corresponds most closely to the reaction coordinate. Taking the stretching vibrational frequency as 2000 $cm^{-1}$ and the bending frequency as 800 $cm^{-1}$:

$$\ln (k_H/k_D) = (0.187/T)[(1620 - 2000) + (1190 - 800) + 477]$$

$$k_H/k_D = 1.4 \text{ at } 250 \text{ K}$$

Thus, at this point isotope effects do not provide enough information to distinguish between even these extreme examples presented above because of the low frequencies associated with the motion along the reaction coordinate. Of the models presented above, the one which most closely conforms to the experimentally determined activation parameters and kinetic isotope effects is that of a single potential energy barrier and a transition state containing a terminal hydride. Further measurements of temperature dependencies of the isotope effects and tritium kie's may provide the information necessary to more clearly define the nature of hydride fluxionality.

## Conclusion

Hydride fluxionality on $Ru_3$ clusters occurs through a sequence of migrations, each involving the movement of a single bridging hydride ligand from one metal–metal vector to an adjacent unbridged metal–metal bond. The mechanism can be treated as a proton exchange from one metal–metal bond to another. The "intrinsic" free energies of activation are ca. 50 kJ/mol, with the other ligands in the coordination sphere having a minor influence due to steric and electronic effects. The kinetic isotope effects are ca. 1.5, and activation entropies are ca. −30 J/(K mol). The transition state containing a terminal hydride is consistent with the observed activation parameters and deuterium kinetic isotope effects.

**Acknowledgment.** This work was supported by the National Science Foundation through Grant CHE85-20276. We also acknowlege the Alfred P. Sloan Foundation. We thank T. Marder of the University of Waterloo for a copy of DNMR3 and W. Jones of the University of Rochester for the two-site exchange program. We gratefully acknowledge helpful discussions with A. G. Orpen (University of Bristol) and suggestions provided by Professors W. H. Saunders (University of Rochester) and E. Rosenberg (California State University, Northridge).

**Supplementary Material Available:** Figures 1S and 2S, giving observed and calculated $^1H$ NMR line shapes for $(\mu\text{-H})_2Ru_3(\mu_3\text{-}\eta^2\text{-CHCO}_2\text{Me})(CO)_8(PPh_3)$ and $(\mu\text{-H})_2Ru_3(\mu_3\text{-}\eta^2\text{-MeOC}_2\text{Me})(CO)_9$, respectively (2 pages). Ordering information is given on any current masthead page.

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(39) For $(\mu\text{-H})_4Ru_4(CO)_{10}(PPh_2C_2H_4PPh_2)$, the $^1H$ NMR spectra have been interpreted to rule out the possibility of an intermediate containing four $\mu_3$-H ligands, in favor of an intermediate containing four terminal hydrides.[33] However, this distinction depends upon an arbitrary assignment of one hydride resonance. Furthermore, the possibility of stepwise hydride migration via intermediates having $\mu_3$-H ligands or terminal hydrides could not be ruled out.

# Formation of an Agostic Bond by Protonation. Characterization by NMR Spectroscopy of $[(\mu\text{-H})_3M_3(\mu_3\text{-}\eta^2\text{-HCR})(CO)_9][SO_3CF_3]$ (M = Ru, R = Et, $CHPhCH_2Ph$; M = Os, R = Me)

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*Received January 23, 1990*

Protonation of $(\mu\text{-H})_3M_3(\mu_3\text{-CX})(CO)_9$ (M = Ru, X = Et, $CHPhCH_2Ph$; M = Os, X = Me) in $HSO_3CF_3$ solution yields $[(\mu\text{-H})_3M_3(\mu_3\text{-}\eta^2\text{-HCR})(CO)_9]^+$, in which the proton has been shown by $^1H$ and $^{13}C$ NMR spectroscopy to add across a C–M edge. The agostic hydrogen is fluxionally exchanged among all three C–M bonds but does not exchange with the bridging hydrides. These protonated clusters prove to be more susceptible to reductive elimination of $CH_3X$ than their neutral precursors. When M = Ru and X = H, Cl, Br, and Ph, addition of acid causes immediate cluster decomposition. When X = Ph and $CHPhCH_2Ph$, the reductive-elimination products toluene and 1,2-diphenylpropane have been identified.

## Introduction

We have proposed that the reversible formation of an intermediate containing an agostic bond is the first step in the reductive elimination of $CH_3X$ from $(\mu\text{-H})_3Ru_3(\mu_3\text{-CX})(CO)_9$ under CO.[1] Reversible formation of an agostic bond by hydride migration from a metal–metal edge to a metal–carbon edge has been demonstrated in $Fe_3(CO)_9CH_4$, which exists in solution as an equilibrium mixture of tautomers $(\mu\text{-H})_3Fe_3(\mu_3\text{-CH})(CO)_9$, $(\mu\text{-H})_2Fe_3(\mu_3\text{-HCH})(CO)_9$, and $(\mu\text{-H})Fe_3(\mu_3\text{-H}_2CH)(CO)_9$; deprotonation yields $[(\mu\text{-H})Fe_3(\mu_3\text{-HCH})(CO)_9]^-$ (Figure 1).[2] However, $(\mu\text{-H})_3M_3(CO)_9(\mu_3\text{-CH})$ (M = Ru, Os) exists as the single isomer which contains no agostic bond. Also,

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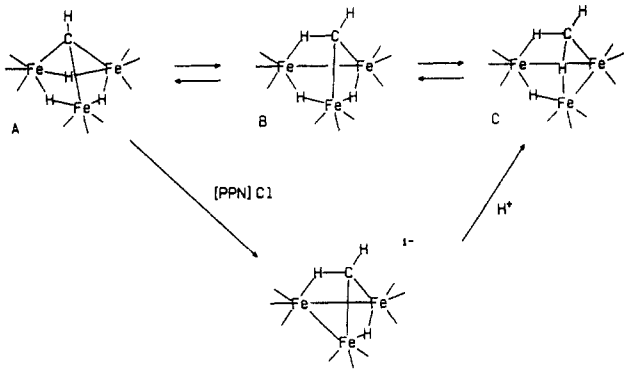


**Figure 1.** Tautomeric equilibria established previously for $H_3Fe_3(CH)(CO)_9$.

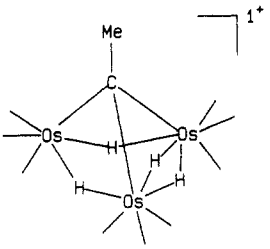


**Figure 2.** Structure proposed previously for the product from the protonation of $(\mu\text{-}H)_3Os_3(\mu_3\text{-}CMe)(CO)_9$.

deprotonation of $(\mu\text{-}H)_3Ru_3(CO)_9(\mu_3\text{-}COMe)$ with KOH yields $[(\mu\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}COMe)]^-$, in which the hydride signal has shifted only slightly downfield from that of the neutral precursor;[3] thus, deprotonation does not result in agostic bond formation in this instance.

