Kinetics and mechanisms of halide ion catalysis of CO substitution reactions in $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ metal carbonyl clusters

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The results of kinetic studies on ligand substitution in $[M_3(CO)_{11}X]^-$ complexes (M = Ru, Os; X = Cl, Br, I) are summarized. The $[Os_3(CO)_{11}X]^-$ complexes react with PPh_3 under mild conditions to initially yield monosubstituted products $[Os_3(CO)_{10}(PPh_3)X]^-$. The rate of CO substitution obeys a first-order equation with respect to the concentration of the complex and does not depend on the ligand concentration. The rates of the reactions decrease in the order Cl > Br > I with $\Delta H^{\neq}$ values increasing from 15 to 18 kcal mol^{-1} and $\Delta S^{\neq}$ values varying from −19 to −13 cal mol^{-1} K^{-1}. The enhanced reactivities of these complexes as well as the low activation energies and negative activation entropies are discussed in terms of the effects of μ-X bridge formation on the transition state of the reaction. Reactions of PPN$[Ru_3(CO)_{11-x}(Cl)]$ (PPN is the bis(triphenylphosphine)iminium cation; x = 0, 1) and PPN$[Ru_3(CO)_9(\mu_3\text{-}I)]$ with alkynes are also reported. The reactivities of alkynes follow the order BuC≡CH ≥ PhC≡CH >> EtC≡CEt ≥ PhC≡CPh. The higher rates of the reactions of monosubstituted acetylenes compared with those of their disubstituted analogs are explained by agostic interaction between the metal atom and the C—H bond in the reaction transition state and by steric effects. The results obtained attest that the reaction with alkynes occurs *via* intermediates containing halide bridges and that μ_3-halide complexes are more reactive than μ_2-halide complexes.

Key words: metal carbonyl clusters; osmium, ruthenium, alkynes; kinetics; catalytic effect of halide ions.

This paper is intended to provide a limited review of our recent studies[1a,b] on the effect of halide ions on the kinetics and mechanism of CO substitution in the $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ metal clusters. Our interest in CO substitution of metal carbonyl halides dates back to 1961, when we reported[2] the rates and mechanisms of reactions of $Mn(CO)_5X$ (X = Cl, Br, I). The results of this study showed that the reactions proceed by dissociative pathways, and that the rates decrease in the order Cl > Br > I. The variations in the reactivity of compounds was explained in terms of electronegativities and polarizabilities of the halide ions, such that the most electronegative and least polarizable Cl^- results in the lowest electron density on Mn and thus less back π-bonding to CO and the weakest M—C bond. This is supported by the fact that rates of reactions increase as the νCO values in the IR spectra increase. However, this paper did not consider the contribution of the transition state to the reaction rate. It was later suggested[3] that site preference in the transition state is more important for determining reactivities of the compounds than the ground state. This suggestion was also supported[4a—c] by molecular orbital calculations. It appeared that *cis*-labilization of CO in $Mn(CO)_5X$ is the greatest when X has potential π-donor character, due to the overlap of its lone pair orbital with an appropriate vacant Mn orbital in the transition state, as we suggested earlier[4d] for dissociative reactions of Werner complexes.

Recently, there has been much greater research interest in metal carbonyl clusters activated by nucleophilic anions as potential homogenous catalysts.[5] In 1972, Prof. P. Chini and co-workers[6] during their seminal research on the syntheses of metal carbonyl clusters were the first to report that halide ions activate clusters such as $Rh_6(CO)_{16}$. They found that in THF solution this cluster readily reacts with halide ions at ambient temperatures to afford $[Rh_6(CO)_{15}X]^-$. However, the reactivities of these anionic clusters have not been studied, except for their role as intermediates in the syntheses of larger and more complicated metal carbonyl clusters. The significance of the nucleophilic activation was noted in 1980 by Kaesz,[7] who studied CO substitution in $Ru_3(CO)_{12}$.

It was believed that activation of the cluster is due either to a nucleophilic attack of the anion on a CO carbon atom to weaken the M—C bond,[8] or it is due to incorporation of the anion in the cluster as an ancillary ligand.[9] As early as at the end of the 1960s we showed[10] that CO substitution in $Fe(CO)_2(NO)_2$ is catalyzed by halide ions, presumably by attack on the CO carbon atom to weaken the Fe—C bond. However, it does appear that the role of the nucleophile in activating CO

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substitution in metal carbonyl clusters is that of an ancillary ligand in the anionic cluster. In order to elucidate the manner in which the halide ligand serves to labilize the substitution of CO groups in clusters, we decided to investigate the kinetics and mechanism of CO substitution in $[M_3(CO)_{11}X]^-$ (M = Os, Ru; X = Cl, Br, I). A brief review of our findings and the conclusions reached are presented here.

