

# Kinetic Deuterium Isotope Effects on $\mu$ -Hydride and Carbonyl Ligand Migrations

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Kinetic deuterium isotope effects have been observed on the axial-radial carbonyl exchange process at hydride-bridged metal atoms in  $H(\mu-H)Os_3(CO)_{10}L$  ( $L = P(C_6H_5)_3$ ,  $CN-t-Bu$ ) and  $(\mu-H)Ru_3(CO)_9(\mu_3-C_2-t-Bu)$  by variable-temperature  $^1H$  and  $^{13}C$  NMR techniques. In  $(\mu-H)_2Os_3(CO)_{10}$  this effect is not observed. Kinetic deuterium isotope effects have also been measured directly on the site exchange of the magnetically inequivalent hydrides in  $(\mu-H)_2Ru_3(CO)_9(\mu_3-CH=C-t-Bu)^{2+}$ , for the mono- and dideuterio derivatives by  $^1H$  and  $^2H$  NMR. The meaning of these isotope effects for the particular ligand migrations involved is discussed.

## Introduction

Although there have been many studies on the ligand mobility of bridging hydrides and carbonyl groups in  $\mu$ -hydrido metal clusters, relationships between the migrations of these two ligands have not been clearly delineated. For instance, in cases where axial-radial exchange of carbonyl groups is observed at metal atoms bridged by a hydride the relationship between motion of the carbonyl ligands and the hydride has not been elucidated. We have previously observed that barriers to axial-radial carbonyl site exchange are 12-20 kJ higher at the hydride-bridged edge of the metal triangle in  $(\mu-H)M_3(CO)_9(\mu_3-L)$  systems ( $M = Ru, Os$ ;  $L = 2-$  or  $3-$ carbon organic ligand).<sup>1-3</sup> However, since there is only one hydride in these systems, its motion cannot be directly observed by NMR techniques and we cannot determine whether hydride motion is actually required for carbonyl site exchange at hydride-bridged metal atoms. In cases where there are two different hydride ligands (e.g.,  $H(\mu-H)Os_3(CO)_{10}L$ ) we have observed that hydride motion can be directly linked to carbonyl group site exchange at a given metal atom.<sup>4</sup> In addition, we recently reported the observation of an apparent deuterium isotope effect on formation of two dicationic dihydrido products from the reaction of the phosphine-substituted organometal cluster  $(\mu-H)Ru_3(CO)_8(\mu_3-C_2-t-Bu)P(C_6H_5)_3$  with sulfuric acid.<sup>5</sup> These results were interpreted in terms of a significant ( $k_H/k_D = 1.5$ ) deuterium kinetic isotope effect on the  $\mu$ -hydride migrations involved in the proposed reaction mechanism. Deuterium kinetic isotope effects on  $\mu$ -hydride migrations have not previously been measured in polyhydrido clusters. The determination of kinetic isotope effects on ligand

migrations may prove to be a valuable tool in understanding the relationships between ligand dynamics and reactivity of polynuclear metal clusters as our initial findings suggest.<sup>5</sup> We have therefore undertaken a study of deuterium kinetic isotope effects in both reactive and nonreactive metal clusters containing  $\mu$ -hydride ligands. We report here our initial findings on the measurement of the deuterium kinetic isotope effects on ligand migrations in the deuterated analogs of  $H(\mu-H)Os_3(CO)_{10}L$  ( $L = P(C_6H_5)_3$ , I;  $C\equiv N-t-Bu$ , II),  $(\mu-H)_2Os_3(CO)_{10}$  (III),  $(\mu-H)Ru_3(CO)_9(\mu_3-C_2-t-Bu)$  (IV), and  $(\mu-H)_2Ru_3(CO)_9(\mu_3-CH=C-t-Bu)^{2+}$  (V) as determined by  $^{13}C$ ,  $^1H$ , and  $^2H$  NMR techniques.

## Results and Discussion

**(A) Kinetic Isotope Effects on Carbonyl Migrations in  $H(\mu-H)Os_3(CO)_{10}L$  and  $(\mu-H)_2Os_3(CO)_{10}$ .** Our previous work on the ligand dynamics of  $H(\mu-H)Os_3(CO)_{10}L$  ( $L = P(C_6H_5)_3$ , I)<sup>4</sup> established a direct link between bridge-terminal exchange of the hydride ligands and axial-radial site exchange of two carbonyl ligands,  $CO_A$  and  $CO_B$ , on the osmium atom bearing the terminal hydride (Figure 1). Since the relationship between hydride and carbonyl site exchange is well understood in this system, it seemed a good starting point for our investigations on deuterium kinetic isotope effects. The  $^{13}C$  NMR of  $D(\mu-D)Os_3(CO)_{10}P(C_6H_5)_3$  at  $-36$ ,  $-25$ , and  $+32$  °C clearly shows a kinetic isotope effect on the averaging of  $CO_A$  with  $CO_B$  when compared visually with its protic analogue at all three temperatures (Figure 1). The peaks between A and B (figure 1) are due to the nonexchanging equatorial carbonyl groups C and G whose chemical shift is observed to change with temperature.<sup>4</sup> The simulated  $^{13}C$  NMR spectra give a value of  $k_H/k_D = 1.5 \pm 0.1$  at all three temperatures. It is difficult to imagine any other process besides simple hydride bridge opening coupled with in-plane rotation of  $CO_A$  and  $CO_B$  to close the hydride bridge on the opposite face of the metal triangle that would explain the observed isotope effect. An estimate of the maximum isotope effect on  $\mu$ -hydride bridge opening can be obtained from the known values of the infrared stretching frequencies for the  $\mu$ -hydride in  $H(\mu-H)Os_3(CO)_{10}L$  and  $D(\mu-D)Os_3(CO)_{10}L$ .<sup>6</sup>

