Effects of Halides and Related Ligands on Reactions of Carbonylruthenium Complexes (Ru^0–Ru^{II})

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Dedicated to Herbert D. Kaesz on the ocassion of his 66th birthday

Keywords: Halides / Homogeneous catalysis / Organometallics / Ruthenium

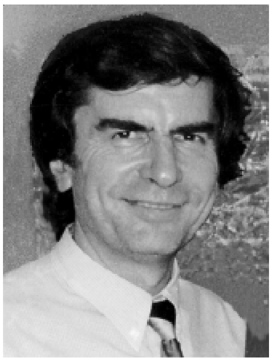
While the primary motivation of fundamental studies on carbonylhalotriruthenium complexes was to understand the promoter effect of halides on certain ruthenium-based catalytic systems of industrial relevance, such complexes have gained significance in their own right due to their remarkable ability to provide low-activation energy pathways for the coordination of organic substrates. Limitations inherent to the fragility of these prototypes led to the design and development of a related family of more sophisticated derivatives where an aminopyridyl group serves as an alternate *hemilabile* ancillary ligand. Studies of their reactivity have revealed the possibility of achieving a number of stoichiometric or moderately catalytic "cluster-mediated" transformations of organic substrates under very mild conditions. Yet, the viability of these systems is still limited to a narrow low-energy domain. By contrast, halotriruthenium derivatives are still seen to function as catalyst precursors under the actual conditions of certain catalytic reactions where they act as sources of ruthenium(II) halide complexes that become the active components of the system. The second part of the review focuses on novel aspects of their fascinating chemistry.

Introduction

The association of carbonylruthenium complexes with halides has long been known to produce remarkably efficient catalyst precursors. Historically, Dombek and Knifton were the first to draw attention on the effects of these "magic" mixtures in two fascinating series of independent reports revealing, respectively, that *enhanced selectivity* in the syngas conversion into ethylene glycol could be achieved in the homogeneous phase with an $Ru_3(CO)_{12}$/iodide system,[1] or by ruthenium "melt" catalysis, where a bromide salt acts both as solvent and co-catalyst.[2] Two anionic species, $[Ru_3(\mu\text{-}H)(CO)_{11}]^-$ and $[Ru(CO)_3X_3]^-$, both directly generated in situ under CO/H_2, were found to be essential for optimum activity.

The CO hydrogenation leading to glycol was proposed to begin with the formation of a formyl species by *intermolecular hydride transfer* from $[Ru_3(\mu\text{-}H)(CO)_{11}]^-$ (or, more probably from $[HRu(CO)_4]^-$ generated in situ)[3] to one of the electrophilic carbonyl groups of the haloruthenium(II) complex.

At that time, however, and even though interesting model studies were done with other metals,[4] the proposed halo(hydroxyalkyl)ruthenium(II) intermediates on the way to glycol remained elusive and were even thought to be too short-lived for proper detection, which may no longer be true on the basis of recent observations (vide infra).



Guy Lavigne was born in Toulouse in 1947. He obtained his Ph.D. ("Doctorat d'Etat des Sciences") from the University of Paris VI under the supervision of Professor Yves Jeannin. In 1979, he joined the group of Professor Jean-Jacques Bonnet at the "Laboratoire de Chimie de Coordination du CNRS" (LCC). After post-doctoral studies at UCLA with Professor Herbert D. Kaesz in 1984, he returned to Toulouse at the LCC/CNRS where he was appointed Research Director in 1988. His research deals with the fundamental aspects of metal-mediated carbon−carbon bond-forming reactions and their application to homogeneous catalysis.

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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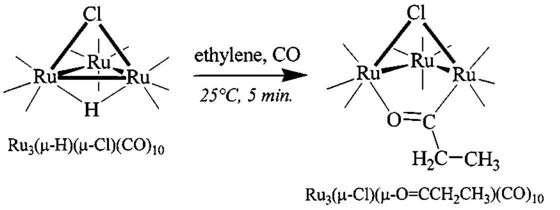
These and related[5] pioneering observations paved the way to a dramatic development of research on Ru-based syngas reactions,[2b] with notable modifications including the use of different promoters such as onium chloride salts and weak acids[6] or even benzimidazoles.[7] The mixture of $[HRu_3(CO)_{11}]^-$ and $[Ru(CO)_3X_3]^-$ (X = Br or I) was later found to be active for various related reactions[8] including, in particular, the oxonation of olefins[9] and their alkoxycarbonylation.[10] Besides, Cenini and co-workers published an interesting phosgene-free process for the carbonylation of aromatic nitro compounds to carbamates, again using mixtures of $Ru_3(CO)_{12}$ and halide salts.[11]

While examining the chemical behavior of the same complexes within a much lower energy domain, Kaesz and co-workers discovered at the same time that the presence of a halide in the ligand shell of a carbonylruthenium cluster results in the regioselective incorporation of phosphane ligands[12] or organic substrates[13] under unprecedented mild conditions. A spectacular report[13] included a reaction between the halide-containing species $Ru_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}$ and ethylene/CO mixtures (5 atm), giving the propionyl complex $Ru_3\{\mu\text{-}C(O)CH_2CH_3\}(\mu\text{-}Cl)(CO)_{10}$ within minutes at 25°C (Scheme 1), thus nicely modeling a key step in olefin hydroformylation, a reaction independently found to be catalyzed by $[Ru_3(\mu\text{-}H)(CO)_{11}]^-$.[14]



Scheme 1. Facile activation of ethylene by a carbonylchlorohydridotriruthenium complex

In attempts to devise an anion route to the above halohydridotriruthenium derivative, Kaesz and Lavigne discovered that $Ru_3(CO)_{12}$ reacts spontaneously at 25°C with onium salts of halides or pseudohalides *in the absence of ion pairing* to give hitherto unknown adducts of the type $[Ru_3(CO)_{12-n}(X)]^-$ ($n = 0-3$) exhibiting remarkably *enhanced substitutional lability.*[15] These *"activated"* species primarily drew attention while appearing as the first formed intermediates on the way to Dombek's catalysts (vide supra). In fact, as explained below in the first part of this review, these and related complexes were further shown to be of specific interest as synthetic tools for a number of stoichiometric or moderately catalytic *cluster-mediated* transformations of organic substrates occurring on a laboratory scale *under very mild conditions*[16] but having no direct relevance to the applied reactions mentioned above.

A renewal of interest for ruthenium/halide systems emerged in 1989 with Keim's report[17] that carbonylruthenium chloride clusters were catalyst precursors for the hydroesterification of ethylene with methyl formate, originally disclosed by Sneeden et al.[18] The reaction was later shown by Petit and co-workers to be much more efficiently catalyzed by the multi-component Ru/iodide/DMF system.[19]

Based on what we knew at that time, carbonylhaloruthenium clusters appeared to us unlikely to survive under the reported experimental conditions. We were thus challenged to re-investigate the hydroesterification reaction with the aim of tracing the transformation of Ru_3/halide precursors toward the formation of the active species. Studies in collaboration with Kalck and co-workers led us to observe that the aforementioned anionic mononuclear carbonylruthenium(II) halide species $[Ru(CO)_3X_3]^-$ was again implied, and could even be used alone as a catalyst precursor.[20] A literature survey indicated that, in spite of the newly established implication of carbonylhaloruthenium(II) complexes as catalyst precursors in a growing number of C−C bond-forming reactions,[21] the present state of knowledge of their reactivity rests essentially on early pioneering studies.[22] Thus, a new research project was undertaken with the aim of filling the gap between the basic knowledge on these compounds and their applied reactions. The first results of our new investigation are summarized in the second part of this review.

