

Mechanistic Studies of the Hydrogenation of Alkynes with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ Using para-Hydrogen as a Probe

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Received December 13, 2001

The reactions of 1-pentyne and acetylene with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ in the presence of para- H_2 at 3–4 atm and 50–60 °C have been studied. An attempt is made to understand the nature of the intermediates in the catalytic hydrogenation process and the mechanistic relationship of the various organometallic clusters formed to each other and to the overall hydrogenation process. It was found that of the four products usually formed by the reaction of terminal alkynes with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$, only the $\sigma\text{-}\pi$ -vinyl complex $\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-CH=CHR})(\mu\text{-H})$ (**A**, R = H or n-Pr) goes on to yield alkene and the starting $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$. The $\mu\text{-}\eta^2$ -acetylido complex $\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-CCR})(\mu\text{-H})$ (**B**), a product that results from the loss of hydrogen, is not formed under these conditions, as might be expected, in the presence of excess H_2 . The $\mu_3\text{-}\eta^2$ -alkyne complex $\text{Os}_3(\text{CO})_9(\text{m-CO})(\mu_3\text{-}\eta^2\text{-HCCR})$ (**C**) is formed when $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ reacts with the subject alkynes in the presence of para- H_2 , but does not react with para-hydrogen. An unstable $\alpha\text{-}\beta$ -unsaturated aldehyde complex $\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^4\text{-RC=CC(O)H})(\mu\text{-H})$ (**E**) is detected, which is thought to go on to form the $\mu_3\text{-}\eta^4$ -metallacyclohexadienone cluster $\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^4\text{-(RC=CH)}_2\text{C(O)})$ (**D**), after loss of hydrogen and addition of a second mole of alkyne. Product **E** is also detected when $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ is reacted with 1-pentyne or acetylene in the presence of para- H_2 . The observation of this complex represents an example of direct detection of C–CO coupling in a transient intermediate on a trimetallic site. Labeling experiments with ^{13}C and deuterio-1-pentyne elucidate the origin of **E**, and the observation of hyperpolarized intermediates using para- H_2 is shown to be a valuable tool for elucidating the entire manifold of reactions.

Introduction

In recent years the use of transition metal clusters as homogeneous catalysts and heterogeneous catalyst precursors for hydrogenation and other transformations of organic compounds has increased considerably.¹ In the particular case of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$, early work showed this cluster to be an effective olefin hydrogenation and isomerization catalyst.^{2–4} More recently, $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ has been shown to be a stereoselective ring-opening metathesis polymerization catalyst for norbornene.⁵

The reactions of alkynes with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ are more complex than with olefins, especially in the case of terminal alkynes where four distinct types of products are obtained: a $\sigma\text{-}\pi$ -vinyl complex, $\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-CH=CHR})(\mu\text{-H})$ (**A**); a $\mu\text{-}\eta^2$ -acetylido complex, $\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-CCR})(\mu\text{-H})$ (**B**); a $\mu_3\text{-}\eta^2$ -alkyne complex, $\text{Os}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-HCCR})$ (**C**); and a $\mu_3\text{-}\eta^4$ -metallacyclohexadienone cluster, $\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^4\text{-(RC=CH)}_2\text{C(O)})$ (**D**)

(Scheme 1).^{6,7} Previous studies have focused on the factors determining the product distribution in these reactions and on the mechanisms of the metal-to-ligand hydrogen transfers.⁷ Recently, we have reported on the mechanisms of H_2 exchange in $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ using para- H_2 and deuterium labeling as probes.⁸ In light of these results we thought it could be useful to examine the reactions of alkynes with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ in the presence of H_2 in order to understand which of the alkyne products is most reactive with H_2 and in the hope of using the hyperpolarization induced by para-hydrogen to expose early intermediates in the reactive process. Such studies should be useful in understanding the competing reactions occurring during catalytic processes involving alkynes on polymetallic sites.

