimentally. Compound 12 was found to be much less air-sensitive than liquid \(\text{PhCCCH}_2\text{Cl}\) as well, another common advantage of solids over related liquids.

Compound 12 was completely characterized spectroscopically, and its exact mass was determined by electron-impact mass spectrometry. Diagnostic \(^1\text{H}\) NMR signals were observed at \(\delta\) 4.96 and 2.39 ppm for the methylene and methyl resonances, respectively, and the \(^{13}\text{C}\) NMR spectrum (Figure 3) helped to identify the acetylenic (\(\delta\) 88.8 (s) and 80.6 (t, \(^2\text{J}_{\text{CH}} = 8.0\))) and \(\text{CH}_2\) carbon (\(\delta\) 58.6 (t, \(^1\text{J}_{\text{CH}} = 156\))) atoms. Note the significant degree of \(\text{sp}^2\) character of the \(\text{CH}_2\) carbon as indicated by the \(^1\text{J}_{\text{CH}}\) coupling constant of 156 Hz. Perhaps the electron-withdrawing nature of the oxygen atom directly bonded to the \(\text{CH}_2\) carbon atom accounts for this NMR value. Unfortunately, while 12 was easier to handle than \(\text{ClCH}_2\text{C}≡\text{CPh}\), the yield of the reaction of 12 with \([\text{Cp(CO)}_2\text{Ru}]^+\) did not exceed that of the propargyl chloride with the ruthenium complex anion.
Figure 3. $^{13}$C NMR Spectrum of $p$-Me$_6$H$_4$S(O)$_2$OCH$_2$C≡CPh (12).
The preparation and reaction of tosylsulfonamide, p-MeC₆H₄S(O)₂NH₂ with (PPh₃)₂PtC₂H₄ were important control reactions, as will be seen later in this dissertation. Analytically pure tosylsulfonamide was prepared by the simple addition of an excess of water to a benzene solution of toluenesulfonyl isocyanate (TSI). The most important spectroscopic features of tosylsulfonamide are its ¹H NMR signals at δ 4.92 (s, br, NH₂) and 2.43 (s, Me) ppm.

The reaction of tosylsulfonamide with (PPh₃)₂PtC₂H₄ was straightforward and gave (PPh₃)₂Pt(tosylsulfonamide) cleanly. The ¹H NMR spectrum of the product showed a broad singlet at δ 3.18 ppm for the NH₂ protons and a singlet at δ 2.27 ppm for the methyl protons. The ³¹P{¹H} NMR spectrum showed a singlet at δ 8.0 ppm (Jₚₚ = 3449), indicating equivalent phosphorus atoms on platinum, and the FAB mass spectrum revealed (PPh₃)₂Pt(tosylsulfonamide) as the parent and base ion peak.

B. Reactions of Ruthenium- and Iron-Containing Propargyl and Allenyl Complexes with Platinum(0) Reagents

From the previous discussion, it would appear that first-row transition metal propargyl compounds do not have a high propensity to form heteronuclear metal-metal bonds with other substrates of first-row transition metals. It was also observed that a second-row transition metal propargyl complex tended to dissociate phosphine ligands (PPh₃) rather than form heteronuclear metal-metal bonds. Thus, an early goal of the research described below was two-fold:
a) Find a suitable substrate (i.e., unsaturated transition-metal species, preferably in the zero or very low oxidation state) to react with a first-row transition metal propargyl or allenyl compounds with the formation of heteronuclear metal-metal bonds, and

b) Use the carbonyl-containing, second row, electron-rich, transition-metal propargyl and allenyl complexes (i.e., Cp(CO)$_2$Ru-R, where R=phenylpropargyl or allenyl) and further explore potential metal-metal bond-forming reactions.

1) Preparations of Cp(CO)$_2$M-(μ-η$^2$;η$^1$-CH$_2$=C=C(R))Pt(PPh$_3$)$_2$ (M = Fe and Ru, R = Ph or H)

Oxidative addition of organic halides and related species to platinum(0) reagents is well known. However, the reaction of platinum(0) reagents with transition-metal-containing complexes to form complexes with heteronuclear metal-metal bonds is considerably less developed (see Introduction). Because of our experience with and knowledge of the types of products observed when transition metal propargyl and allenyl complexes are reacted with Fe$_2$(CO)$_9$ and related species, it was our strategy to prepare possibly related heteronuclear compounds by utilizing platinum(0) reagents.

It was discovered that reactions of ruthenium and iron propargyl and allenyl complexes with platinum(0) reagents proceed via cleavage of the metal-carbon σ-bond of the propargyl or allenyl complex to give directly the new heterobinuclear metal-μ-allenyl compounds Cp(CO)$_2$M-(μ-η$^2$;η$^1$-CH$_2$=C=C(R))Pt(PPh$_3$)$_2$ (Eq. 51). Of special note is the concomitant rehybridization of the propargyl CH$_2$ carbon atom (sp$^3$ to sp$^2$) to give a μ-
allenyl product directly analogous to that obtained from an allenyl complex

\[
\begin{align*}
\text{Cp(CO)}_2\text{MCH}_2\text{C}=&\text{CPh} & \text{or} & \text{Pt}(0) \text{ reagent} \\
\text{Cp(CO)}_2\text{MCH}=&\text{C}=\text{CPh}
\end{align*}
\]

\[\text{M} \rightarrow \text{Pt(PPh}_3\text{)}_2\]

\[\text{M} = \text{Ru, Fe} \]

\[\text{R} = \text{Ph, H} \]

as reactant. This rehybridization is of course not necessary in the case where an allenyl compound is utilized as a reactant. This may account for the more forcing reaction conditions necessary to form the heterobinuclear complexes from propargyl as opposed to allenyl complexes (see Experimental section). Possible mechanistic pathways will be discussed as more evidence is introduced below.

The \(\text{Cp(CO)}_2\text{RuCH}_2\text{C}=\text{CPh} \) (13) reagent reacts cleanly with either \(\text{Pt(PPh}_3\text{)}_4\) or \((\text{PPh}_3\text{)}_2\text{PtC}_2\text{H}_4\) (Eq. 52) to form 14a. The reaction with \((\text{PPh}_3\text{)}_2\text{PtC}_2\text{H}_4\) is higher-yielding (56% yield with \(\text{Pt(PPh}_3\text{)}_4\) compared to 87% using \((\text{PPh}_3\text{)}_2\text{PtC}_2\text{H}_4\)), but the reaction takes longer to complete than the reaction with \(\text{Pt(PPh}_3\text{)}_4\) (20 compared to 9 hours). It is also less
convienent to use \((\text{PPh}_3)_2\text{PtC}_2\text{H}_4\) because this reagent is two additional steps from \(\text{Pt} (\text{PPh}_3)_4\) in the platinum reagents preparatory scheme (i.e., \(\text{Pt} (\text{PPh}_3)_4\) to \((\text{PPh}_3)_2\text{PtCO}_3\) to \((\text{PPh}_3)_2\text{PtC}_2\text{H}_4\)).

Product 14a has been completely characterized spectroscopically. The IR spectrum displays the expected single carbonyl stretch at 1912 cm\(^{-1}\), and the \(^{31}\text{P}(\text{H})\) NMR spectrum shows two doublets \((J_{\text{pp}} = 4.2)\) at \(\delta\) 23.6 and 21.5 ppm, indicating inequivalent phosphorus atoms on platinum. The phosphorus-to-platinum coupling constants indicate that the signal at higher field (\(\delta\) 21.5) is more trans to the metal-metal bond than the one at lower field, as has been explained by Dixon.\(^\text{101}\) The CH\(_2\) protons, which were equivalent (\(\delta\) 2.17) in the starting material (13) now appear as two (inequivalent) doublets \((J_{\text{HH}} = 2.2)\) at \(\delta\) 5.43 \((J_{\text{PH}} = 17.8)\) and 4.89 \((J_{\text{PH}} = 13.5)\) ppm in the \(^1\text{H}\) NMR spectrum. The signals do not coalesce or become equivalent, even in toluene solution at 100°C. The downfield shift of the signals to the more olefinic region of the spectrum is expected, as is the inequivalency of the two protons owing to coordination of the internal carbon-carbon double bond of the allenyl to the ruthenium atom.\(^\text{102}\) The protons are also coupled to the platinum atom, one by 17.8 and the other by 13.5 Hz.

All three carbon atoms of the allenyl ligand of 14a resonate downfield relative to starting 13. The most dramatic shift is that of the CH\(_2\) carbon from \(\delta\) -26.4 to 97.2 ppm. This is consistent with the carbon atom becoming more saturated, i.e., less olefinic. Another large downfield shift is that of the central (\(\beta\)) carbon from \(\delta\) 81.6 to 165.3 ppm, the latter being a value quite typical for the central carbon of a bent allenyl ligand.\(^\text{24,76}\)

Interestingly, this carbon atom also experiences coupling to phosphorus

---

Note: The text seems to have been cut off or not fully transcribed, resulting in a partial and fragmented representation. The full context is not provided, making it difficult to understand the complete meaning or process described.
and platinum ($J_{PC} = 2.3, J_{PtC} = 32$), apparently both coupling interactions being enhanced by the $\pi$-electrons of the allenyl ligand. Of the three signals, the one shifted the least downfield (from $\delta 101.2$ to $149.1$ ppm) is that for the C(Ph) carbon atom. The loss of some electron density at this carbon atom is likely responsible for this shift. Interestingly, coupling between this carbon, $\sigma$-bound to platinum, and the platinum atom was not observed.

Compound 14a is isolated by recrystallization as an orange-yellow, air-stable solid. Purification by chromatography resulted in the transformation of 14a into a new complex. This complex, the mechanism of its formation, and some of its reactivity, will be discussed in detail in the last section of this document (page 240). Confirmation of the structure of 14a was made by a comparison of spectroscopic properties with those of two complexes whose structures were elucidated by X-ray diffraction, as discussed on page 151.

When the reaction of Cp(CO)$_2$RuCH$_2$C=CPh (13) with (PPh$_3$)$_2$PtC$_2$H$_4$ was carried out at room temperature, an intermediate (I) was detected

\[
\text{Cp(CO)$_2$RuCH$_2$C=CPh} + \text{Pt(PPh$_3$)$_2$C$_2$H$_4$} \rightarrow \text{Cp(CO)$_2$RuCH$_2$} \quad \text{(53)}
\]

in the reaction solution by $^1$H and $^{31}$P($^1$H) spectroscopy (Eq. 53). Intermediate I has a $^1$H NMR resonance at $\delta 2.83$ (d, $J_{PH} = 8.5, J_{PtH} = 54.4$) ppm for its magnetically equivalent protons, and its $^{31}$P($^1$H)
spectrum displays two nearly equivalent phosphorus nuclei at δ 27.4 (d, \( J_{PH} = 37.2 \), \( J_{PtP} = 3350 \) and 26.9 (d, \( J_{PP} = 37.2 \), \( J_{PtP} = 3440 \)). The proposed structure of \( \text{I} \) is supported further by a comparison of the chemical shift value of the methylene protons (δ 2.83 ppm) to the chemical shift value of the methylene protons of the manganese-platinum species above, and a series of related \( \text{MCO}_2 \) (\( \text{M} = \text{Fe}, \text{Mn}, \text{W}, \text{Mo} \)) acetylene-bridged complexes\(^{103} \) of the type shown here.

\[
\begin{align*}
[M]\cdot\text{H}_2\text{C} & \quad \begin{array}{c}
\text{C} \\
\text{(CO)}_3\text{Co}
\end{array} \\
\text{(CO)}_3\text{Co} & \quad \begin{array}{c}
\text{C}^{\equiv}\quad \text{R}
\end{array}
\end{align*}
\]

\( [\text{M}] = \text{Cp(CO)}_2\text{Fe}, \text{Mn(CO)}_5, \text{Cp(CO)}_3\text{W}, \text{Cp(CO)}_3\text{Mo}; \text{R} = \text{Ph, Me} \)

The acetylenic dicobalt hexacarbonyl complexes have methylene protons that resonate in the chemical shift range δ 2.78-3.48 ppm, which matches closely the value of δ 2.83 for \( \text{I} \).

Intermediate \( \text{I} \) is the initial piece of evidence necessary to suggest the probable mechanism for the formation of \( \text{14a} \) (and hence other heterobinuclear complexes to be discussed here), as outlined in Scheme 3. After the loss of ethylene and coordination of the carbon-carbon triple bond of \( \text{13} \) to the platinum center, one can envision the rearrangement necessary to break the ruthenium-carbon σ bond to form a zwitterionic intermediate. This is a very critical step in the proposed mechanism, because it logically accounts for the breaking of the ruthenium-carbon bond and the formation of the platinum-carbon bond. The zwitterion resembles the product more than the reactants (or more than \( \text{I} \)) in
structure, so the rest of the proposed reaction pathway is undoubtedly very facile and straightforward, involving rearrangement of the allenyl ligand such that the interior carbon-carbon double-bond is attached to

**Scheme 3.** Possible pathway for reaction of 13 with Pt(0) reagent.

\[
\text{Cp(CO)₂RuCH₂C≡CPh} + \text{"Pt(PPh₃)₂" → Cp(CO)₂RuCH₂C≡CPh} + \text{"Pt(PPh₃)₂"}
\]

ruthenium, nucleophilic attack of the negative platinum terminus on the positive ruthenium, and (concurrent?) loss of carbon monoxide. Note that
this is a third variation on the reaction of a transition metal propargyl complex with an unsaturated metal fragment; in all three cases a zwitterionic intermediate has been proposed and reacted further in a different fashion.

\[
\text{Cp(CO)₂Fe} \rightarrow \text{Fe(CO)₃}
\]

The first example reaction, which gives a product (i.e., 6) without a metal-metal bond, occurs when metal-metal bond formation is unfavorable or when a carbonyl carbon has inserted into a metal-carbon bond. In the second case, a product is formed as a result of complete transfer of the propargyl group as an allenyl ligand from the original transition metal to the second, substrate metal to form 2. This transfer probably occurs because the hard Lewis acid character of the positive terminus (the chromium metal) towards 2-electron ligands (i.e., very weak towards π-allene interaction\(^9\)) enables the zwitterion to fragment into the obtained products. The third product is formed as the result of an attack of a nucleophilic metal on an electrophilic metal from the
zwitserionic intermediate and seems to occur if the two metals involved are not both in the first row of the transition series.

Based upon the reasoning outlined for the third product formed above, one would predict that a first-row transition metal propargyl should react with platinum(0) reagents to form heterobimetallic complexes. Thus, reaction of \( \text{Cp(CO)}_2\text{FeCH}_2\text{C}≡\text{CPh} \) (5) with Pt(PPh\(_3\))\(_4\) was carried out (Eq. 54) and compound 14b was isolated as an air-stable

\[
\text{Cp(CO)}_2\text{FeCH}_2\text{C}≡\text{CPh} + \text{Pt(PPh}_3\text{)}_4 \xrightarrow{\Delta, \text{THF}} \begin{array}{c}
\text{H}_2\text{C} \quad \text{C}≡\text{CPh} \\
\text{Cp} \quad \text{Fe} \quad \text{Pt(PPh}_3\text{)}_2 \\
\text{OC} \\
\text{14b}
\end{array}
\]

orange-brown solid in 80% yield. The solubility properties of 14b and triphenylphosphine were different enough to allow for facile isolation of 14b without PPh\(_3\) contamination. Therefore, Pt(PPh\(_3\))\(_4\) could be used as a reagent in this case. Compound 14b was completely characterized spectroscopically.

The single carbonyl stretching frequency for 14b was observed at 1896 cm\(^{-1}\), slightly lower in energy than for the analogous 14a (1912 cm\(^{-1}\)). The signals for the CH\(_2\) protons in the \(^1\)H NMR spectrum (Figure 4) are also very similar in chemical shift and possess coupling constants similar to those for 14a (δ 5.26 (d, \(J_{\text{HH}} = 2.1\), \(J_{\text{PtP}} = 19.7\)) and 4.83 (d, \(J_{\text{HH}} = 2.1\), \(J_{\text{PtH}} = 14.3\)). The three allenyl carbon atoms resonate at δ 173.3 (C(Ph)), and 96.9 (d, \(J_{\text{PC}} = 3.5\), \(J_{\text{PtC}} = 36.0\), =CH\(_2\)) ppm. Again, these values are very similar to those for 14a.
Figure 4. $^1$H NMR Spectrum of Cp(CO)Fe-(μ-η²,η¹-CH₂=C(Ph))Pt(PPh₃)₂ (14b).
Figure 5. $^{31}$P($^1$H) NMR Spectrum of Cp(CO)Fe-$\mu$-$\eta^2$,-$\eta^1$-CH$_2$=C(Ph))Pt(PPh$_3$)$_2$ (14b).
The $^{31}$P($^1$H) NMR spectrum for 14b (Figure 5) is slightly different than for 14a, however. The most noticeable difference between the two spectra is the nearly non-existent phosphorus-phosphorus coupling constant for 14b (ca 1.0 Hz). Also, while the platinum-phosphorus coupling constants ($J_{P-P}$ for $\delta$ 27.7 is 3500 Hz, for $\delta$ 26.0, 2613 Hz) are similar in value to those of 14a ($\delta$ 23.6 (d, $J_{PP} = 4.2$, $J_{P-P} = 2766$) and 21.5 (d, $J_{PP} = 4.2$, $J_{P-P} = 3689$)), they are reversed relative to their assigned chemical shifts. That is, for 14a the more upfield signal ($\delta$ 21.5) has the larger platinum-to-phosphorus coupling constant, while for 14b the further downfield ($\delta$ 27.7) resonance has the larger value for $J_{P-P}$.

According to Meek, strong field ligands cause the $^{31}$P($^1$H) NMR resonance of a trans phosphorus atom to occur at higher chemical shifts than weaker field ligands. Likewise, the stronger trans influence ligands give typically smaller $J_{P-P}$ values for these phosphorus atoms. Thus, in the case of 14a, the more upfield resonance with the smaller coupling constant is assigned to the triphenylphosphine phosphorus that is more trans to the platinum-carbon $\sigma$ bond, which is expected to be a strong trans influence ligand. This idea was later reinforced by an X-ray crystal structure determination on 16a, which revealed that the phosphine trans to the platinum-carbon bond is the most labilized one because it undergoes replacement by a carbon monoxide ligand (vide infra). In the case of 14b, the strength of Cp(CO)Fe as a trans influence ligand may be much closer to that of the $\sigma$-bound carbon, thus accounting for a difference in the spectral data for 14a and 14b. Whether chemical shift or coupling constant plays the more significant role is uncertain, however. Also, recall that the geometry about platinum is highly distorted square planar (very acute
carbon-platinum-ruthenium angle), and this indicates that the phosphine ligands are not directly trans to the ruthenium/iron or to the carbon of the bridging allenyl ligand.

Unlike the case of the reaction of the ruthenium propargyl complex with platinum(0) reagent, no intermediate was observed in the reaction of the mononuclear ruthenium allenyl complex with (PPh₃)₂PtC₂H₄ (Eq. 55). This may be due in part to the relatively fast rate of reaction at ambient temperature. Two possible mechanistic pathways (among others, of course) can be invoked. These pathways are shown in Scheme 4.

In Path A, the remote (carbon-carbon) π-bond of the allenyl ligand has coordinated to the unsaturated platinum center. One can then envision a shift of coordination from the remote to the interior π bond, followed by the eventual formation of the previously invoked zwitterionic intermediate. There is, of course, the possibility that the allenyl is in equilibrium with a more reactive propargyl species, as shown in Path B. Undoubtedly the equilibrium heavily favors the allenyl, since the propargyl complex could not be detected. However, the propargyl form may be so reactive that once it is formed it immediately reacts with the unsaturated platinum center and thus drives the equilibrium toward the reactive propargyl complex. The rest of the mechanism of Path B is analogous to that proposed in Scheme 3. Note that the intermediate I' in
Scheme 4. Possible pathway for reaction of Cp(CO)₂RuCH=CH with Pt(0) reagent.

**Path A:**

\[
\text{Cp(CO)₂RuCH=CH₂} + \text{"Pt(PPh₃)₂"} \rightarrow \text{Cp(CO)₂Ru-CH}
\]

**Path B:**

\[
\text{Cp(CO)₂RuCH=CH₂} \rightarrow \text{Cp(CO)₂RuCH₂C=CH}
\]
Scheme 4 is likely to be more conducive to $\sigma$ bond formation between the $\gamma$-carbon and platinum due to less steric hinderance at this position (H vs. Ph). Although it is impossible to differentiate between the two mechanisms early in the course of the reaction, it is an attractive proposal that the zwitterionic intermediate is involved in the overall process. Without this proposed key intermediate, the rearrangement of $\sigma$ bonds and $\pi$ bonds on going from reactants to product is more difficult to visualize.

