# The Important Role of Some Ancillary Ligands in the Chemistry of Carbonylmetal Cluster Complexes − Selected Reactivity of Triruthenium Clusters Containing Deprotonated 2-Aminopyridines

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*Dedicated to my former mentors, Professors Luis A. Oro, Peter M. Maitlis and Víctor Riera*

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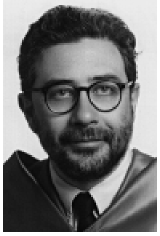
The presence of deprotonated 2-aminopyridines (apy ligands) as face-capping ancillary ligands in carbonyltriruthenium cluster complexes facilitates their reactivity (mild reaction conditions) and increases the regioselectivity of their reactions. This is probably due to the hemilabile character of the apy ligands that help maintain the cluster nuclearity and also provides reaction pathways of low activation energy. Thus, the presence of apy ligands in triruthenium cluster complexes of the type $[Ru_3(\mu\text{-}H)(\mu_3\text{-apy})(CO)_9]$ has allowed an extensive and regioselective derivative chemistry that is surveyed in this review. A comparative study of the reactivity of 2-amino-, 2-mercapto- and 2-hydroxypyridines with triruthenium clusters is followed by a survey of selective reactions of apy-bridged triruthenium cluster complexes that covers substitution processes, protonation reactions, oxidative addition of hydrogen, hydrosilanes and hydrostannanes, reactions with alkynes and diynes, reactions of coordinated alkenyl and ynenyl ligands, synthesis and reactivity of cationic non-hydridic clusters, preparation of higher-nuclearity clusters and some catalytic applications.

## I. Introduction

Regioselectivity is a major concern in the derivative chemistry of carbonyl transition metal cluster complexes.[1] Mixtures containing mono- and/or dinuclear complexes are frequently formed as reaction products and, even when no cluster fragmentation occurs, single products are seldom observed.[2]

The above statement is particularly true for the derivative chemistry of the most common ruthenium and osmium cluster starting materials, such as $[Ru_3(CO)_{12}]$, $[Os_3(CO)_{12}]$ and many of their trinuclear derivatives. The low regioselectivity of many of their reactions is a consequence of some intrinsic characteristics of this type of compounds: (a) they are saturated species (48 valence electrons) with high kinetic stability, frequently requiring thermal or photochemical activation to undergo chemical transformations; (b) metal−metal bonds are rather weak and are easily cleaved under thermal or photochemical conditions; and (c) due to their polynuclear nature, cluster complexes may undergo transformations at more coordination sites than mononu-



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**MICROREVIEWS:** This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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clear species and, consequently, once the corresponding activation energy has been reached (particularly if this is high), their reactions often lead to mixtures of products.

Ligand (generally CO) dissociation is usually a requisite for reactions of saturated carbonyl transition metal cluster complexes, since a vacant site is often necessary for the incoming reagent to enter the coordination shell of the cluster complex.[3,4] It is implicit that the lower the activation energy of this step, the more selective the reaction will be, since the risks of cluster fragmentation and reactions at different cluster coordination sites are diminished. To ensure selectivity, a low activation energy should be associated with an appropriate energy minimum. Several methods have been devised to reduce the activation energy of reactions of such cluster complexes, the following being the most important ones:

(a) To carry out the reactions in the presence of trimethylamine oxide.[5] This reagent can react with coordinated CO to give $CO_2$, in the presence of the appropriate ligand, even at very low temperatures (−78 °C).

(b) To start from "activated" cluster complexes containing weakly coordinating ligands.[6] Acetonitrile is easily displaced by many reagents from complexes such as $[M_3(CO)_{12-x}(MeCN)_x]$ (M = Ru,[6a] Os;[6b] $x$ = 1, 2 or 3). These complexes are normally prepared by treating the parent carbonylmetal complexes with acetonitrile in the presence of the appropriate amount of trimethylamine oxide. Alkenes[6c] and dienes[6d] have also been used as weakly coordinating ligands.

(c) Redox catalysis.[7] The substitution of CO by other ligands can be carried out under mild conditions (room temperature) by performing the reactions in the presence of catalytic amounts of strong reducing reagents, such as the benzophenone ketyl radical anion.

(d) Chemical catalysis. The presence of catalytic amounts of hard anions, such as halides, pseudohalides, carboxylates (as $PPN^+$ salts, in the absence of ion pairing),[8] or methoxide[9] or hydride[10] sources can promote the substitution of CO ligands by other ligands.

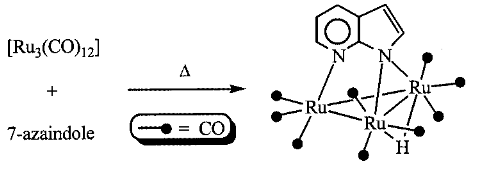
As far as reactivity is concerned, cluster complexes containing bridging ligands with hard-donor atoms[11] are a particular case among carbonyl transition metal cluster complexes because they exhibit an *enhanced substitutional lability*,[12] undergoing reactions under mild conditions. Such ancillary ligands have been termed as *hemilabile* ligands.[12] Although a few examples of bridging monodentate hemilabile ligands are known (chloride,[13] isocyanate[14]), most hemilabile ligands are bidentate and contain both soft- and hard-donor atoms.[15,16] As carbonyl transition metal cluster complexes have soft metal atoms, the softer donor atom of the ligand binds strongly to the metal atom(s), while coordination of the harder donor atom should be labile enough to provide reaction pathways of low activation energy. In addition to helping prevent cluster breakup, these ligands direct the cluster reactivity to reaction sites close (usually *cis*) to the hard-donor atom, thus inducing regioselective reactions.

As long as it is not inconvenient to a particular research project to have a hemilabile ligand attached to the metal cluster, and provided the right hemilabile ligand is chosen, cluster compounds containing a hemilabile ligand have been shown to be the starting materials of choice for studying cluster−ligand interactions,[15,17] for exploring the reactivity of cluster-coordinated ligands,[15,17] and for preparing cluster catalysts.[18]

During the last ten years, Lavigne's and Cabeza's groups have shown that deprotonated 2-aminopyridines (apy) are superb hemilabile ligands in carbonyltriruthenium cluster complexes. This microreview comments on the synthesis and selected reactivity of apy-bridged carbonyltriruthenium cluster complexes. A comparative study of the reactivity of 2-amino-, 2-mercapto- and 2-hydroxypyridines with triruthenium clusters is followed by a survey of selective reactions of apy-bridged cluster complexes that comprises not only substitution processes, but also oxidative additions, protonation reactions, reactions of coordinated ligands, preparation of higher-nuclearity clusters and some catalytic applications. The review is concluded by describing the properties of apy ligands, highlighting the great influence that such ancillary ligands have on the reactivity of the cluster compounds they are coordinated to.