However, a study of the electronic structure of $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CX)(CO)_9$ prompted us to try protonation as a means of inducing agostic bond formation. Fenske–Hall approximate molecular orbital calculations for $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CX)(CO)_9$ (X = H, Cl, Br) have indicated that the HOMO of these clusters is mainly Ru–C bonding in character.[4] Therefore, protonation of these clusters was expected to occur at the Ru–C bond, forming an agostic Ru–H–C interaction.

In 1976 Johnson and co-workers[5] reported the protonation of $(\mu\text{-}H)_3Os_3(\mu_3\text{-}CMe)(CO)_9$ with $HSO_3F$, yielding a product characterized as $[(\mu\text{-}H)_4Os_3(CO)_9(\mu_3\text{-}CMe)]^+$ (Figure 2). They reported that the $^1H$ NMR spectrum of the product contained three high-field resonances attributed to bridging hydrides: −12.85 (br s, 1 H), −16.62 (s, 2 H), and −16.81 (br s, 1 H) ppm. In the years since this work it has become recognized that agostic hydrogen resonances appear at high field, as do hydride resonances.[6] Therefore, we decided to reinvestigate the protonation of $(\mu\text{-}H)_3M_3(\mu_3\text{-}CX)(CO)_9$ (M = Ru, Os; X = alkyl, aryl, halide, H). Some of these results have been described in a preliminary communication.[7]

## Experimental Section

**General Considerations.** $^1H$ and $^{13}C$ NMR spectra were recorded on either a JEOL FX-90Q 90-MHz or a Varian Gemini 300-MHz spectrometer. Spectra of trifluoromethanesulfonic acid solutions were recorded on the FX-90 spectrometer with external lock ($D_2O$) and the sample in a 5-mm tube. Chemical shifts were referenced to TMS in a capillary insert in the center of the 5-mm tube. Chromium(III) acetylacetonate ($Cr(acac)_3$; 0.02 M) was added as a relaxation agent for $^{13}C$ NMR spectroscopy of the neutral clusters. Reagent grade solvents were used without further purification. Trifluoromethanesulfonic acid was obtained commercially and used as obtained from the freshly opened ampule or after trap-to-trap vacuum distillation. Workup of the protonated cluster solutions involved pouring the cluster/acid solution over ice, extracting with dichloromethane or pentane, and purifying the residue from the organic layer by thin-layer chromatography (TLC) on silica gel, eluting with hexane or hexane/dichloromethane solutions.

**Syntheses of Starting Materials.** $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CR)(CO)_9$ (R = H,[8] Cl,[8] Br,[8] Ph,[8] Et,[9] $CCHPhCH_2Ph$[9]), $Ru_3(CO)_{12}$,[10] $(\mu\text{-}H)_4Ru_4(CO)_{12}$,[11] and $(\mu\text{-}H)_3Os_3(\mu_3\text{-}CMe)(CO)_9$[12] were prepared according to previously published procedures. $(\mu\text{-}D)_3Ru_3(\mu_3\text{-}CCDPhCHDPh)(CO)_9$ was prepared as described below. Standard samples of 1,2-diphenylpropane, *cis*- and *trans*-1,2-diphenylpropene, and 2,3-diphenylpropene were prepared as described in the supplementary material.

**Protonation of $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CEt)(CO)_9$ in $Ru_3(\mu_3\text{-}CEt)(CO)_9$ in $HSO_3CF_3$.** $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CEt)(CO)_9$ (139.7 mg) was dissolved in $HSO_3CF_3$ (0.5 mL), producing a yellow solution with no gas evolution. $^1H$ and $^{13}C$ NMR spectra were recorded immediately (spectra A). A selectively decoupled $^{13}C\{sel\text{-}^1H\}$ NMR spectrum was also recorded. The $^1H$ and $^{13}C$ NMR spectra showed no broadening of the agostic hydrogen, hydride, or carbonyl resonances at −65 °C. Upon workup, $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CEt)(CO)_9$ (44.7 mg, 32%) and $Ru_3(CO)_{12}$ (32.8 mg, 22%) were recovered as the major products. The $^{13}C$ NMR spectrum of unprotonated $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CEt)(CO)_9$ was also recorded (spectrum B).

(A) $[(\mu\text{-}H)_3Ru_3(\mu_3\text{-}HCEt)(CO)_9]^+$: $^1H$ NMR ($HSO_3CF_3$, 22 °C) 3.25 (q, 2 $H_a$, $CH_2$), 1.28 (t, 3 $H_b$, $J_{ab}$ = 6 Hz, $CH_3$), −9.45 (s, 1 H, RuHC), −18.37 (s, 3 H, RuHRu) ppm, referenced to external TMS; $^{13}C$ NMR ($HSO_3CF_3$, −20 °C) 184.1 (s, 3 C, axial CO), 182.2 (d, 6 C, $J_{CH}$ = 12 Hz, equatorial CO), 143.3 (d, 1 C, $J_{CH}$ = 58 Hz, RuHC), 45.1 (t, 1 C, $J_{CH}$ = 137 Hz, $CH_2$), 22.2 (q, 1 C, $J_{CH}$ = 127 Hz, $CH_3$) ppm, referenced to $HSO_3CF_3$ at 125.02 ppm.

(B) $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CEt)(CO)_9$: $^{13}C$ NMR ($CDCl_3$, 22 °C) 238.8 (s, 1 C, $\mu_3$-C), 190.6 (d, 6 C, $J_{CH}$ = 11.6 Hz, equatorial CO), 189.7 (s, 3 C, axial CO), 53.6 (t, 1 C, $J_{CH}$ = 129 Hz, $CH_2$), 24.5 (q, 1 C, $J_{CH}$ = 126 Hz, $CH_3$) ppm.

**Protonation of $(\mu\text{-}H)_3Os_3(\mu_3\text{-}CMe)(CO)_9$ in $HSO_3CF_3$.** $(\mu\text{-}H_3)Os_3(\mu_3\text{-}CMe)(CO)_9$ (34.3 mg) was dissolved in $HSO_3CF_3$ (0.5 mL), and its $^1H$ NMR spectrum was immediately recorded (spectrum A). The $^1H$ NMR spectrum at −60 °C showed no broadening of the high-field resonances. $(\mu\text{-}H)_3Os_3(\mu_3\text{-}CMe)(CO)_9$ (29.8 mg, 87%) was the only product recovered upon workup.

A second sample of $(\mu\text{-}H)_3Os_3(\mu_3\text{-}CMe)(CO)_9$ (17.8 mg) was dissolved in $HSO_3CF_3$. This sample was allowed to partially decompose at room temperature for 1 day before its $^1H$ NMR spectrum was recorded (spectrum B).