Compound 15a was characterized spectroscopically, and unequivocal confirmation of its structure was obtained by X-ray diffraction analysis by Professor A. L. Rheingold and co-workers. This compound is one of two in this dissertation that was prepared and completely characterized by Shuchart.76 The IR spectrum ($\nu_{C=O} = 1912$ cm$^{-1}$) and $^{31}$P($^1$H) NMR ($\delta 27.7$ (d, $J_{PP} = 4.3, J_{PtP} = 2852$), 21.8 (d, $J_{PP} = 4.3, J_{PtP} = 3620$)) spectrum are very similar to those of 14a. The $^1$H NMR spectrum showed a signal for the CH proton ($\delta 6.61$ (m, $J_{PtH} = 33.0$)) in addition to the typical CH$_2$ resonances ($\delta 5.44$ (d, $J_{HH} = 2.5, J_{PtH} = 19.2$) and 4.66 (d, $J_{HH} = 2.5, J_{PtH} = 15.0$)). In the $^{13}$C($^1$H) NMR spectrum the central allenyl carbon ($\delta 168.0$) and CH$_2$ carbon ($\delta 95.6$ (d, $J_{PC} = 3.1, J_{PtC} = 36.5$)) have chemical shift values and coupling constants that are analogous to 14a, but the CH carbon, $\sigma$-bound to the platinum, is now observed coupled to platinum ($\delta 114.7$ (d, $J_{PC} = 85.0, J_{PtC} = 725$)). The fact that this platinum-to-carbon coupling was not observed in 14a (or 14b) is probably due to the quaternary (14a) vs. CH (15a) nature of the carbon atoms in question. That is, the intensity enhancement due to spin-lattice relaxation from dipole-dipole interaction with directly attached protons afforded 15a by the
presence of the hydrogen atom$^{102}$ may allow for the observation of the coupling in the $^{13}$C($^1$H) NMR spectra of these compounds. The significantly weaker intensity of the quaternary carbon resonances of 14a and 14b does not allow for such $^{13}$C NMR observations under saturated solution conditions even after 18 hours of continuous scanning (with normal relaxation times, etc.). Structural features of 15a will be discussed below as these relate to other structural data collected on similar complexes.

As expected, the iron allenyl compound Cp(CO)$_2$FeCH=C=CH$_2$

\[
\text{Cp(CO)$_2$FeCH=C=CH$_2$} \quad \text{RT, THF} \quad \text{H$_2$C} \quad \text{C} = \text{C} \quad \text{H} \\
\text{Cp} \quad \text{Fe} \quad \text{Pt(PPh$_3$)$_2$} \\
\text{OC} \quad 15b
\]

reacted with (PPh$_3$)$_2$PtC$_2$H$_4$ (Eq. 56) to form the orange, air-stable powder (15b) in good yield (60%). A complete spectroscopic investigation of 15b was carried out.

As in the case of 14b, the carbonyl stretching frequency for 15b observed in the IR spectrum ($v_{C=O} = 1899$ cm$^{-1}$) is of lower energy than that of the ruthenium analogue 15a. Also, the $^{31}$P($^1$H) NMR data (δ 30.99 (d, $J_{PP} = 1.0, J_{PtP} = 2925$) and 27.7 (d, $J_{PP} = 1.0, J_{PtP} = 3415$)) shows a much weaker phosphorus-to-phosphorus coupling of the inequivalent phosphorus nuclei. The $^1$H NMR data for the CH (δ 7.03 (m, $J_{PH} = 36.8$)) and CH$_2$ (5.43 (d, $J_{HH} = 1.0, J_{PtH} = 10.0$) and 4.67 (d, $J_{HH} = 1.0, J_{PtH} = 10.1$)) protons are very similar to those for 15a and the signals for the three allenyl carbons (δ 176.4 (=C=), 122.3 (dd, $J_{PC} = 4.5, J_{PC} = 80.2, J_{PtC} = 715$),
Figure 6. $^{13}$C ($^1$H) NMR Spectrum of Cp(CO)Fe-(μ-η$^2$⁻η$^1$-CH$_2$=C=H)Pt(PPh$_3$)$_2$ (15b)
CH) and 94.3 (d, J_{PC} = 2.9, J_{PtC} = 41.7, -CH_2) are as expected for the 15a analogue. For example, the CH carbon, σ-bound to the platinum atom, is coupled to said platinum with J_{PtC} = 715 Hz (Figure 6).

Thus it has shown that four binuclear species (14 and 15) can be prepared and that their spectroscopic properties can be used to draw analogies amongst them. Only subtle differences were noted among the compounds spectroscopically, so it is assumed that all four conform to the same structure, one of which (15a) was unequivocally determined by X-ray crystallography. As will be shown, subtle differences may mean a great deal when reactivity is in question, though.

Some $^{13}$C NMR data for the heterobinuclear compounds discussed above are summarized in Table 3. Also in Table 3 is a series of data from several other research groups who have prepared binuclear complexes containing a related bridging allenyl ligand. Each of these compounds will now be discussed in terms of bonding and structure (as appropriate) by a comparison of $^{13}$C NMR spectroscopic data for the bridging allenyl-type ligands.

This second type of binuclear $\mu$-allenyl compound is the more common $\mu$-\(\eta^2,\eta^1\)-type (as compared to the $\mu$-\(\eta^2,\eta^3\) type discussed on page 103), exemplified by the work here as well as by that of Seyferth, Mathieu, Casey, and their co-workers. Another binuclear complex has been prepared by Carty and co-workers that has been postulated to have a structure like those to be discussed presently. However, this compound will be discussed later as its spectroscopic properties more closely match those of a different type of structure. With the exception of the compound \(k\), the $^{13}$C NMR data correlate very well for the four different types of
Table 3. Comparison of $^{13}$C NMR data$^a$ for binuclear $\mu$-$\eta^1,\eta^2$-allenyl complexes ($^1J_{CH}$ values in Hz).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$=C=, C_\beta$</th>
<th>C(R), $C_\alpha$</th>
<th>CH$<em>2$, $C</em>\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cp}_2\text{Fe}_2(\text{CO})_3(\mu-\eta^1,\eta^2-CH=CH(t-Bu))^+$ ($k$)$^{30}$</td>
<td>152.0</td>
<td>145.6 (167)</td>
<td>123.7 (161)</td>
</tr>
<tr>
<td>$\text{Fe}_2(\text{CO})_6(\mu-S-R'')(\mu-\eta^1,\eta^2-\text{CR}=\text{CR}_2)$ ($l$)$^{27}$</td>
<td>177.7 - 171.8</td>
<td>148.6 - 113.2</td>
<td>115.4 - 93.4</td>
</tr>
<tr>
<td>R = H, Me; R' = H, Et R'' = Et, t-Bu,</td>
<td></td>
<td></td>
<td>(167 - 163)</td>
</tr>
<tr>
<td>$\text{Fe}_2(\text{CO})_6(\mu-\eta^2,\eta^1-\text{C(Ph)}=\text{C(H)}\text{Ph})$</td>
<td>175.5</td>
<td>127.8</td>
<td>93.2 (166)</td>
</tr>
<tr>
<td>($\mu-\eta^1,\eta^2-(\text{CH}=\text{C}=\text{CH}_2)$ ($m$)$^{28}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Cp}(\text{CO})M(\mu-\eta^2,\eta^1-\text{CH}_2=\text{C}=\text{C(R)})\text{Pt(PPh}_3)_2$</td>
<td>176.4 - 163.3</td>
<td>150.1 - 112.4</td>
<td>98.4 - 94.3 (160)</td>
</tr>
<tr>
<td>M = Ru, Fe; R = H, Ph ($14$, $15$)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$At 25°C in CD$_3$CN ($k$), CDCl$_3$ ($m$), or C$_6$D$_6$ or CD$_2$Cl$_2$ ($l$).
complexes. The central carbon ($C_\beta$), in the compounds 1, m, and 14/15, is the most diagnostic signal for this class of complex; this signal ranges from $\delta 177.7$ to $163.3$ ppm for the different metals, ligands, and general nature of the compounds under discussion. Likewise, the $C_\gamma$-carbon resonances for the three types of compounds fall in the narrow range of $\delta 115.4$ to $93.2$ ppm. Also, the $^1J_{CH}$ values for these resonances are in the range 167 to 160 Hz, indicating sp$^2$ hybridization for these carbon atoms.

The largest range of $^{13}$C NMR resonance values for a particular atom is that for the so-called $\sigma$-bound or $C_\alpha$ carbon ($\delta 150.1$ to $112.4$ ppm). However, a closer examination of the data reveals that related substituents on the $C_\alpha$ carbon give rise to similar chemical shifts, and therefore two distinct ranges are observed. That is, if the substituent on the $C_\alpha$ carbon is hydrogen, the range narrows from $\delta 127.8$ to $112.4$ ppm.
the substituent is Ph or Et, the range is narrowed and shifted downfield to δ 150.1 to 148.2 ppm.

Accounting for the $^{13}$C NMR resonances of the cationic compound $k$ is more difficult. The most downfield signal (δ 152.0 ppm), which is not coupled to any protons, is undoubtedly the central allenyl carbon resonance. The most upfield resonance (δ 127.3 ppm, $^{1}J_{CH} = 161$ Hz) is probably due to the σ-bound or C$_{α}$ carbon, as it falls into the appropriate range as discussed above. The third resonance (δ 145.6 ppm, $^{1}J_{CH} = 167$ Hz) is much farther downfield than expected for a C$_{γ}$ carbon resonance (compare to compound 1 (δ 115.4 ppm) where R = Me, R' = H and R'' = CMe$_{3}$), and can be accounted for by assuming that the positive charge of the compound is responsible for the dramatic downfield chemical shift.

Structurally, only the compounds 14/15 and 1 can be compared to reinforce the $^{13}$C NMR spectroscopic data. In 15a (i.e., M = Ru, R = H, L = PPh$_{3}$), a slight lengthening of the interior (π-bound) carbon-carbon double bond from a typical allene double bond length$^{105}$ (1.31 Å to 1.38 Å) was observed. Likewise, the compound 1 (R = H, R' = H, R'' = CMe$_{3}$) displays a longer interior (1.363 Å) than remote (exoskeletal, 1.335 Å) carbon-carbon double bond. Thus, the two complexes containing similar μ-allenyl ligands, but of markedly different composition otherwise are observed to be structurally as well as spectroscopically ($^{13}$C NMR) similar. Based upon such correlation, the compounds $k$ and $m$ can be reasoned to be structurally similar as well.
2) Control Reactions with (PPh$_3$)$_2$Pt(CO)$_2$

One of the most interesting reactions of the series of four binuclear compounds (14 and 15) is that with carbon monoxide. However, before attention is given to that topic, a set of control reactions will be discussed.

Authentic (PPh$_3$)$_2$Pt(CO)$_2$ was prepared by exposing a freshly prepared solution of (PPh$_3$)$_2$PtC$_2$H$_4$ to carbon monoxide atmosphere for a few minutes and subsequently isolating the pink solid.$^{106}$ The compound was then reacted with the allenyl complexes (Cp(CO)$_2$MCH=C=CH$_2$, M = Ru, Fe) in THF at room temperature for 2 hours to prepare 15a and 15b in 90 and 87% yield, respectively (Eq. 57). The reactions of the propargyl complexes (5 and 13) with (PPh$_3$)$_2$Pt(CO)$_2$ were not as straightforward, however.

For example, the ruthenium propargyl complex (13) did not react with (PPh$_3$)$_2$Pt(CO)$_2$ in THF at room temperature. Instead, the solution had to be heated at reflux temperature for 2 hours to drive it to

\[
\begin{align*}
\text{Cp(CO)$_2$MCH=C=CH$_2$} & \quad \text{RT, THF} \\
+ & \quad \text{(PPh$_3$)$_2$Pt(CO)$_2$}
\end{align*}
\]

\[
\begin{align*}
\text{RT, THF} & \quad \text{OC-Pt(PPh$_3$)$_2$} \\
\text{a, M = Ru; b, M = Fe}
\end{align*}
\]

\[
\begin{align*}
\text{Cp(CO)$_2$RuCH$_2$C=CPt(CO)$_2$} & \quad \Delta, \text{THF} \\
+ & \quad \text{(PPh$_3$)$_2$Pt(CO)$_2$}
\end{align*}
\]

\[
\begin{align*}
\text{H$_2$C} & \quad \text{Ph} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{M} \\
\text{C} & \quad \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{Cp} & \quad \text{OC} \\
\text{Ru} & \quad \text{Pt(PPh$_3$)$_2$} \\
\text{14a}
\end{align*}
\]
completion (Eq. 58) in 92% yield. Although not apparent now, this result is very important in the justification of a new transient species that will be discussed later (page 178). This result also serves to point out a reactivity difference between mononuclear allenyl and propargyl complexes of ruthenium and iron with platinum(0) reagents. The result of the reaction of \((\text{PPh}_3)_2\text{Pt}(\text{CO})_2\) with the iron propargyl (5) is even more striking.

In this case, a solution of the iron propargyl (5) with \((\text{PPh}_3)_2\text{Pt}(\text{CO})_2\) in THF was heated at reflux temperature for 24 hours. Only about 10% of the starting materials was converted to 14b, as evidenced by \(^1\text{H}\) and \(^{31}\text{P}(^1\text{H})\) NMR spectral data. Again, it will be shown later (page 178) that this is exactly the result that was expected. Also, the results presented here seem to suggest that Path A of Scheme 4 (page 138) may represent the course of reaction for the allenyl complexes with platinum(0) reagents. In other words, if the initial coordination of the propargyl species to platinum does not readily occur, it is likely that the extremely facile reaction of the allenyl complexes with platinum(0) reagents does not proceed via involvement of a propargyl intermediate. On the other hand, no explanation can be offered as to why the iron propargyl complex 5 reacts with \(\text{Pt}_(\text{PPh}_3)_4\) at elevated temperature but not with \((\text{PPh}_3)_2\text{Pt}(\text{CO})_2\). The best explanation is simply that the carbonyl ligands in \((\text{PPh}_3)_2\text{Pt}(\text{CO})_2\) are more strongly coordinated (less labile) than the phosphines in \(\text{Pt}_(\text{PPh}_3)_4\).
C. Reactions of Binuclear Complexes with Fe₂(CO)₉, Ru₃(CO)₁₂, and Carbon Monoxide

Unlike the heterobinuclear complexes prepared by Young²⁴ and Shuchart,⁷⁶ compounds 14 and 15 show one important feature, namely, the presence of the remote double bond of the bridging allenyl ligand that is not involved in bonding to a transition metal. This unsaturation was exploited, as it was in the case of the propargyl and allenyl functionalities of the mononuclear propargyl and allenyl complexes, respectively, for further expansion of cluster nuclearity.

1) Fe₂(CO)₉

The reaction of the heterobinuclear compound 14a with Fe₂(CO)₉ was conducted in THF at ambient temperature over a rather long period (36 hours). Two new complexes were prepared and separated from one another by chromatography on alumina (Eq. 59). The less polar (i.e., first to be removed from the column with less polar solvent) compound (16a) turned out to be a simple carbon monoxide-for-triphenylphosphine substitution product of 14a. This compound is also observed as a major side-product in the reaction of Cp(CO)₂RuCH₂C≡CPh (13) with (PPh₃)₂PtC₂H₄ if the reaction is carried out at room temperature over long
reaction times (18 - 36 hours). The yield of 16a produced in this reaction can be diminished somewhat, however, if the THF used as solvent is saturated with ethylene before the reaction is allowed to commence.

Spectroscopically, compound 16a is very similar to 14a. The IR spectrum now consists of two stretches in the carbonyl region (2019 (s) and 1947 (s)) rather than one, as expected from the presence of carbonyl ligands on each of two distinctively different metal centers (Figure 7).

The presence of a single phosphine ligand in compound 16a can be ascertained by examination of the $^{31}$P$^{1}$H) NMR spectrum. The phosphorus nucleus of 16a gives a singlet at $\delta$ 24.4 ppm with a $J_{PtP} = 3277$ Hz. Of interest is the value of the platinum-to-phosphorus coupling constant. This is an intermediate value between the two couplings of the phosphorus nuclei to platinum of 14a (2766 and 3689 Hz). Therefore, one cannot infer whether the lone phosphine of 16a is cis or trans to the heteronuclear metal-metal bond from these data alone.

That complexes 14a and 16a differ only in one ligand can be clearly seen upon examination of their $^1$H and $^{13}$C$^1$H) NMR spectra. Interestingly, the signals for the CH$_2$ protons are seen as slightly broadened singlets (i.e., very small geminal coupling) ($\delta$ 5.60 (s, br, $J_{PtH} = 17.7$) and 5.02 (s, br, $J_{PtH} = 14.3$)) rather than weakly coupled doublets, and yet platinum-to-hydrogen couplings of typical magnitude are still observed. The $^{13}$C$^1$H) NMR signals for the three allenyl carbon nuclei of 16a are also in close agreement with those for 14a ($\delta$ 163.3 (d, $J_{PC} = 5.0$, =$C-$), 148.2 ( =$C$(Ph)), and 98.4 (=CH$_2$)). No coupling between the C(Ph) carbon and the platinum nucleus was observed.
Figure 7. IR Spectrum of Cp(CO)Ru-(µ-η²,η¹-CH₂=C=CH₂)Pt(PPh₃)(CO) (16a).
The structure of 16a could not be determined with certainty from a spectroscopic data comparison for two reasons, however. Based upon the $^{31}\text{P}({}^1\text{H})$ NMR data, the substitution of carbon monoxide for triphenylphosphine at platinum and of phenyl for hydrogen at the $\sigma$-bonded carbon atom indicated the likely existence of a different structure for 16a (i.e., compared to that of 15a, determined by X-ray diffraction). More significant is the obvious difference in chemical reactivity between 14a and 16a that led to uncertainty in assignment of structure. For example, compound 16a is stable toward chromatography on Grade III alumina (6% $\text{H}_2\text{O}$) whereas compounds 14 and 15 either decompose or react to form other materials. Thus, a structure determination was carried out on 16a. An ORTEP drawing of 16a is given in Figure 8, and selected bond distances and angles can be found in Table 4.

Yellow crystals of 16a were obtained from hexane/CH$_2$Cl$_2$ at room temperature. The structure of 16a actually differs little from that of 14b.$^{76}$ As in the case of 14b, the molecule of 16a is comprised of a Cp(CO)Ru and a Pt(PPh$_3$)$_2$ fragment held together by a metal-metal bond (2.668 Å) and a bent allenyl ligand that is $\sigma$-bonded to platinum and $\eta^2$-attached to ruthenium by the interior carbon-carbon double bond of the bridging allenyl ligand. The interior double bond of the allenyl ligand has a bond length of 1.402 Å, elongated somewhat from a typical uncoordinated allene $C=\text{C}$ bond length,$^{105}$ while the remote $C=\text{C}$ bond length (1.313 Å) is typical of an uncoordinated carbon-carbon double bond. The allenyl ligand is bent about the central carbon at an angle of 148.5°.
Figure 8. ORTEP Drawing of Complex 16a.
Table 4. Selected bond distances (Å) and angles (degrees) for 16a.

<table>
<thead>
<tr>
<th>Distances</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Ru</td>
<td>Ru-Pt-C10</td>
</tr>
<tr>
<td>Pt-P</td>
<td>Ru-Pt-C1</td>
</tr>
<tr>
<td>Pt-C1</td>
<td>Cl-Pt-P</td>
</tr>
<tr>
<td>Pt-C10</td>
<td>P-Pt-C10</td>
</tr>
<tr>
<td>Ru-C2</td>
<td>C8-C9-C10</td>
</tr>
<tr>
<td>Ru-C3</td>
<td>Pt-C10-C9</td>
</tr>
<tr>
<td>Ru-C4</td>
<td></td>
</tr>
<tr>
<td>Ru-C5</td>
<td></td>
</tr>
<tr>
<td>Ru-C6</td>
<td></td>
</tr>
<tr>
<td>Ru-C7</td>
<td></td>
</tr>
<tr>
<td>Ru-C9</td>
<td></td>
</tr>
<tr>
<td>Ru-C10</td>
<td></td>
</tr>
<tr>
<td>Cl-O1</td>
<td>1.140 (12)</td>
</tr>
<tr>
<td>C2-O2</td>
<td>1.155 (15)</td>
</tr>
<tr>
<td>C8-C9</td>
<td>1.313 (9)</td>
</tr>
<tr>
<td>C9-C10</td>
<td>1.402 (9)</td>
</tr>
</tbody>
</table>
Of special note is the highly distorted square planar arrangement of ligands around the platinum center. The extremely acute Ru-Pt-C1 angle of 52.4° is most striking. The remaining 307.6° around the platinum atom is divided up rather evenly among the other three angles: C10-Pt-P = 101.7°; P-Pt-C1 = 97.8°; C1-Pt-Ru = 108.3.

The other isolable product from the reaction of 14a with Fe₂(CO)₉ is 17, a trinuclear cluster possessing a unique, open "L-shaped"

![Diagram of 17]

arrangement of metal atoms. The similarities and differences between the spectroscopic properties of 17 and the binuclear complexes are intriguing.

The IR spectrum has become more complicated, as expected, and it contains three broad vC=O absorptions located at 2025 (s), 1996 (vs), and 1954 (m) cm⁻¹. That the remote carbon-carbon double bond of the allenyl is involved in bonding to a transition metal (in this case ruthenium) is evident upon examination of the ¹H NMR spectrum (Figure 9). The CH₂ proton resonances, still inequivalent, are now shifted upfield relative to those of the binuclear complexes (δ 3.86 (d, Jₜʰ = 5.1, Jₚʰ = 12.7) and 2.82 (d, Jₜʰ = 5.1, Jₚʰ = 21.1)). This upfield shift indicates that the CH₂ carbon is less olefinic, which is expected if this carbon is now involved in bonding to the ruthenium atom.
Figure 9. $^1$H NMR Spectrum of Cp(CO)Ru($\mu$-$\eta^2,\eta^2,\eta^1$-CH$_2$C=Ph)Fe(CO)$_3$Pt(PPh$_3$)(CO) (17).
The $^{13}$C($^1$H) NMR spectrum of 17 provides a good example of the typical upfield shift of carbonyl carbon resonances as one proceeds from a first to a third row metal. The iron carbonyls resonate at $\delta$ 213.6 (d, $J_{PC} = 4.3$, $J_{PCC} = 50$), the ruthenium carbonyl at $\delta$ 203.5 ppm, and finally the platinum CO at $\delta$ 191.7 ppm (d, $J_{PC} = 4.9$). The chemical shifts of the three allenyl carbon atoms are all somewhat different from those of the binuclear starting material. The central carbon has shifted downfield to $\delta$ 187.7 (d, $J_{PC} = 5.0$), the carbon $\sigma$-bound to platinum has also shifted downfield to $\delta$ 152.2 (d, $J_{PC} = 2.7$), and the CH$_2$ carbon has moved upfield to $\delta$ 13.4 ppm. The downfield shift of the signal for the carbon bound to platinum can be explained by the presence of the carbonyl ligand on platinum. This carbon monoxide ligand will enhance deshielding of this carbon atom, via back $\pi$-bonding to remove electron density from the platinum, and thus result in a downfield chemical shift. The upfield shift of the CH$_2$ carbon resonance is due to its becoming more hydrogen saturated, as noted in the discussion of its $^1$H NMR spectrum. At first, one might have guessed that the downfield shift of the central allenyl carbon was due to less bending at this position of the ligand. An examination of the X-ray structural data (Figure 10 and Table 5) does not support this idea, however ($<$C11-C12-C13 = 149.7°).