I. Chemistry of "Anion-Promoted" Ruthenium Cluster Complexes Under Mild Conditions

I.1 Catalysis of CO Displacement by Phosphanes in $Ru_3(CO)_{12}$ in the Presence of Anionic Nucleophiles

In 1984, we made the intriguing observation that addition of catalytic amounts of $[(PPh_3)_2N]Cl$ to a THF solution containing a mixture of $Ru_3(CO)_{12}$ and triphenylphosphane, results in the rapid formation of the monosubstituted derivative $Ru_3(CO)_{11}(PPh_3)$ at 25°C[15] (Equation 1).

$$Ru_3(CO)_{12} + PR_3 \xrightarrow[\text{THF, 25°C}]{\substack{\text{onium salt of Nu}^{-}{*}\\ \text{(catalytic amounts)}}} Ru_3(CO)_{11}(PR_3) + CO \quad (1)$$

(*) $Nu^- =$ (i) CN^-, CH_3COO^-, F^-, Cl^-, Br^-, or I^-;
or, (ii) $[BHR_3]^-$ or $[HRu(CO)_4]^-$

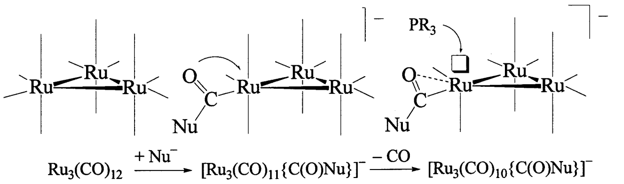
Whereas the thermally induced substitution (ca. 2 h, 90°C) was known to give only the "thermodynamic" trisubstituted derivative $Ru_3(CO)_9(PPh_3)_3$,[23] catalysis by the salt under highly dissociating conditions (i.e. in the absence of ion pairing) appeared as a valuable means to *selectively* trap the kinetic substitution product. The system was rapidly extended to a range of nucleophilic anions [see Equation 1, catalysts type (i)] whose relative efficiencies were established on the basis of a preliminary kinetic study revealing a zero-order rate dependence on $[Ru_3(CO)_{12}]$. The effect of these ions was interpreted in terms of the enhanced substitutional lability of the methoxycarbonyl adducts $[Ru_3\{\eta^1\text{-}C(O)OMe\}(CO)_{11}]^-$ established by Ford[24] in stoichiometric reactions with phosphanes (see Equations 2−3)[25] or molecular hydrogen (sequence of Equations 2 and 4),[26] and independently applied to ^{13}CO enrichment by Darensbourg.[27]

$$Ru_3(CO)_{12} + OCH_3^- \rightarrow [Ru_3(CO)_{11}\{C(O)OCH_3\}]^- \quad (2)$$

$$[Ru_3(CO)_{11}\{C(O)OCH_3\}]^- + PR_3 \rightarrow Ru_3(CO)_{11}PR_3 + CO + OCH_3^- \quad (3)$$

$$[Ru_3(CO)_{11}\{C(O)OCH_3\}]^- + H_2 \rightarrow Ru_3(\mu\text{-}H)(CO)_{11}]^- + HC(O)OCH_3 \quad (4)$$

It was suggested[15b] (Scheme 2) that CO labilization by the oxygen atom of a transient nucleophile-CO adduct "C(O)Nu" would allow the phosphane to reach the metal center. The increased basicity brought by this incoming ligand would then cause a reduction of the δ^+ character of the carbon atom, thereby facilitating the expulsion of the nucleophilic anion Nu^- and its intermolecular transfer to a neighboring cluster for the propagation of the effect.



Scheme 2. Proposed pathway for anion-promoted CO labilization (the square box denotes a vacant coordination site)

While reasoning that the simplest nucleophilic anion H^- is likely to give the same type of transient adduct $[Ru_3\{\eta^1\text{-}C(O)H\}(CO)_{11}]^-$ (or $[Ru_3\{H\}(CO)_{12}]^-$), we were able to show that catalysis of CO displacement by phosphanes into $Ru_3(CO)_{12}$ can also be efficiently carried out by *intermolecular hydride transfer*, using simple hydridic reagents like potassium tri-*sec*-butylhydroborate (K-Selectride) or $[HRu(CO)_4]^-$ as catalysts [Equation 1, catalyst type (ii)].[28] The latter procedure, exceeding the performance of the sodium benzophenone ketyl catalyst proposed earlier by Bruce,[29] is of high practical synthetic utility since "super hydrides" are found in any chemical laboratory. Significantly, the catalytic substitution can also be initiated by adding few crystals of $[PPN][Ru_3(\mu\text{-}H)(CO)_{11}]$ to a THF solution of $Ru_3(CO)_{12}$ and phosphane under CO.[28] In that case, however, an induction period is required for the latter anion to generate the actual hydride transfer agent $[Ru_3\{\eta^1\text{-}C(O)H\}(CO)_{11}]^-$ (or $[Ru_3\{H\}(CO)_{12}]^-$[30]). The mechanism proposed at that time for the formation of such adducts[28] found further support in the results of a more recent kinetic study reported by Shore,[30c] indicating that $^{13}CO/^{12}CO$ exchange in $[Ru_3(\mu\text{-}H)(CO)_{11}]^-$ is governed by competition between two parallel pathways, namely, a dissociative pathway (zero-order in anion and zero-order in CO) and an associative step (first-order in anion and first-order in CO), the latter becoming increasingly significant with increasing concentration of ^{13}CO. Thus, just like in the water gas shift reaction[30] [and also like in the hydride transfer occurring in the glycol synthesis (vide supra)], the preceding substitution reaction is governed by an associative step.

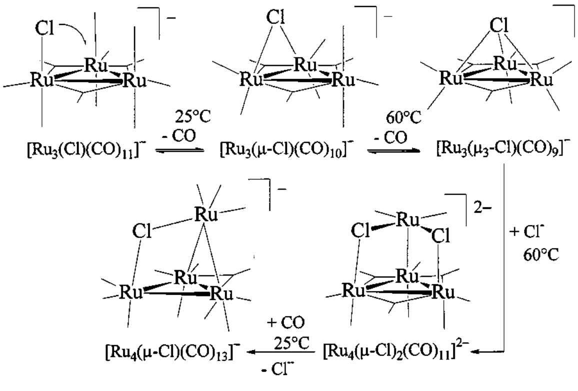
For anionic nucleophiles such as halides and pseudohalides, the nature of the initial site of attack proposed in Scheme 2 cannot be ascertained since the first formed adducts are very short-lived. Competitive nucleophilic attack at CO and at the metal center was reasonably suggested by Ford on the basis of a thorough kinetic study.[31]

I.2 Intramolecular Halide-Promoted CO Labilization and Its Application to the Controlled Activation of Unsaturated Substrates

Whereas the primary adducts discussed above are involved in the catalysis of phosphane substitution, we will now see that the subsequent anionic derivatives $[Ru_3(Cl)(CO)_{12-n}]^-$ ($n = 1-3$) are of synthetic utility when the incoming ligands are unsaturated organic substrates.

I.2.1 Equilibria within Ru_3/Halide Systems

The complete elucidation of the precise nature of these halide adducts rests on the concerted efforts of several groups.[15,20,32–35] Though Scheme 3 displays all equilibria appearing within the $Ru_3(CO)_{12}$/chloride system, the present paragraph deals only with the first three adducts $[Ru_3(Cl)(CO)_{12-n}]^-$ ($n = 1-3$), whereas further re-arrangement to tetranuclear species occurring under specific conditions will be discussed in section II.1.



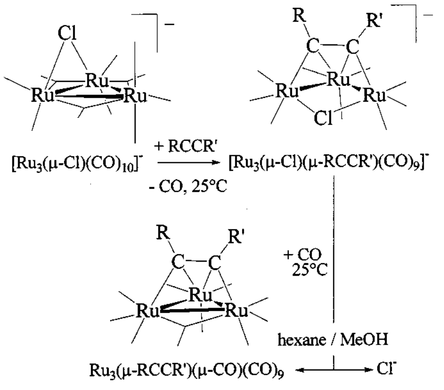
Scheme 3. Equilibria within Ru_3/halide systems

In the first observable adduct, $[Ru_3(Cl)(CO)_{11}]^-$ (readily obtained at 25 °C), the halide ligand occupies an axial coordination site onto the metal triangle.[33] It then slowly labilizes one vicinal CO at 25 °C while moving into an edge-bridging position to yield $[Ru_3(\mu\text{-}Cl)(CO)_{10}]^-$. Finally, it may still use one more electron pair to coordinate in a face-bridging position with concomitant CO labilization to form $[Ru_3(\mu_3\text{-}Cl)(CO)_9]^-$. However, this requires the assistance of thermal activation (60 °C) and a stream of inert gas to evacuate the released CO.[34]

I.2.2 Activation of Alkynes under Ambient Conditions

Opening of the halogen bridge in $[Ru_3(\mu\text{-}Cl)(CO)_{10}]^-$ or $[Ru_3(\mu_3\text{-}Cl)(CO)_9]^-$ provides a low-activation-energy path for the reaction of these complexes with alkynes at 25 °C, giving only one species $[Ru_3(\mu\text{-}Cl)(\mu\text{-}RCCR)(CO)_9]^-$ in quantitative yield within few minutes (Scheme 4).[34][36]

