Carbon–Metal Hydrogen Interchange in Organometal Clusters of Ruthenium and Osmium

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Facile carbon–metal hydrogen exchange is demonstrated by the scrambling of deuterium into the hydrocarbon ligand from the hydride position of $(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}CH_3CH_2C\text{=}C\text{=}C(H)CH_3)Os_3(CO)_9$ (I) at 110 °C in a sample initially 80% enriched in deuterium at the hydride position by ^1H NMR techniques. Deuterium was incorporated into the allenic hydrogen position and the methylene hydrogens but not into the methyl groups. The observed scrambling is interpreted in terms of reversible formation of a 46e alkyne complex $(\mu_3\text{-}\eta^2\text{-}CH_3CH_2C\equiv CCH_2CH_3)Os_3(CO)_9$. The analogous ruthenium complex I′ was also deuteriated in the hydride position (76%), and the scrambling of deuterium was observed by ^1H NMR during its isomerization to the corresponding allylic isomer $(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}CH_3CH_2C\text{=}C(H)\text{=}CCH_3)Ru_3(CO)_9$ (II). A scrambling pattern similar to that seen for I is observed. These results are considered in terms of the known differences in the ligand dynamics of the organic ligands in structural types I and I′, and a two-step mechanism is proposed for the isomerization of I′ to II.

Introduction

The oxidative addition–reductive elimination of C–H bonds in transition-metal-coordinated hydrocarbon ligands has been well-studied in the case of mononuclear transition-metal complexes.[1] In the case of the trinuclear cluster $(\mu\text{-}H)_2(\mu\text{-}CH_2)Os_3(CO)_{10}$ metal–carbon hydrogen interchange is a reversible[3] process whose exact rate is not known.[2] Many other thermally induced hydrogen transfers from ligand to metal and from metal to ligand in polynuclear systems have been reported.[3,4] We report here a more detailed study of the carbon–metal hydrogen interchange in the complex $(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}CH_3CH_2C\text{=}C\text{=}C(H)CH_3)Os_3(CO)_9$ (I) for which we previously noted what

I
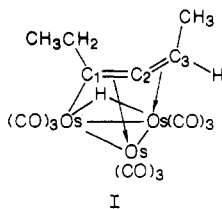
appeared to be hydrogen exchange between the hydride and the organic ligand[5] as well as a study of the role that this process plays in the rearrangement of the ruthenium analogue of I (I′) to its $\mu_3\text{-}\eta^3$-allylic isomer (II) (eq 1).

I′   II   (1)
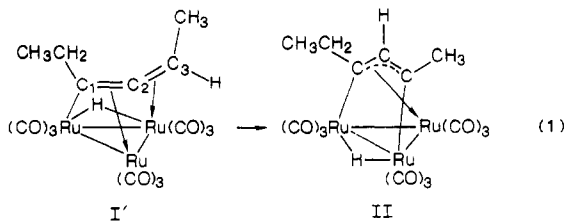
(1) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

(2) Shapley, J. R.; Calvert, R. B. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

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Results and Discussion

A sample of I, 80% deuteriated in the hydride position, was prepared by dissolution of the complex in CF_3COOD (stirred at room temperature for several days) followed by quenching in D_2O and recrystallization. The percentage of deuterium incorporation was evaluated by ^1H NMR.

Heating a sample of deuteriated I in toluene-d_8 in a vacuum-sealed NMR tube at 110 °C for 2 h resulted in several changes in the ^1H NMR spectrum of I (Table I). Relative integration of the two methyl groups to the hydride showed a decrease in the deuterium content in this position (i.e. incorporation of hydrogen). Similar comparative integration with the allenic hydrogen at 3.1 ppm reveals that deuterium has been incorporated into the allenic position. Incorporation of deuterium into the allenic hydrogen position is also evidenced by the observation of a singlet resonance at 1.98 ppm between the doublet of allenic methyl ($CH_3(a)$, Table I, Figure 1). The resonance is shifted off center by a small deuterium isotope effect on the chemical shift of the $CH_3(a)$ group. Even more interesting is the observation of a doublet superimposed on the triplet of the ethyl group methyl at 1.08 ppm ($CH_3(b)$). Relative integration of the methyl groups to the doublet of quartets observed for the methylene protons H_c and $H_{c'}$ (Table I) verifies that there is significant deuterium incorporation into the methylene protons. In our preliminary report of carbon–metal hydrogen interchange in I scrambling into the methylene group was not detected at 60 MHz.[5] Since there is no observable change in the multiplicity of the allenic proton H_d and the methylene protons H_c and $H_{c'}$, we can safely assume that there has been no deuterium incorporation into $CH_3(a)$ or $CH_3(b)$. Utilizing the relative intensity data obtained, we calculated that there is 26% D in the hydride position, 31% D in the allenic hydrogen position, and 25% D in the methylene protons. This corresponds, approximately, to a random distribution of deuterium between these three positions in complex I. No further change in deuterium distribution is realized by continued heating of the sample at 110 °C. These observations can be readily explained by the reversible formation of a 46e alkyne complex, $(\mu_3\text{-}\eta^2\text{-}CH_3CH_2C\text{=}CCH_2CH_3)Os(CO)_9$ (Scheme I). This 46e