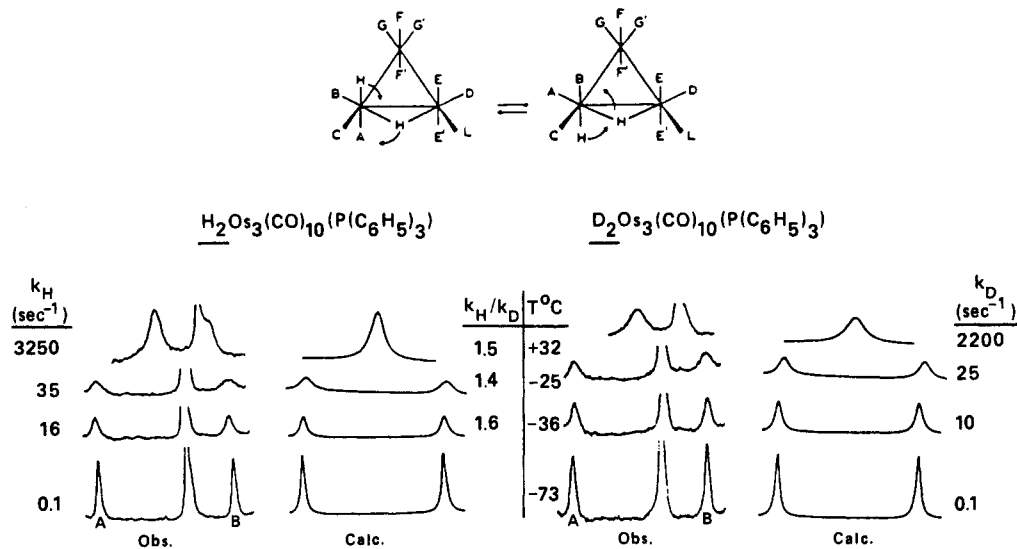
(1) S. Aime, L. Milone, D. Osella, M. Valle, and E. W. Randall, *Inorg. Chim. Acta*, **20**, 217 (1976).

(2) S. Aime, O. Gambino, L. Milone, E. Sappa, and E. Rosenberg, *Inorg. Chim. Acta*, **15**, 53 (1975).

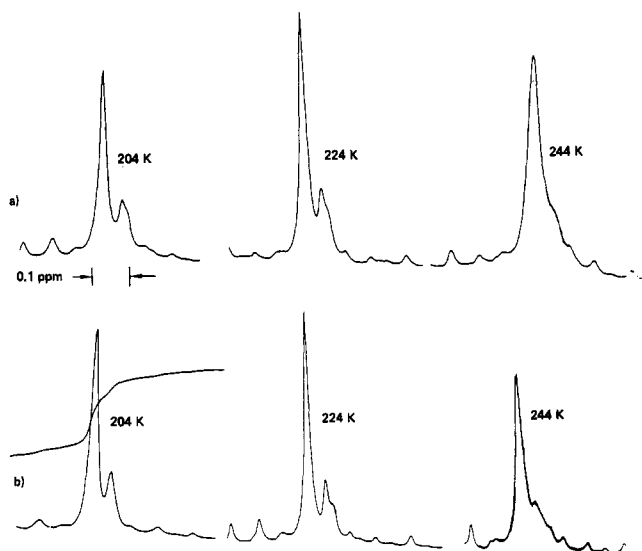
(3) S. Aime, D. Gobetto, D. Osella, L. Milone, and E. Rosenberg, *Organometallics*, **1**, 640 (1982).

(4) S. Aime, D. Osella, L. Milone, and E. Rosenberg, *J. Organomet. Chem.*, **213**, 207 (1981).

(5) C. Barner-Thorsen, E. Rosenberg, G. Saatiijan, A. Aime, L. Milone, and D. Osella, *Inorg. Chem.*, **20**, 1592 (1981).



**Figure 1.** Observed and calculated variable-temperature  $^{13}\text{C}$  NMR spectra of the carbonyl region of  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{P}(\text{C}_6\text{H}_5)_3)$  (left) and  $\text{D}(\mu\text{-D})\text{Os}_3(\text{CO})_{10}(\text{P}(\text{C}_6\text{H}_5)_3)$  (right) in  $\text{CD}_2\text{Cl}_2$  at 20.1 MHz.



**Figure 2.** Variable-temperature  $^1\text{H}$  NMR of the *tert*-butyl methyl resonances of *cis*- plus *trans*- $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-Bu})$  (upper) and  $\text{D}(\mu\text{-D})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-Bu})$  (lower) in  $\text{CD}_2\text{Cl}_2$  at 500 MHz.

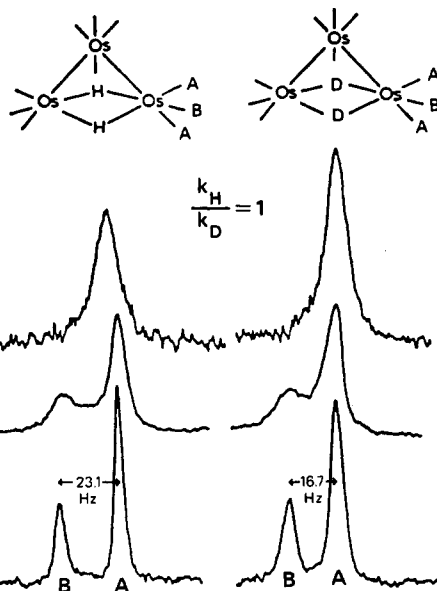
The calculated value for the primary isotope is  $k_{\text{H}}/k_{\text{D}} = 2.7$ . That this value is larger than the observed value is not surprising in view of the expected nonlinearity of the transition state.<sup>7</sup> In addition, the slight broadening of the  $^{13}\text{C}$  NMR resonances observed for  $\text{D}(\mu\text{-D})\text{Os}_3(\text{CO})_{10}\text{P}(\text{C}_6\text{H}_5)_3$  in the low-temperature limit, which is probably caused by incompletely relaxed quadruple coupling could contribute to the diminution of the observed  $k_{\text{H}}/k_{\text{D}}$  value. This was taken into account in the line-shape analysis however, by assigning a shorter intrinsic  $T_2$  to the deuterated species. Shapley and Keister recently suggested exchange of  $\text{CO}_A$  with  $\text{CO}_B$  and  $\text{H}_A$  with  $\text{H}_B$  in these systems could take place via a doubly H-bridged transition state.<sup>8</sup> The isotope effects reported here do not distinguish between this transition state and one having two terminal hydrides.

