

# Novel Synthesis, Solution Structure, Dynamics, and Protonation of $H(\mu-H)Ru_3(CO)_{11}$

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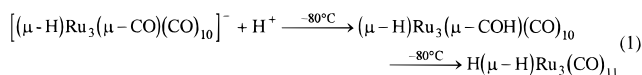
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The reaction of the lightly stabilized cluster  $Ru_3(CO)_{11}(NCCH_3)$  with  $H_2$  quantitatively affords  $H_2Ru_3(CO)_{11}$ , which is sufficiently stable under an  $H_2$  atmosphere to be characterized by  $^1H$  and  $^{13}C$  spectroscopy. In solution, the structure of the dihydride product is different from that previously reported, and it corresponds to a novel bonding scheme, intermediate between those of the two structures previously reported for  $H_2M_3(CO)_{11}$  species ( $M = Fe, Ru, Os$ ). The stereochemical nonrigidity of the title compound is investigated by VT  $^{13}C$  NMR spectroscopy, and an exchange mechanism involving edge hopping of the bridging hydride in concert with the motion of the carbonyl ligands is proposed. The reactivity of the title compound with  $CF_3COOH$  is also investigated. At low temperature, the addition of the strong acid to the cluster yields a reversible O-protonation at the bridging carbonyl site. When the temperature is raised, the formation of  $(\mu-H)Ru_3(\mu-\eta^3-OOCF_3)(CO)_{10}$  is observed.

## Introduction

$H(\mu-H)Ru_3(CO)_{11}$  was first reported by Keister in 1980 as the product of the protonation reaction of  $[(\mu-H)Ru_3(\mu-CO)(CO)_{10}]^-$  at low temperature.<sup>1</sup> He showed that the initial protonation occurs at the oxygen site of the bridging carbonyl with a subsequent rearrangement to a dihydride species:



Protonation at the oxygen site of the  $[(\mu-H)M_3(\mu-CO)(CO)_{10}]^-$  ( $M = Fe, Ru, Os$ ) anion appears then to be a common trait of the iron triad.<sup>2</sup> However, in the case of Ru and Os, the hydroxycarbyne-containing species (structure **I** in Chart 1) readily evolves to a more stable tautomer containing a bridging and a terminal hydride ligand. On the basis of the close analogy of their IR spectra, it was suggested that  $H(\mu-H)Ru_3(CO)_{11}$  has the same structure (**III**) as the previously reported  $H(\mu-H)Os_3(CO)_{11}$ .

A remarkable feature of the reactivity of  $H(\mu-H)Ru_3(CO)_{11}$  is the easy loss of molecular hydrogen to yield the coordinatively unsaturated " $Ru_3(CO)_{11}$ " species.<sup>1</sup> Thus  $H(\mu-H)Ru_3(CO)_{11}$  may act as a "lightly stabilized" system, and it was found to promptly react, at low temperature, with alkynes to afford the previously unaccessible  $Ru_3(CO)_{11}(\eta^2\text{-alkyne})$  derivatives.<sup>3</sup>

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Conversely,  $H(\mu-H)Os_3(CO)_{11}$  is more stable, and thermal activation leads to disproportion into  $(\mu-H)_2Os_3(CO)_{10}$  and  $Os_3(CO)_{12}$ .<sup>4</sup>