Reactions of CO substitution in $[Os_3(CO)_{11}X]^-$ complexes (X = Cl, Br, I)

The reactions of CO substitution in $[M_3(CO)_{11}X]^-$ (M = Os, Ru) are orders of magnitude faster than the corresponding reactions of $M_3(CO)_{12}$ (see Ref. 11). This is an unexpected behavior because both for a dissociative and for an ordinary second-order associative pathway it would appear that the anionic complex should be the slower to react. For example, the negative charge on the complex puts a greater electron density on the metal which causes more back π-bonding to CO resulting in a stronger M—C bond and a slower rate of dissociation for CO replacement. Likewise an associative pathway is also expected to give rise to a slower reaction for the anionic complex, because a nucleophile will attack a neutral substrate more readily than it will attack a negatively charged substrate.

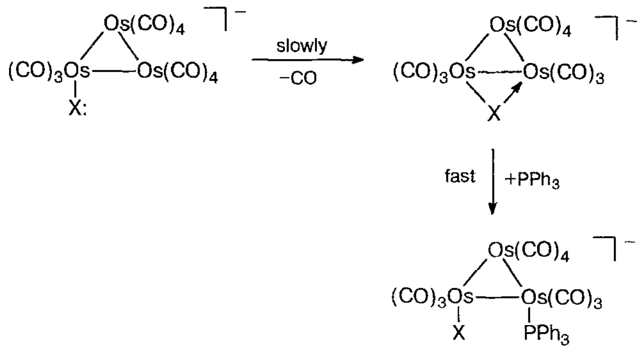
It therefore appeared to us that the anionic complexes should be subjected to detailed investigation in an attempt to understand their apparent anomalous behavior. The first complexes chosen for study were $[Os_3(CO)_{11}X]^-$ (X = Cl, Br, I), because their reactions were of such a rate that they could be conveniently monitored by changes in the IR spectra in the region of C—O stretching. It was found that the rate of reaction (1) is described by a first-order equation with respect to the concentration of $[Os_3(CO)_{11}X]^-$ and is zero-order with respect to the PPh_3 concentration.

$$[Os_3(CO)_{11}X]^- + PPh_3 \longrightarrow [Os_3(CO)_{10}(PPh_3)X]^- + CO \quad (1)$$

X = Cl, Br, I

Such a rate law generally indicates a dissociative pathway, however the activation parameters, *viz.* small $\Delta H^{\neq}$ values (15—18 kcal mol^{-1}) and negative $\Delta S^{\neq}$ values (−19 to −13 cal mol^{-1} K^{-1}), are typical of associative processes. This seemingly peculiar kinetic result now allows us to offer a possible explanation for the anomalous behavior mentioned above that the anionic complex reacts much faster than does the corresponding neutral cluster. Considering the well known property of halide ions to act as bridging ligands between neighboring metals,[12] one may infer that the rate-determining step may involve intramolecular displacement of CO by the adjacent halogen ligand as it forms a bridged intermediate. This mechanism is consistent with the observed first-order rate law; in addition, one of the three unshared electron pairs of the halide ion can readily attack the neighboring metal to maintain its stable electron count as it loses CO with its σ-bonded electron pair. The proposed mechanism for reaction (1) giving the monosubstituted product is depicted in Scheme 1.