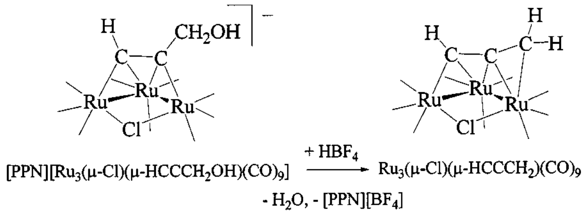
The kinetics of this reaction were investigated by Basolo.[37] The halide ligand appears to be so lightly coordinated to the metal core in the latter anionic species that its displacement by a CO ligand can be readily catalyzed by a



Scheme 4. Halide-promoted reaction of alkynes with $Ru_3(CO)_{12}$

protic solvent like methanol. Hence, if a biphasic hexane/methanol solvent mixture is used, the neutral complex $Ru_3(\mu\text{-RCCR})(\mu\text{-CO})(CO)_9$ transfers itself to the hexane phase, from which it can be recovered pure without chromatographic workup.[34][36] The latter complex is the kinetic product of the reaction between $Ru_3(CO)_{12}$ and alkynes, and is not observable under thermal activation.[38]

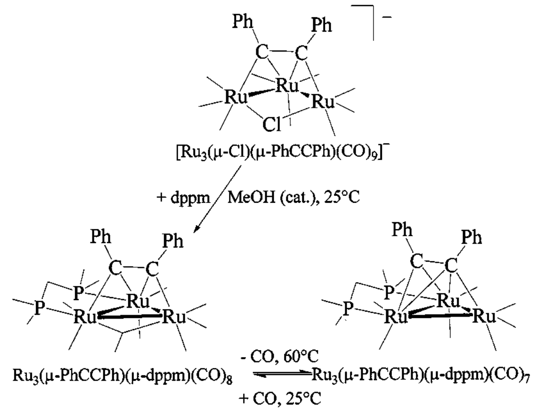
Slight modifications of the above synthetic strategy allowed the preparation of various alkyne-, alkynyl-[34][36] or allenyltriruthenium[39] complexes. For example, the new allenyl complex $Ru_3(\mu\text{-Cl})(\mu\text{-HCCCH}_2)(CO)_9$ was readily obtained within a few minutes by reaction of the anionic chlorotriruthenium complex with propargylic alcohol followed by proton-induced dehydration of the cluster-bound ligand (Scheme 5).[39]



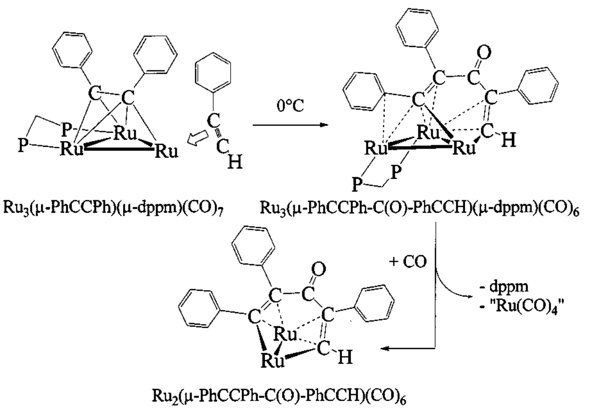
Scheme 5. Facile dehydration of a cluster-bound alkynol

Significantly, the first and still unique prototype of unsaturated 46e⁻-alkynetriruthenium complex, $Ru_3(\mu_3\text{-}\eta^2\text{-PhCCPh})(\mu\text{-dppm})(CO)_7$, was also prepared from the anionic alkynedecacarbonylchlorotriruthenium derivative by methanol-induced halide abstraction in the presence of dppm according to the sequence shown in Scheme 6.[40]

While the synthetic utility of the halide appeared obvious in light of the above reactions, we rapidly faced a new problem while attempting to achieve a full transformation of the "activated" alkyne directed toward the liberation of an oligomeric substrate. This is illustrated in Scheme 7.[41] We first made the encouraging observation that the cluster-bound alkyne ligand in the triruthenium complex $Ru_3(\mu\text{-PhCCPh})(\mu\text{-dppm})(CO)_7$ could be readily engaged in C−C bond formation with an incoming phenylacetylene molecule within minutes at 0 °C, giving the coordinatively unsaturated "fly-over"-type complex $Ru_3[\mu\text{-PhCCPh-C(O)-PhCCH}](\mu\text{-dppm})(CO)_6$ where the dialkenyl ketone fragment HC=CPh−C(O)−PhC=CPh appeared as the result of an intramolecular alkyne/CO/alkyne coupling.[41] Bearing in mind the existence of a patented process for the synthesis of hydroquinone using $Ru_3(CO)_{12}$ as a catalyst precursor,[42] we treated the newly formed derivative with CO, hoping to release a cyclic ketone or a quinone. However, this resulted in successive losses of the supporting dppm ligand and of one metal center, ending with the formation of a stable dimetallic fly-over species. It was thus becoming clear that the elimination of the free organic molecule (probable under forcing conditions, but not observed under those of our experiment) would take place only from a low-nuclearity fragment after complete degradation of the cluster (see Scheme 7, ancillary ligands omitted for clarity).



Scheme 6. Synthesis of the first prototype of an unsaturated alkyne-triruthenium cluster complex and observation of a "windshield-wiper" motion of the alkyne ligand onto the metal triangle

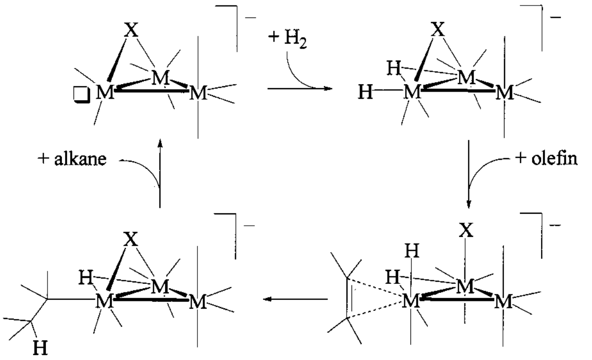


Scheme 7. Intramolecular akyne/CO/alkyne coupling

A modification of our strategy was thus required in order to observe full transformations of organic substrates on the metal core (see section I.3).

I.2.3 Activation of Olefins

In 1986, Gladfelter and co-workers reported that olefins can be readily hydrogenated at ambient temperature in the presence of the isocyanatotriruthenium cluster complex $[Ru_3(NCO)(CO)_{10}]^-$,[43] another member of the growing family of "anion-promoted" triruthenium clusters.[16] The system was understood in terms of the ability of the pseudohalide $X^- = NCO^-$ to function reversibly as a one- or three-electron donor, thereby helping to maintain similar relative energies of the intermediates. The catalytic reaction observed with ruthenium was modeled with osmium (Scheme 8) for which the alkyl intermediate was intercepted, using succinoyl anhydride as the olefin.[44]

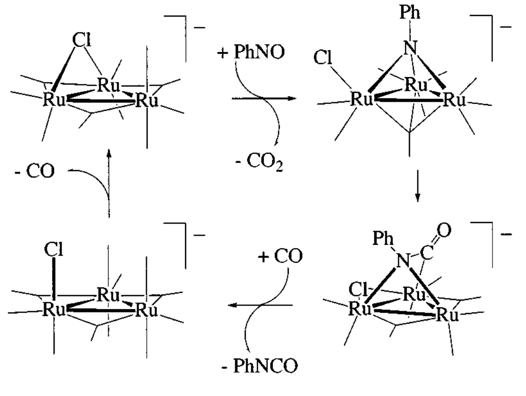


Scheme 8. Mechanism of the anion-promoted olefin hydrogenation proposed by Gladfelter and co-workers; the square box appearing in the scheme denotes a vacant coordination site on the metal center

A limitation of the system for $X^- = Cl^-$ appeared to be the facile reductive elimination of HCl from the anionic halohydrido intermediate, giving the anion $[HRu_3(CO)_{11}]^-$, a pathway related to the one shown in Equation 4.

I.2.4 Carbonylation of Nitrosobenzene

In connection with the above-mentioned discovery by Cenini et al. of a promoter effect of halides on the ruthenium-catalyzed synthesis of carbamates from aromatic nitro compounds,[11] Geoffroy and co-workers were able to show that the lightly coordinated halide in $[Ru_3(\mu\text{-}Cl)(CO)_{10}]^-$ can be engaged in bridge-opening/closing reactions assisting both the coordination of nitrosobenzene prior to NO bond cleavage and the carbonylation of the incipient nitrene intermediate to give phenyl isocyanate (Scheme 9).[45]



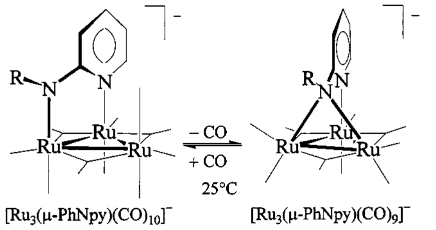
Scheme 9. Mechanism of the anion-promoted conversion of nitrosobenzene into isocyanate, as proposed by Geoffroy and co-workers

However, given that such a transformation occurs only under very mild conditions, there is no evidence for its value as a model for the effective carbonylation of aromatic nitro compounds, which is known to take place only under more forcing conditions.