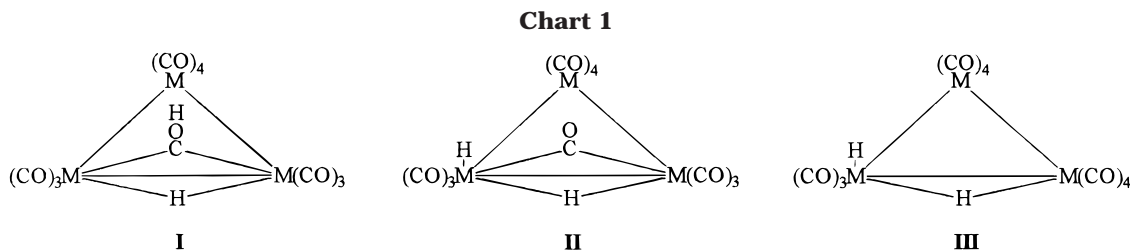
The remarkable discrepancy in their reactivities is in apparent contradiction with the proposed similarity of their structures. To gain more insight into the peculiar properties of  $H(\mu-H)Ru_3(CO)_{11}$ , we undertook a detailed investigation of its solution structure, dynamics, and reactivity with  $CF_3COOH$ .

## Results and Discussion

**Synthesis and Solution Structure of  $H(\mu-H)Ru_3(CO)_{11}$ .** The protonation reaction of  $[(\mu-H)Ru_3(\mu-CO)(CO)_{10}]^-$  with  $CF_3COOH$  was followed by means of  $^{13}C$  NMR spectroscopy, and we found that the thermodynamically favored isomer does not possess the proposed structure **III**. In fact, the  $^{13}C$  NMR spectrum clearly shows that—at 183 K, when the proton NMR spectrum consists of two narrow hydride doublets—there is a well-defined absorption in the region of the bridging carbonyl resonances. However, the sample synthesized by this procedure is not stable enough to allow a complete NMR characterization, so an alternative preparation was explored that would avoid the fast decomposition of  $H(\mu-H)Ru_3(CO)_{11}$ .

The new procedure parallels the previously reported one for the synthesis of  $H(\mu-H)Os_3(CO)_{11}$ .<sup>4</sup> It is based on the assumption that the "lightly stabilized"  $Ru_3(CO)_{11}(NCCH_3)$  compound releases the acetonitrile ligand to yield the coordinatively unsaturated " $Ru_3(CO)_{11}$ " species, which promptly reacts with  $H_2$  to afford  $H(\mu-H)Ru_3(CO)_{11}$ . The use of a large excess of  $H_2$  avoids the decomposition of  $H(\mu-H)Ru_3(CO)_{11}$ ; in fact, under these

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conditions, it appears quite stable and only minor amounts of Ru<sub>3</sub>(CO)<sub>12</sub> may be detected after several hours. The H<sub>2</sub> atmosphere allows the complete NMR investigation of H( $\mu$ -H)Ru<sub>3</sub>(CO)<sub>11</sub> over a sufficiently large temperature range, but unfortunately we could not record the IR spectrum under these conditions. The formation of H( $\mu$ -H)Ru<sub>3</sub>(CO)<sub>11</sub> by this route is very clean, and it can be conveniently carried out in an NMR tube at 213 K (CD<sub>2</sub>Cl<sub>2</sub> as solvent). The signal due to free acetonitrile ( $\delta$  = 1.98 ppm) gradually increases with the concomitant growth of two hydride resonances at -12.06 (terminal hydride) and -18.92 ppm (bridging hydride) ( $^2J_{H,H}$  = 1.9 Hz). Whereas the <sup>1</sup>H NMR spectrum closely resembles that reported for the related H( $\mu$ -H)Os<sub>3</sub>(CO)<sub>11</sub> derivative (-10.3 and -20.0 ppm),<sup>5</sup> the <sup>13</sup>C-NMR spectrum of a <sup>13</sup>C enriched sample of H( $\mu$ -H)Ru<sub>3</sub>(CO)<sub>11</sub> at 183 K clearly shows the presence of a bridging CO resonance at 267.9 ( $J_{C,C}$  = 21 Hz) (11) ppm in addition to 10, equally intense resonances in the terminal carbonyl region at 183.6 (1), 184.9 (9), 187.4 (8), 191.3 ( $J_{C,H_{bridge}}$  = 9 Hz) (6), 192.3 ( $J_{C,H_{term}}$  = 12 Hz,  $J_{C,H_{bridge}}$  = 4 Hz) (2), 193.9 ( $J_{C,C}$  = 30 Hz) (10/7), 194.0 ( $J_{C,C}$  = 30 Hz) (7/10), 194.5 (5), 196.3 ( $J_{C,H_{term}}$  = 15 Hz) (3), and 201.7 ( $J_{C,C}$  = 21 Hz) (4) ppm (Figure 1). The assignment of several of these CO resonances was performed by observing the  $J_{C,H}$  and  $J_{C,C}$  coupling patterns. The  $J_{C,H}$  values appear rather different from the corresponding ones reported for H( $\mu$ -H)Os<sub>3</sub>(CO)<sub>11</sub>.<sup>5</sup> In fact, in the Ru derivative there are two  $^2J_{C,H}$  couplings involving the terminal hydride, of 15 and 12 Hz, respectively, whereas only one  $^2J_{C,H}$  of 23 Hz has been observed in the case of the Os compound.