Scheme 1



As mentioned earlier, although the rate of reaction (1) obeys first-order kinetics, low $\Delta H^{\neq}$ values and negative $\Delta S^{\neq}$ values are unusual for dissociative reactions with evolution of CO. Such reactions are known[13] to generally have $\Delta H^{\neq}$ values of ~30 kcal mol^{-1} and positive $\Delta S^{\neq}$ values. These low $\Delta H^{\neq}$ values and negative $\Delta S^{\neq}$ values suggest that there is considerable intramolecular reorganization in the reaction transition state, which energetically favors CO dissociation from the metal center. For mononuclear complexes, $M(CO)_5X$, where it is believed[3,4] that the overlap of an unshared pair orbital with an appropriate empty metal orbital stabilizes the reaction transition state, M—X bond strengthening and geometrical relaxation may also occur, but these reactions all have large $\Delta H^{\neq}$ values and very positive $\Delta S^{\neq}$ values.[2,14] The differences in activation parameters suggest that the halide ligands play a different role in activating CO in mononuclear complexes from that in metal cluster complexes. Similar activation parameters were reported[15] for CO substitution in $[Ru_3(CO)_{11}(CO_2Me)]^-$ with $P(OMe)_3$, for which the rate-determining step is CO dissociation from the metal complex. Although it was speculated that the enhanced reactivity of the metal cluster methoxycarbonyl adduct may perhaps result from *cis*-labilization of the methoxycarbonyl group, the structure of the active intermediate remains unknown. Intramolecular CO substitution in the $Os_3(CO)_{11}$dppm complex (dppm = $Ph_2PCH_2PPh_2$) has also been reported.[16] This reaction is much faster than that of $Os_3(CO)_{11}L$ (L — phosphorus-containing ligands) for which $\Delta H^{\neq}$ = 22 kcal mol^{-1} and $\Delta S^{\neq}$ = −9.6 cal mol^{-1} K^{-1}. The enhanced reactivity and the negative $\Delta S^{\neq}$ value were explained by the attack of the free P atom of dppm on an adjacent Os atom in the transition state of the reaction.

These results and the isolation[17] of the $[Os_3(\mu\text{-}NCO)(CO)_{10}]^-$ complex and other similar species[9,18] suggest that anions can activate CO abstraction from metal clusters by stabilizing the reaction transition state through the formation of an X^- bridge, since this transformation of bonds would coordinatively saturate the reaction transition state. The small $\Delta H^{\neq}$ values and the very negative $\Delta S^{\neq}$ values for these reactions indicate a great extent of X—Os bond formation in the transition state.

As indicated earlier, CO substitution in $Os_3(CO)_{12}$ is orders of magnitude slower[11] than the corresponding reactions of $[Os_3(CO)_{11}X]^-$. Furthermore the reactions of $Os_3(CO)_{12}$ undergo a dissociative pathway with $\Delta H^{\neq}$ = 38.6 kcal mol^{-1} and $\Delta S^{\neq}$ = 24.2 cal mol^{-1} K^{-1}. Qualitative observations indicate that $Os_3(CO)_{11}L$ compounds react at about the same rates as the parent cluster. These results show that replacement of CO by a stronger σ-donor phosphorus-containing ligand does not significantly affect the reactivity of the cluster. It was concluded that the Os—CO bonds in these anion complexes were not disturbed significantly, based on an X-ray structural study of $[Os_3(CO)_{11}X]^-$ (X = Br, I).[19] That the replacement of CO by a halide ion has a dramatic effect on the rate of CO substitution, whereas PR_3 does not, is probably due to the fact that the P atom does not possess a pair of electrons to interact with the neighboring Os atom and assist CO displacement. Thus, it appears that at least for the present the mystery of halide ion activation can be given a possible explanation.

Mechanisms of reactions of triruthenium carbonyl halide clusters with alkynes

CO substitution in $[Ru_3(CO)_{11}X]^-$ clusters is much faster than in the corresponding Os complexes discussed in the previous section. For this reason reactions of Ru-containing complexes with PPh_3 are too fast to be studied by conventional methods. Therefore, for these complexes, the slower reactions with alkynes were investigated (reactions (2)—(4)).[1b]

$$[Ru_3(CO)_{11}(Cl)]^- + RC{\equiv}CR' \rightarrow \rightarrow [Ru_3(CO)_9(\mu\text{-}Cl)(\mu\text{-}\eta^2\text{-}RC{\equiv}CR')]^- + 2\ CO \qquad (2)$$