We have also measured the variable-temperature  $^1\text{H}$  NMR spectra of  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-Bu})$  and  $\text{D}(\mu\text{-D})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-Bu})$ .

(6) J. R. Shapley, J. B. Keister, M. R. Churchill, and G. DeBoer, *J. Am. Chem. Soc.*, **97** (1978).

(7) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(8) J. B. Keister and J. R. Shapley, *Inorg. Chem.*, **21**, 3304 (1982).



**Figure 3.** Variable-temperature  $^{13}\text{C}$  NMR of the carbonyl region of  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  (left) and  $(\mu\text{-D})_2\text{Os}_3(\text{CO})_{10}$  (right) in  $\text{CD}_3\text{C}_6\text{D}_5$  at 20.1 MHz.

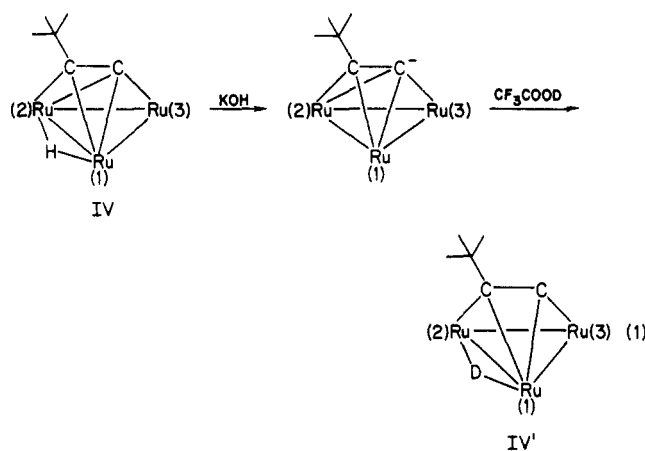
$\text{D}(\mu\text{-D})\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-Bu})$ . The solid-state structure of this adduct has the isocyanide in an axial position *trans* to the terminal hydride.<sup>9</sup> In solution both the *cis* and *trans* isomers exist and are interconverted by the same bridge-terminal hydride exchange observed for the phosphine adducts.<sup>8,9</sup> At 500 MHz the two *Bu-t*-methyl resonances for the *cis* and *trans* isomers are partially resolved at  $-60^\circ\text{C}$  ( $\delta$  1.58 and 1.49 (relative intensity = 3.6:1 in  $\text{CD}_2\text{Cl}_2$ ) for both the deuterated and protic samples (Figure 2). As the temperature is increased, a definite difference in the rate of averaging of the two signals between the deuterated and protic samples is seen with the deuterated sample averaging distinctly more slowly. Unfortunately, due to the instability of this adduct in solution,<sup>9</sup> the appearance of impurity peaks prevented a detailed line-shape analysis for this system. We feel, however, that the experiments do demonstrate the generality of the kinetic isotope effects in the  $\text{D}(\mu\text{-D})\text{Os}_3(\text{CO})_{10}\text{L}$  class in at least a qualitative sense and that our more quantitative results for the phosphine

(9) R. D. Adams and N. M. Golembeski, *Inorg. Chem.*, **18**, 1909 (1979).

adduct are not due to anomalous effects arising from interaction of the deuterium with the carbonyl ligands.

In sharp contrast to the results reported here for  $H(\mu-H)Os_3(CO)_{10}L$  we observe no deuterium kinetic isotope effect on the rate of exchange of the magnetically inequivalent carbonyl groups  $CO_A$  and  $CO_B$  on the hydride-bridged metal atoms in  $(\mu-D)_2Os_3(CO)_{10}$  when compared with  $(\mu-H)_2Os_3(CO)_{10}$  (Figure 3). Line-shape analysis gives a value of  $k_H/k_D = 1.0$ . Indeed, these carbonyl groups on  $(\mu-D)_2Os_3(CO)_{10}$  appear to average slightly faster than those on  $(\mu-H)_2Os_3(CO)_{10}$ . This is due to a significant isotope effect on the chemical shift of  $CO_B$  (the unique carbonyl group that is in the plane of the metal triangle) of 6 Hz (0.3 ppm) to higher field making the chemical shift difference between this carbonyl group and the other two carbonyl groups on the hydride-bridged metal atoms smaller. Two general mechanisms are consistent with these results. First, intramolecular carbonyl exchange involving a simple pinwheel rotation and not involving any motion of the hydride bridges. On the other hand, intermolecular exchange of CO to produce small amounts of  $H(\mu-H)Os_3(CO)_{11}$  that is known to be undergoing rapid intra- and intermolecular exchange at these temperatures could account for these observations.<sup>6,10</sup> The fact that coupling between the exchanging carbonyl groups and the hydride ligands is lost at the high-temperature limit and that  $(\mu-H)_2Os_3(CO)_{10}$  begins to decompose in this temperature range (+110 °C) also suggests that intermolecular exchange may be promoting the intermolecular site exchange processes observed. In any case, the absence of a kinetic isotope effect on carbonyl migration in  $(\mu-H)_2Os_3(CO)_{10}$  strongly suggests that bridging hydride motion is not involved in the rate-determining step and lends support to the idea that kinetic isotope effects can be used to differentiate mechanisms of carbonyl averaging in metal clusters. Furthermore, these results indicate that the higher barrier to carbonyl site exchange at the coordinately unsaturated centers of  $(\mu-H)_2Os_3(CO)_{10}$  when compared with the saturated  $H(\mu-H)_2Os_3(CO)_{10}L$  is due to a more rigid (i.e., nonmoving) metal hydrogen framework. It seems unlikely therefore that this same bonding framework would allow carbonyl site exchange at much lower activation energies in the more crowded transition-state structure " $(\mu-H)_2Os_3(CO)_{10}L$ " as suggested by Keister and Shapley.<sup>8</sup> The evidence to date therefore seems to support the bis terminal-geminal hydride as the most likely transition state.<sup>6</sup>