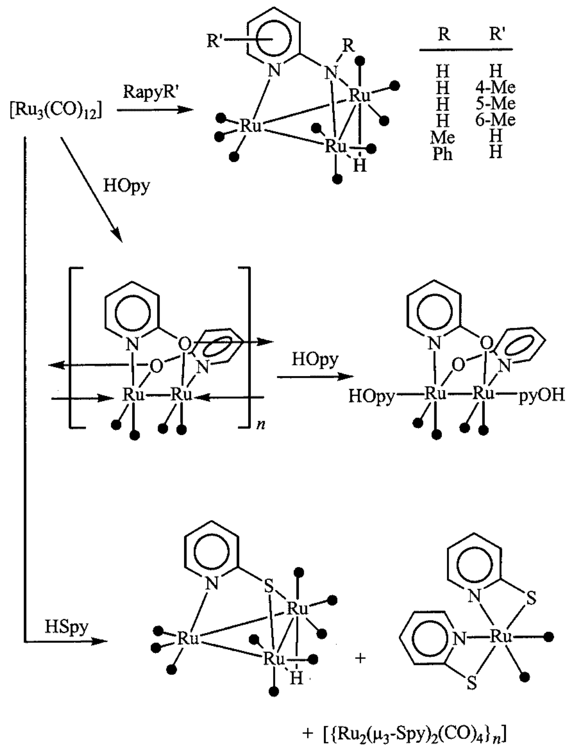
## II. Comparative Reactivity of 2-Amino-, 2-Mercapto- and 2-Hydroxypyridines with Triruthenium Clusters

We reported the synthesis and X-ray structure of the first carbonyltriruthenium cluster containing an apy ligand in 1988.[19] It was prepared by treating $[Ru_3(CO)_{12}]$ with 7-azaindole in refluxing hexane (Scheme 1). This work was prompted by the finding that ethylene glycol and methanol could be prepared from synthesis gas using a combination of $[Ru_3(CO)_{12}]$ and 7-azaindole as catalyst precursors.[20]



Scheme 1

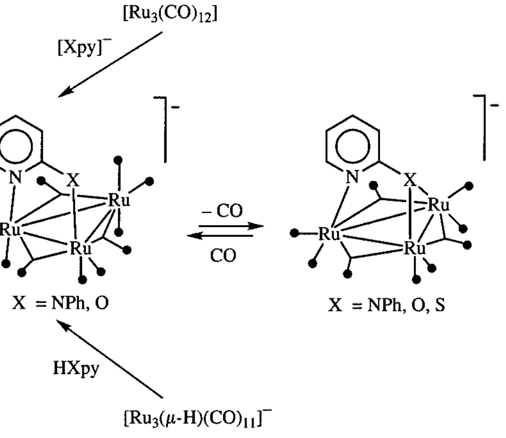
These results led us to examine the reactivity of $[Ru_3(CO)_{12}]$ with a series of 2-amino-, 2-mercapto- and 2-hydroxypyridines. These ligand precursors are structurally very similar, but differ in their acid-base properties. All reactions need thermal activation (60−110 °C). 2-Aminopyridines (Hapy) afford only trinuclear hydrido derivatives containing face-capping ligands, regardless of the presence of substituents on the pyridine ring or on the exocyclic nitrogen atom, and regardless of the ratio of the reactants (Scheme 2).[21] However, 2-mercapto- and 2-hydroxypyridine (HSpy and HOpy, respectively) lead to several products depending on the ratio of the reactants. No evidence was obtained for the presence of an intermediate trinuclear complex in the reactions of $[Ru_3(CO)_{12}]$ with 2-hydroxypyridine.[21] The complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}Spy)(CO)_9]$ was isolated in a low yield because it reacts readily with 2-mercaptopyridine to give polymeric $[\{Ru_2(\mu_3\text{-}Spy)(CO)_4\}_n]$ (analogous to the polymer derived from 2-hydroxypyridine) and/or monomeric $[Ru(Spy)_2(CO)_2]$ (Scheme 2).[22]



Scheme 2

In parallel to our work, Lavigne's group studied the reactions of $[Ru_3(CO)_{12}]$ with deprotonated 2-anilino-, 2-mercapto- and 2-hydroxypyridines (Phapy, Spy and Opy, respectively) and showed that the results were comparable with those of the reactions of $[Ru_3(\mu\text{-}H)(CO)_{11}]^-$ with the neutral ligands (Scheme 3).[23] While only a face-capping derivative was observed for the Spy ligand, both edge-bridging and face-capping derivatives were observed for the Phapy and Opy ligands. Interestingly, interconversion of the decacarbonyl and nonacarbonyl derivatives of the Phapy ligand is observed under milder conditions (25 °C, CO or inert gas purge), while interconversion of the corresponding Opy derivatives is not observed (the decacarbonyl Opy complex could only be partially decarbonylated after prolonged refluxing under a stream of inert gas).[23]

The very mild conditions under which the above-mentioned interconversion of the anionic Phapy derivatives takes place indicate that the reversible opening of the amido bridge in $\mu_3$-apy ligands is a low activation energy process. Although such a bridge opening has been observed only in very few occasions in neutral cluster complexes containing $\mu_3$-apy ligands (vide infra), it is believed that in their reactions such an opening may also be responsible for their high reactivity.[23] This, in addition to the higher stability of the trinuclear apy derivatives than that of the Opy and Spy complexes, makes the apy ligands excellent ancillary ligands for triruthenium cluster complexes. This statement is demonstrated by the rich, easy and regioselective derivative chemistry commented in the following section of this review.



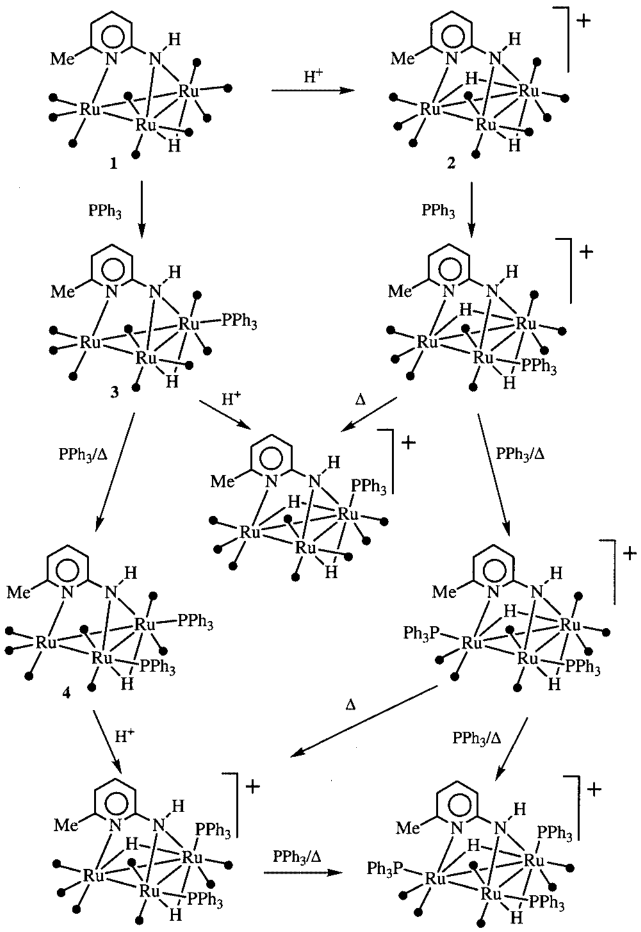
Scheme 3

## III. Selected Reactivity of Triruthenium Clusters Containing Deprotonated 2-Aminopyridines

As starting material, we chose the complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}apyMe)(CO)_9]$ (**1**, HapyMe = 2-amino-6-methylpyridine, Scheme 4) because the presence of the methyl group on the pyridine ring facilitates the monitoring of the reactions by NMR spectroscopy, without sterically interacting with other ligands. In addition, the presence of the N−*H* hydrogen atom results in an appropriate solubility/insolubility of the complexes in polar/nonpolar solvents.