(A) $^1H$ NMR ($HSO_3CF_3$, 22 °C): 3.39 (s, 3 H, $CH_3$), −10.64 (s, 1 H, OsHC), −19.25 (s, 3 H, OsHOs) ppm, referenced to external TMS.

(B) $^1H$ NMR ($HSO_3CF_3$, 22 °C): 3.31 (s, 3 H), −10.64 (s, 1 H), −12.20 (s, 1 H), −19.29 (s, 3 H) ppm, referenced to external TMS.

**Protonation of $(\mu\text{-}H)_3Os_3(\mu_3\text{-}CMe)(CO)_9$ in $HSO_3F$.** $(\mu\text{-}H)_3Os_3(\mu_3\text{-}CMe)(CO)_9$ (17.8 mg) was dissolved in $HSO_3F$ (0.5 mL), and its $^1H$ NMR spectrum was immediately recorded. Upon workup, $(\mu\text{-}H)_3Os_3(\mu_3\text{-}CMe)(CO)_9$ (13.2 mg, 74%) was recovered.

$^1H$ NMR ($HSO_3F$, 22 °C): 3.39 (s, 3 H, $CH_3$), −10.64 (s, 1 H, OsHC), −19.25 (s, 3 H, OsHOs) ppm.

**Protonation of $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CCHPhCH_2Ph)(CO)_9$ in $HSO_3CF_3$.** $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CCHPhCH_2Ph)(CO)_9$ (200 mg) was dissolved in $CDCl_3$, $Cr(acac)_3$ (0.02 M) was added as a relaxation

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agent, and $^1H$ and $^{13}C$ NMR spectra were recorded (spectra A). The sample was purified by TLC, eluting with hexane to remove the $Cr(acac)_3$, and then it was dissolved in $HSO_3CF_3$ (0.5 mL) and $^1H$ and $^{13}C$ NMR spectra were immediately recorded (spectra B). The sample was then allowed to decompose at room temperature. After 4 days the decomposition was complete (the agostic hydrogen and hydride resonances in the $^1H$ NMR spectrum had completely disappeared). The sample was worked up by pouring the cluster/acid solution over ice and extracting with pentane. The pentane solution was then evaporated to dryness, and $^1H$ and $^{13}C$ NMR spectra of the extracted organic residue were recorded (spectra C).

A second sample of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCHPhCH}_2\text{Ph})(CO)_9$ (20 mg) was dissolved in $HSO_3CF_3$ (0.5 mL) and placed in a 5-mm NMR tube. The sample was then allowed to decompose at room temperature with the progress of the reaction followed by monitoring the disappearance of the agostic hydrogen and hydride signals at −8.8 and −17.9 ppm by $^1H$ NMR spectroscopy. The sample was stable for 3 days.

(A) $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCHPhCH}_2\text{Ph})(CO)_9$: $^1H$ NMR ($CDCl_3$, 22 °C) 7.45–7.05 (m, 10 H, Ph), 5.20 (m, 1 H, CH), 3.82–3.39 (m, 2 H, $CH_2$), −17.67 (s, 3 H, RuHRu) ppm (small resonances due to impurities (<25% of the 1 H resonance at 5.20 ppm) were noted at 2.89 (s), 2.25 (s), 1.22 (br) ppm); $^{13}C$ NMR ($CDCl_3$, 22 °C) 239.9 (s, 1 C, $\mu_3$-C), 190.6 (s, 3 C, CO), 189.9 (s, 3 C, CO), 189.2 (s, 3 C, CO), 74.5 (d, 1 C, $J_{CH}$ = 122 Hz, CHPh), 51.4 (t, 1 C, $J_{CH}$ = 128 Hz, $CH_2$) ppm (resonances due to phenyl substituents were found between 148.7 and 125.6 ppm but were not assigned).

(B) $[(\mu\text{-H})_3Ru_3(\mu_3\text{-HCCHPhCH}_2\text{Ph})(CO)_9]^+$: $^1H$ NMR ($HSO_3CF_3$, 22 °C) 7.70–7.06 (m, 10 H, Ph), 4.48 (m, 1 H, CH), 3.77–3.22 (m, 2 H, $CH_2$), −8.99 (s, 1 H, RuHC), −18.08 (s, 3 H, RuHRu) ppm, referenced to $HSO_3CF_3$ resonance at 11.07 ppm; $^{13}C$ NMR ($HSO_3CF_3$, 22 °C) 185.3 (s, 3 C, axial CO), 183.5 (d, 3 C, $J_{CH}$ = 12 Hz, equatorial CO), 182.2 (d, 3 C, $J_{CH}$ = 10 Hz, equatorial CO), 148.8 (d, 1 C, $J_{CH}$ = 56 Hz, RuHC), 147.7 (s, 1 C, Ph), 139.0 (s, 1 C, Ph), 129.1 (1 C, Ph), 128.8 (2 C, Ph), 127.8 (2 C, Ph), 126.9 (1 C, Ph), 66.8 (d, 1 C, $J_{CH}$ = 131 Hz, CH), 50.3 (dd, 1 C, $CH_2$) ppm, referenced to $HSO_3CF_3$ resonance at 126 ppm.

(C) Extracted organic products: $^1H$ NMR ($CDCl_3$, 22 °C) 7.37–6.93 (m), 3.52 (br), 2.84–2.77 (m), 1.42, 1.35, 1.18, 0.86–0.74 (m) ppm (integrals could not be determined due to the poor quality of the spectrum); $^{13}C$ NMR ($CDCl_3$, relative intensities given) 128.2 (32), 127.6 (d, $J_{CH}$ = 166 Hz, 17), 127.3 (d, $J_{CH}$ = 157 Hz, 69), 126.1 (36), 125.7 (d, $J_{CH}$ = 154 Hz, 14), 125.4 (14), 125.0 (d, $J_{CH}$ = 154 Hz, 34), 123.6 (14), 123.4 (12), 45.1 (20), 40.9 (16), 37.1 (21), 34.7 (7), 33.2 (40), 31.0 (16), 28.8 (205), 28.5 (23), 26.0 (14), 24.9 (11), 23.6 (17), 21.8 (14), 21.4 (82), 20.1 (24), 13.0 (q, $J_{CH}$ = 124 Hz, 99) ppm.

**Protonation of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCHPhCH}_2\text{Ph})(CO)_9$ with $HSO_3CF_3$ in $CD_2Cl_2$.** $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCHPhCH}_2\text{Ph})(CO)_9$ (200 mg) was dissolved in $CD_2Cl_2$ (0.5 mL) with TMS added as an internal standard. One drop of $HSO_3CF_3$ was added to this solution, which was mixed by shaking. Then the $^1H$ NMR spectrum was recorded, but no change was visible except for the addition of the acid resonance at 11.55 ppm. Two more drops of acid were added to the solution, but the $^1H$ NMR spectrum again remained unchanged, so a few more drops of acid were added (ca. 0.3 mL of acid was added in total). This time gas evolution was observed upon mixing, so the $^1H$ NMR spectrum of this solution was immediately recorded (spectrum A). Multiple decomposition products were noted in the spectrum. The cluster/acid solution was then allowed to completely decompose before being worked up by pouring over ice and extracting with pentane. The $^1H$ NMR spectrum of the extracted organic residue was recorded (spectrum B).