We measured the spin-lattice relaxation time of the two hydrides at 213 K (both show a  $T_1$  value of 3.5 s at this temperature at 400 MHz) and then evaluated the proton-proton distance in H( $\mu$ -H)Ru<sub>3</sub>(CO)<sub>11</sub> by applying

the usual equation for homonuclear dipolar interaction:<sup>6</sup>

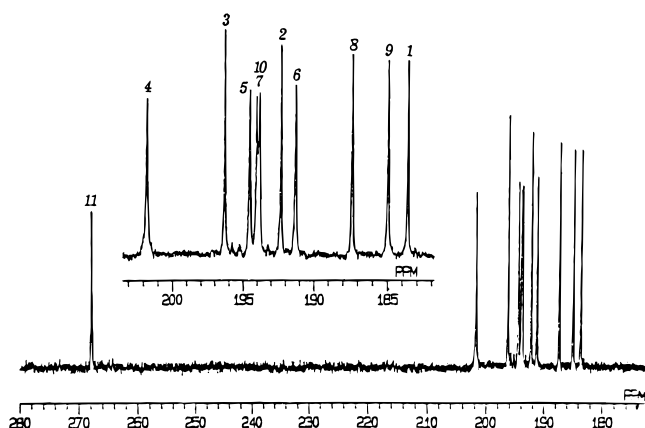
$$\frac{1}{T_1} = \frac{3}{10} \left( \frac{\mu_0}{4\pi} \right)^2 \gamma_H^4 \hbar^2 \tau_c \left( \frac{1}{1 + \omega_0^2 \tau_c^2} + \frac{4}{1 + 4\omega_0^2 \tau_c^2} \right)$$

where  $\mu_0$  is the magnetic susceptibility in the vacuum,  $\gamma_H$  is the gyromagnetic ratio for the proton, and  $\tau_c$  is the molecular correlation time for the complex at 213 K. By considering a  $\tau_c$  value of 172 ps as previously evaluated for Ru<sub>3</sub>(CO)<sub>12</sub> at the same temperature,<sup>7</sup> we obtained an  $r_{HH}$  value of 2.62 Å. Assuming a Ru-H distance of 1.79 Å for the bridging hydride and 1.65 Å for the terminal hydride,<sup>8</sup> we can estimate an HRu<sub>1</sub>H angle of 99.1°.

On the basis of the <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data, it is then evident that the structure of H( $\mu$ -H)-Ru<sub>3</sub>(CO)<sub>11</sub> is rather different from that previously suggested (III), the main difference being the presence of a bridging CO ligand, which is reminiscent of the bonding scheme found in the hydroxycarbyne moiety (I) and in the anionic [( $\mu$ -H)Ru<sub>3</sub>( $\mu$ -CO)(CO)<sub>10</sub>]<sup>-</sup> derivative.<sup>9</sup> A schematic representation of the proposed structure (II) is shown in Chart 2.