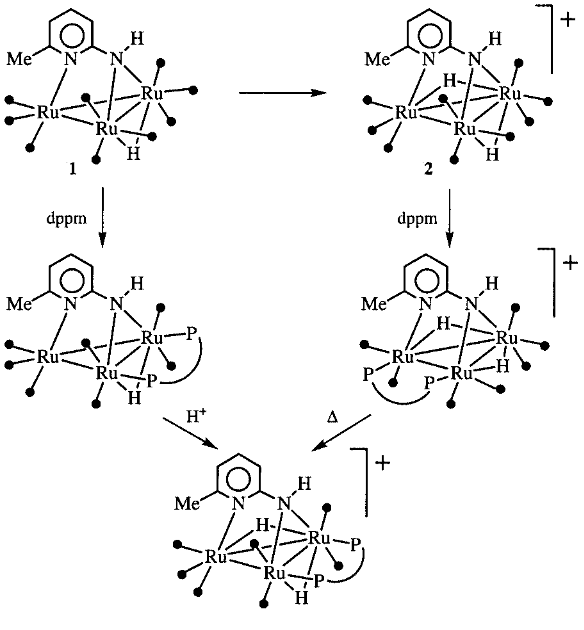
### III.a. Reactions with Phosphanes

Simple carbonyl substitution reactions are frequently used to determine the position of reactive sites in cluster complexes. Schemes 4 and Scheme 5 show the reactivity of complex **1** and its protonated derivative $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}apyMe)(CO)_9]^+$ (**2**) with triphenylphosphane[24,25] and bis(diphenylphosphanyl)methane,[26] respectively. It is remarkable that all reactions are regioselective and that the successive substitutions take place stepwise. Moreover, the first substitutions occur instantaneously at room temperature, while further substitutions require gentle heating (60−70 °C). With triphenylphosphane, under kinetic conditions, the substitutions take place in positions *cis* to the bridging amido fragment and/or *cis* to the hydrido ligand, indicating a strong *cis*-labilizing effect of these ligands. The rigidity of the dppm ligand results in the coordination of the two P atoms at the equatorial sites on adjacent metal atoms. In the case of some cationic complexes, the kinetic products isomerize on heating resulting in the thermodynamic products by dissociative mechanisms (such isomerizations are inhibited by the presence of the free phosphanes in solution). Stable neutral methoxycarbonyl derivatives (not



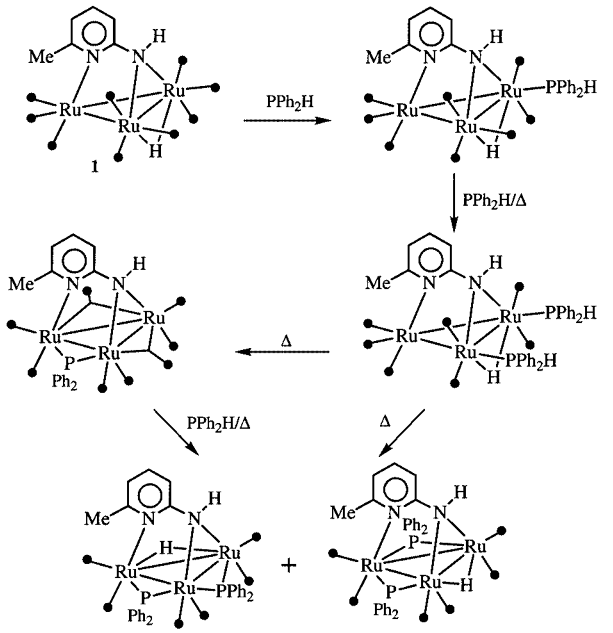
Scheme 4

represented in Schemes 4 and Scheme 5) are produced when the cationic complexes are treated with potassium methoxide.[24−26]



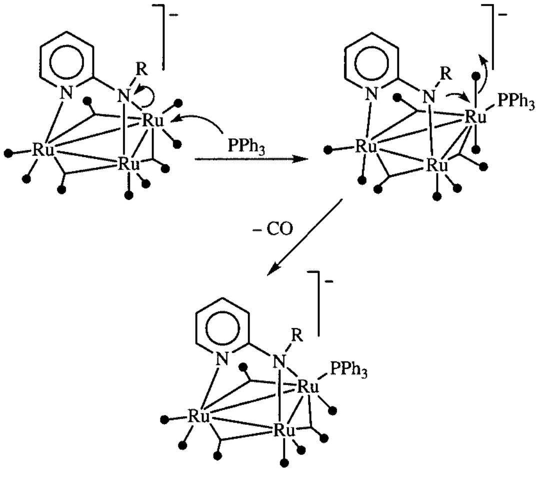
Scheme 5

Facile activation of the P−H bond of diphenylphosphane has been observed on heating diphenylphosphane derivatives of complex **1** (Scheme 6).[27]



Scheme 6

Basolo and Lavigne studied the mechanism of exchange of CO by phosphane ligands in a series of anionic complexes $[Ru_3(\mu_3\text{-}Rapy)(CO)_9]^-$, having different R substituents on the exocyclic N atom (Scheme 7).[28] Second-order kinetics were found (associative-type mechanism), which is consistent with a two-step process in which the first step is the coordination of the phosphane with the concomitant opening of an Ru−N arm. This adduct evolves into the final substituted product. The energy barrier for the second step depends on the nucleophilicity of the amido group. In fact, the initial adduct can be isolated when R = Ph, but it is too short-lived when R = Me. These results clearly demonstrate the hemilabile character of the apy ligands in these complexes.



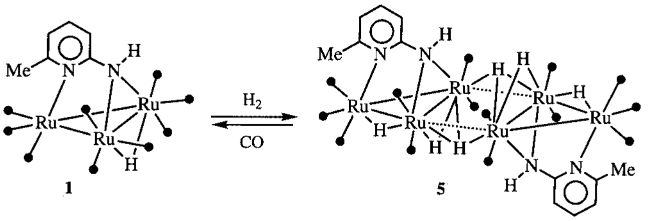
Scheme 7

### III.b. Reactions with Hydrogen, Silanes and Stannanes

The reactions of these three reagents with unsaturated organic substrates are of great practical importance and need the intermediacy of metal catalysts. We wondered whether such reactions could be promoted by apy-bridged triruthenium clusters.

Prior to this study, the reactivity of carbonyltriruthenium cluster complexes with these three reagents had been relatively uninvestigated. This is probably because their reactions with $[Ru_3(CO)_{12}]$ frequently give products of different nuclearity, i.e. $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$,[29] $[Ru_2(SiR_3)_2(CO)_8]$ and $[Ru(ER_3)_2(CO)_4]$ (E = Si, Sn).[30] Interestingly, a few trinuclear products containing $ER_3$ groups have been obtained using $[Ru_3(MeCN)(CO)_{11}]$,[31] $[Ru_3(\mu\text{-}H)(CO)_{11}]^-$,[32] or ligand-bridged clusters[33] as starting materials.

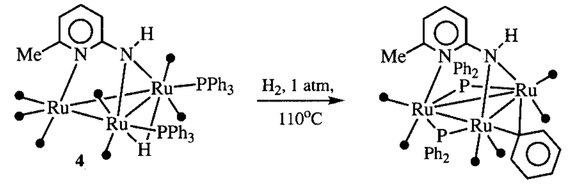
Complex **1** is an efficient catalyst precursor for the homogeneous hydrogenation of alkynes to alkenes and dienes to monoenes.[34] This catalytic activity prompted us to study the stoichiometric reactions that might be involved in the catalytic process. The reaction of complex **1** with hydrogen (1 atm, 110 °C) leads to the hexanuclear hexahydrido 92-electron derivative $[Ru_6(\mu_3\text{-}H)_2(\mu\text{-}H)_4(\mu_3\text{-apyMe})_2(CO)_{14}]$ (**5**, Scheme 8),[35] erroneously formulated as $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-apyMe})(CO)_8]$ when it was first reported.[34] This remarkable complex consists of two unsaturated (46-electron) trinuclear units connected to each other through two bridging hydride ligands. The shortest Ru···Ru distance between the two trinuclear units is 3.292(3) Å, too long to be considered an Ru−Ru bond. It regenerates complex **1** when exposed to carbon monoxide (1 atm, 20 °C), but undergoes CO substitution instead of ligand addition when treated with P(*p*-tolyl)$_3$ at room temperature. Complex **5** is even more effective than **1** as a catalyst precursor for the homogeneous hydrogenation of diphenylacetylene under very mild conditions (1 atm, 50 °C).[36]