(A) $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCHPhCH}_2\text{Ph})(CO)_9 + HSO_3CF_3$: $^1H$ NMR ($CD_2Cl_2$, 25 °C) 6.78–6.55 (m), 6.24–6.04 (m), 5.04–4.89 (m), 4.79 (s), 4.08–3.81 (m), 3.44, 3.24 (m), 3.10 (m), 2.95, 2.82, 2.67–2.12 (m), 1.05–0.90 (m), 0.78, 0.70, −9.58 (s), −10.33 (s), −18.62 (s), −20.89 (s) ppm. The integral ratio of signals at −9.58 and −18.62 ppm is 1:3.

(B) Organic products: $^1H$ NMR ($CDCl_3$, 25 °C) 7.27–7.13 (m, 10 H, Ph), 3.05–2.70 (m, 3 H, CH and $CH_2$ of 1,2-diphenylpropane), 2.16 (s), 1.24 (d, 3 H, $J$ = 6.4 Hz, $CH_3$ of 1,2-diphenylpropane) ppm. Weak signals (<10% of the other signals in the spectrum) were noted at 4.25 (s), 4.19 (s), 3.78 (s), and 0.99–0.84 (m) ppm. The resonance at 2.16 (s) ppm is very strong and is assigned to residual acetone left behind in the NMR tube after cleaning.

**Synthesis of $(\mu\text{-D})_3Ru_3(\mu_3\text{-CCDPhCHDPh})(CO)_9$.** $(\mu\text{-H})\text{-}Ru_3(\mu_3\text{-}\eta^3\text{-MeOCPhCPh})(CO)_9$ (578 mg) was dissolved in cyclohexane (75 mL) and placed in a Parr bottle. The solution was flushed with nitrogen three times, pressurized with deuterium gas (45 psi), and then heated at 75 °C for 16 h. The solvent was removed by vacuum, and the residue was separated by TLC, eluting with hexane/$CH_2Cl_2$ (80:20). $(\mu\text{-D})_3Ru_3(\mu_3\text{-CCDPhCHDPH})(CO)_9$ (ca. 85% deuteriated in the hydride position, determined by integration vs the phenyl hydrogen resonances) was isolated as the second yellow band.

$(\mu\text{-D})_3Ru_3(\mu_3\text{-CCDPhCHDPh})(CO)_9$: $^1H$ NMR ($CDCl_3$, 22 °C) 7.83–7.02 (m, 10 H), 5.19 (s, 0.11 H), 3.67 (m, 0.30 H), −17.68 (s, 0.44 H) ppm.

**Protonation of $(\mu\text{-D})_3Ru_3(\mu_3\text{-CCDPhCHDPh})(CO)_9$ in $HSO_3CF_3$.** $(\mu\text{-D})_3Ru_3(\mu_3\text{-CCDPhCHDPh})(CO)_9$ (55.8 mg) was dissolved in $HSO_3CF_3$ (0.5 mL), and the $^1H$ NMR spectrum was immediately recorded (spectrum A). The cluster/acid solution was allowed to stand at room temperature for ca. 3 h before a second $^1H$ NMR spectrum was recorded (spectrum B). No starting cluster was recovered upon workup.

(A) $^1H$ NMR ($HSO_3CF_3$, 22 °C, relative peak heights given): 7.3 (m), 0.91 (s, 77), 0.62 (s, 54), −8.95 (s, 74), −18.03 (s, 55) ppm, referenced to $HSO_3CF_3$ resonance at 11.12 ppm.

(B) $^1H$ NMR ($HSO_3CF_3$, 22 °C, relative peak heights given): 7.3 (m), 0.91 (s, 107), 0.62 (s, 72), −8.95 (s, 82), −18.03 (s, 75) ppm, referenced to $HSO_3CF_3$ resonance at 11.12 ppm.

**Protonation of $H_3Ru_3(CPh)(CO)_9$ in $HSO_3CF_3$.** $(\mu\text{-H})_3Ru_3(\mu_3\text{-CPh})(CO)_9$ (210 mg) was dissolved in $HSO_3CF_3$ (0.8 mL), and its $^1H$ and $^{13}C$ NMR spectra were immediately recorded (spectra A). $(\mu\text{-H})_3Ru_3(\mu_3\text{-CPh})(CO)_9$ was not recovered, but $Ru_3(CO)_{12}$ and $(\mu\text{-H})_4Ru_4(CO)_{12}$ were recovered upon workup. In a separate NMR tube, toluene (25 μL) was mixed in $HSO_3CF_3$ (0.5 mL) and its $^{13}C$ NMR spectrum was recorded (spectrum B).

(A) $(\mu\text{-H})_3Ru_3(\mu_3\text{-CPh})(CO)_9$ in $HSO_3CF_3$: $^1H$ NMR (−30 °C) 6.87 (br), 5.81 (br), 5.51 (br), 2.55 (br), 1.93 (s), −14.22 (s), −18.00 (br), −20.53 (br) ppm, referenced to $HSO_3CF_3$ resonance at 10.98 ppm; $^{13}C$ NMR ($HSO_3CF_3$, −30 °C) 189.2 (s), 188.2 (s), 181.3 (s), 178.8 (s), 138.3 (s, 1 C), 128.6 (d, 2 C), 127.8 (d, 2 C), 124.4 (s, 1 C), 19.6 (q, 1 C, $J_{CH}$ = 126 Hz) ppm, referenced to $HSO_3CF_3$ resonance at 125.0 ppm ($J_{CH}$ for the resonances at 128.6 and 127.6 ppm could not be determined due to masking of the doublets by the acid resonances in the $^{13}C$ NMR spectrum).

(B) Toluene in $HSO_3CF_3$: $^{13}C$ NMR ($HSO_3CF_3$) 138.4 (s, 1 C), 128.6 (d, 2 C), 128.1 (d, 2 C), 124.4 (s, 1 C), 19.6 (q, 1 C, $J_{CH}$ = 126 Hz) ppm.