Results

The reaction of 1-pentyne with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ in the presence of 3–4 atm of para-enriched hydrogen was

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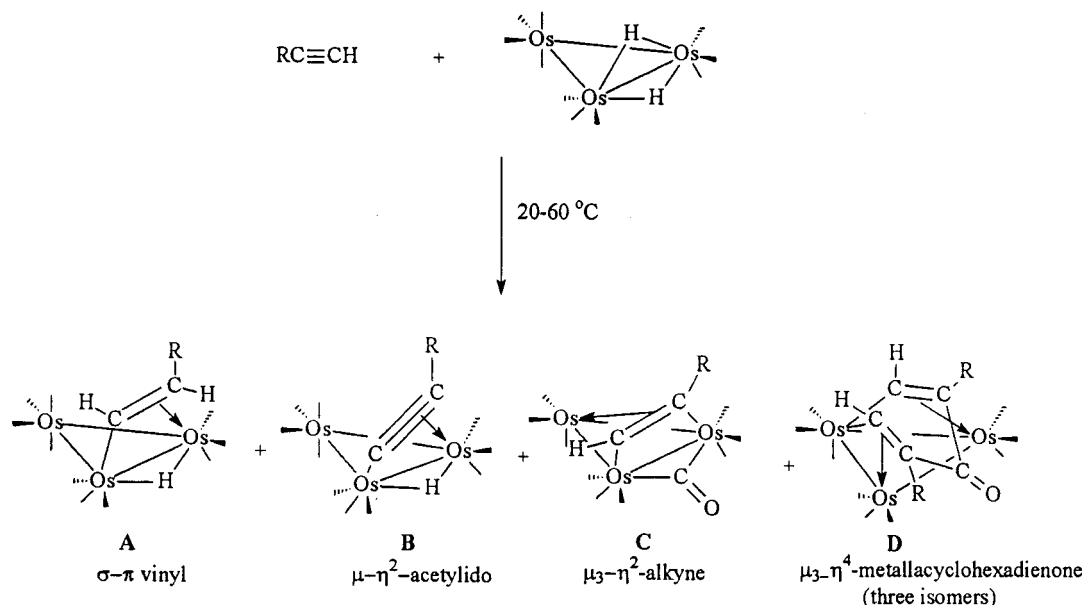
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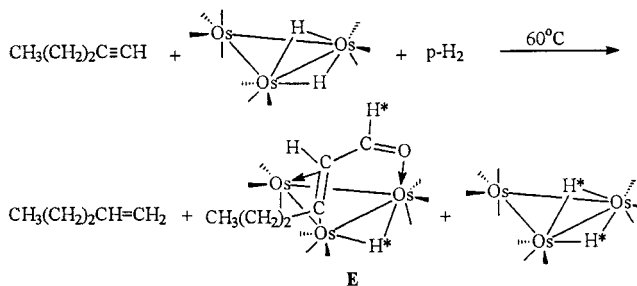
Scheme 1. Products Resulting from the Reaction of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ with Terminal Alkynes

followed at 60 °C by ^1H NMR. After 60 s a spectrum was recorded, and the presence two hyperpolarized resonances were detected, an absorption–emission doublet of doublets at 10.13 ppm ($J_{\text{HH}} = 3.4$ and 2.4 Hz) and an absorption–emission doublet at –13.76 ppm ($J_{\text{HH}} = 2.4$ Hz). A negatively polarized resonance at –11.5 ppm that can be assigned to $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ was also detected (Figure 1a). At this time a small amount of 1-pentene is also detected, as evidenced by the presence of its olefinic resonances at 5.90 and 5.05 ppm.

We know that the intense negative signal at –11.5 ppm must result from an unobserved intermediate in which the longitudinal relaxation processes are different for the two hydrides (Figure 2).^{8–10} As a consequence of the presence of this intermediate, the A_2 spin system of para-hydrogen is transformed into an AX spin system (the intermediate) and then back into an A_2 spin system in the final product ($\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$). Due to the transient presence of the AX system, symmetry is broken and polarization evolves, through various relaxation mechanisms, such that the upper states are populated and an emission signal is observed (Figure 2). In all the reported cases where this negatively polarized signal is observed the intermediate involved is of the general type $\text{Os}_3(\text{CO})_{10}\text{L}(\mu\text{-H})\text{H}$, in which L is CH_3CN or a solvent molecule.^{8–10}