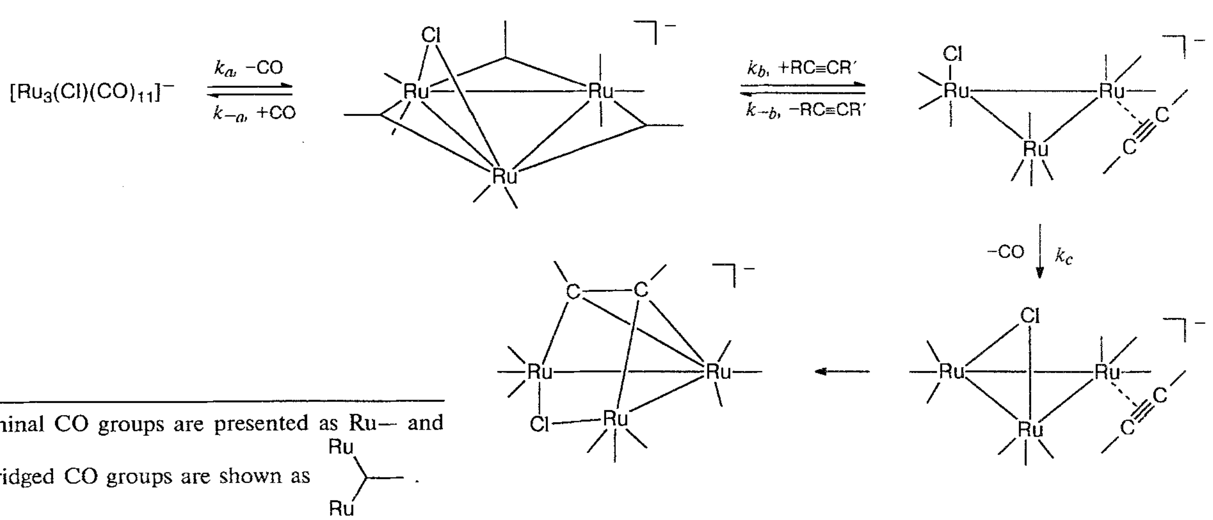
$$[Ru_3(CO)_{10}(\mu\text{-}Cl)]^- + RC{\equiv}CR' \rightarrow \rightarrow [Ru_3(CO)_9(\mu\text{-}Cl)(\mu\text{-}\eta^2\text{-}RC{\equiv}CR')]^- + CO \qquad (3)$$

$$[Ru_3(CO)_9(\mu_3\text{-}I)]^- + PhC{\equiv}CPh \rightarrow \rightarrow [Ru_3(CO)_9(\mu\text{-}I)(\mu\text{-}\eta^2\text{-}PhC{\equiv}CPh)]^- \qquad (4)$$

It should be mentioned that complexes based on a triruthenium framework are the most thoroughly studied[5] systems with respect to anion activation. The bulk of this research has dealt with syntheses and homogeneous catalysis, but a qualitative thermodynamic investigation[20] has also been carried out and two recent kinetic studies have been reported. One of these papers[21] deals with reactions of $Ru_3(CO)_{12}$ with PPNX to form $[Ru_3(CO)_{12-a}X]^-$ (a = 1 to 3), while the other[22] reports the kinetics of catalytic hydrogenation of PhC≡CPh using $Ru_3(CO)_8(\mu\text{-}H)(\mu_3\text{-}ampy)PPh_3$ (ampy is 2-amino-6-methylpyridine). To our knowledge no detailed kinetic study had been reported on the reactivities of triruthenium carbonyl halide anionic clusters. This prompted us to study reactions of these clusters with alkynes.

$[Ru_3(CO)_{11}(Cl)]^-$. It has been reported previously[18c,d] that halide ions can promote reactions of $[Ru_3(CO)_{12}]$ with alkynes; the products of reactions (2)—(4), along with the products of further halide displacement were fully characterized. Plots of $\ln A_t$ vs. time for the reactions of $[Ru_3(CO)_{11}(Cl)]^-$ with alkynes (see reaction (2)) do not yield straight lines. Instead, the reaction becomes slower as more CO is evolved. Since

Scheme 2*



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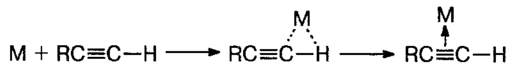
* Teminal CO groups are presented as Ru— and the bridged CO groups are shown as Ru Ru .

the rate of the reaction depends on the CO concentration, the kinetic data were obtained under constant CO pressure (p_{CO}). It was found that the rate of the reaction increases with an increase in the concentration of alkyne and decreases with an increase in p_{CO}. Plots of $1/k_{os}$ *vs.* p_{CO}/[alkyne] yield straight lines. These results are consistent with a reaction mechanism (Scheme 2), where $[Ru_3(CO)_{11}(Cl)]^-$ loses a CO ligand to form $[Ru_3(CO)_{10}(\mu\text{-}Cl)]^-$, which then reacts with alkyne to form the reaction product. The initial step of CO substitution is apparently similar to that described in the previous section for the reaction between $[Os_3(CO)_{11}X]^-$ and PPh_3. Since RC≡CR is a poorer nucleophile than PPh_3, CO more favorably competes with RC≡CR for the active intermediate and, in the case of alkynes, the return to the starting substrate may occur in the initial equilibrium step.