Orange crystals of 17 for X-ray diffraction work were obtained from a mixture of hexane and dichloromethane. The molecule of 17 consists of three fragments, Pt(CO)PPh$_3$, Fe(CO)$_3$, and Cp(CO)Ru, attached in an L-shaped arrangement of the metal atoms. The Pt-Fe-Ru angle is 84.1°, nearly a right angle, and open enough so as not to allow for a bonding interaction between platinum and ruthenium (simple calculations
Figure 10. ORTEP Drawing of Cluster 17.
Table 5. Selected bond lengths (Å) and angles (degrees) for 17.

<table>
<thead>
<tr>
<th>Distances</th>
<th></th>
<th>Angles</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Fe</td>
<td>2.528 (2)</td>
<td>C1-O1</td>
<td>1.124 (17)</td>
</tr>
<tr>
<td>Pt-P</td>
<td>2.291 (3)</td>
<td>C2-O2</td>
<td>1.132 (16)</td>
</tr>
<tr>
<td>Pt-Cl</td>
<td>1.874 (12)</td>
<td>C3-O3</td>
<td>1.153 (15)</td>
</tr>
<tr>
<td>Pt-C13</td>
<td>2.022 (9)</td>
<td>C4-O4</td>
<td>1.122 (15)</td>
</tr>
<tr>
<td>Ru-Fe</td>
<td>2.761 (2)</td>
<td>C5-O5</td>
<td>1.160 (14)</td>
</tr>
<tr>
<td>Ru-C2</td>
<td>1.832 (13)</td>
<td>C11-C12</td>
<td>1.431 (13)</td>
</tr>
<tr>
<td>Ru-C6</td>
<td>2.238 (16)</td>
<td>C12-C13</td>
<td>1.362 (13)</td>
</tr>
<tr>
<td>Ru-C7</td>
<td>2.221 (18)</td>
<td>C13-C26</td>
<td>1.493 (11)</td>
</tr>
<tr>
<td>Ru-C8</td>
<td>2.172 (11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-C9</td>
<td>2.214 (9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-C10</td>
<td>2.211 (15)</td>
<td>Pt-Fe-Ru</td>
<td>84.1 (1)</td>
</tr>
<tr>
<td>Ru-C11</td>
<td>2.214 (9)</td>
<td>Fe-Pt-C13</td>
<td>54.0 (3)</td>
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<tr>
<td>Ru-C12</td>
<td>2.116 (9)</td>
<td>Fe-Pt-C1</td>
<td>104.4 (4)</td>
</tr>
<tr>
<td>Fe-C3</td>
<td>1.752 (12)</td>
<td>Cl-Pt-P</td>
<td>97.3 (4)</td>
</tr>
<tr>
<td>Fe-C4</td>
<td>1.792 (12)</td>
<td>P-Pt-C13</td>
<td>104.4 (3)</td>
</tr>
<tr>
<td>Fe-C5</td>
<td>1.767 (12)</td>
<td>C11-C12-C13</td>
<td>149.7 (9)</td>
</tr>
<tr>
<td>Fe-C12</td>
<td>1.981 (10)</td>
<td>Pt-C13-C12</td>
<td>114.2 (6)</td>
</tr>
<tr>
<td>Fe-C13</td>
<td>2.116 (10)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
showed that the platinum and ruthenium atoms are 3.55 Å apart -- nearly 1 Å farther apart than would be expected for a metal-metal bond. The Fe-Pt-C13 angle is again very acute for a square planar platinum(II) complex (54.0°). Unlike in the case of 16a (or 15a76), both carbon-carbon double bonds are lengthened from a typical allenyl double bond, indicating that both π bonds are involved in bonding to transition metals. It is interesting that the Fe(CO)3 fragment appears to have inserted into what is expected to be a strong metal-metal (Pt-Ru) bond. Note also that initially the ruthenium was involved in bonding to the interior double bond of the μ-allenyl, but that in 17 it is bonded to the remote π-bond. Finally, the carbonyl-for-phosphine substitution at platinum is also intriguing and emphasizes a key property of several complexes that has been and will be observed throughout this dissertation-- triphenylphosphine ligands on platinum are quite labile.

It was thought that the open arrangement of metal atoms in 17 could be closed under appropriate conditions to form a triangulated trinuclear cluster. Thus, cluster 17 was subjected to thermal (60°C for 24 hours) and photochemical conditions as per Eq. 60. There was no reaction
under the thermal conditions. Irradiation with 254 nm lamps led to the
dissociation of the carbonyl ligand on the platinum to form a new
compound, possibly the closed trinuclear cluster C17. However, C17 was
never isolated in a pure form owing to its inherent instability in solution
and toward chromatography. Also, the reaction in Eq. 60 could never be
driven past about 50% consumption of the starting 17, and long irradiation
times resulted in decomposition of 17 and C17. Only $^1$H NMR (CH$_2$
protons: δ 3.75 (d, $J_{HH} = 3.0, J_{PH} = 9.0$) and 3.61 (d, $J_{HH} = 3.0, J_{PH} = 8.0$))
and $^{31}$P($^1$H) NMR (δ 26.2 (s, $J_{PP} = 3398$)) data were obtained for C17. An IR
spectrum of the reaction solution consisted of a complex set of many
overlapping bands owing to the presence of both 17 and C17.

A reactivity difference between the ruthenium-platinum binuclear
complex 14a and the analogous 14b was observed upon reaction of each
with Fe$_2$(CO)$_9$. The situation was further complicated by the instability of

\[
\begin{align*}
\text{H}_2\text{C} & \text{C} = \text{C} \text{Ph} \\
\text{C} & \text{Fe} \text{C} \text{C} \text{P} \text{(PPh}_3)_2 \text{Fe} = \text{C} \text{Fe}{\text{Fe}}_2(\text{CO})_9 \\
\text{OC} & \text{14b} \\
\end{align*}
\]

the complexes obtained from the reaction in Eq. 61. For example, the iron
analogue of 16a, compound 16b is not stable in deuterated solvents for
complete $^{13}$C($^1$H) NMR spectroscopic characterization. The IR, $^1$H NMR,
and $^{31}$P($^1$H) NMR spectral data for 16b are all in line with data for 16a,
however.

The IR spectrum for 16b contains two carbonyl stretches at 2014 (s)
and 1962 (s) for the two distinctively different carbonyl ligands in the
complex. The CH$_2$ proton signals in the $^1$H NMR spectrum are typical of those observed for other binuclear complexes ($\delta$ 5.50 (d, $J_{HH} = 1.6$, $J_{PH} = 20$) and 4.99 (d, $J_{HH} = 1.6$, $J_{PH} = 16$)), and the $^{31}$P($^1$H) NMR spectrum displays a singlet at $\delta$ 26.9 ($J_{PP} = 3381$). These data are nearly identical to those for 16a. Chromatographic properties of 16b on alumina (eluted in 25:1 hexane/ether) are also identical to those of 16a.

The other product of Eq. 61, compound 18, has yet to be elucidated structurally. Upon chromatography it behaves as a typical trinuclear cluster such as 17 (elution from Grade III alumina with 3:1 hexane/diethyl ether), but spectroscopic properties are quite different and rather unusual.

The IR spectrum of 18 displays four bands (2028 (s), 2000 (m), 1985 (vs), 1931 (s) cm$^{-1}$) in the carbonyl region. The $^1$H NMR spectrum is quite simple, however, in that besides the obvious phenyl resonances, only one doublet at $\delta$ 2.05 ($J_{PH} = 3.6$, $J_{PP} = 35$) is observed. No signal for a cyclopentadienyl (Cp) ligand was observed, suggesting that a CpRu(CO) fragment is not present in the compound 18. The $^{13}$C($^1$H) NMR spectrum is also suggestive of the presence of an Fe(CO)$_3$ fragment owing to the appearance of a resonance at $\delta$ 217.5 (s, $J_{PC} = 33$) ppm for the carbonyl carbon atoms. As mentioned on page 156, this signal is significantly farther downfield than would be expected for carbonyl ligands bound to ruthenium or platinum. Other probable assignments in the $^{13}$C($^1$H) NMR spectrum include the central allenyl carbon resonance at $\delta$ 194.2 and a corresponding one for the CH$_2$ carbon at $\delta$ 86.5 ppm.

The $^{31}$P($^1$H) NMR spectrum for 18 (Figure 11) is very interesting. It consists of two doublets ($\delta$ 19.2 ($J_{PP} = 3682$) and 12.9 ($J_{PP} = 3478$)) coupled
Figure 11. $^{31}$P($^1$H) NMR Spectrum of Unknown Compound 18.
to each other by 3.5 Hz. Interestingly, both signals are also coupled to what appears to be a second platinum nucleus that does not have a phosphine ligand attached to it ($J_{Pt'P} = 215$). Further evidence for this second platinum center was obtained by X-ray fluorescence spectroscopy. In this experiment, a quantitative measurement of the iron-to-platinum ratio in compound 18 could be obtained by comparing the spectrum of 18 to a sample of a known iron-to-platinum ratio. A sample of 18 gave a spectrum consistent with a ratio of two platinum atoms to one iron atom when directly compared to a spectrum of 14b. Unfortunately, due to the low isolated yield and the aforementioned instability of this compound in solution, no further study was carried out on 18.

The reaction of 15a with Fe$_2$(CO)$_9$ (Eq. 62) is very straightforward in that only the trinuclear analogue of 17, compound 19a, was isolated as a new product by chromatography. That is, unlike in the reactions of the phenyl-substituted compounds 14 with Fe$_2$(CO)$_9$, there is no binuclear complex formed as a result of carbon monoxide-for-triphenylphosphine substitution during reaction in Eq. 62. This lack of substitution is also observed upon direct reaction of carbon monoxide with 15a (page 177).
Compound 19a was completely characterized spectroscopically, and its formulation is based upon a comparison of its spectroscopic properties to those of 17, whose structure was determined by X-ray crystallography.

The IR spectrum (2027 (s), 1997 (vs), 1953 (s) cm\(^{-1}\)) for 19a is nearly identical to that for 17, as is the \(^{31}\)P\({\mathrm{^1}}H\) NMR (\(\delta 28.3\) (s, \(J_{\mathrm{PP}} = 3092\)) spectrum. One obvious difference between 17 and 19a is that 19a has a resonance in the \(^1\)H NMR spectrum for the CH proton at \(\delta 7.90\) (d, \(J_{\mathrm{PH}} = 10.7, J_{\mathrm{PtH}} = 47\)) which displays a significantly larger coupling to platinum than the CH\(_2\) protons (\(\delta 3.54\) (d, \(J_{\mathrm{HH}} = 4.9, J_{\mathrm{PtH}} = 11.4\)) and 2.65 (dd, \(J_{\mathrm{HH}} = 4.9, J_{\mathrm{PH}} = 1.1, J_{\mathrm{PtH}} = 19.2\)). The allenyl carbon signals (\(\delta 194.9\) (d, \(J_{\mathrm{PC}} = 2.5, =C=\)), 135.5 (d, \(J_{\mathrm{PC}} = 5.4, J_{\mathrm{PtC}} = 702, =C(H), 13.8\) (s, \(J_{\mathrm{PC}} = 42.3\))) in the \(^{13}\)C\({\mathrm{^1}}H\) NMR spectrum are in line with those of 17, with the obvious exception of the CH carbon resonance. As in the case of the binuclear 15a, this carbon, \(\sigma\)-bound to platinum, displays a \(J_{\mathrm{PtC}}\) of around 700 Hz.

The binuclear complex 15b reacted with Fe\(_2\)\((\mathrm{CO})_9\) in an manner analogous to 15a, to form 19b as the only new isolable product (Eq. 63). It is of particular note that the substituent on the C\(_\alpha\) (\(\sigma\)-bound to platinum) appears to be more important in the determination of the course of reaction than the identity of the other (iron or ruthenium) metal. In other words, in reaction with Fe\(_2\)\((\mathrm{CO})_9\), 15b behaves more like the allenyl-
derived 15a than the iron-containing 14b. This is in direct contrast to the results obtained upon reaction of the mononuclear iron and ruthenium propargyl complexes with Fe$_2$(CO)$_9$. In these reactions, recall that no iron-to-iron metal-metal bond was formed from Cp(CO)$_2$FeCH$_2$C≡CPh (5, Eq. 39) as reagent, but when Cp(CO)$_2$RuCH$_2$C≡CPh (13, Eq. 41) was utilized, iron-to-ruthenium bonds are formed in every new compound obtained. Apparently the presence of the platinum atom or perhaps the steric environment about the C$_\alpha$ atom are more significant factors in determining the reaction products formed than the identity of the metal attached to platinum. In an indirect way, this implies that the bridging allenyl ligand participates in the formation of these L-shaped trinuclear clusters, probably by initial coordination of an unsaturated metal fragment.

Spectroscopically, compound 19b is analogous to 19a. Subtle differences are observed in both the $^1$H and $^{13}$($^1$H) NMR spectra, however. For example, the CH proton ($\delta$ 8.04 (dt, $J_{PH} = 10$, $J_{HH} = 1.2$, $J_{PH} = 48$) is coupled to the phosphorus atom, the platinum atom, and the CH$_2$ protons ($\delta$ 3.41 (dd, $J_{HH} = 1.1$, $J_{HH} = 5.0$, $J_{PH} = 18.3$) and 2.26 (dt, $J_{HH} = 1.1$, $J_{HH} = 4.8$, $J_{PH} = 10$, $J_{PH} = 25$). In the $^{13}$C($^1$H) NMR spectrum, the central allenyl ($\delta$ 193.5 (d, $J_{PC} = 4.0$)) and CH$_2$ ($\delta$ 18.8 (s, $J_{PC} = 46$)) carbons resonate at usual positions, but the CH carbon signal ($\delta$ 139.1 (d, $J_{PC} = 5.0$)) does not show the usual platinum-to-carbon coupling of around 700 Hz observed for compounds 15 and 19a. It is probable that the low signal-to-noise ratio obtained for this spectrum (due to relatively low solubility of 19b) resulted in the satellites being buried in the baseline. The $^{31}$P($^1$H) NMR spectrum ($\delta$ 28.5 (s, $J_{PTP} = 3062$)) is nearly identical to that for 17 and 19a.
Although all four of the heterobinuclear complexes (compounds 14 and 15) reacted with Ru$_3$(CO)$_{12}$, the yields (11 - 34%) and stabilities of the heterotrinuclear clusters obtained were disappointing. The clusters derived from the hydrogen-substituted (i.e., compounds 15) binuclear complexes were easier to handle than the phenyl-substituted analogues.

The reactions of compounds 14 with Ru$_3$(CO)$_{12}$ (Eq. 64) were carried out under conditions similar to those employed above for the reactions with Fe$_2$(CO)$_9$. The spectroscopic properties of compounds 20 were slightly different than for compound 17, however.

For example, the IR spectra of compound 20a (2064 (w), 2036 (s), 2007 (sh), 1996 (vs), 1971 (vs), 1932 (m) cm$^{-1}$ and 20b (2068 (m), 2035 (vs), 2020 (sh), 2004 (vs), 1970 (m), 1960 (w) cm$^{-1}$) in the carbonyl region are very complicated and seem to suggest a more complicated structure than that observed for 17. The possibility of Ru(CO)$_4$ being present (e.g., as the three Ru(CO)$_4$ units of Ru$_3$(CO)$_{12}$ in place of Ru(CO)$_3$ is a possible explanation for this difference in the infrared data.
The $^{31}$P($^1$H) NMR spectral data for 20a (δ 26.2 (s, $J_{PtP} = 3000$)) and 20b (δ 24.7 (s, $J_{PtP} = 2964$)) are more simple. Likewise, the $^1$H NMR data for the CH₂ protons of 20a (δ 3.63 (d, $J_{HH} = 5.5$, $J_{PtH} = 29$) and 2.52 (d, $J_{HH} = 5.5$, $J_{PtH} = 35$)) and of 20b (δ 3.39 (d, $J_{HH} = 5.5$, $J_{PtH} = 25$) and 2.02 (d, $J_{HH} = 5.5$, $J_{PtH} = 30$)) can be compared directly to the data for compound 17. The $^{13}$C($^1$H) NMR spectrum obtained for 20a (before it began to decompose in the CDCl₃ solution) revealed fairly typical allenyl carbon resonances for the central (δ 184.5), C(Ph) (δ 147.4) and CH₂ (δ 22.1 ppm) carbon atoms.

The reactions of compounds 15 with Ru₃(CO)₁₂ (Eq.65) produced

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{C} = \text{CH} \\
\text{C} \quad \text{M} \quad \text{Pt(PPh₃)₂} & \quad \text{Ru₃(CO)₁₂} \\
\text{OC} & \quad \text{RT, THF} \\
\text{15} & \quad \text{M = Ru; b, M = Fe} \\
\end{align*}
\]

slightly more stable compounds 21 as the only new isolable products. Again, no binuclear complexes resulting from carbon monoxide substitution for triphenylphosphine at platinum were observed spectroscopically either in the reaction solution or upon chromatography on alumina. Satisfactory elemental analysis was obtained for 21b, and good FAB mass spectral data (M⁺, and then products of 5 consecutive CO's lost¹⁰⁷) were obtained for both 21a and 21b.

The IR spectra for 21a (2038 (s), 2015 (m), 2000 (w), 1971 (s) cm⁻¹) and 21b (2036 (s), 2010 (vs), 1994 (m), 1970 (m) cm⁻¹) show four bands ranging from 2038 to 1970 cm⁻¹. These correspond to a number of terminal carbonyl ligands. While the $^1$H NMR resonance for the CH proton is buried in the
phenyl region (δ 7.5 - 6.8) for 21a, the CH signal for 21b is observed at δ 7.21 (d, JPH = 10.0, JPTP = 5.0). The CH2 protons resonate upfield from those of the binuclear starting materials, as above, and again indicate that the remote carbon-carbon double bond is involved in bonding to a transition metal. The CH2 protons for 21a are observed at δ 2.66 (s, br) and δ 2.32 (m, Figure 12), and for 21b the CH2 resonances are observed at δ 2.75 (s, br) and δ 2.34 (d, JHH = 4.0, JPTP = 20) ppm. Interestingly, only the more upfield proton in each compound appears to be coupled to platinum and/or phosphorus. The broadness of the more downfield singlets indicates that the CH2 protons are probably coupled to each other, but by less than 1 Hz.