We can assign the hyperpolarized doublet of doublets at 10.13 ppm and the hyperpolarized doublet at –13.76 ppm to a transient species in which a carbonyl group has coupled to the alkyne and is associated with reaction of para-hydrogen to yield an $\alpha\text{-}\beta$ -unsaturated aldehyde, $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-}\eta^2\text{-CH=CHC(O)H})(\mu\text{-H})$ (**E**, Scheme 2). We make this assignment on the basis of the chemical shift of the hyperpolarized resonance at 10.13 ppm and the fact that this resonance exhibits a second coupling ($J_{\text{HH}} = 3.4$ Hz) that must be due to coupling with the proton originally associated with the terminal alkyne (Figure

Scheme 2. Reaction of 1-Pentyne with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ and para-Hydrogen at 60 °C in CDCl_3 (products shown with asterisks are the polarization-enhanced resonances in the proposed intermediate)



1b). This assignment is further corroborated by the fact that when the experiment is repeated using a sample of 20% ^{13}C -enriched $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$, the resonance at 10.13 ppm exhibits ^{13}C O hyperpolarized satellites ($J_{\text{CH}} = 179$ Hz, Figure 1c). Finally, when the same experiment is repeated using 99% 1-deuterio-1-pentyne, the resonance at 10.13 ppm appears as a simple hyperpolarized doublet. The observed coupling between this resonance and the hydride at –13.76 ppm seems to require coordination of the carbonyl oxygen to the same edge of the osmium triangle as the hydride. Furthermore, the magnitude of the coupling between the aldehyde hydrogen and the α -hydrogen requires the *cisoid*-conformation shown (Scheme 2). The structure of **E** is reminiscent of the proposed structures for the previously reported complexes formed when $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ is reacted with vinyl acetate or methyl acrylate.^{11,12} Reversible CO insertion into coordinated vinyl and phenyl groups has been previously observed with triruthenium clusters.^{13,14} The final fate of this species is uncertain at this point, because the final products

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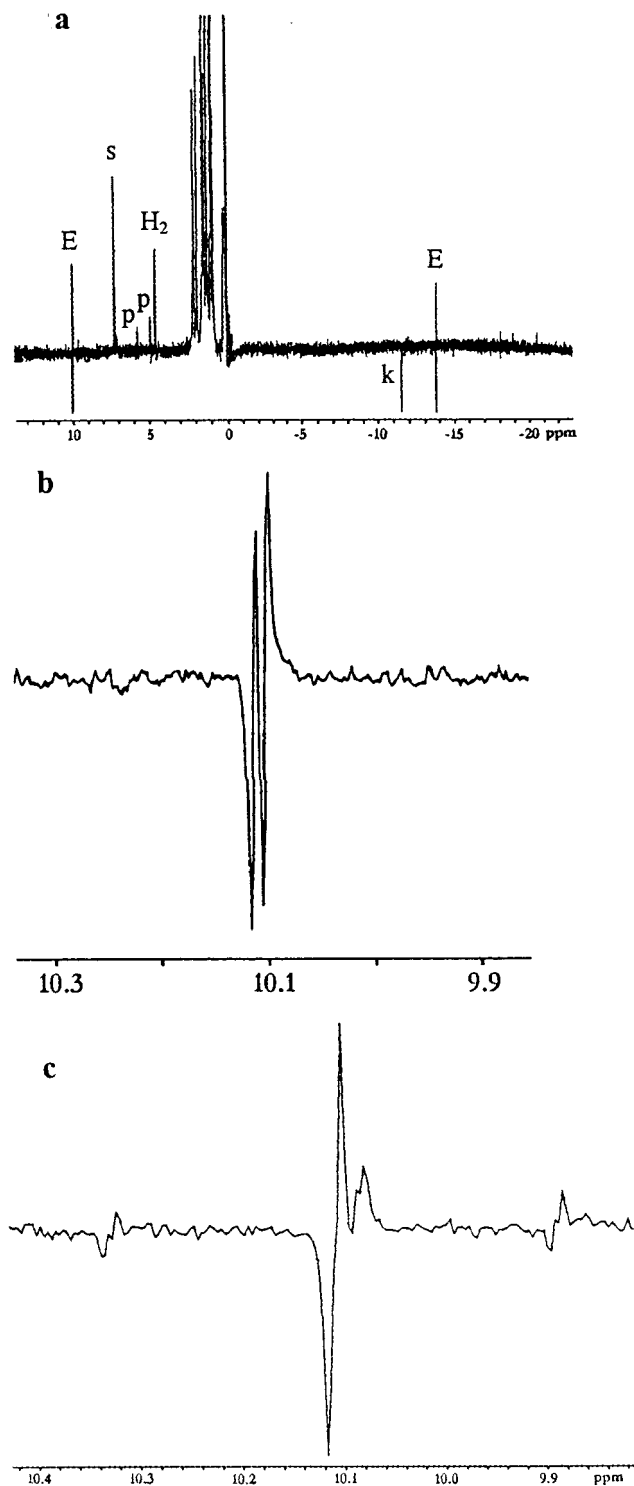