Table I. ^{1}H NMR Chemical Shifts (ppm) for I and I'^{a}

compd	hydride	allenic H	allenic CH$_3$(a)	CH$_2$(H$_c$, H$_c'$)	CH$_3$(b)
I^a	-22.1 (s, 1)	3.1 (q, 1)	1.98 (d, 3)	2.85 (dq, 2)	1.08 (t, 3)
I'^{b}	-20.6 (s, 1)	3.55 (q, 1)	1.64 (d, 3)	2.85 (q, 2)	1.13 (t, 3)

^{a}Measured at 270 MHz in C$_6$D$_6$ or toluene-d_8. ^{b}Measured at 80 MHz in C$_6$D$_6$.

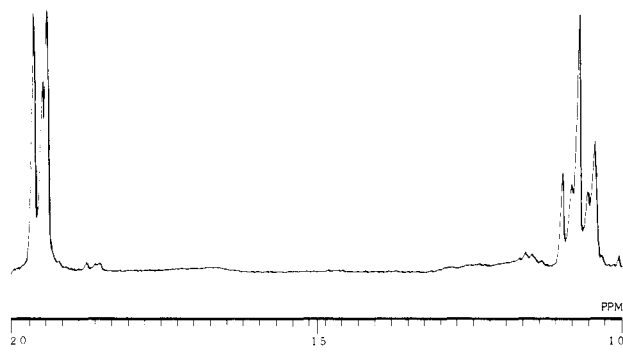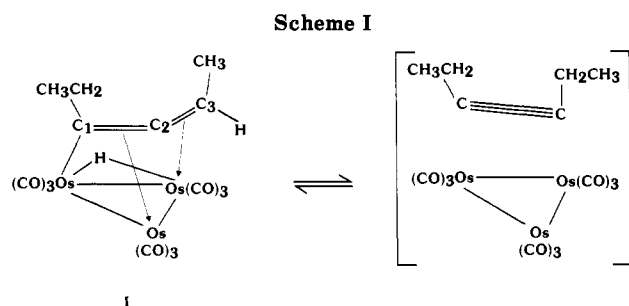**Figure 1.** ^{1}H NMR spectrum of deuteriated I at 270 MHz after heating at 110 °C for 2 h in toluene-d_8 (methyl region only shown).

Scheme I

I

Ln$\left(\frac{n_o}{n_o - n}\right)$

$k = 2.4 \times 10^{-3}$ min^{-1}

t(min) × 10^{-2}

Figure 2. Kinetic plot of the conversion of I' to II ($k = (2.4 \pm 0.3) \times 10^{-3}$ min^{-1}).

species is the likely intermediate from which I is formed by thermolysis of (μ_3-η^2-CH$_3$CH$_2$C≡CCH$_2$CH$_3$)Os$_3$(CO)$_{10}$.[5] We cannot specify the structure of this intermediate, but it is likely to be perpendicular to one edge of the metal triangle.[6] We have heated a sample of proteo-I at 110 °C for 3 days in toluene-d_8 and observed no detectable conversion to its allylic isomer as followed by ^{1}H NMR. These results clearly demonstrate that carbon–metal hydrogen interchange is a facile process whose rate is much faster in the case of I than the rate of isomerization to its allylic isomer.[5]

A sample of I', 76% deuteriated in the hydride position, was prepared by the same method as for I. The sample was heated at 80 °C in benzene-d_6 in a vacuum sealed NMR tube until conversion to II was complete as monitored by ^{1}H NMR (approximately 11 h).[7] The conversion was essentially quantitative since the only new resonances which appeared were attributable to II. Deuterium incorporation was observed in the central allylic hydrogen at 6.5 ppm to the extent of *30%*, into the methylene group of II to the extent of 26%, and the residual deuterium content was observed to be 25% in the hydride position. As for I a doublet was superimposed on the methyl triplet of the ethyl group. Singlet resonances overlapping with the doublets for the hydride and allylic hydrogens were also observed.