**Protonation of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CPh})(CO)_9$ with $HSO_3CF_3$ in $CDCl_3$.** $(\mu\text{-H})_3Ru_3(\mu_3\text{-CPh})(CO)_9$ (29 mg) was dissolved in $CDCl_3$ (0.5 mL) with TMS added as an internal reference, and the $^1H$ NMR spectrum of this solution was recorded (spectrum A). Then 1 drop of $HSO_3CF_3$ was added to this sample, and the $^1H$ NMR spectrum was immediately recorded (spectrum B). Next, separate samples of the acid, toluene, and a mixture of acid and toluene were prepared in $CDCl_3$ with TMS added as an internal reference and their $^1H$ NMR spectra were recorded for comparison. The cluster/acid solution was not worked up.

(A) $(\mu\text{-H})_3Ru_3(\mu_3\text{-CPh})(CO)_9$ in $CDCl_3$: $^1H$ NMR ($CDCl_3$, 22 °C) 7.70–7.10 (m, 5 H), 3.99 (s, impurity), 1.51 (s, impurity), −17.50 (s, 3 H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22 °C) 213.0 (s, 1 C), 190.0 (s, 9 C), 162.0 (s, 1 C), 130.2 (s, 2 C), 128.2 (s, 2 C), 125.2 (s, 1 C) ppm.

(B) $(\mu\text{-H})_3Ru_3(\mu_3\text{-CPh})(CO)_9$ in $CDCl_3$ with $HSO_3CF_3$: $^1H$ NMR ($CDCl_3$, 22 °C, relative peak heights given) 11.06 (s, 1.5), 9.80 (s, 3.7, acid), 6.69 (s, 23, toluene), 4.10 (s, 9.4), 3.47 (s, 12.3), 1.84 (s, 23, toluene), −0.30 (s, 1.9, impurity in acid), −0.52 (s, 4.6), −13.79 (s) ppm, referenced to internal TMS. Peaks due to toluene were off scale.

**Protonation of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CH})(CO)_9$ in $HSO_3CF_3$.** $(\mu\text{-H})_3Ru_3(\mu_3\text{-CH})(CO)_9$ (40 mg) was dissolved in $HSO_3CF_3$ (0.5 mL) and gas immediately evolved from the solution. The $^1H$ NMR spectrum was recorded. No products were recovered upon workup.

$^1H$ NMR ($HSO_3CF_3$, −30 °C): 1.45 (s, br), 1.05 (s), 0.75 (s), 0.31 (s), −13.77 (s) ppm, referenced to $HSO_3CF_3$ resonance at 11.12 ppm.

**Protonation of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCl})(CO)_9$ in $HSO_3CF_3$.** $(\mu\text{-H}_3)Ru_3(\mu_3\text{-CCl})(CO)_9$ (32.9 mg) was dissolved in $HSO_3CF_3$ (0.5 mL), and gas immediately evolved from the solution. After 5 min of mixing not all of the cluster had gone into solution, but in order to avoid further decomposition, the $^1H$ NMR spectrum was recorded immediately.

$^1H$ NMR ($HSO_3CF_3$, −30 °C): 7.7–7.3 (m), 5.43 (s), 4.67 (s), −14.60 (s) ppm, referenced to $HSO_3CF_3$ resonance at 11.07 ppm.

**Protonation of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CBr})(CO)_9$ in $HSO_3CF_3$.** $(\mu\text{-H})_3Ru_3(\mu_3\text{-CBr})(CO)_9$ (27.5 mg) was dissolved in $HSO_3CF_3$ (0.5 mL) at room temperature, and immediate gas evolution occurred. After the solution was mixed for 5 min, some of the cluster still had not gone into solution. However, in order to avoid further decomposition, the $^1H$ NMR spectrum was recorded immediately at −30 °C.

$^1H$ NMR ($HSO_3CF_3$, −30 °C): 0.20 (s), −13.83 (s), −16.97 (s) and −18.39 (s) ppm, referenced to $HSO_3CF_3$ resonance at 11.12 ppm.

**Protonation of $Ru_3(CO)_{12}$ in $HSO_3CF_3$.** $Ru_3(CO)_{12}$ (14.6 mg) was dissolved in $HSO_3CF_3$ (0.5 mL), and the $^1H$ NMR spectrum was immediately recorded. $Ru_3(CO)_{12}$ was recovered upon workup. The $^1H$ NMR spectrum for $Ru_3(CO)_{12}$ in 98% $H_2SO_4$ has been reported and shows a single resonance at −19.4 ppm.[13]

$^1H$ NMR ($HSO_3CF_3$): −19.37 ppm, referenced to external TMS.

**Protonation of $(\mu\text{-H})_4Ru_4(CO)_{12}$ in $HSO_3CF_3$.** $(\mu\text{-H})_4Ru_4(CO)_{12}$ was dissolved in $HSO_3CF_3$ (0.5 mL), and the $^1H$ NMR spectrum was immediately recorded. $(\mu\text{-H})_4Ru_4(CO)_{12}$ was the only product recovered.

$^1H$ NMR ($HSO_3CF_3$): −18.91 ppm, referenced to external TMS.

## Results and Discussion

**Protonation of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CEt})(CO)_9$.** Protonation of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CEt})(CO)_9$ with $CF_3SO_3H$, either as the neat compound or in dichloromethane solution, forms $[(\mu\text{-H})_3Ru_3(\mu_3\text{-}\eta^2\text{-HCEt})(CO)_9]^+$. The product has been characterized by its $^1H$ and $^{13}C$ NMR spectra. The $^1H$ NMR spectrum consists of resonances at 3.25 (q, 2 H, $CH_2$), 1.28 (t, 3 H, $J$ = 6 Hz, $CH_3$), −9.45 (s, 1 H, RuHC), and −18.37 (s, 3 H, RuHRu) ppm, in which the resonances for the ethyl group and the hydrides are shifted slightly upfield from those of the precursor and the new peak at −9.45 ppm is attributed to the agostic hydrogen.

The new resonance observed at −9.45 ppm could reasonably be assigned to either a terminal hydride ligand or an agostic hydrogen, since both will display high-field $^1H$ NMR signals in this region of the spectrum (the terminal hydride resonance of $H(\mu\text{-H})Ru_3(CO)_{11}$ occurs at −11.98 ppm,[14] and the agostic hydrogen signal of $[(\mu\text{-H})Fe_3(\mu_3\text{-}\eta^2\text{-HCH})(CO)_9]^-$ occurs at −10.1 ppm[2]). Definitive evidence for the structural assignment was obtained from the $^{13}C$ NMR spectrum of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CEt})(CO)_9$ in $HSO_3CF_3$. The assignments of the resonances in the $^{13}C$ NMR spectrum of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CEt})(CO)_9$ in $HSO_3CF_3$ were made by comparison with the $^{13}C$ NMR spectrum of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CEt})(CO)_9$ in $CDCl_3$. The resonances in the $^{13}C$ NMR spectrum of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CEt})(CO)_9$ in acid, compared to those of the same cluster in $CDCl_3$, show a trend similar to that seen in the $^1H$ NMR spectrum, namely an upfield shift of the resonances upon protonation. The methylene triplet at 53.6 ($J_{CH}$ = 129 Hz) ppm and the methyl quartet at 24.5 ($J_{CH}$ = 126 Hz) ppm in $CDCl_3$ solution shift upfield to 45.1 ($J_{CH}$ = 137 Hz) and 22.2 ($J_{CH}$ = 127 Hz) ppm, respectively, in acid solution. The $^{13}C$ resonances of the carbonyl ligands also demonstrate this trend. The doublet assigned to the six equatorial CO ligands shifts upfield from 190.6 ($J_{CH}$ = 11.6 Hz) to 182.2 ($J_{CH}$ = 12 Hz) ppm, and the singlet representing the three axial CO ligands shifts upfield from 189.7 to 184.1 ppm upon protonation. The acid, $HSO_3CF_3$, appears at 118.0 (q, $J_{CF}$ = 316 Hz) ppm.