Scheme 8

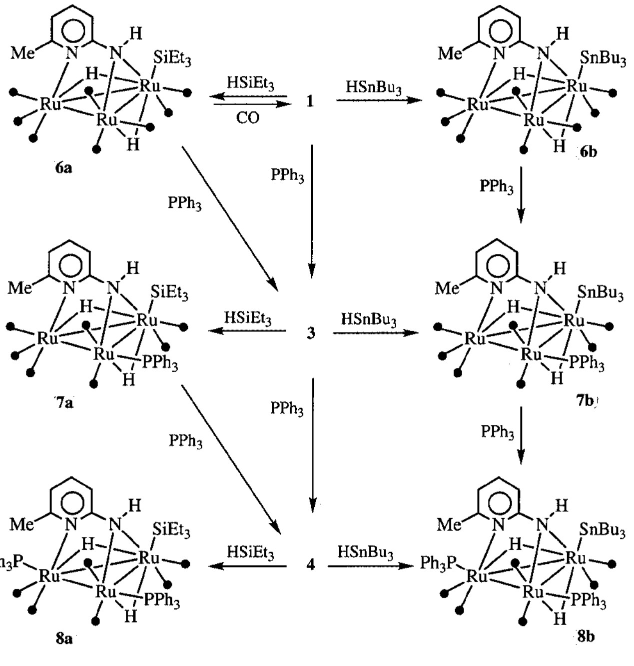
As occurs with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$,[29] the hydrogenation of **1** implies the oxidative addition of hydrogen to a trinuclear cluster complex and the elimination of two CO ligands to give an unsaturated 46-electron species. While the osmium species is stable, the ruthenium species dimerizes to give **5**. Unsaturated 46-electron clusters of ruthenium are very rare. To date, only one trinuclear derivative has been reported, i.e. $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9]$.[37] A hexanuclear complex related to **5**, but containing thioureate instead of apyMe ligands, has also been reported.[38]

While the substituted complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-apyMe})(PPh_3)(CO)_8]$ (**3**; Scheme 4) does not react with hydrogen, the disubstituted derivative $[Ru_3(\mu\text{-}H)(\mu_3\text{-apyMe})(PPh_3)_2(CO)_7]$ (**4**) undergoes two P−C bond activation processes on reaction with hydrogen (1 atm, 110 °C), leading to a complex containing a bridging phenyl group and two bridging diphenylphosphido ligands, i.e. $[Ru_3(\mu\text{-}Ph)(\mu_3\text{-apyMe})(\mu\text{-}PPh_2)_2(CO)_6]$ (Scheme 9).[39] A few more triruthenium clusters containing bridging phenyl groups derived from $PPh_3$ ligands have been reported in the last few years.[17,40−42] It appears that cluster complexes of this type have an unusual ability of stabilizing bridging phenyl groups.



Scheme 9

The clusters $[Ru_3(\mu\text{-}H)(\mu_3\text{-apyMe})(PPh_3)_x(CO)_{9-x}]$ [$x$ = 0 (**1**), 1 (**3**), 2 (**4**)] react with $HSiEt_3$ to give the oxidative substitution products $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-apyMe})(SiEt_3)(PPh_3)_x(CO)_{8-x}]$ [$x$ = 0 (**6a**), 1 (**7a**), 2 (**8a**)]. Similar reactions with $HSnBu_3$ afford $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-apyMe})(SnBu_3)(PPh_3)_x(CO)_{8-x}]$ [$x$ = 0 (**6b**), 1 (**7b**), 2 (**8b**)], which are isostructural with the corresponding silyl derivatives (Scheme 10).[43] The reactions of **6a** and **7a** with $PPh_3$ results in the elimination of $HSiEt_3$, rendering the complexes **3** and **4**. However, similar reactions with the tin-containing compounds **6b** and **7b** afford the substitution products **7b** and **8b**, respectively. Further, while **6b** is stable under carbon monoxide, the silyl derivative **6a** regenerates complex **1** under the same conditions. These reactions, which represent the first systematic study of the reactivity of triruthenium clusters with silanes and stannanes, demonstrate



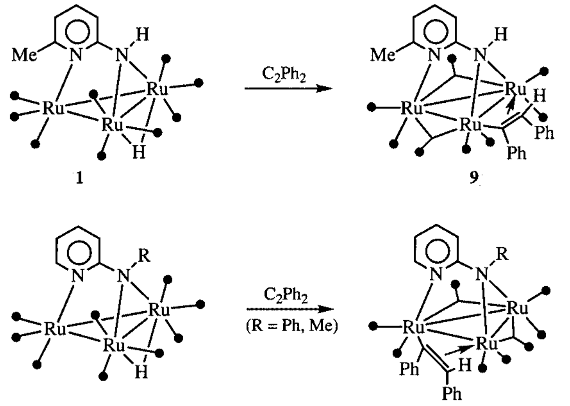
Scheme 10

that the hydrido(stannyl) complexes are much more stable than the hydrido(silyl) derivatives towards the elimination of the corresponding triorganostannanes or triorganosilanes.

### III.c. Reactions with Alkynes

Alkynes have always attracted the attention of organometallic cluster chemists because of their versatile reactivity.[44] They are good ligands that bind strongly to the metal atoms, and are prone to undergo facile insertion processes and coupling reactions with other ligands.

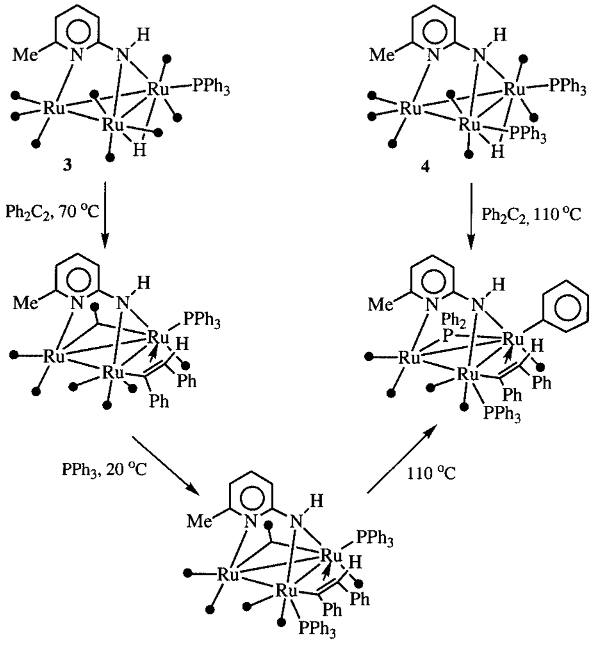
Cluster complexes of the type [$Ru_3(\mu\text{-}H)(\mu_3\text{-apy})(CO)_9$] react easily (10−20 min, 40−60 °C) with alkynes to give derivatives that contain edge-bridged alkenyl ligands. For steric reasons, the position of the alkenyl group within the clusters depends on the presence or absence of substituents on the amidic N atom (Scheme 11).[23,45]



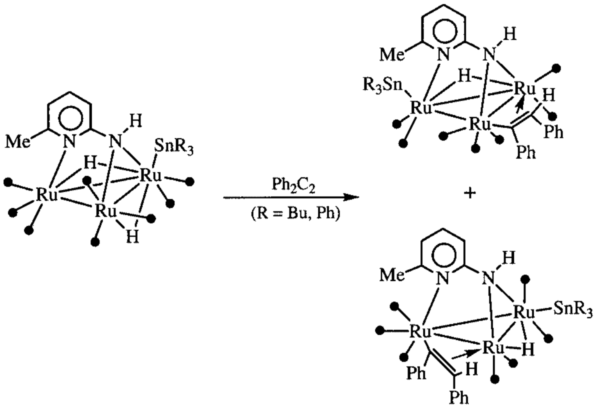
Scheme 11

The phosphane-substituted complexes **3** and **4** also react with diphenylacetylene to give alkenyl derivatives (Scheme 12).[46,47] The conditions needed for the reaction of the disubstituted complex **4** (110 °C, 75 min) induced the cleavage of a P−C bond giving a phenyl derivative that can be isolated.[47] The monosubstituted alkenyl derivative [$Ru_3(\mu_3\text{-apyMe})(\mu\text{-PhCH=CPh})(PPh_3)(CO)_7$] promotes the catalytic hydrogenation of diphenylacetylene under mild conditions (1 atm, 80 °C). A kinetic analysis of this reaction indicated the presence of intermediate trinuclear clusters as catalytic species.[48]