**Dynamic Behavior.** Upon an increase in the temperature from 183 to 233 K, all the <sup>13</sup>C signals except the peak at 196.3 ppm broaden, as indicative of a carbonyl-scrambling process. For the elucidation of the exchange mechanism, the <sup>13</sup>C-2D-EXSY<sup>10</sup> experiment performed at 188 K in CD<sub>2</sub>Cl<sub>2</sub> is very informative (Figure 2). All of the carbonyls are shown to exchange pairwise, except carbonyl 3. On the basis of the above-reported assignment, the following pairwise exchanges take place: 1 ↔ 2, 4 ↔ 8, 5 ↔ 10, 6 ↔ 9, 7 ↔ 11.

At this temperature, no exchange of the hydride resonances is detected, and carbonyl 3 shows a trans



**Figure 1.** <sup>13</sup>C-NMR spectrum of a <sup>13</sup>C-enriched sample of H( $\mu$ -H)Ru<sub>3</sub>(CO)<sub>11</sub> (CD<sub>2</sub>Cl<sub>2</sub>, 183 K).

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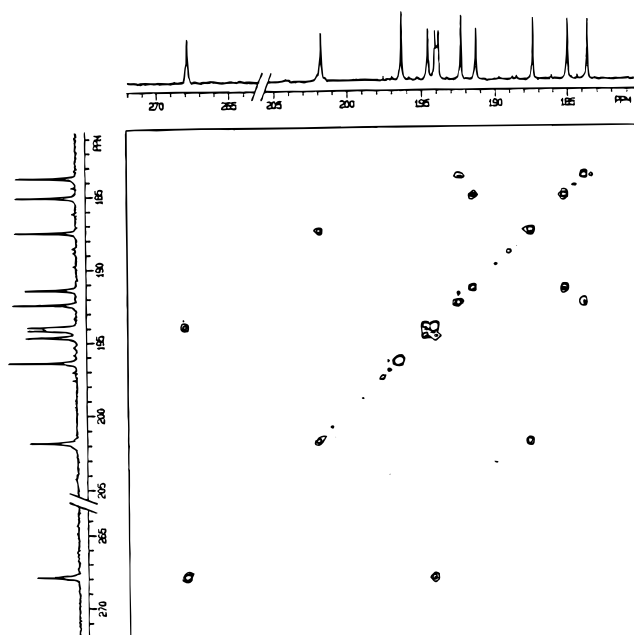
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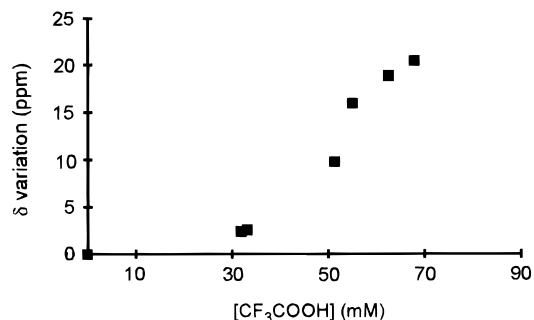
**Figure 2.** Contour plot of a  $^{13}\text{C}$ -2D-EXSY experiment for  $\text{H}(\mu\text{-H})\text{Ru}_3(\mu\text{-CO})(\text{CO})_{10}$  ( $\text{CD}_2\text{Cl}_2$ , 188 K, 100.25 MHz,  $\tau_m = 0.5$  s).

coupling with the terminal hydride, so we propose an exchange mechanism that involves edge hopping of the bridging hydride from the  $\text{Ru}_1\text{-Ru}_3$  to  $\text{Ru}_1\text{-Ru}_2$  edge in concert with the mutual opening and closing of the bridging carbonyl **11** and of the axial carbonyl **7** (Scheme 1). The rapid switch forward and backward of such a dynamic process produces enantiomerization of  $\text{H}(\mu\text{-H})\text{Ru}_3(\mu\text{-CO})(\text{CO})_{10}$ , similar to that reported for  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{11}$ ,<sup>11</sup> but with the significant difference that in the latter case terminal hydride motion is involved.