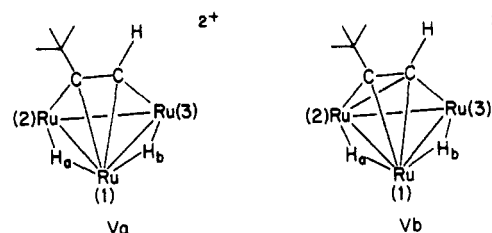
**(B) Deuterium Kinetic Isotope Effects on Carbonyl Migrations in  $(\mu-H)Ru_3(CO)_9(\mu_3-C_2-t-Bu)$ .** In order to investigate the link between hydride motion and carbonyl site exchange in  $(\mu-H)M_3(CO)_9(\mu_3-C_2-t-Bu)$  (IV) complexes we synthesized  $(\mu-D)Ru_3(CO)_9(\mu_3-C_2-t-Bu)$  (IV') by neutralization of the corresponding anion with  $CF_3COOD$  (eq 1) and compared their variable-temperature  $^{13}C$  NMR in the temperature range of +26 to +60 °C. A comparison of the variable-temperature  $^{13}C$  NMR of  $(\mu-H)Ru_3(CO)_9(\mu_3-C_2-t-Bu)$  and  $(\mu-D)Ru_3(CO)_9(\mu_3-C_2-t-Bu)$  is shown in Figure 4 and reveals that the axial-radial carbonyl exchange is distinctly slower in  $(\mu-D)Ru_3(CO)_9(\mu_3-C_2-t-Bu)$  than in  $(\mu-H)Ru_3(CO)_9(\mu_3-C_2-t-Bu)$ . A line-shape analysis of the spectra gave a  $k_H/k_D = 2$  at all four temperatures. The value of  $k_H/k_D$  can only be considered approximate



since the line-shape analysis was complicated by overlap with the coalesced signal from the axial and radial carbonyl groups  $CO(D)$  and  $CO(E)$  on  $Ru(3)$  (Figure 4). It is clear, however, that the kinetic deuterium isotope effect is measurable and is similar in magnitude to those observed for the  $H(\mu-H)Os_3(CO)_{10}L$  systems.

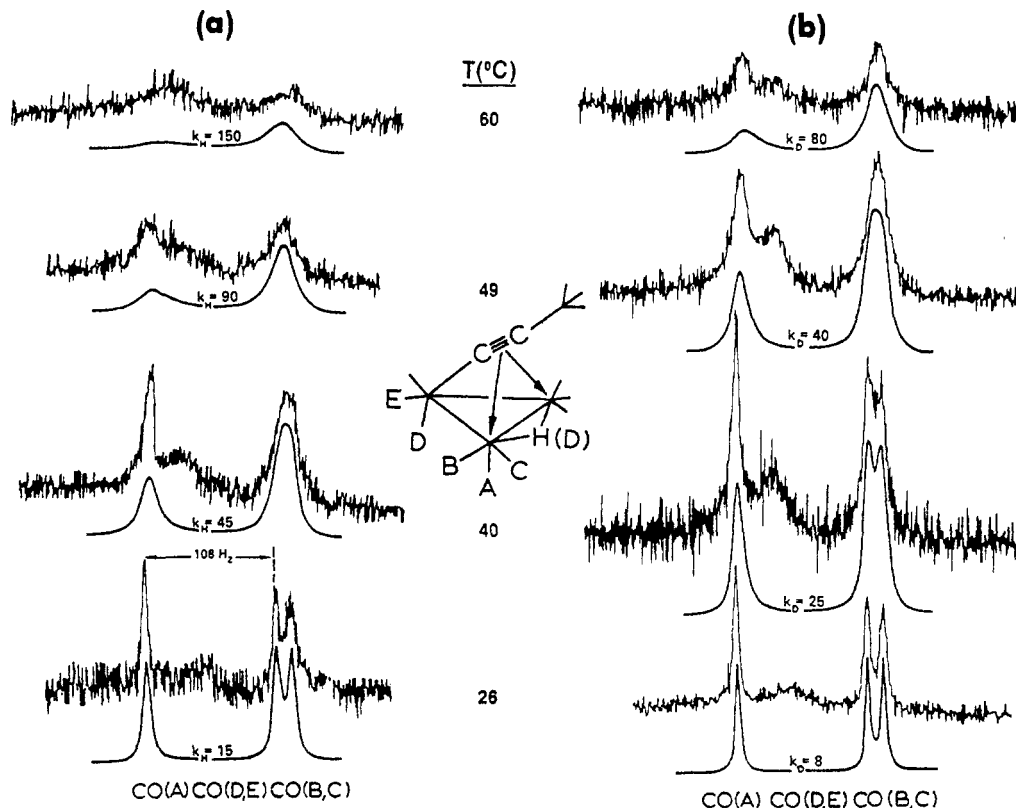
The site exchange of carbonyl groups at the hydride-bridged metal atoms in  $(\mu-H)M_3(CO)_9(\mu_3-L)$  systems must involve some motion of the hydride bridge and two possibilities for this motion exist: (1) opening of the hydride bridge to a terminal hydride on alternate sides; (2) a transition from  $\mu_2$  to  $\mu_3$ -hydride bonding where the hydride moves from an edge-bridging to a face-bridging mode allowing a  $C_3$  rotation of the carbonyl groups. We cannot differentiate between these alternatives at the present time. The IR stretching frequencies vary as  $M-H > \mu_2$ - $M-H > \mu_3$ - $M-H$ ,<sup>10</sup> which would seem to favor the latter.