The 31P(1H) NMR spectra of 21a (δ 25.0 (s, JPTP = 2840)) and of 21b (δ 24.1 (s, JPTP = 2854)) are nearly identical. The 13C(1H) NMR spectra are also very similar. The central, CH, and CH2 carbons for 21a (δ 196.9 (s), 166.6 (d, JPC = 4.0) and 44.4 (s)), respectively, as well as those for 21b (δ 196.7 (s), 167.4 (d, JPC = 4.0), and 44.9 (s)), are all shifted downfield relative to the analogous carbons of compounds 17 and 19, where the iron is at the "elbow" position. Apparently, the remote carbon-carbon double bond is not interacting with the Cp(CO)M metal atom as strongly as in 17 and 19, thus accounting for the 25 ppm or so downfield shift. Support for this conclusion can be seen in the IR data as well. None of the carbonyl stretching frequencies of compounds 21 are of less energy than 1970 cm⁻¹; therefore, one would not expect a large amount of electron density on the Cp(CO)M center being reduced by back π-bonding to the carbonyl ligand on M. Unfortunately, countless attempts at obtaining crystals of 21b suitable for an X-ray structural analysis were unsuccessful.
Figure 12. $^1$H NMR Spectrum of Cp(CO)Ru-$(\mu-\eta^2,\eta^2,\eta^1$-$\text{CH}_2$-$\text{C}=$C(H))Ru(CO)$_3$Pt(PPh$_3$)(CO) (21a).
Compounds 17 and 19 - 21 represent a novel, unprecedented L-shaped arrangement of three distinctively different metal environments (i.e., Pt(PPh₃)(CO) coupled with Cp(CO)M and M'(CO)₃, with M and M' being all combinations of Fe and Ru where the "end" metals are not involved in bonding to one another or to the same atom of the bridging ligand). Typical 48-electron trinuclear clusters that do not contain platinum or palladium adopt a triangulated arrangement of metal atoms, such as in Ru₃(CO)₁₂:[¹⁰⁹]

\[
\begin{array}{c}
\text{(CO)}_4 \\
\text{Ru} \\
\text{(CO)}_4 \text{Ru} \quad \text{Ru(CO)}_4
\end{array}
\]

Owing to the inherent stability of platinum(II) or palladium(II) 16-electron square planar complexes, triangulated (closed) clusters containing one platinum or palladium atom commonly exist as 46- rather than 48-electron species.[¹¹⁰] This readily accounts for the lack of a closed, triangulated arrangement of metal atoms in the 48-electron clusters 17 and 19 - 21. A comparison of spectroscopic data (specifically ¹³C NMR data) of the L-shaped clusters and of other trinuclear clusters bridged by an allenyl ligand may prove insightful, though.
Trinuclear, bridging-allenyl clusters have only been prepared by a few research groups. Only two types of these clusters are known, the

\[ \text{H}_2\text{C} \quad \text{C} = \text{C} \quad \text{R} \quad \begin{array}{c} \text{(CO)}_3\text{M}' \to \text{M}'\text{(CO)}_3 \\ \text{Cp}\text{(CO)}_2 \end{array} \]

\[ \text{M} = \text{Mo, W} \]
\[ \text{M}' = \text{Fe, Ru} \]
\[ \text{R} = \text{Me, Ph, p-tolyl} \]

\[ \begin{array}{c} \text{H} \\ \text{C} = \text{C} \quad \text{CH}_2 \quad \begin{array}{c} \text{(CO)}_3\text{M'} \to \text{M} \text{(CO)}_3 \\ \text{Co}\text{(CO)}_2 \end{array} \quad \text{Cp}\text{(CO)}\text{Ru} \quad \text{R} \end{array} \]

\[ \text{q} \]

\[ \begin{array}{c} \text{i-Pro} \\ \text{C} = \text{C} \quad \text{CH}_2 \quad \begin{array}{c} \text{(CO)}_3\text{Ru} \to \text{Ru}\text{(CO)}_2 \\ \text{PPh}_2 \end{array} \quad \text{Ru} \quad \text{Co} \quad \text{(CO)}_2 \end{array} \]

\[ \text{r} \]

\[ \begin{array}{c} \text{H} \\ \text{C} = \text{C} \quad \text{R} \quad \begin{array}{c} \text{(CO)}_3\text{Fe} \to \text{Fe}\text{(CO)}_3 \\ \text{Fe}\text{(CO)}_3 \end{array} \quad \text{(CO)}_3\text{Fe} \quad \text{R} \end{array} \]

\[ \text{s} \]

\[ \begin{array}{c} \text{Me} \\ \text{C} = \text{C} \quad \text{CH}_2 \quad \begin{array}{c} \text{(CO)}_3\text{Os} \to \text{Os}\text{(CO)}_3 \\ \text{Os}\text{(CO)}_3 \end{array} \quad \text{Os}\text{(CO)}_3 \quad \text{H} \end{array} \]

\[ \text{t} \]

\[ \text{R} = \text{COMe, C(O)OMe} \]
Table 6. Comparison of $^{13}$C NMR data for trinuclear $\mu$-allenyl clusters.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$=C=, \text{or } C_\beta$</th>
<th>C(R), or C$_\alpha$</th>
<th>CH$<em>2$, or C$</em>\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp(CO)$_2$M-($\mu$-$\eta^2,\eta^2,\eta^1$-CH$_2=C=C(R))$M'$_2$(CO)$_6$</td>
<td>161.6 - 155.9</td>
<td>136.4 - 114.1</td>
<td>27.8 - 27.0</td>
</tr>
<tr>
<td>(n)$_2^4$ M = Mo, W; M' = Fe, Ru; R = p-tolyl, Ph, Me</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cp(CO)Ru-($\mu$-$\eta^2,\eta^2,\eta^1$-CH$_2=C=\text{CPh})$M$_2$(CO)$<em>6$ (p)$</em>{76}$</td>
<td>186.6 - 179.8</td>
<td>160.3 - 150.2</td>
<td>13.5 - 11.5</td>
</tr>
<tr>
<td>M = Fe, Ru</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cp(CO)Ru-($\mu$-$\eta^1,\eta^2,\eta^2$-CH=C=CH$_2$)Co$_2$(CO)$_5$ (q)</td>
<td>153.0 - 151.4</td>
<td>116.5 - 115.8</td>
<td>59.5 - 57.7</td>
</tr>
<tr>
<td>(two isomers)$_{76}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CO)$_3$Ru-($\mu$-$\eta^1,\eta^2,\eta^2$-C(Pr)=C=CH$_2$)-Ru$_2$(CO)$_5$(μ-PPh$<em>2$) (r)$</em>{30}$</td>
<td>172.0</td>
<td>142.7</td>
<td>20.1 (161)</td>
</tr>
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</table>
Table 6, cont.

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<tr>
<th>Complex</th>
<th>$C_\beta$</th>
<th>$C_\alpha$</th>
<th>$C_\gamma$</th>
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<tr>
<td>[(CO)$_3$Fe-(μ-$\eta^1$,$\eta^2$,$\eta^2$-C(OEt)=C=C(R)H)</td>
<td>146.1 - 145.3</td>
<td>201.9 - 200.0</td>
<td>38.1 - 27.7</td>
</tr>
<tr>
<td>Fe$_2$(CO)$_6$\textsuperscript{3-} (s) \textsuperscript{33}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cp(CO)M-(μ-$\eta^2$,$\eta^2$,$\eta^1$-CH$_2$=C=C(R))</td>
<td>194.9 - 187.7</td>
<td>152.2 - 135.5</td>
<td>18.8 - 13.4</td>
</tr>
<tr>
<td>Fe(CO)$_3$Pt(PPh$_3$)(CO) (17 and 19)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M= Ru, Fe; R= H, Ph</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cp(CO)M-(μ-$\eta^2$,$\eta^2$,$\eta^1$-CH$_2$=C=C(H))</td>
<td>196.7 - 196.6</td>
<td>167.4 - 166.6</td>
<td>44.9 - 44.4</td>
</tr>
<tr>
<td>Ru(CO)$_3$Pt(PPh$_3$)(CO) (20 and 21)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M= Ru, Fe</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}All spectra recorded at 25°C in CD$_2$Cl$_2$ or CDCl$_3$.  


typical $\eta^1,\eta^2,\eta^2$-closed, triangulated arrangement of metal atoms, and the L-shaped structures discussed above. With the exception of the compounds s (prepared by Mathieu and co-workers$^{33}$), which are anionic and contain one carbon atom each that resonates considerably downfield ($\delta$ 201.9 to 200 ppm) as compared to neutral species, the $^{13}$C NMR signals for the $\mu$-allenyl carbon atoms follow one key trend: The central allenyl carbon ($C_\beta$) resonates the farthest downfield, the $\text{CH}_2$ (or $\text{CH}_R$) carbon ($C_\gamma$) the most upfield, and the $\sigma$-bound carbon ($C_\alpha$) somewhere in-between (see Table 6).

The range for the central allenyl carbon ($C_\beta$) signals is $\delta$ 186.6 to 145.3 ppm, which is very similar to the corresponding range for the binuclear $\mu-\eta^1,\eta^2$-allenyl central carbon resonances ($\delta$ 177.7 to 152.0 ppm) in Table 3. This, of course, suggests some similarity in structure between the closed trinuclear and these binuclear complexes, particularly (and possibly only) in regard to the C-C-C angle about the central allenyl carbon. However, no relationship between binuclear and trinuclear structure based only upon $^{13}$C NMR data can be implied.

The $\text{CH}_2$ carbon ($C_\gamma$) resonances for the trinuclear $\mu$-allenyl clusters fall in the range $\delta$ 38.1 to 11.5 ppm, excluding the clusters q, which have been incompletely characterized. These values are shifted significantly upfield from those of the binuclear complexes and indicate that the remote C-C double bond of the allenyl ligand is involved in bonding to a transition metal.

Again excluding the compound s (where $\delta$ 200 ppm for the $\sigma$-bound carbon is due to the negative charge on an adjacent atom), the range for the $C_\alpha$ carbon atoms in the $^{13}$C NMR spectroscopic data is $\delta$ 160.3 to 114.1
ppm. Interestingly, in direct contrast to the behavior observed for the binuclear $\mu$-$\eta^1,\eta^2$-allenyl complexes, the chemical shift value for this carbon atom reveals little dependence upon the nature of the attached substituent. For example, the compound $n$ ($M = W$, $M' = Ru$, $R = Ph$), with a phenyl substituent on the $\alpha$-carbon atom, shows the most upfield signal ($\delta 114.1$ ppm). The compound $p$, where $M = Fe$ and $L = PPh_3$, also has a phenyl substituent on the $C_\alpha$ atom, but its chemical shift value is $\delta 160.3$ ppm. Thus it is clear that the accumulated data for the trinuclear $\mu$-allenyl clusters are not as straightforward to interpret as are the data for the binuclear complexes.

Interestingly, the data for the L-shaped clusters prepared here compare well to those for the closed, triangulated clusters in Table 6. The central allenyl carbon signal range is from $\delta 196.7$ to $187.7$ ppm, only slightly more downfield than the range for the closed triangulated clusters ($\delta 186.6$ to $145.3$ ppm). The range for the $CH_2$ carbon ($\delta 44.9$ to $13.4$ ppm) and $\sigma$-bound carbon ($\delta 167.4$ to $135.5$ ppm) signals fit into the ranges outlined for the closed, triangulated clusters above. Of course, one must rely on several different types of spectroscopic data ($^1$H and $^{31}$P NMR, mass spectrometric, etc.) and often structural data (X-ray diffraction) to make an assignment as to the class of trinuclear cluster prepared. Later an assignment of the structure of a gold-containing trinuclear $\mu$-allenyl cluster will be made based upon a combination of several different spectroscopic techniques. (Eventually, an X-ray crystallographic study will be carried out to confirm such an assignment.)
3) With Carbon Monoxide

An important property of the heterobinuclear metal $\mu$-$\eta^1,\eta^2$-allenyl compounds (14 and 15) is that of fragmentation into mononuclear species, usually caused by an electrophilic or $\pi$-acid reagent. The reaction of each of the four binuclear species (14 and 15) with carbon monoxide was extensively studied to determine the role of the carbon monoxide, as well as the role of the fragments themselves, in the process. As will be seen in the case of compound 14a, the fragmentation chemistry can yield new and interesting species as well.

a) Reactions of 14 and 15 with Carbon Monoxide (and Reversal of This Reaction with Argon)

The reaction of 14b with carbon monoxide proceeds over 18 hours at room temperature to produce $\text{Cp(CO)}_2\text{FeCH}_2\text{C}=\text{CPh}$ (5) and $(\text{PPh}_3)_2\text{Pt(CO)}_2$ (Eq. 66). However, recall (page 147) that in the reaction of 5 with $(\text{PPh}_3)_2\text{Pt(CO)}_2$ that less than 10% of the starting material 5 was converted to 14b, even during 24 hours in THF at reflux temperature. This result explains the fact that the ambient temperature reversal of Eq. 66 does not occur. As will be seen below, the reaction in Eq. 66 is unique to the
heterobinuclear complex 14b. That is, neither compound 15 nor 14a behaves in this manner.

As in Eq. 66, the course of the reaction in Eq. 67 was followed by $^1$H and $^{31}$P($^1$H) NMR spectroscopies. Hence, the signals for the mononuclear allenyl complexes could be observed as appearing and then increasing in intensity in the $^1$H NMR spectrum at the expense of 15 over the course of the reaction. Likewise, the appearance of signals for (PPh$_3$)$_2$Pt(CO)$_2$ (as ascertained by comparison of spectroscopic data to those in the literature$^{70}$) in the $^{31}$P($^1$H) NMR spectrum at the expense of resonances for 15 was observed as well.

Of particular note is the reversible nature of the process in Eq. 67 upon a change of the atmosphere from carbon monoxide to argon. In fact, the reaction can be driven in both directions at least three times without significant decomposition. The feasibility of the reverse reaction was indicated by control experiments where authentic (PPh$_3$)$_2$Pt(CO)$_2$ was reacted with the ruthenium and iron mononuclear allenyl complexes under similar reaction conditions. That is, the ease of the reaction of platinum(0) reagents, such as Pt(PPh$_3$)$_4$, (PPh$_3$)$_2$PtC$_2$H$_4$, and (PPh$_3$)$_2$Pt(CO)$_2$ with the allenyl complexes was duly noted (vide supra). This is in direct contrast to the relative lack of reactivity of Cp(CO)$_2$FeCH$_2$C=CPh with (PPh$_3$)$_2$Pt(CO)$_2$. 
The reaction of the ruthenium propargyl-derived 14a with carbon monoxide and its subsequent reversal under ambient conditions (unlike its iron-containing analogue, 14b) requires special attention in the present discussion. As shown in Eq. 68 below, the phenylallenyl complex 22 is proposed as the ruthenium-containing product of the forward reaction at ambient temperature of this completely reversible process.

\[
\begin{align*}
\text{H}_2\text{C} & \equiv \text{C} = \text{CPh} \\
\text{Cp} & \text{Ru} - \text{Pt}((\text{PPh}_3)_2) \\
\text{OC} & \text{14a} \\
\text{CO, RT} & \text{18 h} \\
\end{align*}
\rightarrow
\begin{align*}
\text{Cp}((\text{CO})_2\text{RuC(Ph)=C=CH}_2 \\
\text{22} \\
\text{(PPh}_3)_2\text{Pt(CO)}_2
\end{align*}
\]

The apparently lower-energy pathway of the reaction of 22 with \((\text{PPh}_3)_2\text{Pt(CO)}_2\) in the reverse direction of Eq. 68, as compared to the reaction of \(\text{Cp}((\text{CO})_2\text{RuCH}_2\text{C}=\text{CPh} \text{ (13)}\) with \((\text{PPh}_3)_2\text{Pt(CO)}_2\), is completely consistent with the general results obtained for reaction of the parent allenyl complexes \(\text{Cp}((\text{CO})_2\text{MCH}=\text{C}=\text{CH}_2 \text{ (M = Fe, Ru)}\) with \((\text{PPh}_3)_2\text{PtC}_2\text{H}_4\).

That heat was required to drive the control reaction of \(\text{Cp}((\text{CO})_2\text{RuCH}_2\text{C}=\text{CPh} \text{ (13)}\) with \((\text{PPh}_3)_2\text{Pt(CO)}_2\) to completion is also consistent with the experimental conditions (i.e., higher temperature) necessary to prepare compounds 14 from the mononuclear starting materials 13 and \(\text{Pt(PPh}_3)_4\). The initial evidence for the phenylallenyl 22 was obtained from a \(^1\text{H} \) NMR spectrum (Figure 13, \text{C}_6\text{D}_6 \) solvent): \(\delta \) 7.8 - 6.9 (m, Ph), 4.49 (s, Cp), 4.28 (s, CH\(_2\)). More evidence than a simple proton NMR spectrum was required to support the existence of 22, however.

It was proposed that the existence of 22 could be further strengthened by examination of the reaction chemistry of this complex.
Figure 13. $^1$H NMR Spectrum of $\text{Cp(CO)}_2\text{RuC(Ph)=C=CH}_2$ (22).
Thus, a solution of 14a was reacted with carbon monoxide and then the 22 formed in situ was treated with other reactive substrates. An example

\[
\begin{align*}
    \text{Cp(CO)}_2\text{RuC(Ph)=C=CH}_2 + \text{Fe}_2(\text{CO})_9 & \rightarrow 22 + (\text{PPh}_3)_2\text{PtFe}_2(\text{CO})_8 \\
    \quad + (\text{PPh}_3)_2\text{Pt(CO)}_2 & \rightarrow 16a + \text{Fe}(\text{CO})_4\text{PPh}_3
\end{align*}
\]

(Major)

(Minor)

(69)

reagent was Fe_2(CO)_9 (Eq. 69). After fragmentation of 14a as per the usual carbon monoxide purge for 18 hours, Fe_2(CO)_9 was added as a solid, under the carbon monoxide atmosphere. After a total reaction time of 5 hours (3 hours under carbon monoxide, 2 hours under argon), only unreacted 22, (PPh_3)_2PtFe_2(CO)_8, Fe(CO)_4PPh_3, and a very small amount of 16a were observed as products. Interestingly, no evidence for any of the bi- and trinuclear compounds from Eq. 41 was obtained by ^1\text{H} NMR spectroscopy. This suggests that the reaction products observed in Eq. 41 resulted from the interaction of iron carbonyl fragments with a reactive phenylpropargyl complex (i.e., 13), and not with the phenyllallenyl complex 22.

This result leads to two significant conclusions. First, since the myriad of products obtained in Eq. 41 resulted from interaction between a propargyl species (Cp(CO)_2RuCH_2C=CPH (13)) and Fe(CO)_x (x = 3 or 4) fragments, one can postulate that no propargyl species (i.e., 13) was present in the reaction solution of Eq. 69 to react with the iron carbonyl fragments. Thus, it is likely that an isomerization from 22 to 13 (Eq. 70) does not occur to any observable extent under the conditions in Eq. 69. It is

\[
\text{Cp(CO)}_2\text{RuC(Ph)=C=CH}_2 \xrightarrow{\text{?}} \text{Cp(CO)}_2\text{RuCH}_2\text{C}=\text{CPH}
\]

(70)
important to note that while Shuchart observed that some products obtained from the reactions of Fe$_2$(CO)$_9$ with the propargyl complex 13 and with Cp(CO)$_2$RuCH=C=CH$_2$ were analogous, at least two products were formed in the reaction of the allenyl complex with Fe$_2$(CO)$_9$ that do not have 13-derived analogues.$^{76}$ Also, in related work with the Cp(CO)$_3$WCH=CH/Cp(CO)$_3$WCH=C=CH$_2$ pair of complexes, Lin$^{92}$ has discovered different products of reactions of the two isomers with such reagents as amines. This result is in discord with the suggestion put forth in Eq. 70, and instead suggests separate, independent reaction paths for transition metal allenyl and propargyl complexes.

Another type of reaction in which metal allenyl and propargyl complexes react to form related, but different products is cycloaddition.$^{88,89}$ More specifically, the reaction with TSI, $p$-toluenesulfonyl isocyanate, has been closely studied. Under similar reaction conditions, allenyl and propargyl complexes react with TSI to form cycloaddition adducts that appear to be directly analogous (Eq. 71). However, the two species differ as to the relative position of the CH$_2$ carbon atom in the molecules. In the propargyl-derived cycloaddition adduct (PCA) the CH$_2$ carbon is bonded to the nitrogen atom of the TSI. In the allenyl-derived cycloaddition adduct (ACA), the CH$_2$ carbon is bonded to the carbonyl carbon of the TSI. In other words, in each case the original C$_\gamma$ carbon of the C$_3$ ligands is attached to the carbonyl carbon while the original C$_\alpha$ carbon is attached to the nitrogen atom. This suggests that the remote carbon-carbon double bond of the allenyl ligand is involved in the initial nucleophilic attack on the carbonyl carbon of TSI, rather than the carbon-carbon triple bond formed as a result of an isomerization.
before interaction with TSI (See Path A of Scheme 5). If an isomerization to a propargyl species occurred before reaction with TSI, then a PCA product would be expected, as in Path B of Scheme 5. Therefore, the product formed in the reaction of 22 with TSI serves as a means of determining whether 22 is indeed an allenyl complex.

Because of the structural differences between PCA and ACA adducts, $^1$H NMR spectroscopy can be utilized to determine which type of species has been prepared. For example, the CH$_2$ protons of PCA species fall in range $\delta$ 3.5 to 5.0 ppm$^{68}$ whereas the range for ACA CH$_2$ protons is more upfield, $\delta$ 2.5 to 3.5 ppm.$^{68,99}$ If 22 is indeed an allenyl complex, then its cycloaddition adduct upon reaction with TSI should be of the ACA type and a $^1$H NMR spectrum of said adduct can help to show this.

Following the preparation of 22 via fragmentation initiated by carbon monoxide in the usual way in C$_6$D$_6$ (NMR tube) or toluene (larger scale), TSI was added in situ. In each case, an ACA-type complex (23)
**Scheme 5.** Possible reaction pathways for a transition metal allenyl complex with TSI.

**Path A:**

\[
[M]-\text{CH}=\text{C}=\text{CH}_2 \xrightarrow{\text{tosyl-N}=\text{C}=\text{O}} \xrightarrow{\text{ACA}} \xrightarrow{\text{N-tosyl}}
\]

**Path B:**

\[
[M]-\text{CH}_2\equiv\text{CR} \xrightarrow{\text{tosyl-N}=\text{C}=\text{O}} \xrightarrow{\text{PCA}} \xrightarrow{\text{N-tosyl}}
\]
was observed. In C₆D₆, the CH₂ signal was at δ 2.54 ppm, and in CDCl₃ it appeared at δ 3.16 ppm. Unfortunately, because of the presence of the platinum-containing fragments, the reaction was not clean. With excess TSI (Eq. 72), however, the originally prepared 22 was totally converted to

\[
\begin{align*}
14a & \overset{CO}{\longrightarrow} 22 \overset{\text{TSI}}{\longrightarrow} \text{Cp(CO)}_2\text{Ru} & \text{N-Tosyl} \\
\text{(PPh}_3)_2\text{Pt(CO)}_2 \\
\end{align*}
\]  

(72)

23. When only two equivalents of TSI were used, the reaction was only about 60% complete. This is due in part to the consumption of at least one equivalent of TSI by the platinum-containing fragment to form a TSI-containing species. A FAB mass spectrum obtained on this mixture containing 22 and 23 provided further evidence for the existence of the allenyl complex 22 (but not for 23). The fragmentation pattern for 22 consisted of the parent (M⁺ + 1) peak plus peaks resulting from the loss of two consecutive carbon monoxide ligands. In contrast, the fragmentation pattern (EI MS) for Cp(CO)₂RuCH₂C=CH₂ (13) shows the loss of the CO's in a minor fashion only, with the loss of PhC₂CH₂⁺ being much more important.

Even though the existence of 22 has now been implied in several different instances, and even though some spectroscopic properties have been obtained (¹H NMR and mass spectrum, for example), one more key piece of data on this non-isolable compound was desired, namely ¹³C(¹H) NMR spectral data. Because the reaction solution always contains an
unknown platinum species, it was desired to design an experiment in such a way that the only Pt-containing species in solution (for the $^{13}\text{C}(^1\text{H})$ NMR spectral acquisition) be a compound with a known $^{13}\text{C}(^1\text{H})$ NMR spectrum. Since the only carbon-containing parts of the platinum species are the phenyl carbons of the triphenylphosphine ligands, a reagent where carbons are phenyl carbon atoms only was quite desirable. In this way, only one region of the spectrum would be unavailable for the identification of the signals for 22. However, the reagent required to react with $(\text{PPh}_3)_2\text{Pt(CO)}_2$ to form such a simple species must not react with 22. The reagent chosen was diphenylacetylene.