Kinetic data show that the rate of reaction (2) for various alkynes increases in the order PhC≡CPh ≤ EtC≡CEt ≪ PhC≡CH ≤ BuC≡CH. The reactivities of these alkynes are expected to be largely determined by their nucleophilicities, but the experimental results do not support this. For example, EtC≡CEt is a stronger nucleophile than PhC≡CPh, yet they both react with triruthenium carbonyl halide clusters at about the same rate. This is also true of BuC≡CH *vs.* PhC≡CH, which react at about the same rate although alkyl groups are more electron-donating than phenyl.

Larger differences in rates were observed between the reactions of disubstituted acetylenes and monosubstituted acetylenes. The fact that the reactions of monosubstituted acetylenes are faster may be partially attributed to steric restrictions caused by substituents in the disubstituted analogs. Another factor increasing the rates of the reactions of monosubstituted acetylenes is their ability to form "agostic bonds" in the reaction transition state (reaction (5)) which is impossible for disubstituted acetylenes.

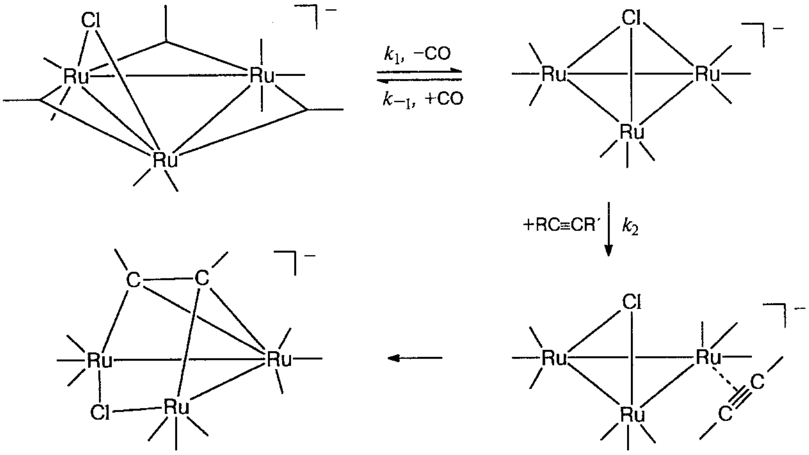

$$\mathrm{M + RC{\equiv}C{-}H \longrightarrow RC{\equiv}\overset{M}{C}{-}H \longrightarrow RC{\equiv}\overset{M}{C}{-}H} \qquad (5)$$

Such C—H/metal interaction was observed in the reactions of alkenes with metal complexes.[23] Kinetic isotope effects were also reported for the reactions of C_6H_6/C_6D_6 with unsaturated metal centers.[24] The reaction of PhC≡CD with $[Ru_3(CO)_{11}(Cl)]^-$ was studied, however, its rate did not differ from that of a similar reaction of PhC≡CH. Although this negative result does not support the proposed agostic interaction, such a reaction pathway cannot be excluded. Isotope effects for this type of interaction are expected to be small, and since the rate of a reaction is a combination of different elementary steps, it is not surprising that a kinetic isotope effect cannot be experimentally detected.

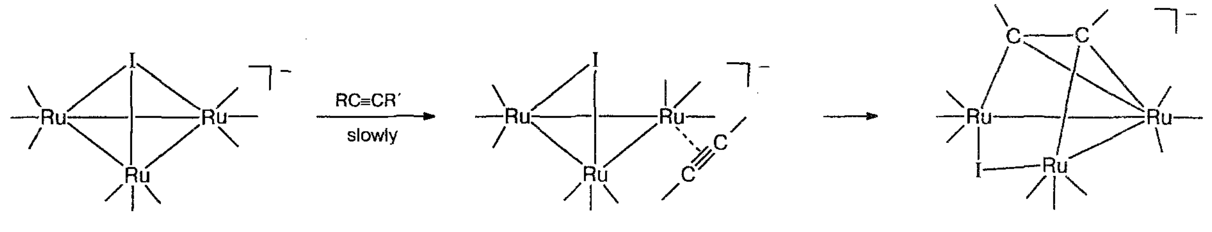
$[Ru_3(CO)_{10}(\mu\text{-}Cl)]^-$. We have studied the reaction of $[Ru_3(CO)_{10}(\mu\text{-}Cl)]^-$ with PhC≡CPh (reaction (3)). At 25 °C, this reaction is too fast to be monitored, so it was studied at lower temperatures. In addition to the expected product (see reaction (2)), $[Ru_3(CO)_{11}(Cl)]^-$ was formed as a side product, which is due to the rapid reaction of $[Ru_3(CO)_{10}(\mu\text{-}Cl)]^-$ with the CO evolved in the main reaction. Although the rate of the reaction increases as the concentration of PhC≡CPh increases, a plot of k_{obs} *vs.* the ligand concentration does not yield a straight line. However, plots of $1/k_{obs}$ *vs.* 1/[PhC≡CPh] show very good linear correlations. These results are consistent with a reaction mechanism involving abstraction of CO from $[Ru_3(CO)_{10}(\mu\text{-}Cl)]^-$ to give $[Ru_3(CO)_9(\mu\text{-}Cl)]^-$, which then reacts with PhC≡CPh (Scheme 3).