I.3 Effects of Related Nitrogen-Based Hemilabile Ancillary Ligands

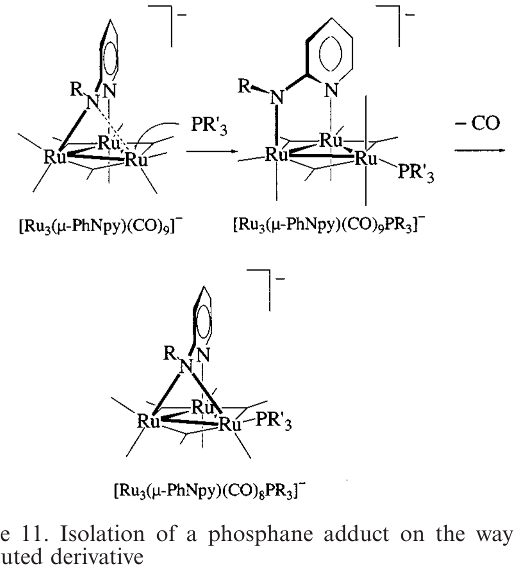
I.3.1 The Basic Concept

Since the adventitious loss of the halide from the above triruthenium species appeared as an undesirable dead end in several cases, we were led to devise a related family of "activated" cluster complexes incorporating aminopyridyl groups as alternate *hemilabile* ancillary ligands. As shown in Scheme 10, whereas the pyridyl group functions as an anchor, the amido group can adopt terminal or bridging coordination modes quite analogous to those occurring with halides (see Scheme 3).[46]



Scheme 10. Reversible CO uptake by a triruthenium cluster incorporating an aminopyridyl group as hemi-labile ancillary ligand

An advantage of aminopyridyl ligands is the possibility to tune their nucleophilicity by modifying the nature of the R group. Second-order kinetics were observed by Basolo for the reactions of anionic (aminopyridyl)triruthenium complexes with phosphanes.[47] The results were consistent with a mechanistic scheme in which nucleophilic attack by the phosphane gives an adduct bearing the amido ligand in



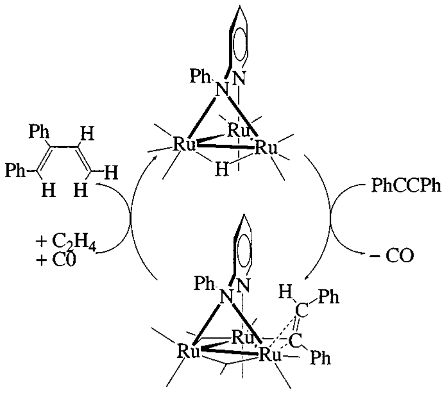
Scheme 11. Isolation of a phosphane adduct on the way to the substituted derivative

terminal position. After isomerization of such an intermediate, further reformation of the amido bridge through intramolecular nucleophilic attack with concomitant CO expulsion leads to the substituted derivative. The energy barrier for the latter step is dependent on the nucleophilicity of the amido group. Thus, whereas the intermediate adduct is trappable with R = Ph, the reaction proceeds directly to the substituted derivative when R = Me.

I.3.2 Activation of Alkynes and Vinyl-Group Transfer Reactions

The hemilabile behavior demonstrated for the above anionic species was suggested to account for the high reactivity of the corresponding protonated complexes $Ru_3(\mu\text{-}H)(\mu\text{-}RNpy)(CO)_9$ whose reactions with phosphanes proved to be too fast, even at −40°C, to be amenable to kinetic studies.

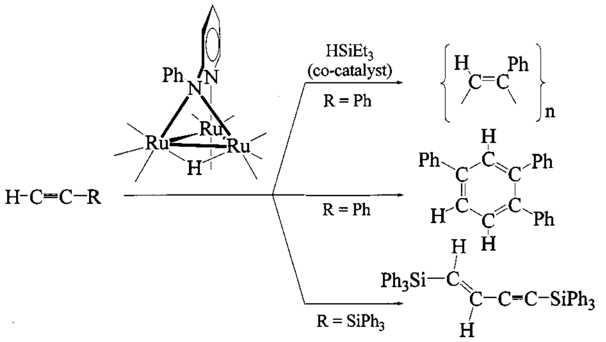
In 1990, we made the original observation that the anilinopyridyl complex $Ru_3(\mu\text{-}H)(\mu\text{-}PhNpy)(CO)_9$ is prone to activate alkynes selectively via the alkenyl intermediate $Ru_3(\mu\text{-}H)(\mu\text{-}PhNpy)(PhC{=}CHPh)(CO)_8$ and to promote the catalytic hydrogenation of diphenylacetylene as well as its stoichiometric hydrovinylation.[46] Whereas the kinetics and mechanism of the former reaction were subsequently investigated in detail by the group of Cabeza and Riera,[48] we became more interested in the second type of transformation which involved C−C bond formation (Scheme 12).



Scheme 12. Cluster-mediated hydrovinylation of diphenylacetylene

The co-dimerization leading to 1,2-diphenyl-1,3-butadiene was understood in terms of an insertion of ethylene into a ruthenium−alkenyl bond followed by β-elimination, a mechanism similar to the one established by Knox for a parallel reaction occurring at a diruthenium center.[49]

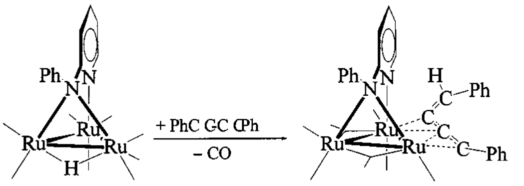
With more reactive 1-alkynes (and in the absence of alkene), multiple alkyne insertions were observed. Curiously, whereas ruthenium is not known to be an efficient alkyne polymerization catalyst, the regioselective polymerization of phenylacetylene to the *cis*-polyphenylacetylene was found to take place within few minutes at room temperature in the presence of the hydrido species $Ru_3(\mu\text{-}H)(\mu\text{-}PhNpy)(CO)_9$ and of triethylsilane (as a co-catalyst) (Scheme 13).[50] By contrast, trimerization was observed in the absence of silane.



Scheme 13. Oligomerization of terminal alkynes in the presence of the (anilinopyridyl)hydridotriruthenium complex as catalyst precursor

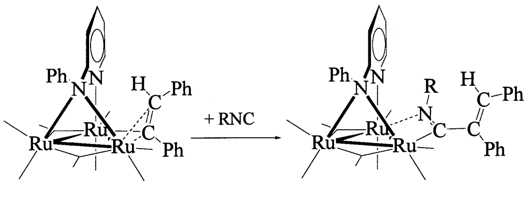
Though polymerization of phenylacetylene under hydrosilylation conditions has been also observed in a few instances with other metals,[51] the promoter effect of the silane as a co-catalyst remains unclear.

With triphenylsilylacetylene as the incoming substrate (and in the absence of silane), a rapid but poorly catalytic dimerization was observed (see Scheme 13), leading selectively to the (*E*)-1,4-bis(triphenylsilyl)but-1-en-3-yne, obtained pure as beautiful crystals appearing on the walls of the glassware. Here again, no intermediates could be detected and our approach to the mechanism had to rely on model studies. First, in order to test the mechanistic possibility of a vinylidene/acetylide coupling,[52] which should have generated a transient butenynyl intermediate,[53] we treated the hydrido complex with a preformed diyne whose insertion into the Ru−H bond was likely to give such an intermediate. Though a butenynyl complex was effectively isolated (Scheme 14),[54] it could not be regarded as a plau'sible intermediate since it was not possible to promote its reductive elimination as an enyne in the presence of an incoming alkyne.