The reaction of diphenylacetylene with the hydrido(silyl) compound [$Ru_3(\mu\text{-}H)_2(\mu_3\text{-apyMe})(SiEt_3)(CO)_8$] (**6a**) gives the alkenyl complex [$Ru_3(\mu_3\text{-apyMe})(\mu\text{-PhCH=CPh})(CO)_8$] (**9**) and $HSiEt_3$.[46] Analogous reactions of hydrido(stannyl) compounds give a mixture of two isomeric hydrido(stannyl)-alkenyl derivatives (Scheme 13).[49] Interestingly, the reactions of the alkenyl complex **9** with tertiary silanes and stannanes give similar mixtures of compounds including (alkenyl)hydrido(silyl) and (alkenyl)hydrido(stannyl) derivatives.[46,49] It should be noted that in all the compounds having alkenyl and $ER_3$ ligands, these ligands are attached to different metal atoms. This may explain why no hydrosilylated or hydrostannated diphenylacetylene is observed when diphenylacetylene and triorganosilanes or triorganostannanes are allowed to react in the presence of complex **1**.



Scheme 12

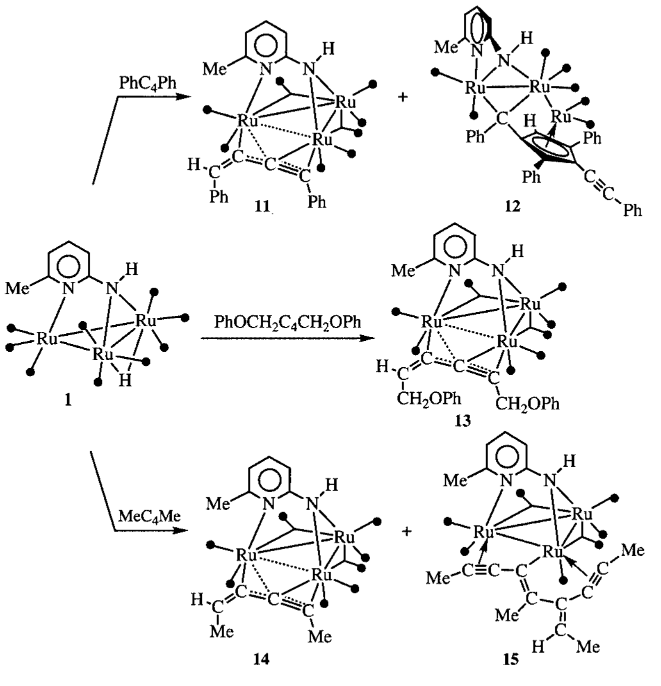


Scheme 13

It has been reported that [$Ru_3(\mu\text{-}H)(\mu_3\text{-Phapy})(CO)_9$] promotes the regioselective polymerization of phenylacetylene to *cis*-polyphenylacetylene, but only in the presence of a catalytic amount of $HSiEt_3$.[50] The role played by the silane remains unknown. In the absence of silane, 1,2,4-triphenylbenzene is obtained. When (triphenylsilyl)acetylene is used as the incoming substrate, a poor catalytic dimerization to (*E*)-1,4-bis(triphenylsilyl)but-1-yn-3-ene is observed.[50]

Compound **1** reacts with diphenylbutadiyne and 1,6-diphenoxyhexa-2,4-diyne in THF at refluxing temperature to give the ynenyl derivatives [$Ru_3(\mu_3\text{-apyMe})(\mu\text{-RC}{\equiv}\text{CC=CHR})(CO)_8$] [R = Ph (**11**), $CH_2OPh$ (**13**); Scheme 14]. These products contain a 1,4-disubstituted butynen-3-yl ligand $\eta^3$-coordinated to two ruthenium atoms. The remarkable compound [$Ru_3(\mu\text{-apyMe})\{\mu_3\text{-}\eta^6\text{-PhCC}_5(C{\equiv}CPh)\text{-}$

$HPh_2\}(CO)_7]$ (**12**), which contains an $\eta^5$-cyclopentadienyl ring and a bridging carbene fragment, has also been obtained from the reaction of **1** with diphenylbutadiyne.[51]



Scheme 14

As diynes contain asymmetric alkyne fragments, there are two possible products resulting from the insertion of one of their alkyne fragments into a metal−hydride bond.[51] While compounds **11** and **13** contain butynen-3-yl ligands that clearly result from one of the two possible insertion regioisomers, compound **12** arises from an unprecedented [3+2]-cycloaddition reaction of an unobserved 1,4-diphenylbutynen-4-yl ligand (of the other insertion regioisomer) with a triple bond of a second diphenylbutadiyne molecule. Both insertion regioisomers have been isolated from the reaction of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}Phapy)(CO)_9]$ with diphenylbutadiyne.[52]

The reaction of complex **1** with an excess of hexa-2,4-diyne in refluxing THF gives the trinuclear derivative $[Ru_3(\mu_3\text{-}apyMe)\{\mu\text{-}\eta^5\text{-}MeC{\equiv}CC({=}CHMe)CMe{=}CC{\equiv}CMe\}(CO)_7]$ (**15**) as the final product (Scheme 14). This compound contains an unprecedented diynedienyl ligand that arises from the coupling of hexa-2,4-diyne with the hex-2-yn-4-en-4-yl ligand of the intermediate $[Ru_3(\mu_3\text{-}apyMe)\ \mu\text{-}MeCH{=}CC{\equiv}CMe)(CO)_8]$ (**14**). This intermediate is the first compound observed in the reaction of **1** with hexa-2,4-diyne, but it could not be isolated free of **15**.[53]

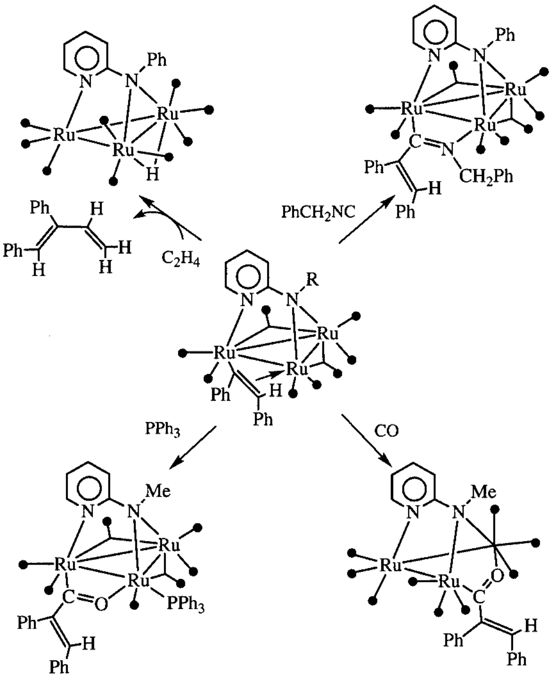
From the results described above, it can be inferred that alkynes can easily be activated in the form of alkenyl (vinyl) ligands by carbonyl(hydrido)triruthenium clusters containing bridging apy ligands. It is worth noting that the presence of the face-capping ligand in the clusters is essential in maintaining the cluster nuclearity, since it is well known that the reactions of alkynes and alkenes with hydridotriruthenium clusters containing edge-bridging ligands provoke the loss of one metal center, rendering bridged dinuclear products.[54]

### III.d. Reactivity of Alkenyl Derivatives

Many of the alkenyl complexes commented on above were considered to be ideal candidates for reactivity studies, including the chemical modification of the alkenyl ligand itself.