Thus, after preparing 22 and $(\text{PPh}_3)_2\text{Pt(CO)}_2$ in the usual way, the reaction solution was treated with diphenylacetylene (Eq. 73). While being

$$\text{14a} \begin{array}{c} \text{CO} \\ \text{(PPh}_3)_2\text{Pt(CO)}_2 \end{array} \xrightarrow{\text{PhC}≡\text{CPh}} \text{22} \xrightarrow{\text{PhC}≡\text{CPh}} (\text{PPh}_3)_2\text{Pt(PhC}≡\text{CPh}) + 22 \quad (73)$$

unreactive towards 22, the diphenylacetylene completely consumed the $(\text{PPh}_3)_2\text{Pt(CO)}_2$ to give $(\text{PPh}_3)_2\text{Pt(PhC}≡\text{CPh})$. Meanwhile, $(\text{PPh}_3)_2\text{Pt(PhC}≡\text{CPh})$ was prepared independently from $(\text{PPh}_3)_2\text{PtC}_2\text{H}_4$ and PhC≡CPh and its $^{13}\text{C}(^1\text{H})$ NMR spectrum recorded for comparative purposes ($\delta 124.9$ (s, br) for C≡C carbons). The most convincing spectral evidence for 22 was then obtained by $^{13}\text{C}(^1\text{H})$ NMR spectroscopy (Figure 14). A comparison of the data obtained for 22 and for $\text{Cp(CO)}_2\text{RuCH}≡\text{C}≡\text{CH}_2$ and $\text{Cp(CO)}_2\text{FeCH}≡\text{C}≡\text{CH}_2$ is presented in Table 7.
Figure 14. $^{13}\text{C}^{(1}\text{H})$ NMR Spectrum of 22, Denoted by $X$. 
Table 7. A comparison of $^{13}\text{C}(^{1}\text{H})$ NMR spectral data$^a$ for the three carbon atoms of the allenyl ($X = \text{CH}=\text{C}=\text{CH}_2$) ligand.

<table>
<thead>
<tr>
<th>$^{13}\text{C}(^{1}\text{H})$ NMR</th>
<th>22</th>
<th>$\text{Cp}(\text{CO})_2\text{RuX}$</th>
<th>$\text{Cp}(\text{CO})_2\text{FeX}^{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$=\text{C}=\ $</td>
<td>206.6</td>
<td>206.1</td>
<td>206.0</td>
</tr>
<tr>
<td>$=\text{C}(\text{R})\ $</td>
<td>68.1 (R = Ph)</td>
<td>58.4 (R = H)</td>
<td>65.2 (R = H)</td>
</tr>
<tr>
<td>$=\text{CH}_2\ $</td>
<td>61.8</td>
<td>63.1</td>
<td>63.4</td>
</tr>
</tbody>
</table>

$^a$Spectral data recorded in CDCl$_3$ or CD$_2$Cl$_2$. $^b$Data obtained by the author as, to his knowledge, this information was not reported in the literature.

The most diagnostic signal is that for the $=\text{C}=\ $ carbon, at around $\delta$ 206 ppm for each compound. The CH$_2$ carbons all resonate around $\delta$ 62 - 63 ppm, and even the $=\text{C}(\text{R})\ $ signals are all in good relative agreement. Thus, based upon the evidence presented, it can be said with a much greater level of confidence that 22 is indeed the proposed phenylallenyl complex.

b) Other Reactions Involving Carbon Monoxide

Another species which was not isolated as a pure material, but was studied indirectly to determine its identity was the intermediate I from Scheme 3. Its structure, based upon $^{1}\text{H}$ and $^{31}\text{P}(^{1}\text{H})$ NMR data was

\[
\text{Cp}(\text{CO})_2\text{RuCH}_2
\]

\[
\text{C} \quad \text{Pt(PPh}_3\text{)}_2
\]

\[
\text{Ph} \quad \text{I}
\]
proposed to be an acetylene complex of a \( (\text{PPh}_3)_2\text{Pt} \) fragment. Intermediate I then, over time, reacts further to form 14a or 16a. Since the complex \( (\text{PPh}_3)_2\text{Pt}(\text{PhC} = \text{CPh}) \) was shown to have a high propensity to react with carbon monoxide to form \( (\text{PPh}_3)_2\text{Pt(CO)}_2 \), it was thought that the reaction of I with excess CO should proceed in the fashion outlined in Eq. 74. The intermediate I for this reaction was prepared simply by treating 13 with

\[
\begin{align*}
\text{I} & \quad \text{CO} \quad \rightarrow \quad \text{13} \\
& \quad \text{(PPh}_3)_2\text{Pt(CO)}_2
\end{align*}
\]

(\text{PPh}_3)_2\text{PtC}_2\text{H}_4 for about one hour at ambient temperature, at which time I was the major species in solution. This reaction was then followed by that given in Eq. 74. Note that in this case, the ruthenium propargyl (13) is recovered with no contamination by the phenylallenyl complex (22). This suggests that I is of the predicted structure that contains a metal-bound acetylene rather than an allenyl-type of ligand. This situation is analogous to the carbon monoxide-induced fragmentation of 14a, 15a, and 15b, all of which contain \( \mu \)-allenyl ligands before reaction with carbon monoxide, and fragment into mononuclear ruthenium or iron allenyl complexes and \( (\text{PPh}_3)_2\text{Pt(CO)}_2 \) during reaction with CO.

As expected, 16a also underwent fragmentation upon exposure of
the reaction solution to carbon monoxide (Eq. 75) to form 22 and several mononuclear Pt-containing species (about 1/2 of the starting 16a reacted in 6 hours). The only reversal of Eq. 75 noted upon changing the atmosphere from carbon monoxide to argon was the reaction of 22, formed in the forward direction, with \((\text{PPh}_3)_2\text{Pt(CO)}_2\) to afford a small amount of the heterobinuclear complex 14a. No reversal of the reaction to reform 16a was observed. Of course, it is possible that the reaction did not reverse because some of the mononuclear platinum species precipitated out of the reaction solution. This process is somewhat common and occurs in several instances in the experiments discussed here. These rather insoluble platinum-containing materials have typical chemical shifts of δ 5-10 ppm in \(^{31}\text{P}(1\text{H})\) NMR spectra with \(J_{\text{Pt-P}}\) values in the range of 3000 to 3800 Hz.

Another important reaction of 16a is that with triphenylphosphine to yield 14a. Unlike the forward direction of the reaction in Eq. 76, where at room temperature in just a few hours 16a is prepared in high yield, the reverse direction requires 18 hours at 100°C in toluene to drive it to 14a. This result implies that 16a is more inert toward ligand substitution than is 14a. The ability of the carbonyl ligand to accept electron density from the platinum atom may explain the stability of 16a, as well as the lack of lability of this carbon monoxide ligand in 16a.
D. General Reactions of the Heterobinuclear Complexes (14 and 15)

Unlike most of the heterobi- and heterotrinuclear μ-allenyl complexes prepared previously in this research group, the heterobinuclear ruthenium-containing 14a and 15a complexes prepared presently were thoroughly investigated for reactivity. As mentioned previously, the remote carbon-carbon double bond of the allenyl group in 14 and 15 that is not involved in bonding to a transition metal was thought to be a potential center of previously unexplored reactivity. In the pages that follow, a clearer picture of the reactivity of this source of unsaturation is developed.

1) With Nucleophiles

Treatment of heterobinuclear metal complexes 14a or 15a with p-tolylsulfonamide, diethylamine, and cyclohexylamine gave no reaction in THF or benzene solution, even at elevated temperature (Eq. 77).

\[
\begin{align*}
\text{Cp} & \quad \text{Ru} \quad \text{Pt(PPh}_3\text{)}_2 \\
\text{OC} & \quad \text{R = Ph, 14a} \\
& \quad \text{R = H, 15a}
\end{align*}
\]

\[
\text{H}_2\text{C} \quad \text{C} = \text{C} \quad \text{R}
\]

\[
p-\text{MeC}_6\text{H}_4\text{S(O)}_2\text{NH}_2
\]

\[
\text{or} \\ \text{HNET}_2 \\
\text{or} \\ \text{C}_6\text{H}_{11}\text{NH}_2
\]

\[
\text{No Reaction (77)}
\]

Even the strong base potassium hydroxide did not react with 15a at 69°C for 18 hours! The reagents sulfur and selenium appeared to cause slow decomposition of 14a (Eq. 78), apparently by removal of
triphenylphosphine from the platinum atom as $E=PPh_3$ ($E = S$ or $Se$).

The reaction of $15a$ with n-BuLi gave a new product (observed via
$D_2O$-insert, $^{31}P\{^1H\}$ NMR only) with $^{31}P\{^1H\}$ NMR spectral data ($\delta 28.0$ (d, $J_{PP} = 4.0, J_{PtP} = 2698$) and 24.3 (d, $J_{PP} = 4.0, J_{PtP} = 3716$)) similar to those for $15a$ and not indicative of an anionic platinum center. $^1J_{PtP}$ for phosphorus nuclei associated with anionic platinum centers are generally greatly decreased in value compared to those of related neutral species. Interestingly, the reaction could not be driven past 50% conversion of $15a$ to this new complex, even with a large excess of the n-BuLi reagent at $69^\circ$C for 24 hours. Removal of solvent from a 1:1 mixture of $15a$/new product led to decomposition of both compounds to yield a red tar.

Replacement of both of the labile triphenylphosphine ligands on the platinum of the heterobinuclear $15a$, rather than reaction at the bridging allenyl ligand, was observed upon treatment of $15a$ with the more basic
triethylphosphine (Eq. 79). Of particular note is the fact that both triphenylphosphine ligands were replaced by triethylphosphine ligands when either an excess or two equivalents of the more basic phosphine was used.

Spectroscopic data for 24 display obvious similarities to those of the other binuclear μ-allenyl complexes, 14 and 15. As expected, due to greater electron density on the platinum atom, and hence on the ruthenium atom as well, caused by the presence of the basic triethylphosphine ligands, the IR stretching frequency for the lone carbonyl ligand is observed at 1892 cm\(^{-1}\). This is 20 cm\(^{-1}\) lower in energy than for 15a. This decrease of the carbonyl stretching frequency is due to a greater degree of back \(\pi\)-bonding of electron density from the ruthenium to the anti-bonding orbital of the C=O. This weakens (and hence lengthens) the bond and causes it to stretch at a lower energy than for 15a.

The \(^1\)H NMR data for the CH (δ 6.42 (m, \(J_{\text{PtH}} = 31\)) and CH\(_2\) (δ 5.41 (m, \(J_{\text{PtH}} = 20\)) and 4.70 (m, \(J_{\text{PtH}} = 13\))) protons is interesting in that no proton-proton couplings can be ascertained. Apparently those protons are strongly coupled to the phosphorus atoms of the triethylphosphine ligands. The result is a complicated multiplet for each signal, rather than the typical doublets with \(^{195}\)Pt satellites observed for 14 and 15. The \(^{31}\)P\(^{(1)}\)H NMR spectrum (δ 23.9 (s, br, \(J_{\text{PtP}} = 3681\)) and 12.4 (s, br, \(J_{\text{PtP}} = 2733\))) displays two widely spaced broad singlets that are actually poorly resolved doublets with a phosphorus-to-phosphorus coupling of < 1 Hz.

The reaction of 14a with 1,3-(diphenylphosphino)propane (dppp) in Eq. 80 is quite clean by NMR spectroscopy, but the isolated yield of 25a is disappointing (40%) owing to the difficulty in its separation from
triphenylphosphine. Unfortunately, 25a decomposes on alumina or Florisil, so only repeated recrystallizations can be utilized to separate the triphenylphosphine from 25a. Relatively clean samples were obtained, however, which provided diagnostic spectroscopic data.

For example, the lone carbonyl ligand on the ruthenium atom of 25a was identified by IR spectroscopy (1901 cm⁻¹), and the two inequivalent phosphorus atoms on platinum could be observed by ³¹P{¹H} NMR spectroscopy (δ 4.0 (d, Jₚₚ = 22.5, Jₚₚ = 2526) and 1.1 (d, Jₚₚ = 22.5, Jₚₚ = 3427)). That the phosphorus atoms of 25a have a higher electron-density than those of 14a is evidenced by the 20 ppm upfield (more shielded) chemical shift. The stability of the platinum-phosphorus bonds is evidenced by the appearance of a Pt(dppp)⁺ fragment (rel. intensity 9.2) in the FAB mass spectrum. Finally, the ¹H NMR data for the CH₂ protons (δ 6.12 (d, Jₚₕ = 2.2, Jₚₕ = 24) and 5.56 (d, Jₚₕ = 2.2, Jₚₕ = 15)) is indicative of the proposed μ-allenyl formulation for 25a.

The yield for the reaction of 15a with dppp (Eq. 81) was almost 10% higher than for the reaction of 14a with dppp, so the product 25b was more completely characterized spectroscopically than 25a. In addition to very similar IR (νC=O = 1902 cm⁻¹), ¹H NMR (CH proton: δ 6.70 (s, Jₚₕ = 37), CH₂ protons, δ 5.59 (s, br, Jₚₕ = 27) and 4.77 (s, br, Jₚₕ = 18)), and ³¹P{¹H} NMR (δ 4.9 (d, Jₚₚ = 20, Jₚₚ = 2502 and 0.4 (d, Jₚₚ = 20, Jₚₚ = 3400))
spectroscopic properties, compound 25b was observed to be similar to 15a by $^{13}\text{C}({}^1\text{H})$ NMR spectroscopy. Specifically, the bridging alleny1 carbon signals of 25b (δ 168.9 (=C=), 112.4 (d, $J_{PC} = 85$, $J_{PtC} = 722$ (CH) and 94.5 (=CH$_2$)) are within 3 ppm, and the coupling constants are within 3 Hz of those for 15a. Purity was established by elemental analysis.

The substitution chemistry observed upon reaction of 14 or 15 with nucleophiles differs from the behavior of related µ-allenyl complexes. Carty and co-workers have found that the central (β) carbon of the µ-η$^1$,$\eta^2$-allenyl ligand of u$^{29}$ is susceptible to nucleophilic attack

![Diagram of chemical structure]

of secondary amines, isocyanides, phosphines, and phosphites to form products such as v.
The $^1$H NMR signals ($\delta 1.64$ (d, $J_{HH} = 6.2$) and $1.16$ (dd, $J_{HH} = 6.2$, $J_{PH} =$ 2.4)) of the CH$_2$ protons for $u$ are positioned extremely upfield compared to those for 14 and 15 ($\delta 4.5 - 6.5$ ppm). Also, a $^{13}$C($^1$H) NMR data comparison of $u$ to our binuclear $\mu$-allenyl complexes suggests another formulation for the $u$ compound. The CH$_2$ carbon resonates at $\delta 29.4$, the C(Ph) carbon at $\delta 99.4$ (my assignment), and the $\beta$-carbon at $\delta 139.1$ (d, $J_{PC} = 5.6$) ppm.$^{29d}$ The corresponding signals for 14a ($\delta 97.2$, 149.1, and 165.3 ppm, respectively), typical for the $\mu$-$\eta^1,\eta^2$-allenyl formulation, do not match the values for $u$. Finally, as has been shown in Eqs. 79 - 81, the $\beta$-carbon of the binuclear complexes 14a and 15a is clearly not electrophilic and/or reactive towards any nucleophilic or basic reagent.

Recently, $u$ was characterized by an X-ray diffraction analysis,$^{29e}$ and the following structure was observed:

```
V P hh
H2C＝C＝C
\downarrow
(CO)$_3$Ru——Ru(CO)$_3$
\downarrow
P Ph$_2$ u'
```

This (u') is an alternative representation of the bonding in a metal binuclear $\mu$-$\eta^1,\eta^2$-allenyl complex, and such a structure accounts for the reactivity and spectroscopic properties of the complex in question (henceforth u').

The $^{13}$C NMR data for u' quite closely match those for the mononuclear $\eta^3$-allenyl and binuclear $\eta^2,\eta^3$-allenyl complexes shown below:
As can be seen from Table 8, the chemical shift of one of the allenyl carbon atoms of the compound $u'$ falls in the range of those of the mononuclear $\eta^3$-allenyl complexes (δ 102.2 to 56.7), and the other (δ 139.1) is fairly close as well. More striking is the CH$_2$ carbon resonance for $u'$, which is very close to the corresponding value for $w$. Indeed, even the reactivities of $w$ and $u'$ are similar, as noted by Casey and co-workers upon reaction of $w$ with

$$\text{Me}_5\text{Cp} \quad \frac{+}{\text{CH}_2} \quad \text{Me}_5\text{Cp}$$

(82)
Table 8. Comparison of $^{13}$C NMR data\textsuperscript{a} for mononuclear $\eta^3$-propargyl complexes and a binuclear $\mu$-$\eta^2,\eta^3$-propargyl complex ($^{1}J_{CH}$ values in Hz).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$C_\beta$, or $\equiv$CCH$_2$</th>
<th>$C_\gamma$, or C(R)</th>
<th>$C_{\alpha}$, or CH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta^5$-Me$_5$Cp(CO)$_2$Re($\eta^3$-C(Me)=C=CH$_2$)$^+$ (w)\textsuperscript{112}</td>
<td>56.7</td>
<td>76.6</td>
<td>29.0 (170)</td>
</tr>
<tr>
<td>$\eta^6$-C$_6$H$_6$(CO)$_2$Mo($\eta^3$-CH=C=CH$_2$)$^+$ (x)\textsuperscript{113}</td>
<td>69.9</td>
<td>74.5 (243)</td>
<td>39.6 (167)</td>
</tr>
<tr>
<td>(Ph$_3$P)$_2$Pt($\eta^3$-C(Ph)=C=CH$_2$)$^+$ (y)\textsuperscript{82}</td>
<td>97.6</td>
<td>102.2</td>
<td>48.4 (170)</td>
</tr>
<tr>
<td>($\eta^5$-MeC$_5$H$_4$)$_2$Mo$_2$(CO)$_4$(\mu-$\eta^2,\eta^3$-CH$_2$C=CH)$^+$ (z)\textsuperscript{114}</td>
<td>118.4</td>
<td>80.8 (227)</td>
<td>76.4 (163 and 170)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}At 25°C in CD$_2$Cl$_2$ (u' and w), CH$_3$NO$_2$ (v), or (CD$_3$)$_2$CO (x).
nucleophiles.\textsuperscript{112}(Eq. 82). The electrophilic nature of the central carbon atom of the coordinated propargyl triple bond in both compounds $u'$ and $w$ is clearly demonstrated. The compounds $x$ and $y$ have been shown to react with nucleophiles at the $\beta$-carbon of the bridging propargyl as well.\textsuperscript{86,113}

Another compound with spectroscopic properties related to compound $u'$ is the cationic compound prepared by Curtis and co-workers (z),\textsuperscript{114} (and independently by Barinov and co-workers\textsuperscript{115}) best thought of as containing a $\mu$-$\eta^2,\eta^3$ propargyl ligand rather than a $\mu$-$\eta^2,\eta^3$-allenyl ligand, from its $^{13}$C NMR data. For example, the two acetylenic carbon atoms bridging the two molybdenum atoms resonate at $\delta$ 118.4 and 80.8 ppm, quite typical for coordinated acetylenic carbon atoms.\textsuperscript{17} However, the $\text{CH}_2$ carbon resonance at $\delta$ 76.4 ppm is not typical for propargyl-type carbons. It is likely that the positive charge situated at the molybdenum atom $\sigma$-bound to this particular carbon accounts for this downfield shift.

The $^1J_{\text{CH}}$ values (163 and 170 Hz for the inequivalent protons) also indicate some sp$^2$ character of the $\text{CH}_2$ carbon atom. The key NMR spectral feature of this compound, however, is the $^1J_{\text{CH}}$ value of 227 Hz for the $\text{CH}$ carbon. This clearly indicates that this carbon is sp hybridized and, therefore, that this bridging ligand is more propargyl- than allenyl-
like. The spectroscopic data for compound z are also quite similar to those for the mononuclear \( \eta^3 \)-allenyl compounds prepared by Krivykh (w) and Casey (w) and discussed previously. In complexes w and x, instead of two metals, only one is involved in \( \mu \)-allenyl bonding interaction.

Unlike the compound u' prepared by Carty and co-workers, which reacted at the \( \beta \)-carbon of the \( \mu \)-allenyl with t-butylisocyanide, compound \( 14a \) reacted via substitution of one of the triphenylphosphine ligands at platinum (Eq. 83). Three interesting aspects of this reaction are worth mentioning. First, although the reaction solution (orange) immediately lightened in color (yellow) upon addition of the isocyanide at \(-78^\circ\text{C}\) dropwise, the reaction was not complete, as ascertained by NMR spectroscopy, until the solution had warmed to room temperature over 8 hours followed by 8 additional hours at that temperature. Second, the other triphenylphosphine ligand on platinum could not be replaced by the isocyanide, even with a large excess of the isocyanide at \(69^\circ\text{C}\) for several hours. However, \( 25c \) does not fragment under these conditions, unlike \( 14a \) when reacted with a large excess of carbon monoxide. Finally, unlike the compound u', which contains the substitution-inert \( \text{Ru}_2(\text{CO})_6 \) core held intact by the bridging phosphido ligands, \( 14 \) and \( 15 \) do not react with nucleophiles at the bridging allenyl ligand. Thus, while the most attractive sight for incoming nucleophiles on compound u' is the \( \text{C}_3 \)
carbon of the bridging allenyl ligand, the most accessible position in 14 or 15 is the platinum atom with its loosely bound triphenylphosphine ligand(s).