In order to exclude a bimolecular pathway for the isomerization of I' to II, we measured the rate of conversion
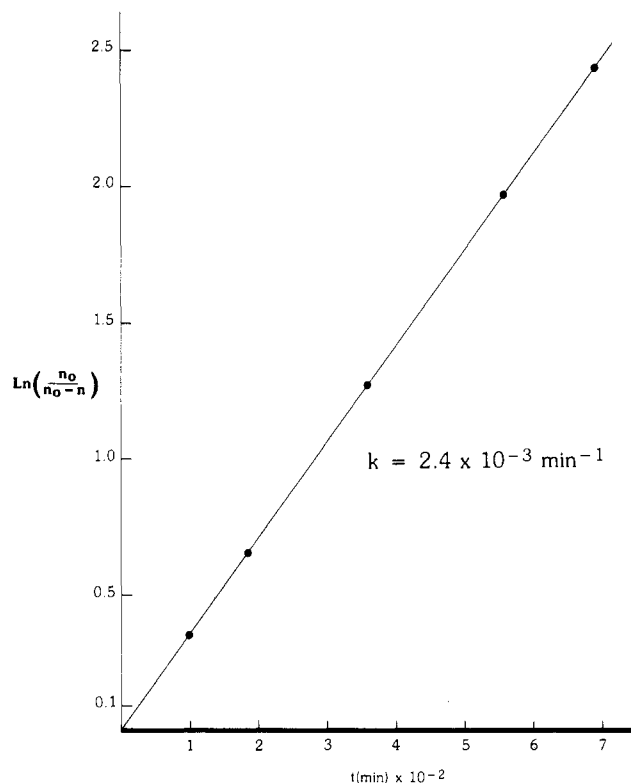
at 80 °C in benzene-d_6. We obtained good first-order kinetics (Figure 2) with $k = (2.4 \pm 0.3) \times 10^{-3}$ min^{-1} ($\Delta G^{\ddagger} \approx 116 \pm 12$ kJ/mol). Although we cannot rigorously exclude a bimolecular pathway in which only one molecule of I' is involved in the rate-determining step, these results are consistent with this isomerization being an intramolecular process. We also followed the rate of conversion I' to II in a sample of I' deuteriated, as above, at the hydride position. We found no significant isotope effect on the rate of conversion. Any isotope effect on isomerization would be difficult to detect since the deuterium is scrambled into three different positions in I' prior to isomerization. This is evident from the fact that a doublet partially overlapping with the methyl triplet at 1.13 ppm is observed, indicating the presence of CHD in the methylene group on unisomerized I'. It should also be noted here that rate of conversion of I' to II is the same in nitrogen and carbon monoxide atmospheres.

These results can be understood in terms of Scheme II where the analogous 46e alkyne intermediate is attained at 80 °C resulting in initial scrambling of deuterium into the methylene positions at a rate faster than the rate of formation of II. It is possible that a simple hydrogen transfer from the methylene carbon to the alkyne carbon takes place from the 46e intermediate followed by reinsertion of the cluster into the remaining C–H bond of the methylene group (pathway a, Scheme II). Alternatively, pathway b (Scheme II) could be operative, where a second C–H insertion by the cluster takes place to give a 48e dihydrido complex where only one of two double bonds of the allene remains coordinated to the cluster. A third

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Scheme II
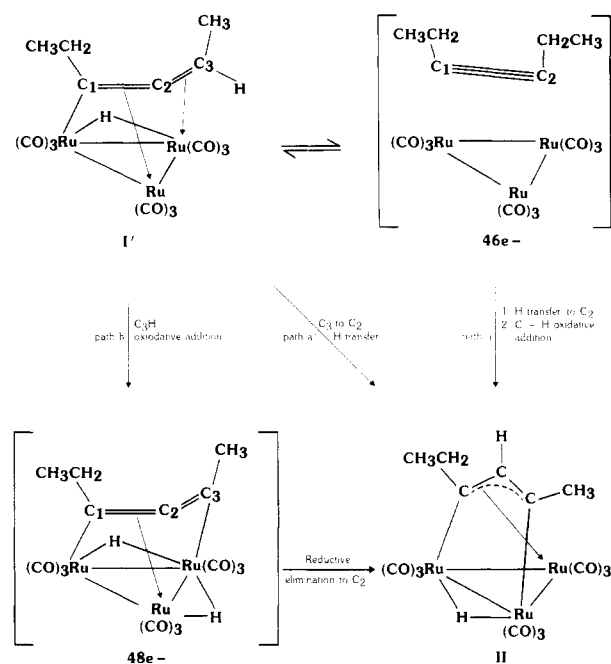
possibility is simple direct hydrogen transfer from an activated form of I′ (path a′, Scheme II). We favor pathway b based on our previous work on the ligand dynamics of the clusters $(\mu\text{-}H)M_3(CO)_9(\mu_3\text{-}\eta^3\text{-}CH_3C\!=\!\!C\!=\!\!C(CH_3)CH_3)$ (M = Ru, Os) where we showed that for these nonisomerizable allenic clusters that the organic ligand was undergoing a wagging motion that was rapid on the NMR time scale at 70 °C ($\Delta G^\ddagger = 56.0 \pm 1$ kJ/mol) for the ruthenium case while the organic ligand was essentially rigid at this temperature for the osmium case ($\Delta G^\ddagger = 80.6 \pm 1$ kJ/mol) and is not rapid on the NMR time scale until 130 °C. In pathway b it seems reasonable that a flexing motion of the organic ligand would be required for dissociation of one allenic π-bond to occur followed by a second C–H insertion to give the dihydrido 48e intermediate which then goes on to II. Furthermore a bending of the ligand on going from I′ to II is definitely a requirement of the reaction since the C–C–C angle in I is 144° while the same angle in II is 117°.[9,10] If attainment of the 46e intermediate alone were enough to induce isomerization as pathway a suggests, then rearrangement of I to its allylic isomer would occur at 110 °C at a reasonable rate. In any case even though we cannot rigorously distinguish between these mechanistic alternatives, these results illustrate that rapid carbon–metal hydrogen interchange is not a sufficient condition for the intramolecular rearrangement studied here (eq 1) and some further activation of the organic ligand is required. These studies demonstrate that reversible carbon–metal hydrogen interchange at α-C–H bonds can be a facile process in trinuclear organometallic complexes of ruthenium and osmium containing η^3-hydrocarbon ligands. The observed difference in activation