Figure 1. (a) ^1H NMR of the reaction of 1-pentyne with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ in the presence of 1 atm para-H_2 at 60°C recorded after 60 s (s = solvent, k = $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$, p = pentene), (b) ^1H NMR of the resonance of the doublet of doublets at 10.13 ppm, (c) ^1H NMR of the resonance at 10.13 ppm obtained from the sample of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ containing 20% ^{13}C and showing the ^{13}C satellites.

isolated from these NMR experiments are only 1-pentene, $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$, and trace amounts of **A** and **D**. Complex **C** is not a precursor to **E** because, in a separate

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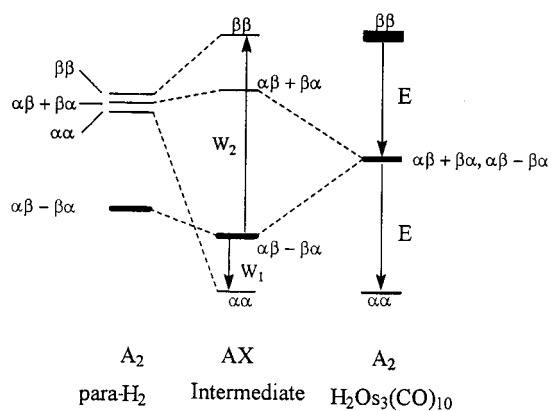


Figure 2. Evolution of the polarization of states during the formation of negatively hyperpolarized $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$.

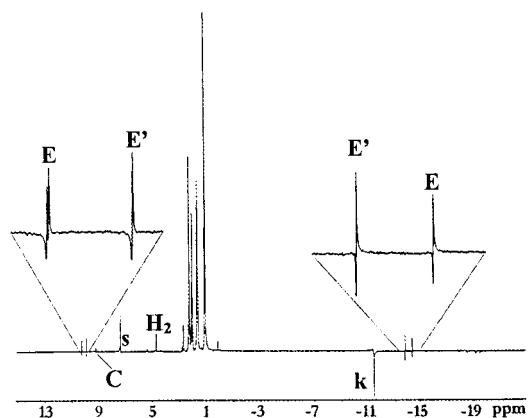


Figure 3. ^1H NMR of the reaction of 1-pentyne with $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ in the presence of 1 atm para-H_2 at 25°C recorded after 60 s (s = solvent, k = $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$).