At temperatures higher than 233 K, a progressive broadening of the hydride resonances takes place, as previously observed in ref 1. This behavior was ascribed to the mutual exchange of terminal and bridging hydrides.

**Reaction with  $\text{CF}_3\text{COOH}$ .** Upon successive addition of aliquots of  $\text{CF}_3\text{COOH}$  to a solution of  $\text{H}(\mu\text{-H})\text{Ru}_3(\mu\text{-CO})(\text{CO})_{10}$  at 183 K, all the  $^{13}\text{C}$  resonances display significant shifts. The most pronounced shift is observed for the bridging carbonyl peak: its chemical shift increases with the acid concentration in solution, as shown in Figure 3.

The observed behavior may be explained by a fast reversible protonation of  $\text{H}(\mu\text{-H})\text{Ru}_3(\mu\text{-CO})(\text{CO})_{10}$ . The large variation of the  $^{13}\text{C}$  chemical shift of the bridging carbonyl suggests that the protonation occurs at this site. Although in an organic solvent a clear-cut distinction between H-bonding and protonation appears somewhat difficult, we believe that the addition of  $\text{CF}_3\text{COOH}$  to  $\text{H}(\mu\text{-H})\text{Ru}_3(\text{CO})_{11}$  indeed implies the formation of an O-H bond. In fact, as we add  $\text{Et}_3\text{NH}^+\text{Cl}^-$  or  $\text{CH}_3\text{COOH}$  to  $\text{H}(\mu\text{-H})\text{Ru}_3(\text{CO})_{11}$ , nothing happens, although such weak acids would have been expected to act as H-donors in hydrogen-bond formation.<sup>12</sup> Thus it appears that a



**Figure 3.** Chemical shift variation vs  $\text{CF}_3\text{COOH}$  concentration plot for the bridging carbonyl of  $\text{H}(\mu\text{-H})\text{Ru}_3(\mu\text{-CO})(\text{CO})_{10}$  (50 mM in  $\text{CD}_2\text{Cl}_2$ ).

protonation scheme analogous to that responsible for the formation of  $[(\mu\text{-H})\text{Ru}_3(\mu\text{-COH})(\text{CO})_{10}]^-$  from the  $[(\mu\text{-H})\text{Ru}_3(\mu\text{-CO})(\text{CO})_{10}]^-$  anion takes place. The oxygen atom on the bridging carbonyl in  $\text{H}(\mu\text{-H})\text{Ru}_3(\mu\text{-CO})(\text{CO})_{10}$  maintains the high Lewis basicity of the parent  $[(\mu\text{-H})\text{Ru}_3(\mu\text{-CO})(\text{CO})_{10}]^-$ . This view is further supported by the similar  $^{13}\text{C}$  chemical shift values found for the bridging CO's in the two compounds ( $\delta = 284.5$  was reported for  $[(\mu\text{-H})\text{Ru}_3(\mu\text{-CO})(\text{CO})_{10}]^-$ ).<sup>13</sup>

When the temperature of a solution containing an excess of  $\text{CF}_3\text{COOH}$  is raised, a net transformation of  $\text{H}(\mu\text{-H})\text{Ru}_3(\mu\text{-CO})(\text{CO})_{10}$  to  $(\mu\text{-H})\text{Ru}_3(\mu\text{-}\eta^3\text{-OOCFF}_3)(\text{CO})_{10}$  takes place. The latter compound has been unambiguously characterized on the basis of its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. The proton spectrum of this compound in  $\text{CD}_2\text{Cl}_2$  consists of a hydride resonance at  $-12.16$  ppm. The  $^{13}\text{C}$  analysis reveals the presence of six different carbonyl resonances in the relative intensity ratio of 1:1:2:2:2:2 at 204.1, 203.3, 197.3 ( $J_{\text{C,H}} = 3.0$  Hz), 191.7, 190.9 ( $J_{\text{C,H}} = 15.3$  Hz), and 182.4 ( $J_{\text{C,H}} = 4.6$  Hz) ppm, respectively, and two quartets centered at 114.0 ppm ( $J^{13}\text{C},^{19}\text{F} = 288$  Hz) and 161.1 ppm ( $J^{13}\text{C},^{19}\text{F} = 42$  Hz), assigned to the  $\text{CF}_3$  and  $\text{COO}$  groups, respectively.