One interesting point is that the abstraction of CO has a very low $\Delta H^{\neq}$ value and a negative $\Delta S^{\neq}$ value. Similar regularities were observed in the previously described CO substitution in the osmium halide carbonyl complexes, $[Os_3(CO)_{11}(X)]^-$, by PPh_3. These were explained in terms of the formation of a halide bridge,

Scheme 3



Scheme 4



which stabilizes the transition state, resulting in a low $\Delta H^{\neq}$ value and a negative $\Delta S^{\neq}$ value. Though the kinetic data on the abstraction of CO from the $[Os_3(CO)_{10}(\mu\text{-}Cl)]^-$ complex are missing, the reaction of $[Os_3(CO)_{11}(Cl)]^-$ has a higher $\Delta H^{\neq}$ value (15.7 kcal mol^{-1}) and a less negative $\Delta S^{\neq}$ value (−19.1 cal mol^{-1} K^{-1}) than that of $[Ru_3(CO)_{10}(\mu\text{-}Cl)]^-$, which reflects a greater tendency of ruthenium complexes than osmium complexes to form bridges.

The reaction of $[Ru_3(CO)_{10}(\mu\text{-}Cl)]^-$ with PhC≡CH (see reaction (2)) is so fast that data on its rate were only obtained at −40 °C. Under the experimental conditions used, the rate of the reaction obeys a first-order equation with respect to concentrations of the complex and PhC≡CH. The observed rate constants of the reaction of PhC≡CH are larger than the rate constants of the abstraction of CO from $[Ru_3(CO)_{10}(\mu\text{-}Cl)]^-$, determined for its reaction with PhC≡CPh. These results suggest that $[Ru_3(CO)_{10}(\mu\text{-}Cl)]^-$ is the species that reacts with PhC≡CH under the given conditions (see Scheme 2). This may be due to the fact that PhC≡CH is much more reactive than PhC≡CPh (see above). The much higher reactivity of PhC≡CH allows the alkyne to react with $[Ru_3(CO)_{10}(\mu\text{-}Cl)]^-$ before the complex loses CO.

$[Ru_3(CO)_9(\mu_3\text{-}I)]^-$. The fact that $[Ru_3(CO)_9(\mu\text{-}I)]^-$ is the species that reacts with diphenylacetylene, has been directly observed in the reaction of PhC≡CPh with ruthenium iodide carbonyl complexes. Reaction (4) occurs much more slowly than the similar reaction of the corresponding chloride complex. It starts with as $[Ru_3(CO)_{10}(\mu\text{-}I)]^-$ rapidly loses one CO group to form the μ_3-I complex, which then slowly reacts with the alkyne to form the final product. The rate of the reaction corresponds to first order with respect to the concentrations of both the complex and the alkyne. An associative reaction mechanism is consistent with second-order kinetics, and is further supported by the low $\Delta H^{\neq}$ and negative $\Delta S^{\neq}$ values. The associative reaction pathway may be favored by the transformation of μ_3-I into μ_2-I in the reaction transition state or active intermediate (Scheme 4).

The fact that the rate of reaction (4) with PhC≡CH is about 20 times higher than the rate of the corresponding reaction with PhC≡CPh is also consistent with the proposed associative mechanism. The lower rate of the reaction of the μ_3-I complex compared with that of the chloride complex is not clearly understood. One might expect that the higher electronegativity of Cl atom compared with I would increase the electrophilicity of the metal atom and enhance the reactivity of the complex.

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