**(C) Deuterium Kinetic Isotope Effects in  $(\mu-H)_2Ru_3(CO)_9(\mu_3-HC=C-t-Bu)^{2+}$ .** We felt an accurate assessment of the size of the deuterium isotope effect on a hydride exchange process could be obtained by direct observation of hydride exchange in a dihydrido cluster. A good candidate for this study is the dication  $(\mu-H)_2Ru_3(CO)_9(\mu_3-HC=C-t-Bu)^{2+}$  which has structure Va or Vb based on  $^1H$  and  $^{13}C$  NMR data.<sup>5</sup> With  $(\mu-H)Ru_3(CO)_9(\mu_3-C_2-t-Bu)$  or  $(\mu-D)Ru_3(CO)_9(\mu_3-C_2-t-Bu)$  as a starting material, we could selectively make the HH, HD, and DD complexes.  $(\mu-H)_2Ru_3(CO)_9(\mu_3-CH=C-t-Bu)^{2+}$  undergoes



a reversible intramolecular hydride site exchange that results in a coalescence of the two hydride resonances (at  $\delta -14.3$  and  $-15.1$ ) at +57 °C ( $G^{\ddagger}_{320K} = 62.7$  kJ/mol<sup>-1</sup>). Solutions of  $(\mu-H)(\mu-D)Ru_3(CO)_9[DC\equiv CC(CH_3)_3]^{2+}$  and  $(\mu-D)_2Ru_3(CO)_9[DC\equiv CC(CH_3)_3]^{2+}$  were prepared by dissolving  $(\mu-H)Ru_3(CO)_9(\mu_3-C_2-t-Bu)$  or  $(\mu-D)Ru_3(CO)_9(\mu_3-C_2-t-Bu)$  in  $D_2SO_4$ . The variable-temperature  $^1H$  NMR for  $(\mu-H)_2Ru_3(CO)_9(\mu_3-CH=C-t-Bu)^{2+}$  and  $(\mu-H)(\mu-D)Ru_3(CO)_9[DC\equiv CC(CH_3)_3]^{2+}$  were measured at 200 MHz in the temperature range of +25 to +57 °C. The  $^2D$  NMR spectrum of  $(\mu-D)_2Ru_3(CO)_9[DC\equiv CC(CH_3)_3]^{2+}$  was measured in the same temperature range at 77 MHz (500 MHz for  $^1H$  NMR) since the lower resonance frequency of deuterium required a higher field to get below coalescence at room temperature. Simulated  $^1H$  and  $^2D$  NMR spectra

(10) We have measured the variable-temperature  $^{13}C$  NMR of  $H_2Os_3(CO)_{11}$  in the range of -80 to +30 °C. Dynamic behavior similar to I and II is observed below -30 °C, but above this temperature a different process sets in which simultaneously averages all carbonyl groups at the hydride-bridged osmium atoms. We currently are investigating how the variation in the free CO pressure and cluster concentration affects the rate of this process.



**Figure 4.** Observed and calculated variable-temperature  $^{13}\text{C}$  NMR spectra of the carbonyl region of  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-C}_2\text{-}t\text{-Bu})$  (left) and  $(\mu\text{-D})\text{Ru}_3(\text{CO})_9(\mu_3\text{-C}_2\text{-}t\text{-Bu})$  in  $\text{CDCl}_3$  at 25.1 MHz.

for  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CH}=\text{C-}t\text{-Bu})^{2+}$ ,  $(\mu\text{-H})(\mu\text{-D})\text{Ru}_3(\text{CO})_9[\text{DC}=\text{CC}(\text{CH}_3)_3]^{2+}$ , and  $(\mu\text{-D})_2\text{Ru}_3(\text{CO})_9[\text{DC}=\text{CC}(\text{CH}_3)_3]^{2+}$  were calculated at or near coalescence. The observed and calculated spectra are shown in Figure 5. The ratios of  $k_{\text{HH}}/k_{\text{HD}} = 1.44$  and  $k_{\text{HH}}/k_{\text{DD}} = 1.80$  reveal the deuterium isotope effect to be roughly additive. A single step concerted process would give multiplicative isotope effect ratios and a two-step process (where  $k_{\text{H}_2} \approx k_{\text{H}_1}$ ) would be expected to give additive isotope effects for hydride site exchange. These two alternatives cannot be differentiated on the basis of these data. The situation where one hydride migrates much faster than the other is ruled out by these results. We have not been able to assign the infrared stretching frequencies for the  $\mu$ -hydrides and the  $\mu$ -deuterides in  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-C}_2\text{-}t\text{-Bu})$  and  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CH}=\text{C-}t\text{-Bu})^{2+}$ . With use of known values of the metal hydrogen stretching frequencies for related  $\mu$ -hydrido species in the literature, a predicted value of  $k_{\text{H}}/k_{\text{D}} = 2\text{--}3.5$  is obtained for the primary deuterium isotope effect.<sup>11</sup>

The variable-temperature  $^{13}\text{C}$  NMR spectrum of  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CH}=\text{C-}t\text{-Bu})^{2+}$  and  $(\mu\text{-D})_2\text{Ru}_3(\text{CO})_9[\text{DC}=\text{CC}(\text{CH}_3)_3]^{2+}$  have also been examined from +26 to +67 °C. Six sharp resonances at  $\delta$  188.1, 187.7, 184.2, 183.1, 182.1, and 181.3 (relative intensity = 1:1:2:2:2:1) at 26 °C are observed for  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CH}=\text{C-}t\text{-Bu})^{2+}$ . The  $^{13}\text{C}$  NMR of  $(\mu\text{-D})_2\text{Ru}_3(\text{CO})_9[\text{DC}=\text{CC}(\text{CH}_3)_3]^{2+}$  at 26 °C shows considerable broadening of all these resonances except the one at  $\delta$  183.1. As the temperature of  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CB}=\text{C-}t\text{-Bu})^{2+}$  is increased to +67 °C, where hydride site exchange is rapid on the NMR time scale, averaging of the two most downfield resonances (which are assigned to two of the axial carbonyls<sup>12</sup>) and