In principle, this product might be formed by oxidative addition of a  $\text{CF}_3\text{COOH}$  molecule to the coordinatively unsaturated  $\text{Ru}_3(\text{CO})_{11}$  species (path i, Scheme 2). If this reaction path is correct, the use of  $\text{CF}_3\text{COOD}$  instead of  $\text{CF}_3\text{COOH}$  should yield only  $(\mu\text{-D})\text{Ru}_3(\mu\text{-}\eta^3\text{-OOCFF}_3)(\text{CO})_{10}$ . Since the  $^1\text{H}$  NMR hydride resonance of the product is detected when  $\text{CF}_3\text{COOD}$  is used, we rule out the possibility that (i) is the only path responsible for the observed transformation. Tentatively, we suggest an alternative pathway, involving protonation of  $\text{H}(\mu\text{-H})\text{Ru}_3(\mu\text{-CO})(\text{CO})_{10}$  and successive elimination of  $\text{H}_2$  and  $\text{CO}$  from the  $[\text{H}(\mu\text{-H})\text{Ru}_3(\mu\text{-COH})(\text{CO})_{10}]^+$  species followed by the reaction with the  $\text{CF}_3\text{COO}^-$  anion to yield the product (path ii).

### Concluding Remarks

These findings unambiguously support the view that the solution structure of  $\text{H}(\mu\text{-H})\text{Ru}_3(\mu\text{-CO})(\text{CO})_{10}$  differs significantly from that of  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{11}$ . It represents a third structural form for the  $\text{H}_2\text{M}_3(\text{CO})_{11}$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) species, intermediate between the hydroxycarbonyl-containing species (**I**) and the all-terminal-CO structure of  $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{11}$  (**III**).

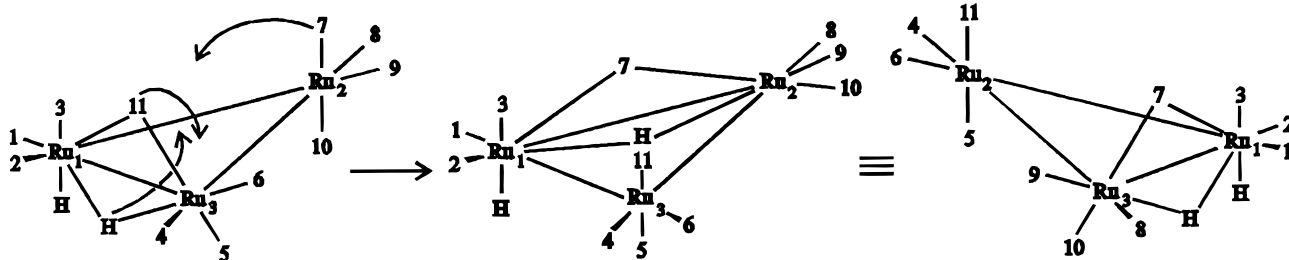
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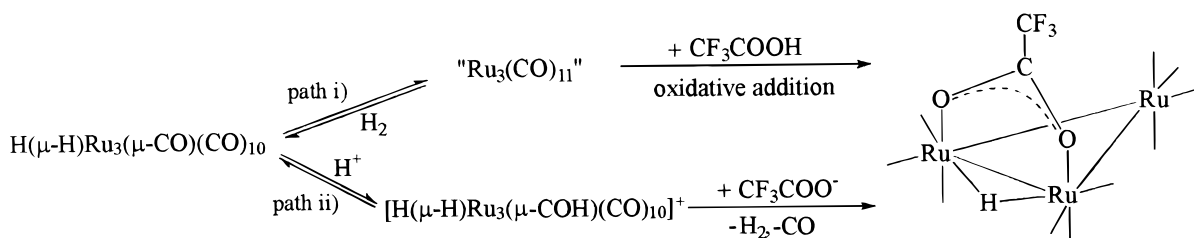
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Scheme 1