energies for this process between the osmium and ruthenium cases could be due to either stronger metal–carbon bonds or more rigid metal–metal bonds expected in the osmium complex I. Finally, it should be noted that the diphenylacetylene analogue of the 46e cluster proposed in Scheme I has been shown to be a stable but reactive complex at ambient temperature which can be generated by vacuum sublimation of $Os_3(CO)_{10}(C_2C_6H_5)_2$ at 250 °C.[12]

Experimental Section

Experimental Materials. $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ were purchased from Strem Chemicals. Compounds I[5] and I′[6] were prepared by known literature procedures from $H_2Os_3(CO)_{10}$ and $Ru_3(CO)_{12}$, respectively, using 3-hexyne purchased from Aldrich. Toluene-d_8 and benzene-d_6 were purchased from Aldrich and dried over molecular sieves before use. Deuteriotrifluoroacetic acid was purchased from Aldrich and used as received.

Spectra. ^{1}H NMR spectra of I were obtained at 270 MHz on a JEOL GX-270. ^{1}H NMR spectra of I′ and spectra following the conversion of I′ to II were recorded on an IBM NR80 operating at 80 MHz. It was extremely important to use long relaxation delays (5–7 s) and no more than a 35° pulse in order to get true line intensities for the hydride resonances in I, I′, and II since the relaxation times for the hydride protons are very long (5–25 sec).[11] All spectra were recorded at 24 (270 MHz) or 28 °C (80 MHz) after samples were heated at 80 or 110 °C in a temperature-controlled oil bath. Chemical shifts are referenced to TMS indirectly by reference to residual protons in the deuteriated solvents used.

Preparation of Deuteriated I. A sample of I (100 mg, 0.11 mmol) was stirred under nitrogen with 5.0 mL of CF_3COOD for 10 days at room temperature. The pale yellow solution was added dropwise to 10.0 mL of D_2O at 5 °C. The mixture was extracted with $CDCl_3$ (2 × 5.0 mL), washed with D_2O (2 × 2.0 mL), dried over $MgSO_4$, rotary evaporated and taken up in the minimum amount of hot heptane, recrystallized at -20 °C (yield 60 mg), and identified by ^{1}H NMR (Table I).

Preparation of Deuteriated I′. A sample of I′ (59 mg, 0.093 mmol) was stirred under nitrogen with CF_3COOD (1.5 mL, 19.8 mmol) for 9 days at room temperature. The yellow solution was then added dropwise to 5.0 mL of D_2O (99.75% D, Baker) at 5 °C and stirred overnight. The mixture was extracted with CCl_4 and the CCl_4 solution washed with D_2O, dried ($MgSO_4$), filtered, evaporated in vacuo, recrystallized from hexane at -20 °C, and identified by ^{1}H NMR.

Kinetic Measurements on the Isomerization of I′ to II. A 30.0-mg (0.045-mmol) sample of I′ was added to a 1.0-mL volumetric flask and diluted to the mark with benzene-d_6; 0.5 mL of this solution was transferred to an NMR tube and sealed under vacuum after three freeze–thaw cycles to remove the dissolved oxygen. The sample was then heated at 80 °C in a constant temperature bath and the ^{1}H NMR spectrum monitored at 30-min intervals. The relative concentrations of I′ and II were calculated for each spectrum by relative integration of the hydride resonances for I′ and II and checked against the relative intensities of the allenic proton quartet at 3.55 ppm and the allylic proton doublet at 6.66 ppm.

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