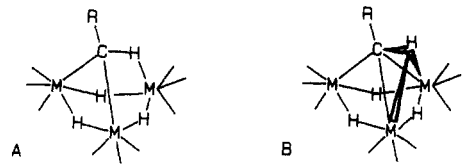


**Figure 3.** Possible structures for $[(\mu\text{-H})_3M_3(\mu_3\text{-}\eta^2\text{-HCR})(CO)_9]^+$ (M = Ru, R = Et, $CHPhCH_2Ph$; M = Os, R = Me). Structure A is preferred.

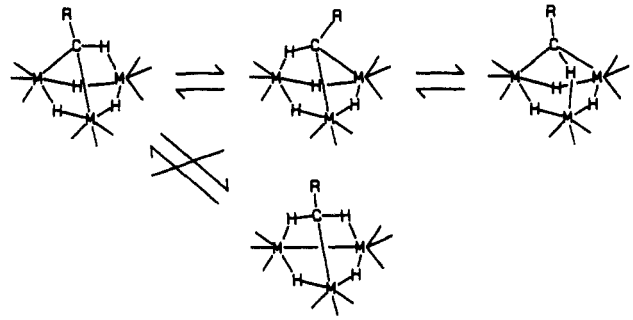

**Figure 4.** Mechanism for fluxional migration of the agostic hydrogen and for exchange of hydrides and the agostic hydrogen of $[(\mu\text{-H})_3M_3(\mu_3\text{-}\eta^2\text{-HCR})(CO)_9]^+$ (M = Ru, R = Et, $CHPhCH_2Ph$; M = Os, R = Me).

The methylidyne carbon resonance undergoes the largest shift upon protonation. In $CDCl_3$, this signal appears as a singlet at 232.8 ppm. In $HSO_3CF_3$, this signal shifts upfield by 89.5 ppm to appear as a doublet at 143.3 ($J_{CH}$ = 58 Hz) ppm. Coupling between the methylidyne carbon and the hydrogen that resonates at −9.45 ppm in the $^1H$ NMR spectrum was confirmed by selective decoupling. The C–H coupling constant is characteristic for a methylidyne carbon involved in an agostic bond. For example, for $[(\mu\text{-H})Fe_3(\mu_3\text{-}\eta^2\text{-HCH})(CO)_9]^-$ the methylidyne carbon resonance appears as a doublet at 118.5 ppm with $J_{CH}$ = 65 Hz.[2] A second example is the tautomeric equilibrium mixture $HFe_2Co(\mu_3\text{-CPh})(CO)_9/Fe_2Co(\mu_3\text{-}\eta^2\text{-HCPh})(CO)_9$, in which the resonance for the $\mu_3$-HCPh ligand appears as a doublet at 189.4 ppm with $J_{CH}$ = 59.5 Hz (cf. 281.4 ppm for the $\mu_3$-CPh ligand).[15]

Workup of the acid solution by pouring over ice and extracting with dichloromethane recovers $(\mu\text{-H})_3Ru_3(\mu_3\text{-CEt})(CO)_9$ in 32% yield along with a significant amount of $Ru_3(CO)_{12}$. $Ru_3(CO)_{12}$ must be formed upon workup, because no resonance for $[(\mu\text{-H})Ru_3(CO)_{12}]^+$ (−19.37 ppm in $HSO_3CF_3$) is observed in the spectrum of the acid solution.[13] This evidence confirms the reversible formation of an agostic bond in $[(\mu\text{-H})_3Ru_3(\mu_3\text{-}\eta^2\text{-HCEt})(CO)_9]^+$.

The proposed structure for $[(\mu\text{-H})_3Ru_3(\mu_3\text{-}\eta^2\text{-HCEt})(CO)_9]^+$ is shown in Figure 3A. The static structure, having $C_s$ symmetry, should yield three high-field signals in the $^1H$ NMR spectrum, while the $^{13}C$ NMR spectrum should show five signals for the carbonyl ligands. The higher apparent symmetry can be explained if the agostic hydrogen migrates to each of the three Ru–CEt vectors at a rate that is fast on the NMR time scale, thus creating apparent $C_{3v}$ symmetry (Figure 4, upper path). Another structure that is consistent with the spectral data is one in which the agostic proton is capping a $CRu_2$ face (Figure 3B). Fast exchange of this structure would also generate apparent $C_{3v}$ symmetry and the observed spectra. However, to date there is only one cluster reported that may

(13) Knight, J.; Mays, M. J. *J. Chem. Soc. A* **1970**, 711.
(14) (a) Keister, J. B. *J. Organomet. Chem.* **1980**, *190*, C36. (b) Nevinger, L. R.; Keister, J. B.; Maher, J. *Organometallics*, in press.
(15) Barreto, R. D.; Fehlner, T. P. *J. Am. Chem. Soc.* **1988**, *110*, 4471.

contain a face-capping agostic proton, and even in this case the preferred structure is edge-bridged.[15] Therefore, an edge-bridged structure is favored, but a face-capped structure is an attractive intermediate for the edge-hopping exchange process proposed. Low-temperature $^1H$ NMR spectroscopy at −65 °C shows no signs of broadening of the high-field signals. No broadening of the carbonyl resonances is observed in the $^{13}C$ NMR spectrum of $[(\mu\text{-}H)_3Ru_3(\mu_3\text{-}\eta^2\text{-}HCEt)(CO)_9]^+$ at −65 °C, implying that this exchange process is very facile.

**Protonation of $(\mu\text{-}H)_3Os_3(\mu_3\text{-}CMe)(CO)_9$.** In our hands, protonation of $(\mu\text{-}H)_3Os_3(\mu_3\text{-}CMe)(CO)_9$ by dissolution in either $HSO_3F$ or $HSO_3CF_3$ at 22 °C produced two high-field signals in the $^1H$ NMR spectrum at −10.64 (s, 1 H) and −19.29 (s, 3 H) ppm, completely analogous to the spectrum of $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CEt)(CO)_9$ in $HSO_3CF_3$. Repeated attempts to reproduce the results reported by Johnson and co-workers were unsuccessful (with the possible exception of the resonance at −12.85 ppm, vide infra).