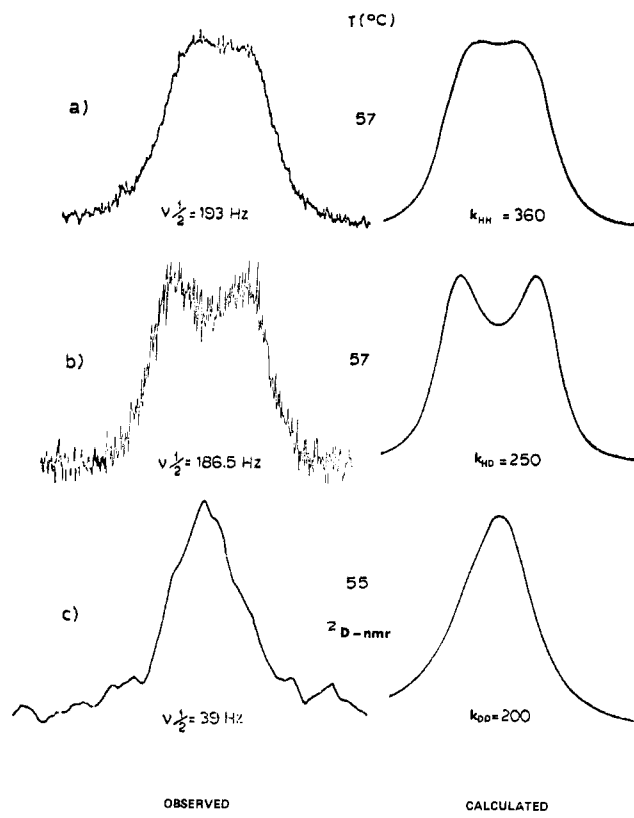
averaging of several of the upfield resonances (radial carbonyls) is observed to give five sharp resonances at  $\delta$  187.9, 183.6, 183.1, 183.0 and 181.6 (relative intensity = 2:2:1:2:2). The observed changes in the  $^{13}\text{C}$  NMR spectra can be understood in terms of the introduction of a  $C_{2v}$  symmetry plane that can be the result of either hydride migration around the cluster for structure Vb or of hydride migration around the cluster coupled with an oscillatory motion of the organic ligand pivoting at one of the acetylenic carbons for Va. The averaging of these carbonyls is observed to be slower for  $(\mu\text{-D})_2\text{Ru}_3(\text{CO})_9[\text{DC}=\text{CC}(\text{CH}_3)_3]^{2+}$  as expected since introduction of the  $C_{2v}$  plane directly depends on hydride migration rates for both Va and Vb. Averaging of radial with axial carbonyl groups is *not* observed in the temperature range examined, and hydride site exchange is rapid with respect to this process in  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CH}=\text{C-}t\text{-Bu})^{2+}$ . It appears that in  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CH}=\text{C-}t\text{-Bu})^{2+}$  motion of the two bridging hydride ligands is apparently independent of carbonyl axial-radial site exchange, an observation which is in sharp contrast with the results obtained for  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}\text{L}$  ( $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{C}\equiv\text{N-}t\text{-Bu}$ ) and  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-C}_2\text{-}t\text{-Bu})$ . This may be due to the fact that there are two hydride bridges in  $(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-CH}=\text{C-}t\text{-Bu})^{2+}$  that open one at a time with their motion coupled only to the movement of the organic ligand, leaving two of three metals always bridged.

### Conclusions

We have documented here four examples of a deuterium kinetic isotope effect on various ligand migrations. These results lend support to the mechanism proposed to explain the deuterium kinetic isotope effect observed in the re-

(11) H. D. Kaesz in "Transition Metal Hydrides", R. Bau, Ed., American Chemical Society, Washington, D.C., 1900 *Adv. Chem. Ser. No.* 167.

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**Figure 5.** (a) Observed and calculated  $^1\text{H}$  NMR of the hydride region of  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9[\text{HC}\equiv\text{C}(\text{CH}_3)_3]^{2+}$  at 200 MHz in  $\text{H}_2\text{SO}_4$ . (b) Observed and calculated  $^1\text{H}$  NMR of the hydride region of  $(\mu\text{-H})(\mu\text{-D})\text{Ru}_3(\text{CO})_9[\text{DC}\equiv\text{C}(\text{CH}_3)_3]^{2+}$  (V) at 200 MHz in  $\text{D}_2\text{SO}_4$ . (c) Observed and calculated  $^2\text{D}$  NMR of the deuteride region of  $(\mu\text{-D})_2\text{Ru}_3(\text{CO})_9[\text{DC}\equiv\text{C}(\text{CH}_3)_3]^{2+}$  in  $\text{D}_2\text{SO}_4$  at 75 MHz.

actions of  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-C}_2\text{-}t\text{-Bu})[\text{P}(\text{C}_6\text{H}_5)_3]$  with  $\text{H}_2\text{SO}_4$ .<sup>5</sup> Furthermore, the absence of a kinetic isotope effect in  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  suggests a significant variability in metal-hydrogen bond strength and the role it may play in the ligand dynamics and the low-temperature reaction chemistry of hydridometal clusters. Although the size of the effect is small, it is measurable by direct observation of the hydride or deuteride nuclei as well as by  $^{13}\text{C}$  NMR and undoubtedly other NMR nuclei. The effects of quadrupolar nuclei on line shapes in site exchanging systems has not been well investigated for metal deuterides, and therefore the  $k_{\text{HH}}/k_{\text{DD}}$  value reported here is tentative. We are currently investigating the  $(\mu\text{-H})_2\text{M}_3(\mu_3\text{-S})(\text{CO})_9$  and  $(\mu\text{-H})_2\text{M}_3(\text{CO})_9(\mu_3\text{-L})$  systems ( $\text{M} = \text{Ru}, \text{Os}$ ;  $\mu\text{-X} = \text{H}$  or  $\text{D}$ ;  $\mu_3\text{-L} = \text{hydrocarbon ligand}$ ) to elucidate this point further. Finally, the kinetic isotope effects observed here define a new class of isotope effects in transition-metal chemistry that are distinct from the "inverse" or thermodynamic isotope effects observed in heavy atom-light atom hydrogen transfers<sup>13</sup> and the larger kinetic isotope effects ( $k_{\text{H}}/k_{\text{D}} = 7\text{--}11$ ) reported for proton transfers from mineral acids to metal carbonyl clusters.<sup>14</sup> Recognition of these three classes of isotope effects may provide a basis for understanding the relative rates of single-step processes in hydridometal cluster reactions.