Scheme 14. Activation of a diyne by insertion into an Ru−H bond and formation of a butenynyl ligand

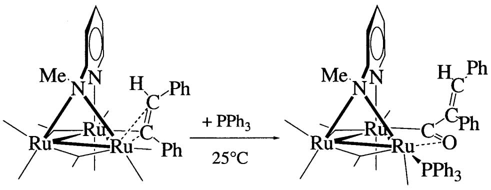
Though not firmly established, the alternate possibility of an alkenyl/acetylide coupling was preferred in light of the parallel observation of a facile alkenyl-group transfer from the alkenyl complex to the α-carbon atom of an incoming isocyanide (Scheme 15).[50][54]



Scheme 15. Alkenyl/isocyanide coupling giving an azabutadienyl ligand

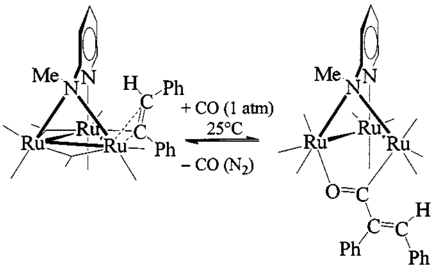
Here, the incorporation of the isocyanide ligand onto the $48e^-$ species occurs at 25 °C by an associative pathway consistent with a mechanistic scheme where the transient opening of the amido bridge (or another weak bond, vide infra) assists the incorporation of the ligand, whereas its subsequent reformation triggers C−C bond formation, in exact parallel with reactions observed earlier with halides and related ancillary ligands.

With the aim of verifying the generality of such a working hypothesis, we treated our alkenyl complex with triphenylphosphane and effectively observed that the incorporation of this ligand also caused migratory CO insertion of the alkenyl group (Scheme 16).



Scheme 16. Phosphane-induced migratory CO insertion of an alkenyl group

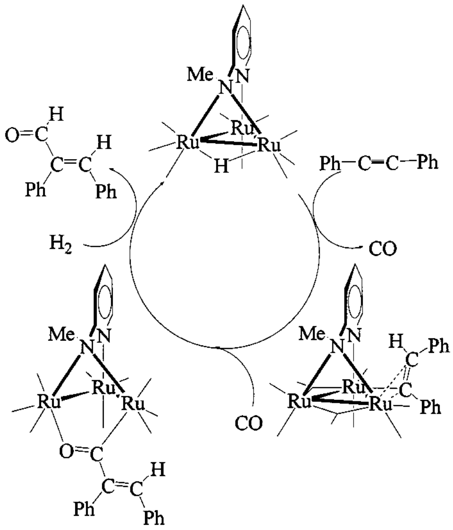
Though obtained within few minutes under very mild conditions, the resulting propenoyl complex proved to be the thermodynamic product of the reaction.[55] Evidence for the existence of a kinetic intermediate was obtained from additional experiments[55] including a preliminary kinetic study carried out by Basolo.[56] Further work indicated that, of course, CO gas itself is readily incorporated and promotes the same migratory insertion. Though the corresponding adduct is stable only under CO, we succeeded in crystallizing it under such conditions (Scheme 17).[50][55]



Scheme 17. CO-induced migratory CO insertion of an alkenyl group

Significantly, *two* carbonyl ligands were incorporated without a detectable intermediate. The fact that an open $50e^-$ cluster was obtained (rather than a closed $48e^-$ species bearing a terminal amido group) raised recurrent questions about the nature of the initial elusive adduct formed upon ligand addition to the alkenyl cluster complex. Indeed, let us remind ourselves that there are three types of weak bonds in this complex whose rupture is plausible: (i) the Ru−N bonds of the amido bridge, (ii) the π interaction between the alkenyl group and the cluster and (iii) the metal−metal bonds. Thus, hypotheses regarding the rupture of any of such bonds may be equally reasonable due to the probable similar magnitude of their respective enthalpies. However, we believe that a more realistic scheme involves *a global expansion of the structure by lengthening of several of these bonds without localized rupture*,[55] as independently demonstrated for another ligand-bridged triruthenium cluster complex.[57] Another notable feature, highlighted by the previous equilibrium, is the ease with which the propenoyl group migrates at the periphery of the cluster.

Following the isolation of the propenoyl adduct, we succeeded in releasing α-phenylcinnamaldehyde upon treatment with CO/H_2 mixtures under very mild conditions. The propenoyl complex could then be tied to a catalytic cycle for the hydroformylation of diphenylacetylene (Scheme 18).[55]



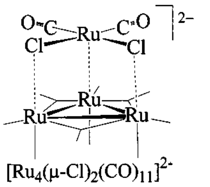
Scheme 18. Catalytic cycle for the hydroformylation of diphenylacetylene showing the isolated intermediates

Though the reaction could cycle catalytically, the viability of the system under non-optimized conditions was affected by a competitive CO insertion into the Ru−N bond of the methylaminopyridyl group, ending with the formation of an inactive carboxamido complex of lower nuclearity.

II. Aspects of the Chemistry of Carbonylhaloruthenium(II) Complexes

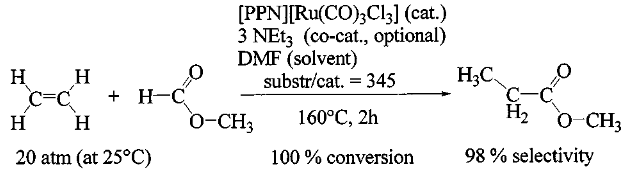
II.1 Evolution of $Ru_3(CO)_{12}$/Halide Mixtures under the Conditions of a Typical Hydroesterification Reaction

Studies reported in this section were undertaken in collaboration with Kalck and co-workers. Philippe Kalck was interested in the use of methyl formate as a valuable feedstock in organic synthesis. The "direct" addition of this substrate to olefins for the production of esters appeared to be a challenging reaction[58] that had been shown by Keim[17] to be catalyzed by $Ru_3(CO)_{12}$ alone or (albeit less efficiently) by the anion $[Ru_3(\mu\text{-}Cl)(CO)_{10}]^-$. A preliminary screening of the above-mentioned series of anionic triruthenium complexes incorporating halides, anilinopyridyl or alkoxypyridyl groups led us to focus on the $Ru_3(CO)_{12}$/[PPN]Cl system, which proved to be highly efficient provided that an amide-type solvent like DMF was used. During the course of preliminary experiments aimed at determining the optimum Ru/Cl ratio, we noted that the $[Ru_3(\mu\text{-}Cl)(CO)_9]^-$ reacts cleanly with an excess of halide at 60 °C to give the novel unsaturated dianionic species $[PPN]_2[Ru_4(\mu\text{-}Cl)_2(CO)_{11}]$ already shown in Scheme 3.[20][59] Strikingly, its structure, of an unprecedented type, gave the image of a mononuclear Ru^{II} complex "$Ru(CO)_2Cl_2$" supported on an anionic triruthenium unit "$[Ru_3(CO)_9]^{2-}$".



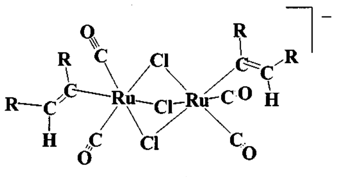
$[Ru_4(\mu\text{-}Cl)_2(CO)_{11}]^{2-}$

Intuitively, the liberation of such a fragment under catalytic conditions was thus conceivable. In fact, the above dianionic cluster species could be used alone as a catalyst precursor, just like other haloruthenium cluster complexes of the same series shown in Scheme 3. After overnight catalytic experiments, the principal species recovered in the reactor was the well-known carbido cluster $[Ru_6(C)(CO)_{16}]^{2-}$. Remembering that this inactive product had been previously detected by Dombek[1] at the end of syngas reactions using Ru/halide mixtures as catalyst precursors (vide supra), we reasoned that the active species in both systems might be the same. Then, different catalytic runs using $[PPN][HRu_3(CO)_{11}]^-$ and $[PPN][Ru(CO)_3X_3]$ (X = Cl, I) either separately, or as mixtures, led us to conclude that under the conditions of our hydroesterification reaction, the best precursor was $[PPN][Ru(CO)_3Cl_3]$ "alone".[59] It was thus appearing that the active species (still elusive) could be generated from either Ru^0 or Ru^{II} precursors. With $[PPN][Ru(CO)_3Cl_3]$, the reaction started without an induction period and proved to be very efficient (Scheme 19).



Scheme 19. Experimental conditions and performances of the catalytic hydroesterification reaction

A DMF complex $[PPN][Ru(CO)_2Cl_3(DMF)]$ appeared to be readily formed by decarbonylation of the above precursor. Interestingly, three closely related alkyl complexes $[PPN][Ru_2(\mu\text{-}Cl)_3(CO)_4RR']$ (R = Et or Me; R′ = Et or Me) were subsequently intercepted in the reactor by quenching the catalytic reaction as the system reached its optimum activity.[60] It was shown that, under the reaction conditions, the alkyl moieties were derived principally from ethylene (by insertion into an Ru−H bond) but also from the alkyl formate [by cleavage of the $O-C(sp^3)$ bond]. Effectively, at that time, the only way to exclusively obtain the dimeric ethyl complex in a pure form proved to be the catalyzed addition of *ethyl* formate to ethylene.