Both the neutral alkenyl complex $[Ru_3(\mu_3\text{-}apyMe)(\mu\text{-}PhCH{=}CPh)(CO)_8]$ (**10**) and its protonated derivative $[Ru_3(\mu\text{-}H)(\mu_3\text{-}apyMe)(\mu\text{-}PhCH{=}CPh)(CO)_8][BF_4]$ (**16**) promote the catalytic hydrogenation of diphenylacetylene under very mild conditions. The neutral complex is more efficient (TOF = 38.8 $h^{-1}$)[55] than the cationic complex (TOF = 29.2 $h^{-1}$)[56] under comparable reaction conditions [333 K, $p(H_2) = 0.573$ atm]. (*Z*)-Stilbene is the kinetic product, but it is progressively isomerized to (*E*)-stilbene. Hydrogenation of stilbenes to 1,2-diphenylethane was not detected. Detailed chemical and kinetic studies on these reactions indicated the presence of intermediate trinuclear clusters as catalytic species in both cases.

Lavigne's group has studied a number of very interesting C−C bond-forming reactions starting from $[Ru_3(\mu_3\text{-}Rapy)(\mu\text{-}PhCH{=}CPh)(CO)_8]$ (R = Ph or Me), that are outlined in Scheme 15.

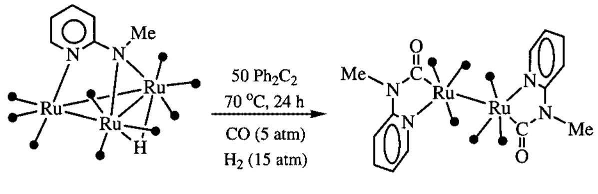


Scheme 15

Stoichiometric ethylene−diphenylacetylene codimerization has been observed on treating $[Ru_3(\mu_3\text{-}Phapy)(\mu\text{-}PhCH{=}CPh)(CO)_8]$ with ethylene.[57] The mononuclear complex $[Ru(PhCH{=}CPhCH{=}CH_2)(CO)_3]$ is a by-product of this reaction. It is proposed that the reaction proceeds by ethylene insertion into the metal−alkenyl group, followed by β-elimination. The elimination of free butadiene competes with the elimination of the mononuclear butadiene complex.

The reaction of [Ru$_3$($\mu_3$-Phapy)($\mu$-PhCH=CPh)(CO)$_8$] with benzyl isocyanide at room temperature leads to [Ru$_3$($\mu_3$-Phapy)($\mu$-PhCH=CPhC=NCH$_2$Ph)(CO)$_8$], which contains an alkenylimino ligand (Scheme 15).[50] This insertion reaction is related to the rapid uptake of triphenylphosphane (room temperature), giving the acyl derivative [Ru$_3$($\mu_3$-Meapy)($\mu$-PhCH=CPhC=O)(PPh$_3$)(CO)$_7$].[58] Second-order kinetics indicate that the initial step is an associative addition of the PPh$_3$ ligand to the metal cluster without CO loss.

In addition, a related 50-electron acyl derivative, i.e. [Ru$_3$($\mu_3$-Meapy)($\mu$-PhCH=CPhC=O)(CO)$_9$], is formed when the alkenyl precursor is exposed to CO (Scheme 15).[58] Hydrogenation (25 °C, 5 atm) of this complex causes the elimination of $\alpha$-phenylcinnamaldehyde and the recovery of the hydrido complex [Ru$_3$($\mu$-H)($\mu_3$-Meapy)(CO)$_9$]. The overall transformation constitutes a stepwise hydroformylation of diphenylacetylene. Attempts to achieve a catalytic process led to the isolation of the catalytically inactive dinuclear derivative [Ru$_2$(MeCOapy)$_2$(CO)$_6$] as the major metal-containing product (Scheme 16).[58] This reaction represents the first (and so far unique) example of the degradation of an apy-bridged triruthenium cluster, probably due to the harsh reaction conditions.



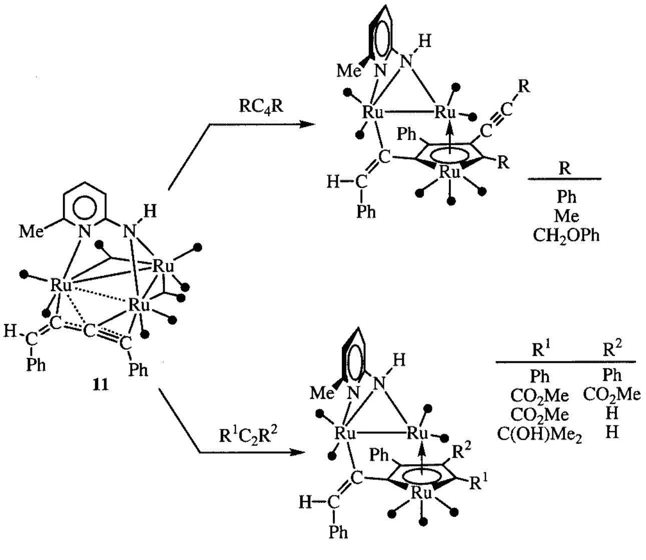
Scheme 16

The reactivity of the ynenyl derivatives [Ru$_3$($\mu_3$-apyMe)($\mu$-RC≡CC=CHR)(CO)$_8$] [R = Ph (**11**), CH$_2$OPh (**13**)] with diynes and alkynes has been studied.[51] In all cases, the products contain a ruthenacyclopentadienyl fragment formed by the coupling of the coordinated ynenyl ligand of the starting material with a triple bond of the new reagent (Scheme 17). While all compounds derived from **11** have the alkenyl C=CHR (R = Ph) fragment with an (*E*) configuration (R *trans* to Ru, Scheme 17), most of the products derived from **13**, have the alkenyl C=CHR (R = CH$_2$OPh) fragment with an (*E*) configuration.

It is interesting to note that all these ruthenacyclopentadienyl derivatives, as well as complex **12** (Scheme 14), have a 5-electron donor apyMe ligand attached to only two metal atoms, a coordination mode previously unobserved for apy ligands in cluster chemistry that strongly supports the hemilabile character of these ligands.

## III.e. Synthesis and Reactivity of Cationic Non-Hydridic Clusters

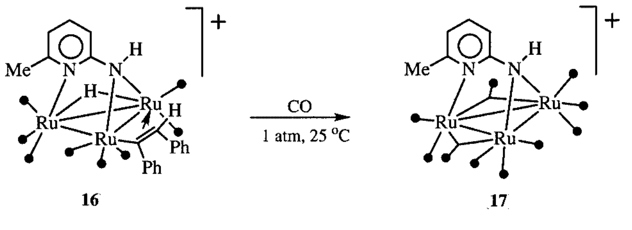
Simple protonation of neutral carbonyl cluster complexes frequently leads to cationic hydridic derivatives.[19,24,25]



Scheme 17

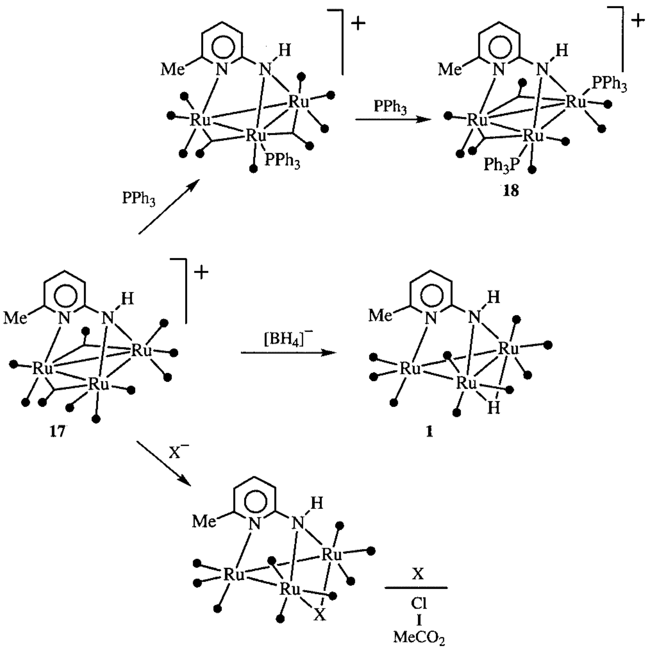
However, very few non-hydridic cationic carbonyl clusters have been described. For ruthenium, prior to the cluster complexes commented on below, only a few examples of trinuclear 50-,[59] 47-[60] or 46-electron[60] species were known.