Compound 25c is a rather unique compound in that all of its ligands— a cyclopentadienyl, carbonyl, phosphine, isocyanide and a bridging allenyl— and the two metals are different. Spectroscopically, 25c has been completely characterized, and its analogy to 14a can be readily drawn. For example, its IR spectrum consists of a single band (1901 cm\(^{-1}\)) in the carbonyl stretching region for the carbon monoxide ligand on ruthenium. The single phosphine is indicated by the \(^{31}\text{P}\{^{1}\text{H}\} \text{NMR}\) spectrum (\(\delta 25.6\) (s, \(J_{\text{PtP}} = 3544\))). Interestingly, the CH\(_2\) protons are not coupled to each other in the \(^1\text{H}\) NMR spectrum, but are coupled to platinum (\(\delta 5.62\) (s, \(J_{\text{PtH}} = 17.0\)) and 4.98 (s, \(J_{\text{PtH}} = 13.0\))). The \(^{13}\text{C}\{^{1}\text{H}\} \text{NMR}\) spectrum displays rather typical resonances for the three \(\mu\)-allenyl carbons (\(\delta 166.5\) (s, \(=\text{C}=\)), 150.1 (s, C(Ph)), 97.0 (s, \(J_{\text{PtC}} = 32.2, =\text{CH}_2\)). The relative stability of the platinum-phosphorus bond is reflected by the appearance of the Pt(PPh\(_3\))t-BuNC\(^+\) fragment (relative intensity 18.9) in the FAB mass spectrum. Interestingly, neither (M\(^+\) - PPh\(_3\)) nor free PPh\(_3^+\) fragments are observed.

It is possible that one of the keys to the reaction chemistry of 14 and 15 is the loss of a labile phosphine from platinum, either before or concurrently with attack by another reagent. It appeared likely that 25 (as well as 16a) would not react in an analogous manner due to the added stability given the ligands on platinum via the presence of a good back \(\pi\)-bonding ligand (16a or 25c) or the chelate effect (25a and 25b). Therefore,
some reaction chemistry of these two types of heterobinuclear complexes was carried out.

An NMR tube reaction of 25a with carbon monoxide (in C₆D₆) showed that complex 25a is related to 14a in structure only. Spectra taken after 4 days at 70°C showed no carbonyl exchange for one or both ends of the dppp ligand, in direct contrast to the facile monosubstitution followed eventually by fragmentation observed during the room temperature reaction of 14a with carbon monoxide. The chelated dppp ligand is simply too tightly bound. Later, reaction of 25a with toluenesulfonyl isocyanate (TSI) was carried out because 14a and 15a reacted with TSI without loss of triphenylphosphine from platinum (pages 220 -230). In other words, the chemistry of compounds 25 and 14a and 15a was shown to be related only when a ligand was not lost from platinum during reaction.

The reaction of 25b with carbon monoxide was also carried out in an NMR tube in C₆D₆, and under essentially the same conditions (70°C for 48 hours) very little reaction to form any characterizable products was observed. Only starting material and a complex mixture of other compounds (1/3 of starting material consumed) were seen in ¹H and ³¹P(¹H) NMR spectra. Compound 25b does appear to be slightly less stable/more reactive than the phenyl-substituted 25a analogue though, based upon the fact that less decomposition was noted in the reaction of 25a with carbon monoxide despite a longer exposure at 70°C. Therefore, several other reactions of 25b were carried out.

Since it is well known that alkyl isocyanides are more basic and better σ-donors of electron density than carbon monoxide (and in turn less effective π-bonding ligands¹¹⁶), it was postulated that possibly t-butyl
isocyanide could displace one end (or even both ends) of the chelated dppp ligand from platinum. Under somewhat forcing conditions (in THF at 69°C for 18 hours), however, no reaction (besides a small amount of decomposition) of t-butyl isocyanide with 25b was observed. Indeed, the chelated dppp ligand is very strongly bound to the platinum atom, and substitution at platinum seems a very unlikely possibility regardless of the basicity of the incoming ligand. Since we have also observed no exchange of the carbonyl ligand on ruthenium for triethylphosphine, dppp, or t-butyliocyanide ligands, even under forcing conditions, it follows that the most interesting chemistry of 25a and 25b must involve the bridging allenyl ligand rather than the apparently inert metal centers. In other words, if the loss of a triphenylphosphine ligand from the platinum atom of a molecule of 14 or 15 is the key to its reactivity, then the reaction chemistry of 25a and 25b must be limited because neither compound has the ability to readily lose a ligand from platinum.

Recall that the L-shaped trinuclear clusters, such as 17, are all characterized by the replacement of a triphenylphosphine ligand on platinum by a carbon monoxide ligand. One way to test whether or not such a substitution is necessary for the formation of these clusters was to carry

![Diagram](image-url)
out the reaction of 25b with Fe$_2$(CO)$_9$. Complex 25b has been shown to be inert toward displacement of one or both ends of the chelated phosphine ligand under forcing conditions. This reaction (Eq. 84) yielded a small amount of a yellow compound (26) upon chromatography on Grade III alumina. The proposed structure given in Eq. 84 is based upon the available spectroscopic data.

The IR spectrum of 26 (2014 (s), 1978 (vs), 1963 (s), 1912 (vs), 1792 (vw) cm$^{-1}$) in the carbonyl stretching region consists of four strong or very strong terminal carbonyl bands, and one quite weak band that very likely corresponds to a bridging carbonyl ligand. The $^{31}$P($^1$H) NMR spectrum (Figure 15) for 26 consists of two inequivalent resonances ($\delta$ 10.4 (d, $J_{\text{PP}} = 2604$) and 2.5 (d, $J_{\text{PP}} = 3280$)), coupled to each other by 21 Hz., but these do not indicate anything structurally about 33. On the other hand, the $^1$H NMR spectrum consists of broadened resonances for the CH ($\delta$ 6.73) and CH$_2$ ($\delta$ 5.43) protons, indicating that the remote carbon-carbon double bond of the $\mu$-allenyl ligand is not involved in bonding to a transition metal, and that apparently the CH$_2$ protons are equivalent, or nearly so. The FAB mass spectrum displays peaks for the M$^+$ ion, as well as separate peaks for the ions resulting from loss of 5 consecutive carbon monoxide ligands, FePt(dppp)C$_3$H$_3^+$, and Pt(dppp)C$_3$H$_3^+$ (base peak).
Figure 15. $^{31}\text{P}(^1\text{H})$ NMR Spectrum of Unknown Compound 26.
Based upon the spectroscopic data above, the structure of 26 is given as shown here:

The major difference between clusters 17 and 26 is that the remote carbon-carbon double bond of the μ-allenyl ligand of 26 is not involved in bonding to a transition metal. The other obvious difference is the introduction of a bridging carbon monoxide ligand on 26. The changes effected by the μ-allenyl ligand and bridging carbon monoxide ligand suggest a dative bond (from iron to ruthenium) to satisfy the 18-electron rule for each Group 8 metal. An alternative, drastically different structure for 26, could be as below:

Notice that instead of a bridging carbonyl ligand, an acyl carbonyl has been suggested to account for the lowest energy vC=O absorption in the IR
spectrum of 26'. The closed, triangulated arrangement of metal atoms in this proposed structure is also a significant departure from the open, L-shaped arrangement of metal atoms in 17. Since no hydrogen-to-platinum coupling is observed in the proton NMR spectrum for 26, it is possible that a structure such as (26') is realized because the μ-acylallenyl ligand is not involved in bonding to the platinum atom. Such a non-bonding situation would be unprecedented in this chemistry. That is, each cluster prepared by this research group and by others has been characterized by interactions between each metal and the bridging allenyl ligand of the cluster. Unfortunately, the low yield of cluster 26 prepared in Eq. 85 precluded its further study.

2) With Electrophiles

In the study of the reactivity of the binuclear μ-allenyl compounds with electrophilic reagents, the goal was to find a reagent that would react without fragmentation or decomposition of the bimetallic framework. It was discovered that some reagents did not react at all. However, in general, reactions of the heterobinuclear complexes with electrophiles proved to be more interesting than those with nucleophiles because electrophiles react at the bridging allenyl ligand rather than at platinum.

Three reagents, all of different types, did not react with complexes 14a or 15a. The first was an activated olefin, diphenylmethylene malononitrile ((CN)₂C=CH₂). This compound consists of a polar carbon-carbon double bond, with the positive carbon attached to the electron-withdrawing cyano groups. However, either this carbon atom was not
electrophilic enough to react, or some other electronic or steric factor was responsible for the lack of reaction with 14a even at 69°C.

The second unsuccessful reaction involved the moderately active methylating agent dimethyl sulfate \((\text{CH}_3\text{O})_2\text{SO}_2\). Again, no reaction was noted with 15a at 69°C. The less active methylation reagent CH3I was unreactive toward 15a as well and, as will be shown below, more reactive alkylating agents completely destroyed 15a.

The third unsuccessful reaction occurred with dihydrogen \((\text{H}_2)\) gas at elevated temperatures and normal atmospheric pressure. Apparently standard-pressure catalysis (hydrogenation) utilizing 15a is not possible, but nevertheless the maintenance of the integrity of the heteronuclear metal-metal bond under these conditions is interesting.

At the other extreme, two reagents literally destroyed the binuclear compound 15a, with which they came in contact. Triethylhexafluorophosphate is considered to be a very strong alkylating agent, and upon reaction with 15a, even at -78°C, a myriad of signals in the \(^1\text{H}\) and \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra was detected. Unfortunately, no source of positive alkyl or aryl functionality produced a clean, isolable product upon reaction with 15a.

The second reagent that destroyed some of the heteronuclear complexes was chlorosulfonyl isocyanate \((\text{ClS}(\text{O})_2\text{N=C=O})\). This reagent was tried owing to the success of \(p\)-toluenesulfonfonyl isocyanate (TSI) in reaction with 14a, 15a, and other \(\mu\)-allenyl heterobinuclear complexes (pages 220 -230). Apparently the greater electron-withdrawing ability of the chloride (vs. \(p\)-tolyl) substituent on the sulfonyl sulfur atom has either rendered the compound too reactive, or it has led to a different type of
reaction (for example, oxidative addition, followed by decomposition) to occur which essentially destroys the heterobinuclear compound.

Other activated olefins and acetylenes reacted with heterobinuclear complexes 14a and 15a leading to fragmentation of the compounds into mononuclear ruthenium- and platinum-containing species. For example, fumaronitrile did not react with 14a at room temperature, but at 69°C fragmentation occurred (Eq. 85) to produce the known (PPh₃)₂Pt(fumaronitrile), a small quantity of the ruthenium phenylallenyl (22), and other, unidentified material. No 

\[
\text{Cp(CO)₂RuCH₂C≡Ph (13)} \text{ was detected, nor were any other platinum-containing species observed in } ^1\text{H or } ^{31}\text{P[}^1\text{H]} \text{ NMR spectra. Apparently the second carbonyl ligand on ruthenium required to form 22 came from another molecule of 14a, as the reaction was carried out under an atmosphere of argon. This also explains the ratio of relative intensities of about of 2:1 for the } ^1\text{H NMR signals of (PPh₃)₂Pt(fumaronitrile)} \text{ vs. } \text{Cp(CO)₂RuC(Ph)=C=CH₂.}
\]

Because activated olefins, such as fumaronitrile, led to fragmentation rather than reaction at the bridging allenyl ligand, activated acetylenes were tried instead. The first of these to be reacted with 15a was dimethylacetylenedicarboxylate (DMAD). Interestingly, a very
similar result to that obtained in the reaction of fumaronitrile with 14a was observed (Eq. 86). The complex Cp(CO)_2RuCH=CH was noted as

![Chemical structure]

the only identifiable ruthenium-containing species. The (PPh_3)_2Pt(DMAD) compound was identified as the only platinum-containing species by comparison of its $^{31}$P(1H) NMR resonance ($\delta$ 23.3 (s, $J_{PtP} = 3729$)) to that reported by Saito and co-workers.\textsuperscript{73} It thus appeared that a less reactive unsaturated species than DMAD would be required to react with 15a without rupture of the heterometallic bond.

Methyl-2-butynoate was a reasonable next choice of this acetylene, because its reactivity compared to DMAD is usually less pronounced owing to the replacement of one of the electron-withdrawing carboxylate groups by the electron-donating methyl group. Under identical reaction conditions, however, the reaction proceeded to only about one-half consumption of the 15a to again form the known (PPh_3)_2Pt(methyl-2-butynoate),\textsuperscript{73} Cp(CO)_2RuCH=CH, and other, unknown compounds. Addition of another equivalent of the activated acetylene at room temperature did not drive the reaction farther to the right, though. Apparently a slow reaction of Cp(CO)_2RuCH=CH with (PPh_3)_2Pt(methyl-2-butynoate) occurred to reform some 15a. This situation was observed again when 15a was reacted with phenylacetylene.
In the case of phenylacetylene as reagent, the increase in the amount of 15a could be observed in the $^1$H and $^{31}$P$^{(1)}$H NMR spectra. In the early stages of the reaction (about 1/2 of the starting 15a consumed), Pt(PPh$_3$)$_4$, Cp(CO)$_2$RuCH=CH=, and only a small amount of (PPh$_3$)$_2$Pt(PhC=CH) were observed among other, unidentified material.

\[
\begin{align*}
\text{H}_2\text{C} & \xrightarrow{\text{PhC}=\text{CH}} \text{Pt(PPh}_3\text{)}_4 + \text{Cp(CO)}_2\text{RuCH}=\text{C}=\text{CH}_2 \\
\text{C}_\text{R} & \xrightarrow{\text{PhC}=\text{CH}} \text{Pt(PPh}_3\text{)}_4 + \text{Cp(CO)}_2\text{RuCH}=\text{C}=\text{CH}_2 \\
\text{OC} & \xrightarrow{\text{PhC}=\text{CH}} \text{Pt(PPh}_3\text{)}_4 + \text{Cp(CO)}_2\text{RuCH}=\text{C}=\text{CH}_2
\end{align*}
\] (Eq. 87). Addition of another equivalent of phenylacetylene did not consume more of 15a, however, but instead, over several hours, some of the Cp(CO)$_2$RuCH=CH= reacted with all of the Pt(PPh$_3$)$_4$ to reform approximately 10% of the original starting 15a. Meanwhile, the relative amount of (PPh$_3$)$_2$Pt(PhC=CH) remained essentially unchanged.

A nearly identical situation to that in Eq. 87 was observed when 15a was reacted with diphenylacetylene (Eq. 88). However, in this case,

\[
\begin{align*}
\text{H}_2\text{C} & \xrightarrow{\text{PhC}=\text{CPh}} \text{Pt(PPh}_3\text{)}_4 + \text{Cp(CO)}_2\text{RuCH}=\text{C}=\text{CH}_2 \\
\text{C}_\text{R} & \xrightarrow{\text{PhC}=\text{CPh}} \text{Pt(PPh}_3\text{)}_4 + \text{Cp(CO)}_2\text{RuCH}=\text{C}=\text{CH}_2 \\
\text{OC} & \xrightarrow{\text{PhC}=\text{CPh}} \text{Pt(PPh}_3\text{)}_4 + \text{Cp(CO)}_2\text{RuCH}=\text{C}=\text{CH}_2
\end{align*}
\] (Eq. 88) (50% Conversion of 15a)

the solution was stirred for 4-8 hours without the addition of another equivalent of free acetylene. Consumption of the small amount of Pt(PPh$_3$)$_4$ and a small increase in the relative intensity of the $^1$H and
Figure 16. Solution Mixture of Eq. 88. X Denotes (PPh$_3$)$_2$Pt(PhC≡CPh).
$^{31}$P($^1$H) NMR signals for 15a were observed. No other changes were noted after another 48 hours (Figure 16).

The reaction in Eq. 88 cannot completely reverse because 25% of the total ruthenium must be lost as intractable material in order that Cp(CO)$_2$RuCH=CH$_2$, with its two carbonyl ligands, be formed. Further, it was thought that the Cp(CO)$_2$RuCH=CH$_2$ present in the reaction mixture could react with (PPh$_3$)$_2$Pt(PhC≡CPh) to reform 15a. In a control reaction it was shown that when a slight excess of

$$\text{Cp(CO)$_2$RuCH=CH$_2$}$$

(slight excess)

$$\text{+}$$

$$\text{(PPh$_3$)$_2$Pt(PhC≡CPh)}$$

$$\rightarrow$$

$$\text{15a + PhC≡CPh + CO (89)}$$

Cp(CO)$_2$RuCH=CH$_2$ was reacted with (PPh$_3$)$_2$Pt(PhC≡CPh) (Eq. 89), complete conversion of the (PPh$_3$)$_2$Pt(PhC≡CPh) to 15a was observed after 2 hours. Stirring the solution at ambient temperature for 5 days, however, resulted in reaction of the newly-formed 15a with PhC≡CPh (as per Eq. 88) to reform a small amount of (PPh$_3$)$_2$Pt(PhC≡CPh). Thus, the results from the reaction described by Eq. 88 would at first sight appear to contradict those of the control reaction (Eq. 89).

Careful examination of the contadictory results, however, suggests a situation analogous to that observed in Eq. 90, where the reaction does

$$\text{Cp(CO)$_2$RuCH=CH$_2$ + (PPh$_3$)$_2$Pt(CO)$_2$}$$

$$\rightarrow$$

$$\text{15a + CO (90)}$$
not proceed under an atmosphere of carbon monoxide, but occurs readily under an atmosphere of argon. In other words, the presence of the excess PhC=CPh (Eq. 88, after any of the ruthenium has been consumed to form \( \text{Cp(CO)}_2\text{RuCH=CCH}_2 \) and intractable material) in solution seems to stabilize the \((\text{PPh}_3)_2\text{Pt(PhC=CPh)}\) with respect to acetylene dissociation and not allow for it to react with the available \( \text{Cp(CO)}_2\text{RuCH=CCH}_2 \) to reform 15a. By contrast, the carbon monoxide on the right side of Eq. 90 is free to escape from the solution when the reaction is carried out under argon. Since carbon monoxide does not build up in the reaction solution, the reaction proceeds to completion. In the control experiment (Eq. 89), however, the slight excess of \( \text{Cp(CO)}_2\text{RuCH=CCH}_2 \) (i.e., a deficient amount of PhC=CPh) present at the start of the reaction insures that plenty of this reagent is available for reaction with \((\text{PPh}_3)_2\text{Pt(PhC=CPh)}\). Hence early, complete reaction to form complex 15a is observed.

Protic acid is another electrophilic reagent of choice for reaction with 15a. Initially, the reaction of 15a with trifluoroacetic acid (Eq. 91), when carried out in a very careful and meticulous manner, produced a relatively clean product, tentatively formulated as 27.

The origin of the second carbonyl ligand in complex 27 is probably from another molecule of 15a. That 27 contains two terminal carbonyl ligands is shown in the IR spectrum (2024 (m) and 1974 (s) cm\(^{-1}\)) of either...
the trifluoroacetate or tetraphenylborate salt. The $^{31}$P($^1$H) NMR spectrum is also useful ($\delta$ 15.1 (d, $J_{PP} = 7.0, J_{PtP} = 4078$), and 14.1 (d, $J_{PP} = 7.0, J_{PtP} = 3946$)), as it indicates that the platinum atom of 27 is more positively charged than that of 15a owing to large phosphorus-to-platinum coupling constants of both phosphorus atoms. The $^{13}$C($^1$H) NMR data for the three proposed allyl carbons ($\delta$ 124.7 (d, $J = 30$, central C$_3$ carbon)), 99.1 (d, $J_{PC} = 32.0, J_{PtC} = 120$, CH$_2$) and 62.5 (d, $J_{PC} = 31.0, J_{PtC} = 130$, other CH$_2$) indicates inequivalency of the two CH$_2$ carbon atoms. The chemical shifts (and $J_{PtC}$ values) may be compared to those of related compounds prepared by Powell (bb)$^{117}$ and Shuchart (aa)$^7$ in Table 9 below, as are the $^{31}$P($^1$H) NMR spectral data. With the exception of the $^{13}$C($^1$H) NMR resonance for the central C$_3$ carbon atom of the compound bb at $\delta$ 219 ppm (which is in error), the data for the three compounds appear compatible.

Another possible formulation for 27 is as follows:

![Diagram](image)

There are several reasons for the rejection of this formulation for 27. First, the IR data clearly indicate the presence of two carbonyl ligands. Also, the
positive charge on the ruthenium would have been noted by a shift to higher energy for the carbon monoxide stretching frequency of the lone electron pair.

<table>
<thead>
<tr>
<th>Table 9. A comparison of some NMR data of allyl complexes.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(^{13}\text{C}[^{1}\text{H}]) NMR</strong></td>
</tr>
<tr>
<td>(solvent)</td>
</tr>
<tr>
<td>Central C</td>
</tr>
<tr>
<td>other carbons</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>(^{31}\text{P}[^{1}\text{H}]) NMR</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

*An error in reporting of this piece of data.

carbonyl. Secondly, the formulation 27' suggests that the central allenyl carbon of 15a is nucleophilic. This would imply that the compound u' prepared by Carty and co-workers\(^{29d}\) and 15 are completely unrelated, which is doubtful. Based upon the available data, compound u' and 15a are certainly not composed of analogous C\(_3\)-bridging ligands, but the two bridging ligands of the compounds are related isomeric forms of one another. Finally, the \(^{31}\text{P}[^{1}\text{H}]\) NMR data suggest that the positive charge of the complex 27 is situated at the platinum center (not at ruthenium), and that the two phosphorus atoms are nearly equivalent. Such a situation is
indicated in the proposed formulation 27 rather than for the formulation of 27\textsuperscript{'}.