$[Ru_2(\mu\text{-}Cl)_3(CO)_4(\eta^1\text{-}RC{=}CHR)_2]^-$

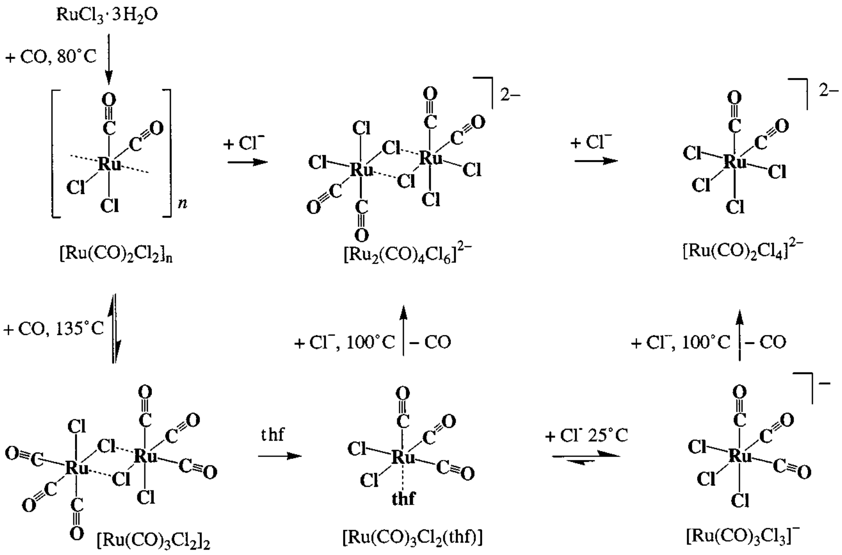
It was amazing to realize that a catalytic run performed in 1997 led to the discovery of the existence of a simple yet hitherto unknown species, some thirty years after its antecedent $[PPN][Ru(CO)_3Cl_3]$(!). Clearly, this revealed that the reactivity of carbonylchlororuthenium(II) species toward unsaturated organic substrates had not been examined in detail, or, at least needed to be revisited.

II.2 Pioneering Observations on Carbonylhaloruthenium(II) Complexes

The present state of knowledge of the chemistry of carbonylchlororuthenium(II) complexes rests on the important pioneering discoveries made in the 1960s and 1970s by several groups[22] amongst which we recognize names that have marked the development of this field: Chatt,[61] Halpern and James,[62] Bruce and Stone,[63] Braca,[64] Calderazzo,[65] Johnson and Lewis,[66] Collmann and Roper,[67] and Wilkinson.[68]

Equilibria involving the principal binary carbonylchloro derivatives are shown in Scheme 20. Chatt[61] was the first to observe that bubbling CO through a solution of $RuCl_3 \cdot 3\,H_2O$ at 85 °C gives a red solution containing a structurally ill-defined polymeric complex $[Ru(CO)_2Cl_2]_n$. Prolonged treatment with CO at 120−140 °C[63] gives the $16e^-$ tricarbonyl unit "$Ru(CO)_3Cl_2$", which spontaneously stabilizes itself by forming halide bridges to give $[Ru(CO)_3Cl_2]_2$.[69] Since the reverse decarbonylation is also operative at high temperature, a mixture of $[Ru(CO)_2Cl_2]_n$ and $[Ru(CO)_3Cl_2]_2$, known as the "yellow solution",[70] is generally obtained. The only way to drive the equilibrium toward the more CO-rich derivative is thus to pursue the carbonylation at room temperature.[59] As originally reported by Bruce and Stone,[63] splitting of the dimer $[Ru(CO)_3Cl_2]_2$ by a donor solvent like THF gives the nice crystalline complex $Ru(CO)_3Cl_2(thf)$ from which THF may be subsequently displaced by a halide anion to give the anionic species $[Ru(CO)_3Cl_3]^-$.

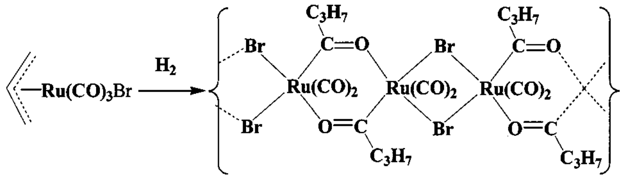
In fact, the complexes shown in Scheme 20 represent the principal possibilities to stabilize the $14e^-$ fragment "$Ru(CO)_2Cl_2$" by using all possible combinations of CO and Cl^- ligands. For a long time, these complexes were mainly regarded as intermediates for the preparation of more elaborate species.[22] For example, ruthenium chemists have long been using the above-mentioned "yellow solution" for the preparation of $Ru_3(CO)_{12}$ (by reduction with CO in the presence of zinc as a halide acceptor),[70] whereas fascinat-



Scheme 20. Interconversion between the principal known carbonylhaloruthenium(II) complexes

ing new complexes are still made nowadays by treatment of $[Ru(CO)_2Cl_2]_n$ with sophisticated phosphanes.[71]

In the early work of Pino et al.[72] we find a rare example of a carbonylhaloruthenium(II) complex bearing a hydrocarbon fragment as the only additional ligand. This is the allyl species $Ru(C_3H_5)(CO)_3Br$, prepared by oxidative addition of allyl bromide to $Ru_3(CO)_{12}$. Such a compound was shown to act as a catalyst precursor for olefin hydrogenation and isomerization,[64c] whereas its reaction with hydrogen gave a structurally ill-defined polymeric acyl species resulting from a hydrogenation of the allyl moiety followed by migratory CO insertion.[64c]

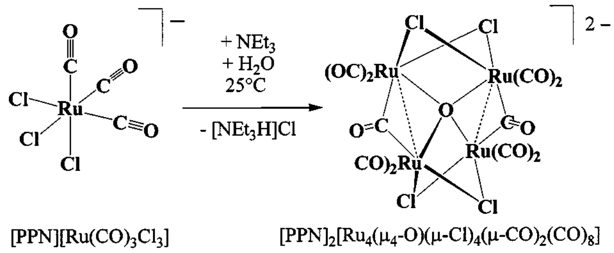


Further treatment of the latter with CO/methanol led to the stoichiometric formation of esters, thus prefigurating the possibility to achieve hydroesterification reactions.

II.3 New Findings in the Footsteps of the Pioneers

II.3.1 Facile Activation of Water

In attempts to trace the evolution of $[PPN][Ru(CO)_3Cl_3]$ under the conditions of a typical hydroesterification reaction, it was noted that treatment of this complex with triethylamine (the optional co-catalyst) resulted in *halide displacement rather than CO substitution*.[73] This provided an indication that the *neutral* fragment "$Ru(CO)_3Cl_2$" might be the reacting entity, whereas the weakly coordinated halide anion could be regarded as a lightly stabilizing ligand for the neutral unit. Furthermore, with wet triethylamine, the known[20] oxo complex $[PPN]_2[Ru_4(\mu_4\text{-}O)(\mu\text{-}Cl)_4(\mu\text{-}CO)_2(CO)_8]$ was obtained,[74] which was indicative of a facile activation of water accompanied by reductive elimination of HCl, trapped as $[NEt_3H]Cl$.



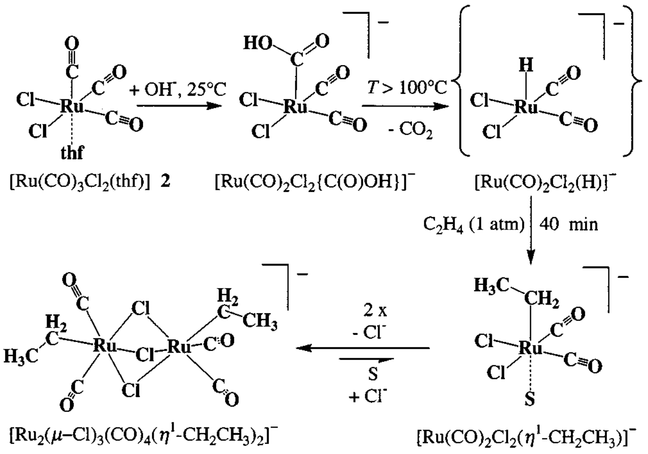
Scheme 21. Facile activation of water by a carbonylchlororuthenium(II) complex with formation of an oxoruthenium(II) species

Though not fully understood, the reaction was thought to involve initial attack of OH^- ions at the carbon atom of a coordinated CO ligand.