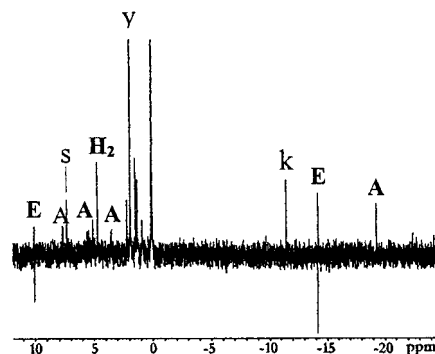
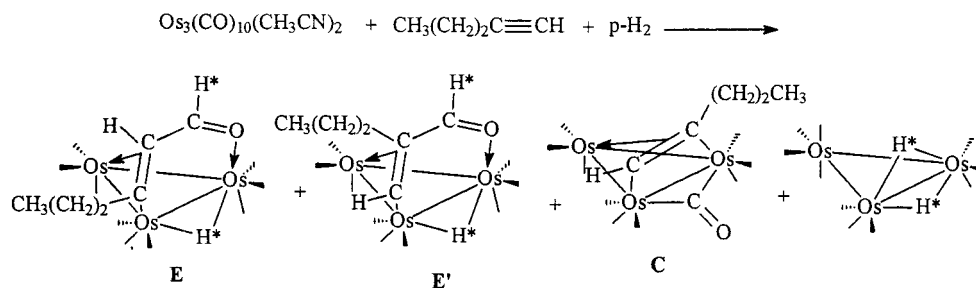
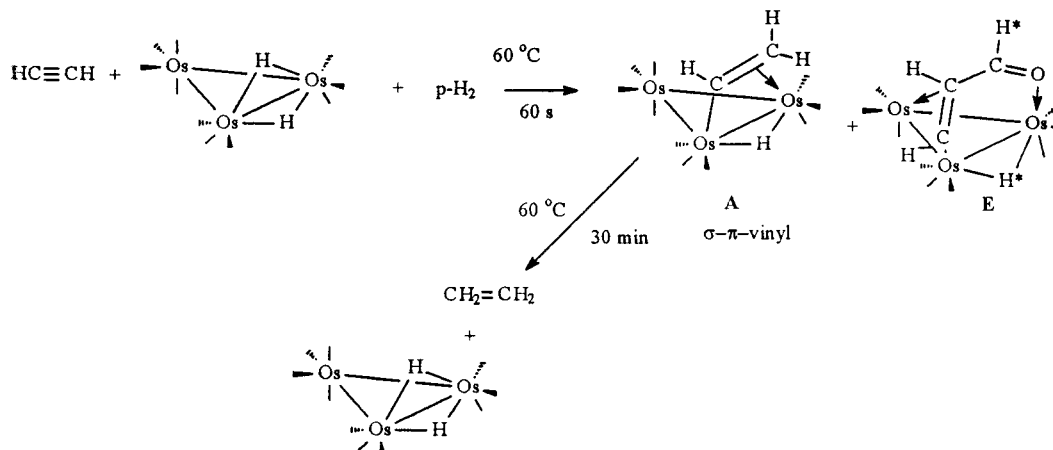


Figure 4. ^1H NMR of the reaction of acetylene with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ in the presence of 1 atm para-H_2 at 60°C recorded after 60 s (s = solvent, k = $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$, y = acetylene).

experiment, it did not react with para-H_2 at 3–4 atm and up to 60°C for several hours.

The reaction of $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ with alkynes at room temperature generally gives only **C**.¹² Of course, in the presence of p-H_2 reaction with $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ to give $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ will be competitive.^{8,9} When the reaction of 1-pentyne with $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ in the presence of para-H_2 is followed by ^1H NMR hyperpolarized signals associated with two isomers of **E**, **E** and **E'** are detected (Scheme 3), as evidenced by the observation of two absorption emission doublets at -13.76 ($J_{\text{HH}} = 2.4$ Hz) and -14.28 ppm (J_{HH}

Scheme 3. Reaction of $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ with 1-Pentyne and para-Hydrogen at 25 °C in CDCl_3 (products shown with asterisks are the polarization-enhanced resonances in the proposed intermediates)**Scheme 4.** Reaction of Acetylene with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ and para-Hydrogen at 60 °C in CDCl_3 (products shown with asterisks are the polarization-enhanced resonances in the proposed intermediates)

= 2.0 Hz), a doublet of doublets 10.13 ppm ($J_{\text{HH}} = 3.4$ and 2.0 Hz), and a doublet at 9.75 ppm ($J_{\text{HH}} = 2.4$ Hz). A negatively polarized signal for $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ is also observed (Figure 3, Scheme 3). Although **C** is observed from the beginning of the experiment, as evidenced by the appearance of its singlet resonance at 9.5 ppm, no pentenes are detected. This indicates that **C** is not active toward hydrogenation.