The \textsuperscript{1}H NMR data for 27 does not support one formulation over another, however (Figure 17). Four separate resonances are observed (\(\delta\) 6.10 (m), 6.03 (dd, \(J_{HH} = 2.3, J_{HH} = 7.2\)), 3.84 (m), and 2.78 (m)), each integrated to one proton. A decoupling experiment showed that the signal at \(\delta\) 3.84 ppm is coupled to each proton: To the signal at \(\delta\) 2.28 ppm by 2.6 Hz, to the signal at \(\delta\) 6.03 ppm by 9.9 Hz, and to the signal at \(\delta\) 6.10 ppm by 2.3 Hz. The tentative assignment of syn vs. anti (to the substituent on the central carbon atom) protons attributes the downfield signals to the syn protons and the more upfield resonances to the anti protons. This assignment is also in agreement with those of Green,\textsuperscript{118} who additionally has observed that the value of \textsuperscript{2}J(geminal) proton couplings for \(\eta^3\)-allyls is very small\textsuperscript{105,119} or non-existent for a great number of compounds. This explains the assignment of the \(\delta\) 3.84 and 6.10 ppm resonances (\(J_{HH} = 2.3\)) as being due to the protons on the same carbon atom. However, no explanation can be offered as to the large difference between the chemical shift values for the anti protons, nor for the corresponding difference in the \textsuperscript{13}C(\textsuperscript{1}H) NMR spectroscopic values for the CH\textsubscript{2} carbon atoms.

Unfortunately, after two successful preparations, including in the second case a methathesis reaction with NaBPh\textsubscript{4} which produced the tetraphenylborate salt of 27, the results given in Eq. 92 became irreproducible. Thus, other acids were reacted with 15a. Most of those acids either destroyed 15a (HCl in ether) or did not react at all (CH\textsubscript{3}CO\textsubscript{2}H). The slightly less acidic\textsuperscript{120} chloroacetic acid (pK\textsubscript{a} of 2.87 compared to 0.50
Figure 17. $^1$H NMR Spectrum of Protonated 15a (27).
for CF₃CO₂H produced some 27 upon low temperature (-78°C) reaction with 15a, but warming to room temperature led to decomposition of this product. So-called superacids, such as HBF₄•OEt₂, were not used because it was thought that CF₃CO₂H was as acidic/reactive as the system could tolerate (the reaction of CF₃CO₂H with 15a occurred at -78°C, not with warming).

Another type of reaction with electrophilic reagents that has been well studied for mononuclear transition metal propargyl and allenyl complexes is cycloaddition. One of the most reactive cycloaddition reagents is tetracyanoethylene (TCNE). In an effort to explore possible interaction of the bridging allenyl ligand with this class of reagent, an exploratory reaction of complex 15a with TCNE was carried out.

Compound 15a reacted quite readily with TCNE at -78°C (Eq. 92) to

\[
\begin{align*}
\text{H}_2\text{C} & \equiv \text{C} = \text{C} \equiv \text{H} \\
\text{C}_\text{Ru} & \equiv \text{C} = \text{C} \equiv \text{H} \\
\text{OC} & \equiv \text{C} = \text{C} \equiv \text{H} \\
\text{Pt(PPh}_3\text{)}_2 & \equiv \text{C} = \text{C} \equiv \text{H} \\
\text{TCNE} & \equiv \text{C} = \text{C} \equiv \text{H} \\
\text{15a} & \equiv \text{C} = \text{C} \equiv \text{H} \\
\text{(PPh}_3\text{)}_2\text{Pt(TCNE)} & \equiv \text{C} = \text{C} \equiv \text{H} \\
\end{align*}
\]

form at least two products that could be identified by (D₂O-insert) NMR spectroscopy on the reaction solution. The first product is the known compound (PPh₃)₂Pt(TCNE), formed as the result of fragmentation of 15a. The second product is most likely an adduct of 15a and TCNE that has maintained the metal-metal bond and bridging C₃ ligand. The (PPh₃)₂Pt(TCNE) NMR data (δ 26.6 (d, Jₚₚ =7.0, Jₚtₚ = 2891) and 19.7 (δ, Jₚₚ = 7.0, Jₚtₚ = 3248 )) provide support for this idea in that they reveal chemical shift values and phosphorus-to-platinum coupling constants
similar to those of the starting complex 15a and other heterobinuclear \( \mu \)-allenyl compounds. Allowing the reaction mixture to warm to room temperature led to the decomposition of this product, however. As will be seen next, a slightly less reactive electrophilic reagent, \( p \)-toluenesulfonyl isocyanate (TSI) provided some novel reaction chemistry with the heterobinuclear complexes 14a and 15a.

The reagent well suited to react with 14a so as not to produce fragmentation, while concurrently generate products stable enough to be isolated and characterized, turned out to be \( p \)-toluenesulfonyl isocyanate (TSI). If the reaction was started at \(-78^\circ C\), no fragmentation was observed. Instead, the new products 28a and 29a were obtained (Eq. 93) and completely characterized spectroscopically. Compound 28a was observed to precipitate out of the reaction solution while 29a was completely soluble under the conditions given in Eq. 93.

That the ruthenium-platinum bond is still intact in 28a is evident
upon examination of the $v_{\text{C=O}}$ region of the IR spectrum ($1924 \text{ (s)}, 1670 \text{ (s)}$ cm$^{-1}$), and the $^{31}\text{P}(^{1}\text{H})$ NMR spectrum ($\delta 21.6 \text{ (d, } J_{PP} = 11, J_{PtP} = 2789)$ and $20.9 \text{ (d, } J_{PP} = 11, J_{PtP} = 3923)$, the former indicating a carbon monoxide on ruthenium and the latter showing the inequivalent phosphorus atoms of the triphenylphosphine ligands on platinum with the appropriate coupling constants. The $^{1}\text{H}$ NMR spectrum (Figure 18) reveals the NH proton ($\delta 12.1 \text{ (s)}$), CH proton ($\delta 5.96 \text{ (s, } J_{PtH} = 10)$), and the methyl group of the tosyl substituent ($\delta 2.43 \text{ (s)}$), indicating an interaction between the bridging allenyl ligand and TSI. The $^{13}\text{C}(^{1}\text{H})$ NMR spectral data for the (former) three allenyl carbon atoms ($\delta 164.5 \text{ (s, } =\text{C=}), 146.2 \text{ (s, } \text{C(Ph)}), \text{ and } 108.4 \text{ (s, } =\text{CH})$) are all very similar to those for the starting material 14a ($\delta 165.3, 149.1, \text{ and } 97.2$), although in the case of 14a, weak coupling between the CH$_2$ carbon and platinum was observed. Further evidence for the formulation of 28a was observed in the FAB mass spectrum (see Experimental section), and purity was established by elemental analysis.

However, in order to unequivocally determine the structure of 28a, a structural analysis was required. Therefore, orange crystals of 28a were grown from a mixture of methylene chloride, ethylene chloride, and hexane and analyzed X-ray crystallographically by Professor Mario Calligaris and co-workers. The ORTEP drawing is presently unavailable, but the important bond lengths and angles appear in Table 10.

The structure of 28a reveals bond formation between the CH$_2$ carbon of 14a and the carbonyl carbon atom of TSI, coupled with a transfer of hydrogen from the CH$_2$ to the nitrogen atom of TSI. The ruthenium-platinum bond length (2.702 Å) compares closely to the corresponding bond length in 15a (2.718 Å), as does the carbon-carbon bond length of the
Figure 18. $^1$H NMR Spectrum of $\text{Cp(CO)}\text{Ru-(p-MeC}_6\text{H}_4\text{S(O)}_2\text{N(H)C(O)}\text{CH}=\text{CPh)}\text{Pt(PPh}_3\text{)}_2$ (28a).
Table 10. Selected bond distances (Å) and angles (degrees) for 28a.

<table>
<thead>
<tr>
<th>Distances</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Ru</td>
<td>2.702 (1)</td>
</tr>
<tr>
<td>Pt-Cl</td>
<td>2.03 (2)</td>
</tr>
<tr>
<td>Ru-C1</td>
<td>2.14 (2)</td>
</tr>
<tr>
<td>Ru-C2</td>
<td>2.04 (2)</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.38 (2)</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.34 (3)</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.52 (3)</td>
</tr>
<tr>
<td>C4-O4</td>
<td>1.22 (3)</td>
</tr>
<tr>
<td>C4-N</td>
<td>1.35 (2)</td>
</tr>
<tr>
<td>C1-C2-C3</td>
<td>139 (2)</td>
</tr>
<tr>
<td>C2-C1-C5</td>
<td>123 (2)</td>
</tr>
<tr>
<td>C2-C3-C4</td>
<td>123 (2)</td>
</tr>
<tr>
<td>C3-C4-O4</td>
<td>120 (2)</td>
</tr>
<tr>
<td>C3-C4-N</td>
<td>114 (2)</td>
</tr>
<tr>
<td>O4-C4-N</td>
<td>126 (2)</td>
</tr>
<tr>
<td>S-N-C4</td>
<td>124 (2)</td>
</tr>
</tbody>
</table>

Carbon atom numbering for 28a.
Figure 19. $^1$H NMR Spectrum of TSI Cycloadduct 29a.
internal (bound to ruthenium) double bond (1.38 Å in each case). One consequence of the addition of TSI at C3 is a lengthening of the C2-C3 bond to 1.34 Å (compared to 1.31 Å in 15a). Otherwise, the core of the molecule is structurally very similar to that of 15a and 16a.

The structure of 29a is derived upon a comparison of its spectroscopic properties to those of the structurally determined 29e (page 234). The IR spectrum of 29a consists of two peaks in the vC=O region (1899 (s) and 1724 (s) cm⁻¹), suggestive of both the terminal carbon monoxide ligand on ruthenium and the organic carbonyl of the (former) TSI. The 31P{1H) NMR spectrum (δ 22.7 (d, JPP = 11.3, JPtP = 2643) and 16.3 (d, JPP = 11.3, JPtP = 3621)) is typical for the two inequivalent triphenylphosphine phosphorus atoms, and the 13C{1H) NMR data for the former C3 carbons of the bridging allenyl ligand (δ 174.5 (d, JPC = 8.5, JPtC = 120, central C), 153.1 (s, NC(Ph)), and 52.5 (s, JPtC = 54.7, CH2)) are easy to assign. The CH2 carbon resonance at δ 52.5 is shifted about 45 ppm upfield relative to that of 14a, indicating that the former C=CH2 bond is now saturated. The AB/ABX splitting pattern for the CH2 protons (δ 3.71 (d, JHH = 21.3, JPH = 17.2) and 2.72 (dt, JHH = 21.5, JPH = 14.5)) is a feature distinctive of all of the 29 complexes (Figure 19). The more upfield resonance shows coupling to phosphorus and not to platinum, whereas the downfield signal shows coupling to platinum and not to phosphorus.

The probable mechanism of formation of 28 and 29 is depicted in Scheme 6, with a somewhat different representation of the structure of 14a as shown below:
When exposed to TSI, the remote carbon-carbon double bond of the original binuclear complex attacks the electrophilic carbon of the TSI forming the zwitterionic, acetylene-bridged, bimetallic tetrahedrane, II. The reader will recall a similar proposed intermediate in Path A of Scheme 5, which forms as a result of an attack of a mononuclear metal allenyl complex on TSI. To date, however, only one pure, isolable mononuclear allenyl/TSI cycloaddition product (prepared from Cp(CO)$_2$FeCH=C=CH$_2$), has been isolated. In the related case where II occurs as an intermediate, the proposed bimetallic tetrahedrane must be more stable than the zwitterionic acetylene complex in Scheme 5. That is, the general observation that mononuclear allenyl/TSI cycloaddition products are unstable (or are unable to be prepared) may perhaps be traced to an inability of this reaction to proceed via a stabilized intermediate, such as the proposed II. Alternatively, the product formed may be somewhat unstable without the assistance provided by the ruthenium atom in such reactions as that of complex 14a with TSI.

Intermediate II, with added stability owing to coordination with ruthenium, can then proceed to the cycloaddition product 29 via nucleophilic attack of the TSI nitrogen atom on the CPh carbon. This
**Scheme 6.** Proposed pathway for the formation of 28 and 29.

(tosyl = p-MeC₆H₄SO₂⁻)

R = Ph, H
L = PPh₃, 1/2 dppp, t-BuNC
L' = PPh₃, 1/2 dppp

---

R = H, Ph
L = L' = PPh₃

---

R = Ph, H
L = PPh₃, 1/2 dppp, t-BuNC
L' = PPh₃, 1/2 dppp
affords product 29, where the ruthenium atom is coordinated to the same
two carbon atoms as in II. It should also be noted that this reaction
pathway appears quite feasible upon examination of the structures of 15a,
a model of II, and 29e via a 3-D graphics program. Only small changes in
bond angles and positions of the three original allenyl carbon atoms are
necessary on proceeding from starting material to product.

In a competitive process, compound 28 is formed via abstraction of a
proton from the CH₂ group by the negatively-charged nitrogen atom of II,
rather than via nucleophilic attack of the nitrogen atom at the CPh carbon
atom. This type of competitive proton transfer process has been observed
by Rosenblum and co-workers¹²⁴ in the reaction of an iron allyl complex
with trichloroacetyl isocyanate (Eq. 94a). However, this process can be

\[
\begin{align*}
\text{(a)} & \quad \text{Cp(CO)₂Fe} & \quad \text{H} \\
& \quad \text{Cl₃CC(O)N=C=O} & \quad \text{NC(O)CCl₃} \\
\end{align*}
\]

\[
\begin{align*}
\text{(b)} & \quad \text{Cp(CO)₂Fe} & \quad \text{Cp(CO)₂Fe} \\
& \quad \text{Me} & \quad \text{Me} \\
& \quad \text{Me} & \quad \text{Me} \\
& \quad \text{Me} & \quad \text{Me} \\
& \quad \text{Me} & \quad \text{Me} \\
& \quad \text{Me} & \quad \text{Me} \\
\end{align*}
\]

foreclosed by employing the 3,3'-dimethylallyl iron complex, which reacts
with the same isocyanate to form the cycloaddition product (Eq. 94b). In
the latter reaction, replacement of the acidic protons by methyl groups
encourages cycloaddition to occur over proton transfer. Because both
cycloaddition and proton transfer-derived products are observed in the
reaction of binuclear complexes with TSI, the CH$_2$ protons must be less
acidic or the nitrogen atom somewhat less basic than the corresponding
ones in the iron allyl complex in Eq. 94a. Otherwise, one product (28 or 29)
should dominate.

Unlike the reaction of 14a with TSI, the reaction of the binuclear
complex 15a with TSI is very complicated. There were no products isolated
in a form pure enough for full characterization. However, the reaction
was studied in detail because of the implication of a side reaction
mechanism based upon a proposed intermediate with 14a. Because the
molecular structures of the analogues of the two major final products
have been determined crystallographically, the only valuable information
to be obtained here is the course of the reaction of binuclear complexes
with TSI. It has been observed that the reactions of 14a and 15a with TSI
occur at relatively comparable rates under similar reaction conditions;
therefore, the information gleaned from one reaction should apply to the
other reaction as well.

The proposed course of the reaction of 15a with TSI is based upon
five different sets of reaction conditions (see Experimental section for
details). In general, fragmentation, observed when TSI is added at room
temperature, can be avoided altogether by simply starting the reaction at
-78°C and allowing the reaction solution to slowly warm to room
temperature. Of interest is an intermediate of possible structure X, which
converts to mononuclear ruthenium- and platinum-containing species
upon being stirred in solution over several hours at room temperature (Eq.
The spectroscopic evidence for X is $^1$H NMR data, presumably for the allenyl protons ($\delta$ 5.15 (d, $J_{PH} = 20$, CH), 3.25 (d, $J_{HH} = 19.5$, 1 H of CH$_2$), and 2.85 (d, br, $J_{HH} = 19.5$, 1 H of CH$_2$)), and a $^{31}$P($^1$H) NMR spectrum ($\delta$ 62.0 (d, $J_{PP} = 15.2$, $J_{PtP} = 137$) 17.0 (d, $J_{PP} = 15.2$, $J_{PtP} = 2711$, Figure 20)). While the $^1$H NMR data are not necessarily insightful, the $^{31}$P($^1$H) NMR spectrum indicates that one of the triphenylphosphine ligands is no longer on the platinum atom, but instead is presently bonded to the ruthenium atom (the more downfield resonance that does not display $^1$J$_{PtP}$ satellites). Other research groups have observed that triphenylphosphine ligands bound to Cp(CO)$_x$Ru tend to resonate in the $\delta$ 70 to 40 ppm range. Typical triphenylphosphine ligands bound to a neutral platinum atom display $^{31}$P NMR resonances significantly upfield from these values (vide supra). Also, the $^1$H NMR data seem to suggest that the remote carbon-carbon double bond of the bridging allenyl ligand is involved in bonding to one of the metals. Further speculation about the structure of X, however, would be just that.

The identity of another intermediate, Y, is completely unknown, but its existence was suggested experimentally. For example, a typical set of reaction solution spectra revealed that as the reaction solution containing
Figure 20. $^{31}\text{P}^{(1}\text{H})$ NMR Spectrum of 15a + TSI Reaction Solution. X Denotes Intermediate X.
an excess of TSI warmed to room temperature, 28b, 29b, and Y were essentially the only identifiable species in solution. After another 3 hours in solution, intermediate Y had been completely consumed to form only 28b and 29b. Spectroscopically, only a cyclopentadienyl resonance could be assigned to Y in a ¹H NMR spectrum, and the ³¹P{¹H} NMR data (δ 33.6 (d, Jpp = 3.6, Jppt = 2912) and 16.2 (d, Jpp = 3.6, Jppt = 3230)) for Y does not suggest anything structurally.

Compounds 28b and 29b are described as analogous to 28a and 29a by a comparison of NMR data. For compound 28b, its ¹H NMR spectral data for the NH (δ 12.4 (s)) and CH (δ 5.91 (s)) protons are a match to the corresponding values for 28a, while the ³¹P{¹H} NMR data (δ 25.4 (d, Jpp = 5.3, Jppt = 2791) and 18.4 (d, Jpp = 5.3, Jppt = 3538) are diagnostic and similar as well. The ¹H NMR (CH₂ protons: δ 3.50 (d, JHH = 22.2, JPtH = 11.7) and 3.15 (dt, JHH = 22.2, JPH = 6.1)) and ³¹P{¹H} NMR (δ 26.3 (d, Jpp = 9.6, Jppt = 2889) and 20.7 (d, Jpp = 9.6, Jppt = 3804) spectral data for 29b are also analogous to the data reported above for 29a.

Compounds 25 reacted with TSI to produce only complexes analogous to 29a and 29b. For example, the robust nature of 25a is further evidenced in its reaction with TSI (Eq. 96). The more typical -78°C, slow addition of standard (i.e., diluted) solution of TSI was replaced in Eq. 96 by a dropwise addition of neat TSI at room temperature.
However, unlike the reactions of 14a and 15a with TSI under these reaction conditions, no fragmentation into mononuclear platinum and ruthenium species was observed. Instead, only 29c, an analogue of 29a, was obtained in 53% yield.

That the structure of 29c is analogous to 29a can be ascertained by an examination of the spectroscopic properties of 29c. The best evidence of an analogy to 29a is seen in the $^1$H NMR spectrum. Specifically, the CH$_2$ protons resonate at the appropriate chemical shifts and with a splitting pattern very similar to that of 29a ($\delta$ 3.41 (d, $J_{PH} = 23, J_{PtH} = 21$) and 2.82 (m)). The more downfield signal is the most diagnostic, as it is coupled to both phosphorus and platinum, while the more upfield signal appears as a broadened multiplet. The chemical shift values of the phosphorus signals are shifted upward by about 5 ppm relative to 25a ($\delta$ 0.47 (d, $J_{PP} = 26.5, J_{PP} = 26.5, J_{PtP} = 3468$)), but the phosphorus-to-platinum coupling constants are very similar. The IR spectrum indicates the presence of both a terminal carbonyl ligand (1894 (s) cm$^{-1}$) and an organic carbonyl (1708 (m) cm$^{-1}$), and the FAB mass spectrum has the base ($M^+$, 1114) and the Pt(dppp)$^+$ fragments as two of its most prominent peaks.

As in the case of the reaction of 25a with TSI, only the analogue of 29a was observed by $^1$H NMR and $^{31}$P($^1$H) NMR spectroscopy (Eq. 97) during an NMR-tube scale reaction of TSI with 25b. The resonances for the CH$_2$ protons at $\delta$ 3.31 and 3.07 ppm appear to be similar in appearance (pseudo-doublet and doublet of triplets, respectively) to those of 29a and 29c,
and the $^{31}$P{$^1$H} NMR spectrum indicates a new product has been prepared ($\delta$ 2.2 (d, $J_{PP} = 24$, $J_{PTP} = 2549$) and -4.0 (d, $J_{PP} = 24$, $J_{PTP} = 3250$)). The NMR spectra were not as clean for 29d as for 29c or 29e below, so a preparatory scale reaction was not carried out.

The cleanest reaction of a heterobinuclear metal $\mu$-allenyl complex with TSI to form an analogue of 29a was that with the isocyanide-for-triphenylphosphine substituted 25c (Eq. 100). The product 29e was identified as an analogue of 29a most readily by its $^1$H NMR spectrum:

$\text{H}_2\text{C} = \text{C} = \text{C} \text{Ph}$

$\text{TSI}$

$\text{C}_{2}$

$\text{Ru} \rightarrow \text{Pt}$

$\text{PPh}_3$

$\text{OC}$

$\text{C}_2\text{H}_4 \text{protons: } \delta \text{ 3.66 (dd, } J_{HH} = 21.6, J_{PH} = 1.8, J_{PtH} = 50) \text{ and 3.29 (dd, } J_{HH} = 21.6, J_{PH} = 6.6). }$

Specifically, as in all of the 29a analogues, the CH$_2$ proton signal most downfield is coupled to platinum while the more upfield signal is not.