II.3.2 A Simple Route to "Unprotected" Alkyl and Alkenyl Complexes

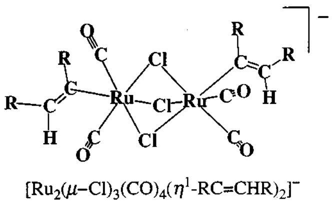
An obvious analogy of the preceding reaction with the basic principle of the water gas shift[24] led us to attempt the generation of a transient hydrido species by treatment of the neutral complex $[Ru(CO)_3Cl_2(thf)]$ with KOH and to examine its ability to insert olefins and, by extension, any unsaturated organic substrate. The logical sequence we envisaged (Scheme 22) effectively allowed a clean preparation of the anionic ethyl complex $[Ru_2(\mu\text{-}Cl)_3(CO)_4(CH_2CH_3)_2]^-$ in a one-pot procedure requiring no ethylene pressure.[75]

Subsequently, it was not a problem to extend the reaction to the case of alkynes and to observe in such cases a parallel



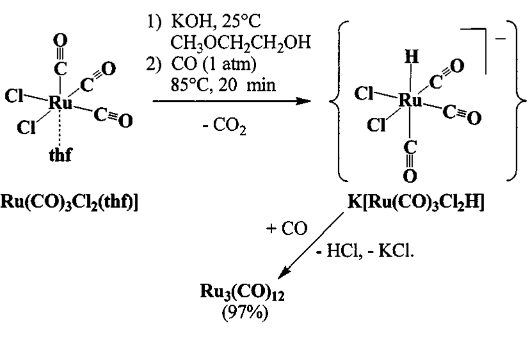
Scheme 22. Proposed mechanism for the formation of the isolated alkyl complex

cis insertion leading to the corresponding isostructural alkenyl derivative $[Ru_2(\mu\text{-}Cl)_3(CO)_4(RC{=}CHR)_2]^-$.[75]



II.3.3 Facile Interconversion $Ru^{II}-Ru^{0}$

A (naive) tentative attempt to intercept the transient hydrido species, generated in the preceding reaction by decarboxylation of the intermediate hydroxycarbonyl species in the presence of CO (and in the *absence* of any unsaturated substrate), led us to observe the formation of $Ru_3(CO)_{12}$ in quantitative yield(!).

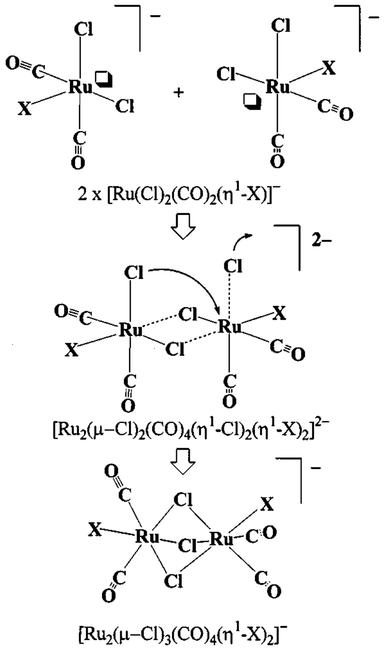


Scheme 23. A facile reduction of Ru^{II} to Ru^{0}

Apart from the interest in the procedure on account of its performance and of the established possibility to run the reaction directly from commercial $RuCl_3$,[75] an important extension of this finding was to establish that an extremely facile reduction of carbonylhaloruthenium(II) precursors to Ru^{0} intermediates can take place by reductive elimination of HCl as soon as traces of water are present. This may have relevance to various catalytic systems involving carbonylhalo derivatives.[76]

II.3.4 A New Binary Carbonylchlororuthenium(II) Species

An intriguing point in the sequence shown in Scheme 22 was the fact that dimerization of the monoanionic alkyl intermediate $[Ru(CO)_2Cl_2(\eta^1\text{-}X)]^-$ (X = R) (observable only in a donor solvent like DMF) gave a monoanionic dimer $[Ru_2(CO)_4(\mu\text{-}Cl)_3(\eta^1\text{-}X)_2]^-$ (by loss of a halide ion, see Scheme 24) rather than the expected dianionic dimer "$[Ru_2(CO)_4(\mu\text{-}Cl)_2(Cl)_2(\eta^1\text{-}X)_2]^{2-}$" (X = R), which might have been isostructural with the known "allchloro" (X = Cl) analog $[Ru_2(CO)_4(\mu\text{-}Cl)_2(Cl)_4]^{2-}$shown in Scheme 20.

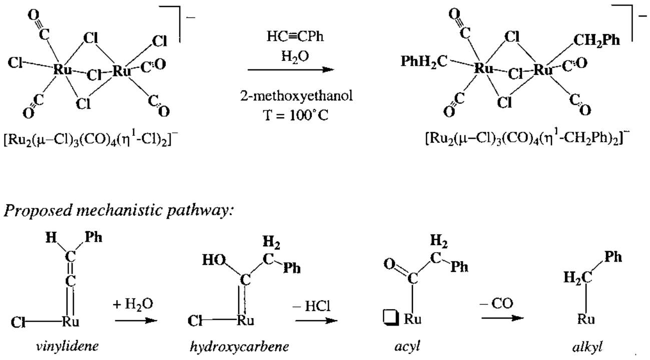


Scheme 24. Aggregation of unsaturated 16-e⁻ haloruthenium fragments and formation of a face-sharing bi-octahedral species (FSBO); the square box appearing in the scheme denotes a vacant coordination site on the metal center

Conversely, the fact that the hypothetical allchloro anion $[Ru_2(CO)_4(\mu\text{-}Cl)_3(\eta^1Cl)_2]^-$ had never been intercepted was also intriguing. In fact, we found that such a compound does exist, and can be simply prepared by thermal decarbonylation of $[Ru(CO)_3Cl_2(thf)]$ in the presence of the appropriate amount of halide (1/2 equiv. per Ru unit).[75] It can be regarded as the simplest association of two neutral units "$Ru(CO)_2Cl_2$" that are lightly stabilized by a weakly coordinating halide.

II.3.5 A Simple Route to Vinylidenes

The simple "non-hydridic" complex $[(PPh_3)_2N][Ru_2(\mu\text{-}Cl)_3(CO)_4(\eta^1\text{-}Cl)_2]$ allows the facile activation of alkynes to give *vinylidenes.*[75] To date, the latter intermediates have not yet been intercepted. Yet, we do observe *the product of their* *clean hydration involving C−C bond activation.* Typically, activation of phenylacetylene gives the benzyl derivative $[Ru_2(CO)_4(\mu\text{-}Cl)_3(\eta^1\text{-}CH_2Ph)_2]^-$ (Scheme 25). The mechanism we propose for such a reaction is fully consistent with the one previously established by Bruce,[77] Bianchini[78] and Esteruelas.[79] In the present case, a transient opening of the halide bridge is believed to provide the vacant site required for alkyne activation, whereas its closure assists the final CO loss.



Scheme 25. Activation of the C−C triple bond of a terminal alkyne by hydration of the transient vinylidene; the square box appearing in the scheme denotes a vacant coordination site on the metal center

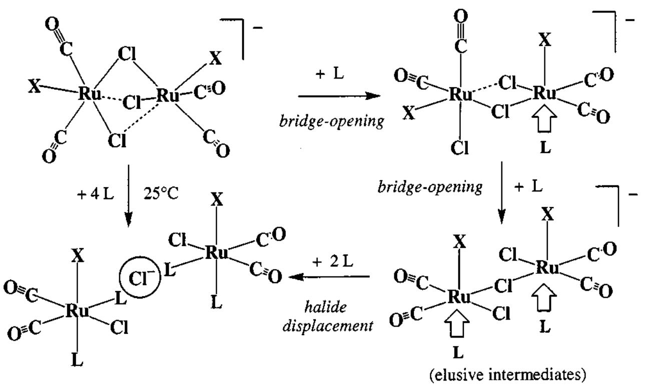
Interestingly, related ruthenium(II) halide complexes have been recently shown by Wakatsuki[80] to catalyze the hydration of alkynes to produce aldehydes and ketones. Unobserved carbenoid species have also been recently postulated as key intermediates in the construction of polycyclic ring systems from enynes involving $[Ru(CO)_3Cl_2]_2$ as a catalyst precursor.[21a]

II.3.6 Aspects of the Reactivity of FSBO (Face-Sharing Bi-Octahedral) Complexes

While the aggregation of carbonylhaloruthenium(II) species is understood to be a means for the unsaturated organometallic fragments to relieve their unsaturation, the reverse reaction, namely, a transient opening of halide bridges, constitutes the main pathway for substrate activation, as illustrated by the preceding reaction (Scheme 25).