Therefore, a structure analogous to that of $[(\mu\text{-}H)_3Ru_3(\mu_3\text{-}\eta^2\text{-}HCEt)(CO)_9]^+$ is proposed for $[(\mu\text{-}H)_3Os_3(\mu_3\text{-}\eta^2\text{-}HCMe)(CO)_9]^+$. Like $[(\mu\text{-}H)_3Ru_3(\mu_3\text{-}\eta^2\text{-}HCEt)(CO)_9]^+$, this cluster must also be fluxional at a rate that is fast on the NMR time scale in order to account for the observed spectrum. Workup of the acid solution recovers $(\mu\text{-}H)_3Os_3(\mu_3\text{-}CMe)(CO)_9$ in 87% yield.

**Protonation of $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CCHPhCH_2Ph)(CO)_9$.** Dissolution of $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CCHPhCH_2Ph)(CO)_9$ in $HSO_3CF_3$ yields a $^1H$ NMR spectrum with two high-field resonances at −8.99 (s, 1 H) and −18.08 (s, 3 H) ppm in addition to the resonances for the 2,3-diphenylpropylidyne substituent. The spectrum is completely analogous to those of $[(\mu\text{-}H)_3Ru_3(\mu_3\text{-}\eta^2\text{-}HCEt)(CO)_9]^+$ and $[(\mu\text{-}H)_3Os_3(\mu_3\text{-}\eta^2\text{-}HCMe)(CO)_9]^+$. The methylidyne carbon resonance for $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CCHPhCH_2Ph)(CO)_9$ in $CDCl_3$ is a singlet at 239.9 ppm, but in $HSO_3CF_3$ it shifts upfield to 148.8 ppm (d, $J_{CH}$ = 56 Hz), behavior clearly indicative of a carbon atom involved in an agostic interaction. The other resonances experience smaller upfield shifts, analogous to those observed for $[(\mu\text{-}H)_3Ru_3(\mu_3\text{-}\eta^2\text{-}HCEt)(CO)_9]^+$.

Protonation of $(\mu\text{-}H)_3Ru(\mu_3\text{-}CCHPhCH_2Ph)(CO)_9$ in $CD_2Cl_2$ was also attempted. Addition of $HSO_3CF_3$ to $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CCHPhCH_2Ph)(CO)_9$ in $CD_2Cl_2$ was accompanied by gas evolution. The $^1H$ NMR spectrum of this solution revealed two signals in the hydride region at −9.58 (s, 1 H) and −18.62 (s, 3 H) ppm, characteristic of a fluxional agostic species. In addition, two other smaller resonances were observed at −10.33 (s) and −20.89 (s) ppm. The highest field signal is most likely due to $[(\mu\text{-}H)Ru_3(CO)_{12}]^+$, while the −10.33 ppm resonance is attributed to an unidentified decomposition product.

**Agostic Hydrogen–Hydride Exchange in Protonated Clusters.** In an attempt to determine whether the agostic hydrogen exchanges with the metal hydrides, $(\mu\text{-}D)_3Ru_3(\mu_3\text{-}CCDPhCHDPh)(CO)_9$ (85% deuteriated in the hydride position) was prepared and then protonated with $HSO_3CF_3$. Exchange between the agostic hydrogen and the hydrides at a rate that is fast on the NMR time scale should yield a less than 1:3 ratio between the height of the agostic hydrogen resonance and the height of the hydride resonance in the $^1H$ NMR spectrum of a partially deuteriated sample because of the differences in zero-point energies. After ca. 3 h at room temperature, the ratio of agostic hydrogen to hydride resonances in the $^1H$ NMR spectrum had decreased by only 19%, from 1.34 to 1.09 based on relative peak heights, almost the same within experimental error (5–10% of peak height). If exchange is occurring, it is at a very slow rate.

The proposed mechanism for the reductive elimination of $CH_3X$ from $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CX)(CO)_9$ calls for the reversible preequilibrium formation of an intermediate containing an agostic bond, as in Figure 1B, by migration of hydrogen from metal–metal bridging to metal–carbon bridging. A similar species was proposed as an intermediate in the methylidyne hydrogen/hydride exchange observed in $(\mu\text{-}H)_3M_3(\mu_3\text{-}CH)(CO)_9$ (M = Ru, Os).[16] Fehlner has demonstrated the existence of such a species as a tautomer of "$Fe_3(CO)_9CH_4$" (Figure 1).[2] However, exchange does not appear to occur between the agostic hydrogen and the hydrides in $[(\mu\text{-}H)_3Ru_3(\mu_3\text{-}\eta^2\text{-}HCR)(CO)_9]^+$.

In most of the previously studied systems in which M–H–M or M–H–C bridges are possible, the M–H–M arrangement is the more stable one, but exchange between the two tautomers can be fast on the NMR time scale. Thus, it is surprising that exchange between the hydrides and agostic hydrogen is slow on the chemical time scale. For $[(\mu\text{-}H)_3Ru_3(\mu_3\text{-}\eta^2\text{-}HCR)(CO)_9]^+$, exchange between the hydrides and the agostic hydrogen could occur by migration of a hydride ligand to one of the two vacant C–M edges. This mechanism (Figure 4, lower path) would generate an intermediate species containing two agostic bonds, similar to one of the tautomers of "$Fe_3(CO)_9CH_4$", $(\mu\text{-}H)Fe_3(CO)_9(\mu_3\text{-}\eta^3\text{-}H_2CH)$, observed by Fehlner (Figure 1C). The equilibrium constant for M–H–M to M–H–C migration is influenced by the identities of M and R, with $K_{Ru} < K_{Fe}$ and $K_{alkyl} < K_H$; for the equilibria in Figure 1, $K(A \rightarrow B) > K(B \rightarrow C)$. The equilibrium constant for the formation of the intermediate $[(\mu\text{-}H)_2Ru_3(\mu_3\text{-}\eta^2\text{-}H_2CEt)(CO)_9]^+$ containing two agostic bonds is likely to be small because of the slow rate of the forward reaction. Fehlner has noted that $\Delta H°$ for the migration of M–H–M to M–H–E is related to the difference in electronegativities of M and E.[19] The positive charge on $[(\mu\text{-}H)_3Ru_3(\mu_3\text{-}\eta^2\text{-}HCR)(CO)_9]^+$ may therefore be a factor responsible for the instability of the tautomer with two agostic hydrogens.

**Protonated Cluster Decomposition Products.** No metal-containing species were recovered upon workup of the decomposed acid solutions. However, some of the metal-containing products of decomposition were characterized in situ via $^1H$ and $^{13}C$ NMR spectroscopy.