The IR spectrum of 29e in the carbonyl region is also diagnostic in that the organic carbonyl (of the TSI adduct) is clearly observed (1714 (m) cm$^{-1}$) in addition to the terminal carbonyl ligand on ruthenium (1908 (s) cm$^{-1}$). The $^{31}$P{$^1$H} NMR spectrum is as simple as expected for a carbonyl
compound with a single phosphorus atom ($\delta 14.6 (s, J_{PH} = 3538)$), an 
upfield shift from the phosphorus resonance of $25c$, and the most 
prominent features of the FAB mass spectrum are the $M^+$ and $M^+ - TSI$
peaks. Purity of $29e$ was established by elemental analysis on crystals 
obtained from a mixture of hexane and methylene chloride. One of these 
crystals was also subjected to an X-ray structural analysis by Dr. Judith 
Gallucci, and the structure appears as an ORTEP drawing in Figure 21 
and pertinent bond distances and angles appear in Table 11.

The structure of $29e$ can be described as comprised of a Pt(PPh$_3$)$_2$
and a Cp(CO)Ru fragment held together by a bridging $\eta^1,\eta^2$-heterocyclic 
bonding ligand. The geometry around platinum is highly distorted square 
planar, with a ruthenium-platinum-C$_5$ angle of $52.9^\circ$. This angle 
compares closely to the analogous angle in $15a$, $16a$, and $17$. The C$_4$-C$_5$
bond distance of $1.47\AA$ is considerably longer than a typical carbon-carbon 
double bond, indicating significant interaction between this $\pi$ bond and the 
ruthenium atom. The C$_5$-C$_6$ bond distance of $1.51\AA$ is typical of a carbon-
carbon single bond, as expected from the structure. The platinum-
ruthenium bond length of $2.66\AA$ is very close to the corresponding bond 
length in $16a$ ($2.67\AA$), but it is shorter than the one in $15a$ ($2.72\AA$). That the 
C$_4$-C$_5$ bond is attached to ruthenium is further apparent owing to the 
equal C$_4$- and C$_5$-to-ruthenium bond lengths ($2.16\AA$).

It has been shown that the heterobinuclear complex $15a$ reacts with 
unsaturated transition metal fragments to form heterotrinuclear 
clusters. It has also been shown that $15a$ reacts with acid differently than 
with TSI to form an $\eta^3$-allyl type compound. A reagent that serves as a 
reactive metal-containing (positively-charged rather than "unsaturated")
Figure 21. ORTEP Drawing of 29e.
Table 11. Selected bond distances (Å) and angles (degrees) for 29e.

<table>
<thead>
<tr>
<th>Distances</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Ru</td>
<td>Ru-Pt-C 5</td>
</tr>
<tr>
<td>2.665 (1)</td>
<td>52.6 (3)</td>
</tr>
<tr>
<td>Pt-P</td>
<td>Ru-Pt-C 20</td>
</tr>
<tr>
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<tr>
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<td>100.3 (4)</td>
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<tr>
<td>Pt-C 20</td>
<td>P-Pt-C 5</td>
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<td>106.8 (3)</td>
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<td>120.3 (5)</td>
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</tr>
<tr>
<td>N2-C36</td>
<td>1.50 (2)</td>
</tr>
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</table>
species, and is also isobal to H$^+$ is PPh$_3$Au$^+$. Its possible catalytic applications, especially when present in conjunction with platinum,$^{125}$ also make it an ideal reagent for reaction with heterobinuclear complexes.

It was discovered that this reagent (PPh$_3$Au$^+$) was more readily obtained in the dark in THF solution from PPh$_3$AuCl utilizing a soluble silver reagent,$^{39,126,127}$ silver triflate, rather than a somewhat insoluble (in THF) thallium$^{128,129}$ reagent. Slow addition of a solution of this

"activated" gold reagent in THF to a -78°C solution of 15a resulted in the formation of the trinuclear cluster 30, as a tan solid (Eq. 99). The compound was characterized spectroscopically.

The lone carbonyl ligand on ruthenium is observed by IR spectroscopy (1899 cm$^{-1}$). The $^{31}$P($^1$H) NMR spectrum displays a signal for the triphenylphosphine phosphorus atom attached to gold at $\delta$ 39.5 (d, $J_{PP}$ = 13) and two signals for the inequivalent phosphorus atoms attached to platinum at $\delta$ 26.5 ($t$, $J_{PP}$ = 13, $J_{PPT}$ = 2600) and 20.5 (d, $J_{PP}$ = 13, $J_{PPT}$ = 4471) ppm. It is interesting that the phosphorus atom attached to gold is coupled to only one phosphorus atom on the platinum, and that it is not coupled to the platinum atom at all. The best explanation for this is that the phosphorus atom of the triphenylphosphine ligand on the gold atom is coupled only to the phosphorus on the platinum atom that is trans to it.
(i.e., the triplet at $\delta$ 26.5), a coupling over three bonds. Meanwhile, the other phosphorus atom on platinum has a very large coupling to platinum, which indicates that this triphenylphosphine ligand is trans to the ruthenium-platinum bond. That the phosphorus on the gold atom is not visibly coupled to platinum may result from such a coupling being over an even number of bonds (2).

The $^1H$ and $^{13}C(^1H)$ NMR spectral data seem to contradict each other as to the type of $\mu$-allenyl group in 30. The $^1H$ NMR resonances for the CH$_2$ protons (8 3.71 (d, $J_{PH} = 4.0$) and 2.21 (d, $J_{PH} = 9.0$)), which are significantly upfield from the CH$_2$ proton signals of 15a, suggest that the remote $\pi$-bond of the allenyl is involved in bonding to a metal, and that the metal is possibly gold (each proton is coupled to a phosphorus atom by a different value of $J_{PH}$, and the gold-phosphorus bond is three bonds away). The resonances for the allenyl carbon atoms ($\delta$ 161.3 (d, $J_{PC} = 73.9$, =C=), 120.8 (d, $J_{PC} = 112$, CH) and 90.1 (s)), however, are very similar to those of 15a ($\delta$ 168.0, 114.7, 95.6) and not those of the heterotrinuclear L-shaped cluster 19a ($\delta$ 194.9, 135.5, 13.8), suggesting that the remote carbon-carbon double bond is not interacting with a metal center. A FAB mass spectrum suggested that at least the formulation of 30, if not the geometry and connectivity proposed, was correct. The only way to be certain, of course, would be to study the structure of 30 via X-ray crystallography. However, attempts at growing good quality crystals have been unsuccessful. Therefore, it was thought that replacement of the hydrogen substituent on the carbon atom bound to platinum with a phenyl group might allow X-ray quality crystals to be grown.

Thus, the reaction of 14a with the activated gold reagent was
Figure 22. $^1$H NMR Spectrum of Gold-Containing Compound 31.
carried out as well (Eq. 100), and a greenish-yellow solid (31) was obtained. Its $^1$H (Figure 22, CH$_2$ protons: δ 3.76 (d, $J_{PH} = 4.0$) and 2.51 (d, $J_{PH} = 8.0$)) and $^{31}$P NMR (δ 39.3 (d, $J_{PP} = 15.6$), 23.2 (dd, $J_{PP} = 11.4$, $J_{PP} = 15.6$, $J_{PTP} = 2535$), and 14.3 (d, $J_{PP} = 11.4$, $J_{PTP} = 4651$)) data are very similar to 30, and its FAB mass spectrum and elemental analysis are again suggestive of the formulation for 31 shown in Eq. 102. Unlike in the case of 30, though, X-ray-quality crystals, faintly yellow in color, were obtained from mixtures of methylene chloride, acetone, and hexane. Unfortunately, Professor Calligaris will not be able to examine these crystals crystallographically until after the completion of this dissertation.

3) Studies Toward the Elucidation of the Mechanism of Formation of Cp(CO)Ru(μ-H)(μ-C(H)(C(O)Me))Pt(PPh$_3$)$_2$ (32)

One of the more intriguing problems encountered by the author has been to determine the mechanism of formation of 32 (Eq. 101), first prepared over two years ago.$^{76}$ The compound was discovered when a sample of 14a or 15a was introduced onto a column of Grade III alumina and chromatographed/eluted with diethyl ether, and it appears to be the product of a simple net addition of a molecule of water to 14a or 15a.
Crystals of the phenyl-substituted derivative were analyzed via X-ray crystallography by Rheingold and co-workers at the University of Delaware. What follows is a discussion of the current understanding of this complex reaction.

To be certain that the alumina was indeed a necessary part of the reaction, the experiment that was performed first was the reaction of 15a with water in an organic solvent. At room temperature in THF or chloroform, no reaction was observed after 24 hours. When chloroform was the solvent, heat was also applied, but no reaction was observed after 48 hours. As has been observed and described above (pages 190 and 214), reaction of 15a with protic acids or hydroxide ion did not produce 32 either. It thus became apparent early that the role of the heterogeneous surface was important in the preparation of 32.

Owing to the difference between a reaction involving stirred reagents in a flask and one occurring on the surface of packing material in a column (stationary phase), several more controllable reaction flask experiments were carried out. Typically, the solid (such as alumina or silica) was stirred vigorously at ambient temperature in a solution of 15a. The reactions were easily monitored by $^1$H and $^{31}$P($^1$H) NMR spectroscopy.
Preliminary investigation showed that the reaction to form 32 from 15a does not occur when THF or diethyl ether is used as solvent. The heterogeneous solids used were silica, activated neutral alumina (essentially no H₂O), and deactivated (6% H₂O, Grade III) neutral alumina. This result was intriguing because complete conversion of 15a to 32 takes 12 hours when chloroform or methylene chloride is utilized as reaction solvent, and deactivated neutral alumina as heterogeneous phase, the reaction requires 24 hours for completion in chloroform when deactivated basic alumina is used, and the reaction takes only 1 hour to complete in chloroform when deactivated acidic alumina is used as stationary phase. The reaction also proceeds to completion in CHCl₃ or CH₂Cl₂ when silica or Florisil (both used as received) is used as the stationary phase. It appears that the reaction requires a chlorinated solvent and a heterogeneous phase that contains at least a small amount of adsorbed water before it will proceed to form 32. A summary of the preliminary investigations of this reaction appears in Table 12.

In order to ascertain the origin of the two hydrogen atoms and one oxygen atom incorporated into 32 from the original 15a, some experiments with deuterated alumina and deuterated solvents were carried out.

In the first experiment, a solution of 15a in diethyl ether was treated with activated deuterated alumina and yielded no 32 (or deuterated 32). This is of course the same result as the one obtained with regular activated alumina with diethyl ether as solvent, and thus it serves as a control reaction or a basis for comparison between deuterated and non-deuterated systems.
Table 12. Several sets of experimental conditions for reaction of Eq. 101.

<table>
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<th>Solvent</th>
<th>SP1</th>
<th>t/Temp</th>
<th>Result</th>
</tr>
</thead>
<tbody>
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<td>CHCl₃ (H₂O)</td>
<td>None</td>
<td>24 h/reflux</td>
<td>NR²</td>
</tr>
<tr>
<td>THF or Et₂O</td>
<td>ANA³</td>
<td>24 h/RT⁴</td>
<td>NR</td>
</tr>
<tr>
<td>THF or Et₂O</td>
<td>DNA⁵</td>
<td>24 h/RT</td>
<td>NR</td>
</tr>
<tr>
<td>THF or Et₂O</td>
<td>silica⁶</td>
<td>18 h/RT</td>
<td>NR</td>
</tr>
<tr>
<td>CH₂Cl₂ or CHCl₃</td>
<td>ANA</td>
<td>24 h/RT</td>
<td>&lt;50% 32</td>
</tr>
<tr>
<td>CH₂Cl₂ or CHCl₃</td>
<td>DNA</td>
<td>12 h/RT</td>
<td>complete 32</td>
</tr>
<tr>
<td>CH₂Cl₂ or CHCl₃</td>
<td>silica/Florisil</td>
<td>12-24h/RT</td>
<td>complete 32</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>ABA⁷</td>
<td>3 h/RT</td>
<td>NR</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>DBA⁸</td>
<td>24 h/RT</td>
<td>complete 32</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>AAA⁹</td>
<td>3 h/RT</td>
<td>NR</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>DAA¹⁰</td>
<td>1 h/RT</td>
<td>complete 32</td>
</tr>
</tbody>
</table>

¹stationary phase; ²no reaction; ³activated neutral alumina; ⁴ambient (room) temperature ⁵deactivated neutral alumina; ⁶silica (TLC grade); ⁷activated basic alumina; ⁸deactivated basic alumina; ⁹activated acidic alumina; ¹⁰deactivated acidic alumina

In the second experiment, a chlorinated solvent (CH₂Cl₂) was used with activated deuterated alumina as stationary phase. After 12 hours, a $^{31}$P($^1$H) NMR spectrum of the reaction solution revealed that some deuterium incorporation into 32 had occurred because the typical doublets for the inequivalent phosphorus atoms appeared as multiplets. This implies that the phosphorus nuclei are interacting with a deuterium atom.
most likely at the bridging position. A long acquisition time 2D NMR spectrum revealed that deuterium incorporation into the methyl group and into the bridging position was about the same, but that no incorporation into the alkylidene-carbon position was taking place. Unfortunately, very few conclusions can be drawn from this experimental result because the amount of deuterium in the compound was not significantly more than the amount of naturally occurring deuterium in the solvent (CH$_2$Cl$_2$).

The most intriguing experimental result came from the reaction of 15a in deuterated chloroform (CDCl$_3$) with deactivated deuterated alumina (6% D$_2$O). In this case, not only was the incorporation of deuterium into the bridging position very high (approx. 90% D into bridging position), but it was also observed that about three times as much deuterium was incorporated into the bridging hydrogen position as into the methyl group. While this suggests little about the mechanism of this reaction, it implies that the two positions (i.e., methyl group and bridging position) are not deuterated in the same fashion or by the same reactive species.

Since the reaction with deactivated basic alumina is slower than the reaction with deactivated neutral alumina (and, of course, deactivated acidic alumina reacts the fastest), an acidic site on the alumina is possibly responsible for the initial attack on 15a. However, initial attack on 15a by a hydrogen radical generated from interaction between the chlorinated solvent and the alumina cannot be ruled out. However, several other mechanistic possibilities can be imagined at this point. Therefore, other sets of reaction conditions were investigated with the intention of
narrowing these possibilities somewhat.

For example, the possibility existed that the reaction could occur on any porous material (even powdered brick) with a large surface area in a wet environment. Popowa sand, a very fine particulate sand, was treated with a solution of 15a in water-saturated methylene chloride, and no reaction, save for a small amount of decomposition to intractable material, was observed after 24 hours. Therefore, a large surface area of the stationary phase alone is not the only requirement necessary for this reaction to occur.

Alumina, silica, and Florisil are all related in that their surfaces consist of oxides, silicates, and other oxygen-containing species. To test whether a simple metal oxide surface was sufficient for reaction, 15a in water-saturated chloroform was stirred with Cr$_2$O$_3$ for 36 hours at ambient temperature. Again, no reaction was observed to form 32. Thus, the reaction must be more complicated than a simple interaction of a generic metal oxide surface with 15a.

A free radical process may also be responsible for the reaction. To test for this, a solution of 15a in THF was charged with 2,2'-azobis(2-methylpropionitrile) (AIBN), a free radical initiator, in addition to the usual amount of deactivated neutral alumina. (Recall that the reaction normally does not occur in THF, hence its choice as solvent in this particular case). A normal free radical process should have commenced under these conditions, but apparently it does not affect the reaction. Solvent dependence is an important factor in this conversion.

Therefore, in a typical experiment that utilized successful reaction conditions (chloroform as solvent, deactivated neutral alumina, see Table
two different types of free radical inhibitors (<1 eq of nitrobenzene or benzoquinone, in separate reaction solutions) were introduced to ascertain whether or not the reaction would now occur. In both cases, the reaction did not occur. This result is the most convincing piece of evidence obtained with regard to the course of the conversion of 15a to 32. Clearly, it suggests that the reaction occurs via a free radical mechanism that is initiated by a chlorinated solvent, and is aided by an acidic, metal oxide/silicate/hydroxyl surface.

Reactions of Cp(CO)Ru(μ-H)(μ-C(H)(C(0)Me))Pt(PPh₃)₂ (32)

In order to determine whether the bridging hydride of 32 has acidic (H⁺) or hydridic (H⁻) character, two experiments were carried out. In the first, no reaction was observed when 32 was treated with hydroxide ion in ethanol (Eq. 102). That is, the bridging hydride ligand was not removed as H⁺ by a strong Brønsted base. This may imply that the 3-center, 2-electron bond in 32 more closely resembles a related bridging boron hydride bond than a terminal hydride ligand bonded to an electron-poor transition metal center such as (CO)₄CoH. Apparently the heterobimetallic anion that would form could not accommodate the negative charge satisfactorily. This is not in line with the observed acidic
nature of Cp(CO)$_2$RuH$_2$\(^{131}\) which easily forms the very stable, nucleophilic Cp(CO)$_2$Ru$^-$ anion. However, in the case of the heterobimetallic 32, one carbon monoxide ligand, necessary for removal of electron density from ruthenium to help stabilize the generated anion, is replaced by an electron-donating alkylidene and a relatively electron-rich platinum center. Thus, the resultant anion would be expected to be much less stable than the neutral 32.

On the other hand, reaction of 32 with tropylium cation apparently resulted in the removal of the bridging hydrogen as a hydride (H$^-$),

\[
\text{Me} \overset{\text{O}}{\text{C}} \overset{\text{H}}{\text{C}} \overset{\text{Ru}}{\text{Pt(PPh$_3$)$_2$}} \quad \overset{\text{C$_7$H$_7$}^+\text{PF$_6^-$}}{\text{THF}} \quad \text{Me} \overset{\text{O}}{\text{C}} \overset{\text{H}}{\text{C}} \overset{\text{Ru}^+}{\text{Pt(PPh$_3$)$_2$}} \quad \text{PF$_6^-$} \quad (103)
\]

resulting in the formation of the cation 33 (Eq. 103). Spectroscopically, compared to 32, 33 displays a slight (expected) shift to higher energy (1912 to 1920 cm$^{-1}$) for the terminal carbon monoxide on ruthenium in the IR spectrum. The absence of the bridging hydride is noted in the $^1$H NMR spectrum (\(\delta 7.74 \ (d, \ J_{PH} = 4.0, \ J_{PtH} = 23, \ \text{CH}) \) and \(1.57 \ (s, \ \text{Me})\)), and the $^{31}$P($^1$H) NMR data (\(\delta 25.2 \ (d, \ J_{PP} = 21, \ J_{PtP} = 2776)\) and \(15.9 \ (d, \ J_{PP} = 21, \ J_{PtP} = 4325)\)) suggest a positive charge near platinum based upon the large $J_{PtP}$ value (4325 Hz) for the phosphorus trans to the ruthenium-platinum bond. The $^{13}$C($^1$H) NMR spectrum for 33 (\(\delta 193.6 \ (s, \ \text{Ru(CO)}), 177.7 \ (s, \ \text{organic CO}), 25.9 \ (d, \ J_{PC} = 3.0, \ \text{Me})\) does not show the CH carbon
unambiguously, but one can assume that this carbon resonance is hidden in the phenyl region of the spectrum. Unfortunately, FAB mass spectral and elemental analyses on 33 were inconclusive. However, it can be seen from this preliminary investigation into the reactivity of 32 that the bridging hydrogen atom is hydridic rather than acidic in character.
APPENDIX
Table 13. Crystal parameters for structures 16a and 17.

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<td>C₃₇H₂₇O₅FePPtRu</td>
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<td>P2₁/n</td>
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Table 14. Data collection and refinement for 16a and 17.

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<td>±11, +42, +16</td>
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<td>3 std./197 reflns.</td>
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</tr>
<tr>
<td>μ(MoKα), cm$^{-1}$</td>
<td>54.80</td>
<td></td>
</tr>
<tr>
<td>temp, K</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td>T(max)/T(min)</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

Table 15. Crystal parameters for structure 29e.
Table 16. Data collection and refinement for 29e.

<table>
<thead>
<tr>
<th></th>
<th>29e</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffractometer</td>
<td>N/A</td>
</tr>
<tr>
<td>monochromator</td>
<td>graphite</td>
</tr>
<tr>
<td>radiation</td>
<td>MoKα (l = 0.71073 Å)</td>
</tr>
<tr>
<td>2θ scan range, deg</td>
<td>4-55</td>
</tr>
<tr>
<td>data collected</td>
<td>h, +k, ±l</td>
</tr>
<tr>
<td>lin. abs. coeff., cm⁻¹</td>
<td>37.81</td>
</tr>
<tr>
<td>indpt. rflns.</td>
<td>10155</td>
</tr>
<tr>
<td>R(merg), %</td>
<td>1.57</td>
</tr>
<tr>
<td>indpt. obsvd. rflns.</td>
<td></td>
</tr>
<tr>
<td>F₀ ≥ nσ(F₀) (n = 5)</td>
<td>4284</td>
</tr>
<tr>
<td>trans. factors</td>
<td>0.71 to 1.0</td>
</tr>
<tr>
<td>scan speed</td>
<td>4° m in ω, max. 4/ref</td>
</tr>
<tr>
<td>R(F), %</td>
<td>4.5</td>
</tr>
<tr>
<td>R_w(F), %</td>
<td>4.6</td>
</tr>
<tr>
<td>back. time/scan time</td>
<td>0.5</td>
</tr>
<tr>
<td>scan range</td>
<td>(1.30 + 0.35tanθ)° in ω</td>
</tr>
<tr>
<td>scan type</td>
<td>ω</td>
</tr>
<tr>
<td>GOF</td>
<td>1.27</td>
</tr>
</tbody>
</table>
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