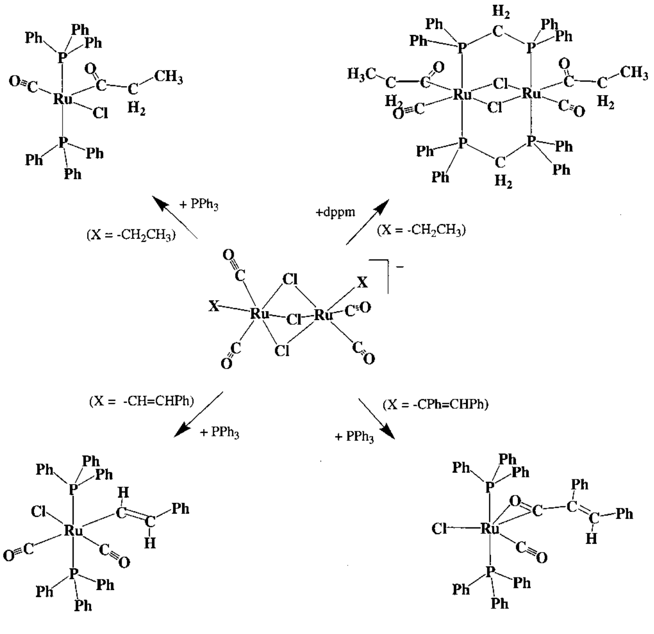
A notable structural feature is that the Ru−Cl bridge bonds that are *trans* to the sigma donor (alkyl, alkenyl) are significantly longer than those *trans* to CO. This suggests the possibility of a selective opening of these bonds through a sequence (Scheme 26) that is reminiscent of the one proposed by Cotton and Poli for related FSBO species.[81]

Thus, the masked unsaturation of these aggregates also allows the facile formation of adducts with a variety of donor ligands, ultimately leading to more elaborate complexes. With L = phosphanes, a rearrangement occurs within the coordination sphere of the final mononuclear species to give the *trans*-P isomer only. If X is an alkyl group, the phosphane also induces migratory CO insertion, giving the $16e^-$-acyl species $[Ru\{C(O)R\}(PR_3)_2(CO)Cl]$ (Scheme 27).[60]



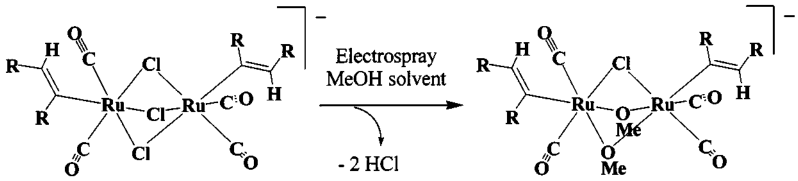
Scheme 26. General scheme for the reaction of face-sharing bi-octahedral species with nucleophiles

If X is an alkenyl group, whether it migrates or not depends on the nature of the starting alkyne. As shown in Scheme 27, we have been able to obtain the alkenyl complex $[Ru(CH=CHPh)(PPh_3)_2(CO)_2Cl]$ from phenylacetylene, and the propenoyl complex $[Ru\{\eta^2C(O)-PhC=CHPh\}(PPh_3)_2(CO)Cl]$ from diphenylacetylene, and to determine their respective structures.[82] It is noteworthy that the same complexes were originally prepared by Ros[83] from $RuH(CO)Cl(PR_3)_2$. The chemistry of these and related derivatives is currently being investigated by Werner[84a,b], Esteruelas[84] and Caulton.[85] With our procedure, retention of the dinuclear structure is possible by using a bridging ligand like bis(diphenylphosphanyl)methane, as exemplified by the facile synthesis of the dimeric acyl complex $[Ru_2(\mu\text{-}Cl)_2\{C(O)CH_2CH_3\}_2(\mu\text{-}dppm)_2(CO)_2]$ (Scheme 27).[86] We are currently exploring the reactivity of the dimers $[Ru_2(\mu\text{-}Cl)_3(CO)_4(\eta^1\text{-}X)_2]$ with a variety of other ancillary ligands and substrates.



Scheme 27. Facile reactions of alkyl- and alkenylcarbonylchloro complexes with phosphanes

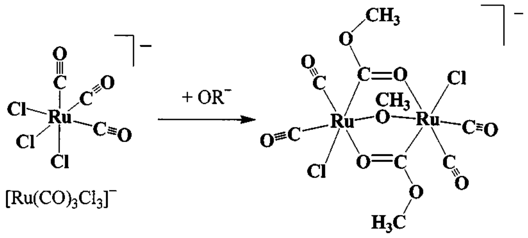
Another aspect of their reactivity is the facile replacement of halides by methoxide ions, which we have observed in some instances. For example, during the course of electrospray mass-spectral analyses of crystals of the dimeric alkenyl complex $[(PPh_3)_2N][Ru_2(\mu\text{-}Cl)_3(CO)_4(\eta^1\text{-}PhC{=}CHPh)_2]$ (whose structure had been ascertained by X-ray diffraction) we observed the ion $[Ru_2(\mu\text{-}Cl)(\mu\text{-}OMe)_2(CO)_4(\eta^1\text{-}PhC{=}CHPh)_2]^-$ when methanol was used as a solvent for the introduction of the samples (Scheme 28).



Scheme 28. Facile replacement of halides by methoxide ligands under the experimental conditions of electrospray mass spectrometry

We are currently exploring various possibilities to induce a systematic replacement of halides by other ancillary ligands through activation of hydrogen−element bonds, starting from compounds like thiols, imidazoles, aldehydes, etc. A full replacement of halides by methoxide ions has been reported by Süss-Fink in related methoxycarbonyl complexes.[87]

Finally we wish to conclude this section by specifying that groups other than the halides may participate in the formation of bridges between the Ru^{II} centers. Typically, in the treatment of $[PPN][Ru(CO)_3Cl_3]$ by methoxide ions, Süss-Fink isolated a complex which probably results from a transformation of the unobserved primary adduct (which we believe is $[PPN][Ru\{C(O)OMe\}(CO)_2Cl_2]$). Once again, a monoanionic aggregate (rather than a dianionic species) is obtained after loss of a halide ion. Interestingly, the new compound bears *terminal* halides and *bridging* methoxycarbonyl groups (Scheme 29).[87]



Scheme 29. Formation of methoxycarbonyl bridges rather than halide bridges in the stabilization of unsaturated carbonylhalo(methoxycarbonyl)ruthenium(II) fragments

Of course, we cannot exclude the same type of aggregation when the hydroxycarbonyl adduct we have observed (Scheme 22) is generated in a noncoordinating solvent. In that case, the whole sequence of Scheme 22 would proceed entirely through dimeric units.

Conclusion

A tantalizing observation about carbonylruthenium clusters incorporating halides or related hard bases as *hemilabile* ancillary ligands is that, in spite of their fascinating reactivity, their ability to catalyze substrate transformations with retention of the polymetallic structure is effective only under very mild conditions that are still too close to those liable to cause their degradation. An illustration of this can be found in our recent report of a *cluster-mediated* hydroformylation of diphenylacetylene.

Significantly, we now find that simple carbonylhaloruthenium(II) derivatives, easily generated from carbonylruthenium (Ru^0)/halide mixtures or by direct carbonylation of $RuCl_3$, are prone to react with olefins or alkynes in the presence of a simple source of hydride to give trappable *alkyl* or *alkenyl* complexes, whereas transient *vinylidene* species are formed from alkynes in the absence of a hydride source. These unsaturated complexes tend to relieve their unsaturation by forming aggregates whose dissociation may in turn release reactive organometallic fragments. Thus, we believe such complexes will provide realistic models for elementary transformations occurring in applied catalysis involving Ru/halide mixtures. An interplay between Ru^{II} and Ru^0 species may be expected in these multicomponent systems, due to the facile and reversible reductive elimination of HCl. Further work aimed at understanding such processes is in progress.

Acknowledgments

The author wishes to express his gratitude to all colleagues and coworkers who have made an important contribution to the research work summarized here, and, in particular, Herbert D. Kaesz, Noël Lugan, Jean-Jacques Bonnet, Philippe Kalck, Fred Basolo, Jean-Yves Saillard and Jean-François Halet. Financial support from the CNRS is also gratefully acknowledged.

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