The presence of the alkenyl and hydride ligands in the cationic complex [Ru$_3$($\mu$-H)($\mu_3$-apyMe)($\mu$-PhCH=CPh)(CO)$_8$][BF$_4$] (**16**) prompted us to study reactions that might induce the reductive elimination of (*Z*)-stilbene, and that would give cationic cluster compounds containing non-hydridic ligands. Although reactions with phosphane ligands only lead to CO-substitution products,[61] complex **16** reacts gently (1 atm, 20 °C) with carbon monoxide giving the cationic complex [Ru$_3$($\mu_3$-apyMe)(CO)$_{10}$][BF$_4$] (**17**) in quantitative yield (Scheme 18). (*Z*)-Stilbene is a by-product of this reaction.[62] No other non-hydridic 48-electron cationic triruthenium cluster complexes were known prior to the publication of complex **17**.



Scheme 18

The reactivity of complex **17** markedly reflects a very high electrophilicity. It easily undergoes CO-substitution reactions on treatment with a variety of nucleophiles, including phosphanes,[62] hydrides, halides and carboxylates (Scheme 19), and is unstable in donor solvents (acetone, THF).[63]



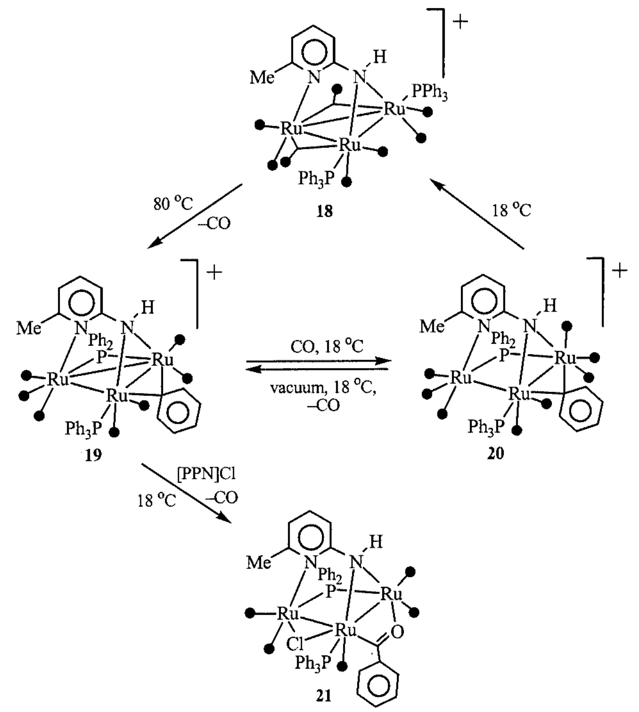
Scheme 19

It is worth noting that the thermal activation of a P−C bond of the disubstituted compound $[Ru_3(\mu_3\text{-apyMe})(PPh_3)(CO)_8][BF_4]$ (**18**) leads to the phenyl derivative $[Ru_3(\mu\text{-Ph})(\mu_3\text{-apyMe})(\mu\text{-PPh}_2)(PPh_3)(CO)_7][BF_4]$ (**19**). Treatment of **19** with carbon monoxide regenerates **18** via the 50-electron intermediate $[Ru_3(\mu\text{-Ph})(\mu_3\text{-apyMe})(\mu\text{-PPh}_2)(PPh_3)(CO)_8][BF_4]$ (**20**) (Scheme 20).[41] These reactions represent the only reversible triphenylphosphane P−C bond activation reaction reported in carbonyl cluster chemistry. The characterization of the neutral acyl derivative $[Ru_3(\mu\text{-PhCO})(\mu\text{-Cl})(\mu_3\text{-apyMe})(\mu\text{-PPh}_2)(PPh_3)(CO)_5]$ (**21**), which arises from the reaction of **19** with [PPN]Cl, supports the formulation assigned to **19**.[41]

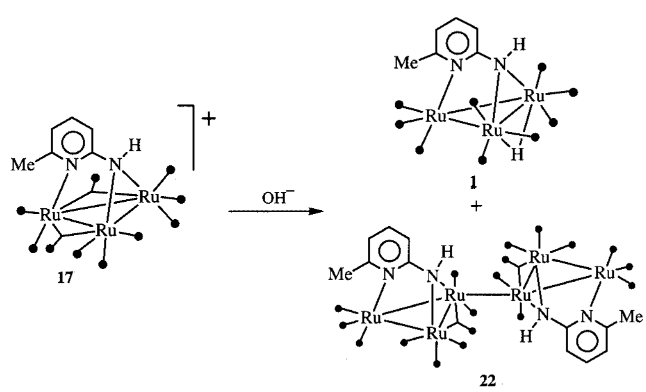
### III.f. Reactions Leading to Higher-Nuclearity Clusters

As part of the study of the reactivity of the cationic complex **17**, we treated it with aqueous NaOH. Two complexes were obtained, i.e. **1** and the hexanuclear derivative $[Ru_6(\mu_3\text{-apyMe})_2(CO)_{18}]$ (**22**) (Scheme 21).[64] The latter is the only example of a hexanuclear cluster consisting of two vertex-linked metal triangles in the chemistry of ruthenium.

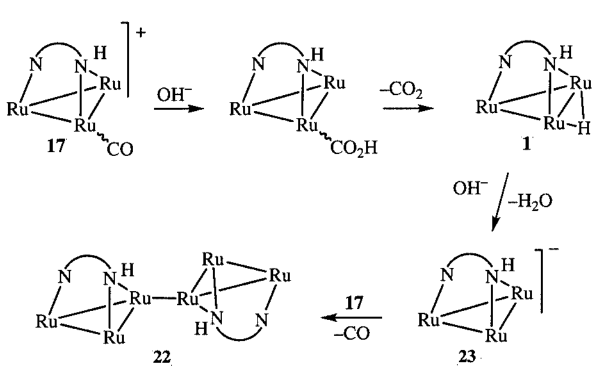
A possible reaction pathway for this transformation is sketched in Scheme 22.[64] It involves the nucleophilic attack of the coordinated CO ligand of complex **17** by the hydroxide anion, to give an unstable hydroxycarbonyl species that rapidly releases $CO_2$, rendering the neutral hydride **1**. Before all of complex **17** has been consumed, complex **1** deprotonates with more $OH^-$ giving the anionic derivative $[Ru_3(\mu_3\text{-apyMe})(CO)_9]^-$ (**23**). Finally, **23** reacts with the remaining complex **17** to give CO and the hexanuclear cluster **22**. This reaction sequence is supported by the facts that **17** does react with **23** to give **2**, and that **1** can be deprotonated with NaOH to afford **23**. Alternatively, compound **22** can also be prepared by zinc reduction of complex **17**.[64]