### Experimental Section

**Materials.** Compounds I-IV and their deuterated analogues were prepared by published literature procedures.<sup>5,6</sup> Solvents

( $\text{CDCl}_3$ ,  $\text{CD}_2\text{Cl}_2$ , and  $\text{CD}_3\text{C}_6\text{D}_5$ ) and acids (95%  $\text{H}_2\text{SO}_4$  and  $\text{D}_2\text{SO}_4$ ) were used as purchased without further purification.

**Spectra.**  $^{13}\text{C}$  NMR were obtained on a JEOL PFT-100 and IBM-NR80 spectrometers operating in the Fourier transform mode using samples that were approximately 15-30% enriched with  $^{13}\text{C}$  by exchange with 0.5 atm of 90%  $^{13}\text{C}$  at 70-100 °C.  $\text{Cr}(\text{acac})_3$  (0.05 M) was used as a relaxation agent for the  $\text{CDCl}_3$ ,  $\text{CD}_2\text{Cl}_2$ , and  $\text{CD}_3\text{C}_6\text{D}_5$  solutions. The viscosity of the  $\text{H}_2\text{SO}_4$  solutions of V and V' was sufficient to shorten the relaxation time of the carbonyl groups so that good  $^{13}\text{C}$  NMR spectra could be obtained.

$^1\text{H}$  NMR were obtained on Varian XL-200 and Bruker WP500 spectrometers operating in the Fourier transform mode.  $\text{D}_2\text{SO}_4$  (10% by volume) was added to the  $\text{H}_2\text{SO}_4$  samples as a field frequency lock.

$^2\text{D}$  NMR were measured on a Bruker-WP500, at 77 MHz operating in the Fourier transform mode. The deuterium resonances due to the deuterides in V' were considerably broadened at 26 °C compared to the same resonances in V as expected from its lower resonant frequency. However, the deuterium lines would also be expected to be intrinsically broader due to the smaller  $T_{2\rho}$  values for deuterium compared with  $T_2$  for protons. The line width of the deuterium resonance of the hydride in IV' at 26 °C was measured to be 4.0 Hz in  $\text{CDCl}_3$ , and this was taken as the value for the resonances in V' at the low-temperature limit in  $\text{D}_2\text{SO}_4$  that could not be obtained experimentally. No field frequency lock was used in the  $^2\text{H}$  NMR experiments, but spectrometer drift was negligible during the 5-10-min spectrum accumulation time.

Temperature was measured to  $\pm 0.5$  °C by a small thermometer in a sample tube containing the same solvent and was checked before and after each run.

**Line-Shape Analysis.** Simulation of the variable-temperature of  $^1\text{H}$ ,  $^2\text{H}$ , and  $^{13}\text{C}$  NMR spectra were performed by using a version of DNMR-4 by Gerhard Binsch modified by Bushweiler. Since DNMR-4 could not accommodate the  $\text{A}_2\text{B}_2\text{C}_2\text{D}_2\text{E}$  system IV with the required two independent sets of rate constants, only the carbonyl ligands on the hydride-bridged metal atoms of IV, Ru(1) and Ru(2), were included in the simulation. The axial-radial exchange at Ru(3) was simulated independently, but the contribution of this process and the higher energy intermetallic exchange to the observed line shapes was not included and the resulting rate constants can only be considered approximate. Rate constants reported here for the  $^1\text{H}$  and  $^2\text{H}$  NMR spectrum simulations can be taken as  $\pm 5\%$  as this was the lower limit for producing observable changes in the calculated spectra near coalescence (55-57 °C).

**Preparation of  $\text{DRu}_3(\text{CO})_9[\mu\text{-C}\equiv\text{C}(\text{CH}_3)_3]$  (IV').** To 500 mg (0.5 mol) of  $[(\text{C}_6\text{H}_5)_4\text{As}]^+[\text{Ru}_3(\text{CO})_9(\mu_3\text{-C}_2\text{-}t\text{-Bu})]^{15}$  in 2.0 mL of  $\text{CD}_2\text{Cl}_2$  at ambient temperature under nitrogen atmosphere was added 1.0 mL of  $\text{CF}_3\text{COOD}$ , dropwise. The solution was evaporated to dryness under vacuum, and the residue was extracted with hot heptane ( $3 \times 5$  mL). The heptane solution was cooled to -20 °C to yield 300 mg (90%) of IV' that was >95% deuterated as determined by  $^1\text{H}$  NMR (a small residual hydride resonance was observed and integrated).

**Preparation of Solutions of  $[\text{X}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-C}_2\text{-}t\text{-Bu})]^{2+}$  (X = H or D).** A 20-30-mg (0.06-0.1-mmol) sample of  $\text{XRu}_3(\text{CO})_9[\mu_3\text{-C}\equiv\text{C}(\text{CH}_3)_3]$  (X = H or D) was dissolved in 0.5 mL of  $\text{X}_2\text{SO}_4$  (X = H or D) in an NMR tube over a period of 1-2 h to give pale yellow solutions that were stable in air for several weeks as evidenced by their  $^1\text{H}$  NMR. The solutions become progressively brown and more viscous after this period even under nitrogen atmosphere. No H for D exchange was observed after dissolution of IV in  $\text{D}_2\text{SO}_4$  or IV' in  $\text{H}_2\text{SO}_4$ .