Scheme 2



Such structural diversity may account for the difference shown by the two complexes in the H<sub>2</sub> elimination process. Tentatively, we suggest that in structure **II** the oxygen atom of the bridging carbonyl provides the basic site for intramolecular activation of one hydride ligand and the H<sub>2</sub> elimination may be envisaged as the coupling reaction of proton and hydride moieties. In this view, the greater inertness of the Os cluster, which was explained in terms of a higher activation entropy,<sup>14</sup> appears to be dependent on the lack of an intramolecular anchoring site for hydride activation. One may think that the Os $\cdots$ ( $\eta^2$ -H<sub>2</sub>) transition state is characterized by a much higher entropic content than that present in a system where the outcoming hydrogen molecule is simultaneously interacting with both a Ru center and the basic oxygen of a bridging carbonyl ligand. Reported examples of related proton transfer are found in the chemistry of nonclassical hydrides. For instance, Morris et al.<sup>15</sup> reported that an intramolecular proton transfer takes place within a transition metal complex from coordinated dihydrogen to a coligand which acts as a base. Another example was recently reported by James

et al.,<sup>16</sup> who showed that a proton transfer occurs from a cation to the associated hydride-containing anion to give an  $\eta^2$ -H<sub>2</sub> complex.

### Experimental Section

All solvents were stored over molecular sieves and purged with nitrogen before use. CH<sub>3</sub>CN was distilled from P<sub>2</sub>O<sub>5</sub>.

H<sub>2</sub> was purchased from SIAD (Bergamo, Italy) and used without further purification. <sup>13</sup>C (99% enriched) was purchased from ISOTECH (Miamisburg, OH). D<sub>2</sub> (99.8%) was purchased from EURISO-TOP (Saint Aubin, France).

Ru<sub>3</sub>(CO)<sub>11</sub>(NCCH<sub>3</sub>) was prepared according to the published method.<sup>17</sup> <sup>13</sup>C-enriched metal carbonyl complexes were prepared by using <sup>13</sup>C-enriched (40%) Ru<sub>3</sub>(CO)<sub>12</sub>, obtained by direct exchange of <sup>13</sup>C with Ru<sub>3</sub>(CO)<sub>12</sub> (200 mg) in cyclohexane (100 mL) at 343 K for 3 days in a sealed vial.

The reactions with H<sub>2</sub> and with CF<sub>3</sub>COOH were carried out directly in a 5 mm resealable NMR tube. For the preparation of ( $\mu$ -H)Ru<sub>3</sub>( $\mu$ - $\eta^3$ -OOCCH<sub>3</sub>)(CO)<sub>10</sub>, the following quantities were used: 0.015 mmol of H( $\mu$ -H)Ru<sub>3</sub>( $\mu$ -CO)(CO)<sub>10</sub> and 0.075 mmol of CF<sub>3</sub>COOH under 200 Torr of H<sub>2</sub>.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a JEOL EX-400 spectrometer operating at 399.65 and 100.25 MHz, respectively.

The nonselective inversion recovery pulse sequence was used to obtain T<sub>1</sub> values. The samples for T<sub>1</sub> measurements were previously degassed via freeze-thaw methodology.

The <sup>13</sup>C-2D-EXSY spectrum was acquired in the absolute mode at 188 K, by using 512 words in the  $f_2$  dimension and 256 words in the  $f_1$  dimension; the mixing time was 500 ms.

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