Scheme 20

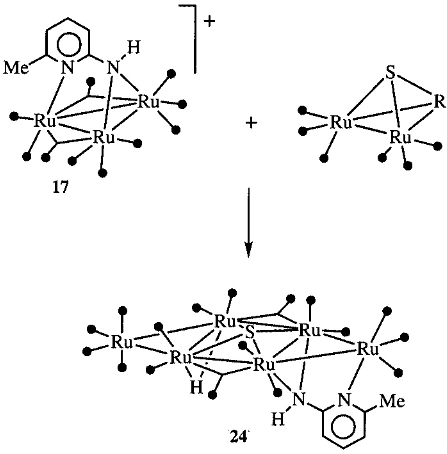


Scheme 21



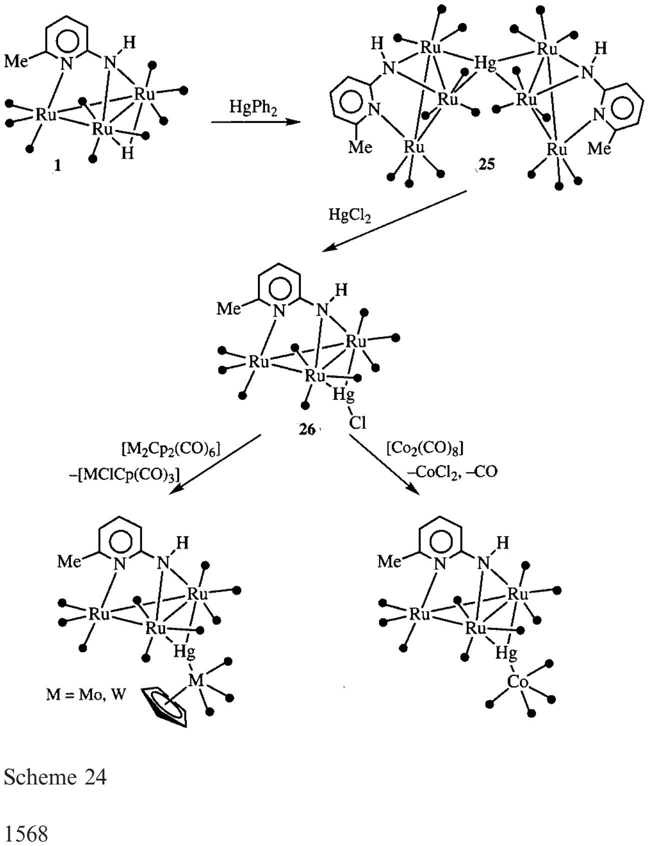
Scheme 22

The hexanuclear compound $[Ru_6(\mu\text{-H})(\mu_4\text{-S})(\mu_3\text{-apyMe})(CO)_{17}]$ (**24**), which consists of two closed trimetal units connected by two metal−metal bonds, has been prepared by reaction of the cationic complex **17** with the anionic cluster $[Ru_3(\mu_3\text{-}S)(CO)_9]^{-2}$ (Scheme 23).[63] Although other related carbonylhexaruthenium cluster compounds containing $\mu_4$-S ligands are known,[38][65] they are electron-rich derivatives since their electron count (94-electrons) has two electrons more than those required by electron-precise clusters containing eight metal−metal bonds (92 electrons). In contrast, compound **24** is electron-precise.



Scheme 23

The reactions of anionic carbonyl clusters with mononuclear cations have often been used to prepare higher-nuclearity cluster compounds.[66] However, no reactions of cationic carbonyl clusters with anionic complexes had been reported prior to the publication of compound **17**. This is probably because cationic non-hydridic clusters were not readily accessible and because a proton transfer from the cation to the anion occurs when cationic hydridic clusters are used. This results in a mixture of two neutral complexes rather than a cluster of higher nuclearity.



Scheme 24

The mercury-containing hexaruthenium cluster $[Ru_6(\mu_4\text{-}Hg)(\mu_3\text{-apyMe})_2(CO)_{18}]$ (**25**) has been prepared by treating complex **1** with diphenylmercury (Scheme 24).[67] This complex reacts with mercury(II) chloride to give $[Ru_3(\mu\text{-}HgCl)(\mu_3\text{-apyMe})(CO)_9]$ (**26**). In both cases, the mercury atoms span the same Ru−Ru edge as the amido moiety.

Redistribution reactions of compound **26** with the metal−metal-bonded dimers $[M_2Cp_2(CO)_6]$ (M = Mo, W) and $[Co_2(CO)_8]$ give mixtures of the mixed-metal clusters $[\{Ru_3(\mu_3\text{-apyMe})(CO)_9\}(\mu\text{-}Hg)ML_n]$ ($ML_n$ = $MoCp(CO)_3$, $WCp(CO)_3$, $Co(CO)_4$] and the corresponding chloro complexes $[MClL_n]$ (Scheme 24).[68] These mixtures can be separated. Besides these reactions, the only additional example of a reaction of a metal cluster containing an HgX (X = halogen) moiety with a neutral complex containing metal−metal bonds is that of $[Ru_3(\mu\text{-}HgI)(\mu_3\text{-}C_2tBu)(CO)_9]$ with $[Ru_3(CO)_{12}]$, which gives $[\{Ru_3(\mu_3\text{-}C_2tBu)(CO)_9\}_2(\mu_3\text{-}Hg)_2Ru(CO)_4]$ as the major product.[69]

## IV. Concluding Remarks

The following are the principal features associated with apy ligands in carbonyltriruthenium clusters:

(a) The apy ligands remain unchanged under most reaction conditions, thus avoiding undesirable side reactions.

(b) The reactions take place under mild conditions (25−100 °C), probably induced by a hemilabile effect of the apy ligands.

(c) Reactivity (CO substitution) is directed to positions *cis* to the apy amido group, thus leading to regioselective reactions in most cases.

(d) The trinuclear cluster framework is preserved during the reactions because of the mild reaction conditions, and because of the anchor effect of the apy ligands, which maintains the metal atoms in adequate proximity.

(e) This type of cluster complexes show an unusual ability to stabilise bridging phenyl groups.

(f) The compounds have a convenient solubility in polar solvents (insoluble in nonpolar solvents), particularly if the exocyclic nitrogen atom is part of an N−H group.

(g) The basicity of the apy ligands can be tuned by introducing substituents on the exocyclic nitrogen atom.

(h) The reactions can easily be monitored by $^1H$ NMR spectroscopy, particularly if the pyridine ring contains a methyl substituent.

Up to date, over a hundred carbonyltriruthenium cluster complexes containing bridging apy ligands have been reported. This wide-ranging cluster chemistry includes quite a few outstanding reactions and products, which have been surveyed in this review. No doubt, this rich derivative chemistry has been facilitated by the presence of deprotonated 2-aminopyridines as ancillary ligands in the clusters.

## Acknowledgments

The author wishes to thank the researchers cited in the references for their contribution to the chemistry surveyed in this review and, in particular, his colleagues and friends José M. Fernández-Colinas and Ignacio del Río. Continuous financial support from the Spanish Ministry of Education is also acknowledged (Projects PB92-1007, PB95-1042, and PB98-1555).

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[1] Throughout this review, the term cluster complex refers to a complex containing at least three metal atoms supported by at least two metal−metal bonds.

[2] For a general overview of cluster reactivity, see: *Metal Clusters in Chemistry* (Eds.: P. Braunstein, L. A. Oro, P. R. Raithby), Wiley-VCH, Weinheim, **1999**.

[3] See, for example: D. J. Darensbourg, in *The Chemistry of Metal Cluster Complexes* (Eds.: D. F. Shriver, H. D. Kaesz, R. D. Adams), VCH Publishers, New York, **1990**, p.171.

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signed to **9** in early publications.[34,46,49] However, subsequent reactivity studies demonstrated that both the alkenyl ligand and the amido fragment span the same Ru−Ru edge.[55]

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