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$\text{RuCl}_3 \cdot \text{H}_2\text{O}$ .

**Registry No.** I, 56398-26-6; I- $d_2$ , 91880-32-9; II, 91880-31-8; II- $d_2$ , 91880-33-0; III, 41766-80-7; III- $d_2$ , 80137-11-7; IV, 57673-31-1; IV', 66973-03-3; V, 76721-83-0; V- $d_2$ , 91897-70-0; V- $d_3$ , 91880-34-1;  $[(\text{C}_6\text{H}_5)_4\text{As}]^+[\text{Ru}_3(\text{CO})_9(\mu_3\text{-C}_2\text{-}t\text{-Bu})]^-$ , 76741-75-8;  $\text{CF}_3\text{COOD}$ , 599-00-8.

## Synthesis, Characterization, and Rearrangements of [(1-Methylcyclobutyl)methyl]platinum(II) Complexes. Very Mild Ring-Strain-Induced Carbon-Carbon Activation

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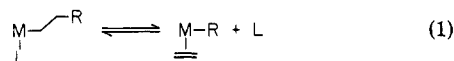
Complexes  $\text{trans-Pt}(\text{PMe}_3)_2\text{ClR}$ , where R = (1-methylcyclobutyl)methyl (mcbm, 1), (adamantyl)methyl (adm, 8), 4-methylpentyl-1,1- $d_2$  (9), and 4-methyl-4-pentenyl (10), and also  $\text{PtCl}(\text{dmpe})(\text{mcbm})$  [dmpe = 1,2-bis(dimethylphosphino)ethane] (2) have been prepared. Pyrolysis of 1 or 2 at 140 °C yields 2-methyl-1,4-pentadiene (12) as the only organic product, and  $\text{trans-HPt}(\text{PMe}_3)_2\text{Cl}$  (13) is isolated in high yield in the case of 1. Added  $\text{PMe}_3$  retards the pyrolysis of 1, leading to formation of  $[\text{HPt}(\text{PMe}_3)_3]\text{Cl}$  (14) and exhibiting kinetics consistent with initial  $\text{PMe}_3$  dissociation. Decomposition of 8 requires heating at 240 °C for hours. Pyrolysis of 9 at 140 °C forms 13 and 4-methyl-1-pentene-1,1- $d_2$  with very little rearrangement of the deuterium label. Treatment of 1 with  $\text{Ag}^+$  in acetone at -80 °C forms  $[\text{trans-Pt}(\text{PMe}_3)_2(\text{mcbm})(\text{acetone})]^+$  (15) that rearranges above -40 °C to  $[\text{cis-Pt}(\text{PMe}_3)_2[1,4,5\text{-}\eta\text{-}(\text{CH}_2)_3\text{C}(\text{Me})=\text{CH}_2]]^+$  (16) and above -10 °C to a mixture of  $[\text{Pt}(\text{PMe}_3)_2(2\text{-}4\text{-}\eta\text{-}2\text{-methylpentenyl})]^+$  (17a) and  $[\text{Pt}(\text{PMe}_3)_2(1\text{-}3\text{-}\eta\text{-}2\text{-methylpentenyl})]^+$  (17b), which is isolated as the  $\text{PF}_6^-$  salt. Reaction of 1 with  $\text{Ag}^+$  in  $\text{CD}_2\text{Cl}_2$  at -80 °C leads within 30 min to direct formation of 16, representing an extremely mild C-C activation step. Reaction of 10 with  $\text{Ag}^+$  at -80 °C followed by warming to -20 °C also generates 16. In contrast, 8 and  $\text{Ag}^+$  from  $[\text{Pt}(\text{PMe}_3)_2(\text{adm})(\text{acetone})]^+$  which is isolable at ambient temperature. Mechanistic implications of these reactions are discussed.

### Introduction

Formation and cleavage of carbon-carbon bonds mediated by transition-metal complexes is a central subject of organometallic chemistry. The activation of saturated hydrocarbons by heterogeneous metal-based catalysts has been a common practice for many years now and can be achieved under remarkably mild conditions in some cases.<sup>1</sup> However, heterogeneous reactions generally are not particularly mild, they are not very selective, and mechanistic details are not readily accessible. Homogeneous reactions hold the promise of being highly selective and of being amenable to testing for mechanistic information that may ultimately be valuable in helping to understand surface reactions.

In our search for homogeneous models for reactions which are components of hydrocarbon reformation, we have become particularly interested in possible carbon-carbon bond activation reactions. A priori, there are a number of C-C bond breaking/forming reactions that could participate in reformation such as  $\alpha$ - or  $\beta$ -alkyl eliminations/insertions,  $\alpha$ - $\gamma$  twofold C-H activation followed by rearrangement or reversible fragmentation of the resulting metallacyclobutanes, and direct bimolecular insertion of an unsaturated metal fragment into a saturated

C-C bond, among others. We consider the last of these to be the least likely. Instead, we make the assumption that successful C-C activation will be a property of already metal-bound alkyl groups. We have chosen to focus initially on  $\beta$ -alkyl insertion/elimination chemistry (eq 1).



Since unsupported Pt is a modest reformation catalyst,<sup>4</sup> and since the synthetic chemistry of Pt alkyls is relatively well worked-out, we have begun our investigation using this metal. In view of the fact that beta-alkyl eliminations are so rarely postulated, we have chosen to initially seek examples of the reaction in that direction.

There are two difficulties in particular that must be overcome to observe  $\beta$ -alkyl elimination. One problem is the propensity for metal alkyls to undergo very facile  $\beta$ -H eliminations, usually irreversibly. In a system which would be catalytically active, the  $\beta$ -H elimination must necessarily

(4) Evidence suggests that in commercial "platforming" the metal component serves mainly to C-H activate, while the C-C rearrangements are largely carbonium ion chemistry catalyzed by acidic sites on the support.<sup>5</sup> Nevertheless, pure Pt will much more slowly catalyze reformation.<sup>6</sup>

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