In a separate series of experiments $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ was reacted with acetylene in the presence of para-hydrogen at 60 °C. At room temperature the reaction of acetylene with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ gives 100% **A**, while in refluxing hexane **C** and **D** become the major products (Scheme 1).^{6,7} In the presence of para-hydrogen, we observe the presence of unpolarized **A** ($R = \text{H}$), as evidenced by multiplet resonances at 3.40, 5.00, 7.61, and -19.38 ppm,^{6,7} hyperpolarized **E**, and unpolarized $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ (Scheme 4, Figure 4). After 30 min unpolarized signals attributable to ethylene are observed as well as the initially detected unpolarized **A**, hyperpolarized **E**, and unpolarized $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$. These results are in sharp contrast to the reaction of 1-pentyne with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ and para-hydrogen where no **A** and hyperpolarized $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ are seen. Furthermore, when **A** ($R = \text{H}$) is reacted with para-hydrogen, only ethylene, unpolarized **A**, and unpolarized $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ are detected. These data and the fact that no olefin is observed in the reaction of $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ with 1-pentyne demonstrate that only the $\sigma\text{-}\pi$ -vinyl complex leads to olefin formation. In the latter stages of the reaction (3 h) we detect the presence of **D**, as evidenced by the presence of two doublets at 8.36 ($J_{\text{HH}} = 7.6$ Hz) and 6.87 ppm.

Finally, in both the reactions with 1-pentyne and with acetylene with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ no **B** is observed. This is not surprising since **B** results from hydrogen loss and would not be expected to form in 3–4 atm of hydrogen.

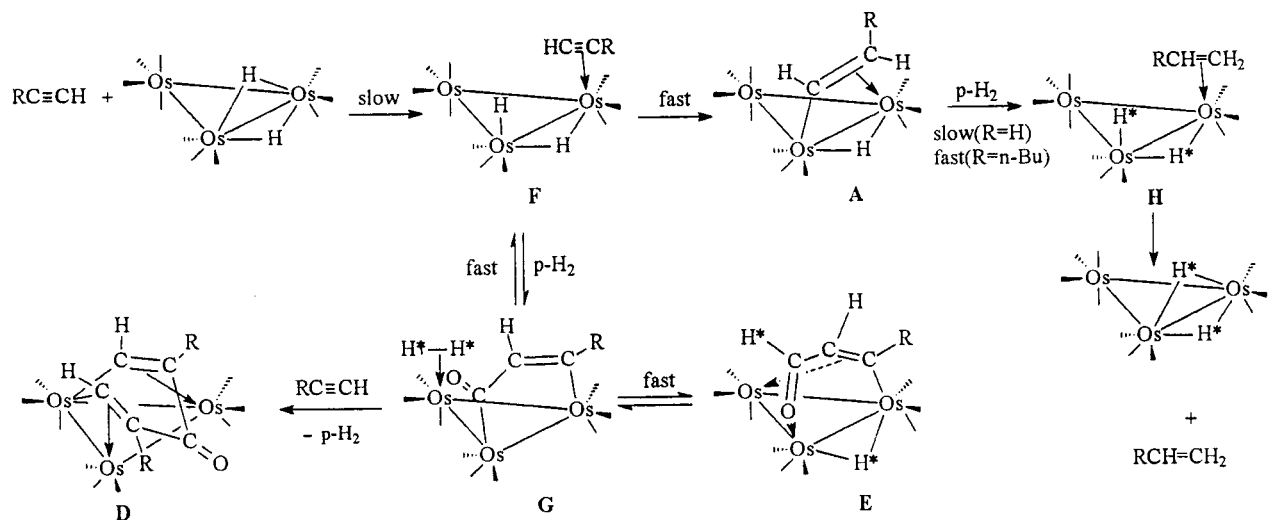
Discussion

The results presented here call for a reaction mechanism that can account for the following observations:

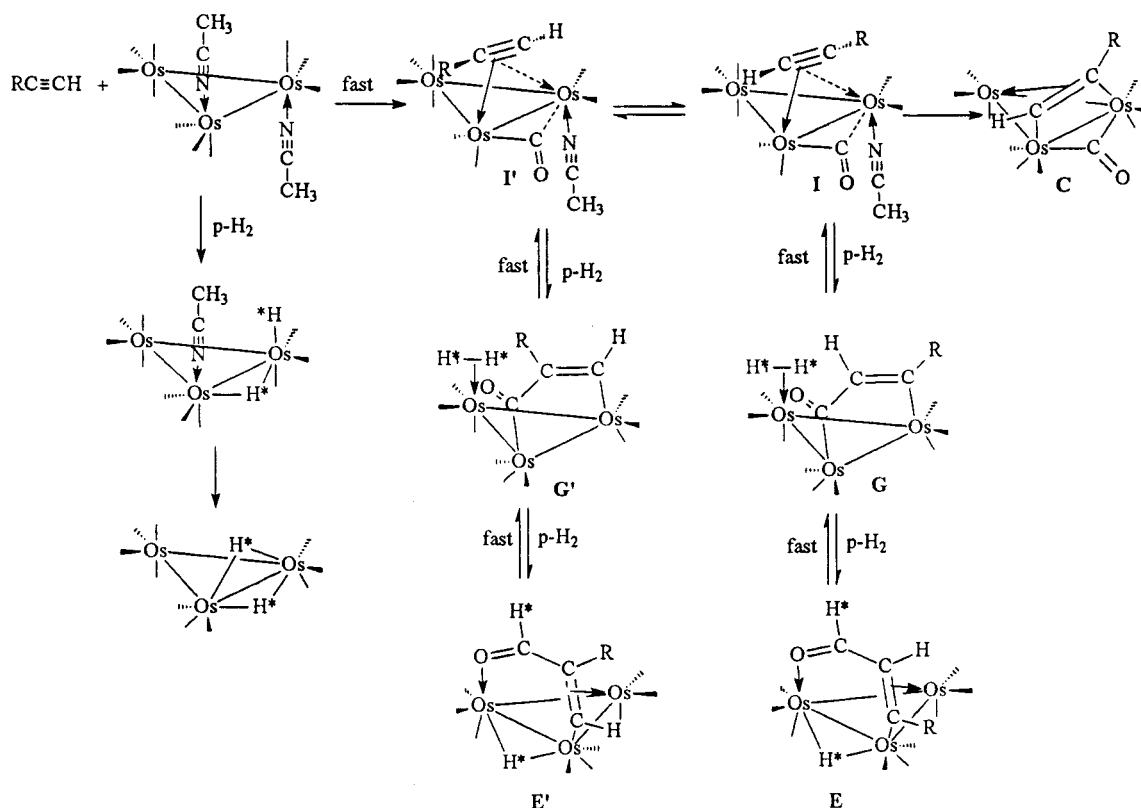
1. The formation of **E** and its sustained presence throughout the experiments conducted.
2. The difference in behavior between acetylene and 1-pentyne in the presence of para- H_2 and $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$.
3. The fact that only one isomer of **E** is formed with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$, while two are formed with $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$.
4. The ultimate fate of **E**.

An attempt to rationalize these observations is presented in Schemes 5 and 6. The fact that neither **A** nor **C** leads to the formation of **E** implies that it must form from an earlier intermediate in the reaction pathway. Also, **E** is maintained in a hyperpolarized state throughout the period of observation (3 h), which implies that it is in a rapid equilibrium with free para-hydrogen. It was previously shown that the initial adduct of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ with terminal alkynes is formed only in low concentration and therefore that it would be a logical precursor to **E**, that is, observable only by polarization enhancement.^{6,7} Finally, it is likely that **E** would be formed by a migratory insertion process from a valence saturated $48e^-$ intermediate since this has been shown to be the case for carbonyl insertion (alkyl migration) in $18e^-$ mononuclear systems.¹⁵ In this case the para-

Scheme 5. Proposed Mechanism for the Reaction of Terminal Alkynes with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ and para-Hydrogen at 60 °C in CDCl_3 (products shown with asterisks are the polarization-enhanced resonances in the proposed intermediates)



Scheme 6. Proposed Mechanism for the Reaction of Terminal Alkynes with $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ and para-Hydrogen at 60 °C in CDCl_3 (products shown with asterisks are the polarization-enhanced resonances in the proposed intermediates)



hydrogen (or alkyne) occupies the coordination site vacated by the migratory insertion, as for CO or phosphane in the mononuclear systems.¹⁵ Indeed, the reverse of a process closely related to that proposed here has been observed in a mononuclear system: in the conversion of $(\text{CO})_2(\text{PPh}_3)_2\text{Os}(\eta^2\text{-C(O)H})\text{H}$ to $(\text{CO})_2(\text{PPh}_3)_2\text{Os}(\eta^1\text{-C(O)H})\text{H}$ and finally to $(\text{CO})_3(\text{PPh}_3)_2\text{Os}$ and H_2 .¹⁶ Putting all this information together we

propose that the alkyne adduct **F** enters into a rapid equilibrium with para-hydrogen to give **G**, which is in rapid equilibrium with **E** (Scheme 5). The proposed migratory insertion to form **G** may have a significant associative component under the elevated pressures of para-hydrogen used here. Reactions of $48e^-$ trimetallic clusters exhibiting associative mechanisms have been reported.¹⁷

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The difference in the behavior of 1-pentene and acetylene in the presence of $p\text{-H}_2$ and $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ is most readily explained by the greater thermodynamic stability of **A** for the less sterically demanding alkyne. This would be expected to slow the reductive elimination for acetylene relative to 1-pentyne, which would result in the formation of intermediate **H** (Scheme 5). The observation of the negatively polarized $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ in the case of 1-pentyne requires intermediate **H**, as explained above (Figure 2), and this seems to preclude the presence of the previously suggested $44e^-$ species, $\text{Os}_3(\text{CO})_{10}$.^{7,12} That negatively polarized $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ is not observed in the case of the acetylene reaction is probably due to the slower conversion of **A** to **H** such that it is masked by unconsumed, unpolarized $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$.

Unlike the reaction of alkynes with $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$, reaction with $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ is fast.¹¹ Previous studies on the reaction of alkynes with $\text{Ru}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ definitively showed that intermediates isostructural with **I** and **I'** (Scheme 6, CO replaces CH_3CN) form prior to slower rearrangement to form **C**.^{18,19} We suggest here that **I** and **I'**, in which the alkyne sits over one edge of the metal triangle, are equally stable and are both trapped by the migratory insertion/ $p\text{-H}_2$ coordination. These intermediates equilibrate with **E** and **E'** slowly on the NMR time scale, but rapidly enough to maintain hyperpolarization. In the case of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$, intermediate **F** sits over only one metal atom, where it would be expected that the conformer with the alkyl chain away from the neighboring metal atom would be much more stable. This conformation allows room for the well-documented bridge-terminal hydride exchange to take place. This process is rapid at 60 °C in the previously examined adducts of the type **F**. Since only this one conformer is populated, only **E** and not **E'** is obtained.

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In summary, the use of para-hydrogen has revealed a previously unobserved migratory insertion-early intermediate, **G** (Schemes 5 and 6). In the absence of para-hydrogen this intermediate would most likely go on to form product **D** (Scheme 5) if sufficient alkyne is present (i.e. in the latter stages of the reaction or with large excesses of alkynes). The observation of negatively polarized $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ has allowed us to exclude a previously proposed $44e^-$ intermediate in favor of **F**.^{8,12} The use of para-hydrogen has also allowed us to obtain information on the early stages of the reaction with regard to the influence of the steric requirement of the alkyne, based on the observation of the number of isomers of **E** and the absence of **A**, in the case of 1-pentyne, and the absence of negatively polarized $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$, in the case of acetylene. Finally, the overall results have enabled us to ascertain that only **A**, of the four products formed from the reactions of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2$ with terminal alkynes, undergoes hydrogenation at 60 °C and 3–4 atm H_2 .

Experimental Section

The ^1H -PHIP (para-hydrogen-induced polarization) NMR spectra were recorded on a JEOL EX 400 spectrometer at a proton resonance frequency of 399.78 MHz. Reagents and solvents were used as received. The hydrogenolysis reactions were conducted in the NMR magnet at 3–4 atm and 25 or 60 °C using a conventional ^1H -multinuclear probe head. Para- H_2 (50% enriched in the para-form) was prepared according to the published methods.^{8–10}

In a typical experiment using hyperpolarized hydrogen, 10 mg of starting compound was dissolved in 0.6 mL of CDCl_3 in a 5 mm resealable NMR tube having a total volume of 3 mL. The solution was frozen, the air was pumped off, and about 1 atm of para- H_2 at 77 K was added. The sample was then warmed to room temperature, vigorously shaken, and introduced into the spectrometer. The first spectrum was recorded 60 s after shaking of the sample. The final pressure inside the tube was estimated using the ideal gas law.

Acknowledgment. We gratefully acknowledge the support of the NATO Science program (E.R. and L.M.) and the Italian Murst (COFIN 2000).

OM011056K