Decomposition of $[(\mu\text{-}H)_3Ru_3(\mu_3\text{-}\eta^2\text{-}HCEt)(CO)_9]^+$ in $HSO_3CF_3$ forms a new species characterized by a $^1H$ NMR signal at −7.59 (s) ppm and $^{13}C$ NMR signals at 179.0 (br, 4 C) and 178.8 (sh, 1 C) ppm. This same signal at −7.59 ppm also becomes visible after about 1 day in the $^1H$ NMR spectrum of the decomposition of $[(\mu\text{-}H)_3Ru_3(\mu_3\text{-}\eta^2\text{-}HCCHPhCH_2Ph)(CO)_9]^+$ in $HSO_3CF_3$. Yarrow and Ford have characterized $[HRu(CO)_5]^+$ in 98% $H_2SO_4$ solution with a $^1H$ NMR signal at −7.23 (s) ppm and $^{13}C$ NMR signals at 180.57 (br, 4 C) and 178.2 (d, 1 C) ppm.[17] Therefore, the species characterized by the resonance at −7.59 ppm is proposed to be $[HRu(CO)_5]^+$, with the differences in the chemical shifts in $HSO_3CF_3$ vs these in $H_2SO_4$ being attributed to solvent effects. Upon further decomposition, other species also form with signals in the hydride region, but these resonances are weak, and the nature of these was not further investigated.

For the case of $[(\mu\text{-}H)_3Ru_3(\mu_3\text{-}\eta^2\text{-}HCCHPhCH_2Ph)(CO)_9]^+$ in $HSO_3CF_3$, the organic product of decomposition was characterized as 1,2-diphenylpropane. Separate samples of protonated cluster were allowed to fully decompose in both neat $HSO_3CF_3$ and $CD_2Cl_2$ solutions. Then, the

(16) VanderVelde, D. G.; Holmgren, J. S.; Shapley, J. R. *Inorg. Chem.* **1987**, *26*, 3077.
(17) Yarrow, P.; Ford, P. C. *J. Organomet. Chem.* **1981**, *214*, 115.

acid solutions were neutralized by pouring over ice and the organic products were extracted with pentane. The $^1H$ NMR spectra of the extracted residues were compared with the $^1H$ NMR spectrum of an authentic sample of 1,2-diphenylpropane, indicating the presence of 1,2-diphenylpropane. While there are other unidentified resonances in the spectrum, the signals for 1,2-diphenylpropane can be located, albeit weakly, as the multiplets at 7.37–6.93 (m) and 2.84–2.77 (m) ppm; the characteristic doublet at 1.22 ppm is masked by other resonances. The $^1H$ NMR spectrum of the residue from acidified $CD_2Cl_2$ solution shows the presence of 1,2-diphenylpropane much more clearly. The large signal at 2.16 ppm is most likely due to residual acetone used to clean the NMR tube. The small multiplet at 0.99–0.84 ppm is probably residual pentane, or another hydrocarbon solvent introduced as an impurity in the cluster sample. The small resonances observed at 4.25, 4.19, and 3.78 ppm are in the range expected for C–H protons adjacent to oxygen-containing organic compounds such as alcohols, ketones, ethers, and esters and may have formed upon workup when the protonated cluster solution was neutralized with $H_2O$. No resonances attributable to the alkene products 1,2-diphenylpropenes or 2,3-diphenylpropene are observed.

Previous work by this research group has demonstrated that reductive elimination from $(\mu\text{-H})_3Ru_3(\mu_3\text{-CX})(CO)_9$ under CO could occur via $\beta$-elimination if $\beta$-hydrogens were present in the starting cluster.[1] $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCHPhCH}_2\text{Ph})(CO)_9$ was shown to form a mixture of alkene products in the presence of CO.[1b] The products reported were 1,2-diphenylpropene (30%), 2,3-diphenylpropene (44%), and 1,2-diphenylpropane (27%). Thus, when $\beta$-ydrogens are present, reductive elimination from $(\mu\text{-H})_3Ru_3(\mu_3\text{-CX})(CO)_9$ under CO forms both alkane and alkenes. However, in the presence of strong acid, only alkane elimination is observed. This result may be due to the ability of excess protons in solution to form agostic bonds and thus to promote reductive elimination over $\beta$-hydrogen elimination.

Shapley and co-workers have reported that dissolution of $(\mu\text{-H})_3Os_3(\mu_3\text{-CH})(CO)_9$ in 98% $H_2SO_4$ results in gas evolution and the formation of $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}O_3SO)$ (67%), which they have isolated and structurally characterized via X-ray crystallography.[18] The $^1H$ NMR spectrum of this complex shows a single resonance at −12.04 (s) ppm. Chromatographic analysis of the gas evolved from the reaction showed it to consist primarily of methane, a significant amount of ethane, and trace amounts of propane, butane, and pentane. They also demonstrated that dissolution of $(\mu\text{-H})_3Os_3(\mu_3\text{-CH})(CO)_9$ in $HSO_3CF_3$ is accompanied by gas evolution, but they were unable to characterize the species detected in solution (thought to be complexes of the trifluoromethanesulfonate ion).

Allowing $[(\mu\text{-H})_3Os_3(\mu_3\text{-}\eta^2\text{-HCMe})(CO)_9]^+$ to decompose in neat $HSO_3CF_3$ solution for 1 day produces a new species characterized by a $^1H$ NMR signal at −12.20 (s) ppm. This resonance is perhaps due to $[(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}O_3SCF_3)]^+$ or $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}O_3SCF_3)$. It is possible that similar species are responsible for the −12.85 ppm signal that Johnson and co-workers originally reported for the protonation of this cluster in $HSO_3F$.

**Protonation of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CPh})(CO)_9$.** Dissolution of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CPh})(CO)_9$ in $HSO_3CF_3$ produces the following $^1H$ NMR spectrum ($HSO_3CF_3$, −30 °C): 6.87 (br), 5.81 (br), 5.51 (br), 2.55 (br), 1.93 (s), −14.22 (s), −18.00 (br), −20.53 (br) ppm. $Ru_3(CO)_{12}$ and $(\mu\text{-H})_4Ru_4(CO)_{12}$ are the only products recovered upon workup of the acid solution. Toluene is observed in the $^1H$ NMR spectrum at 6.87 (br s, phenyl) and 1.93 (s, methyl) ppm and in the $^{13}C$ NMR spectrum at 138.3 (s, 1 C, phenyl), 128.6 (d, 2 C, phenyl), 127.8 (d, 2 C, phenyl), 124.4 (s, 1 C, phenyl), and 19.6 (q, 1 C, $J_{CH}$ = 126 Hz, methyl) ppm. From the spectra obtained from several experiments, it is known that the small resonances observed at −18.00 and −20.53 ppm are not present in the spectrum initially but are observed after a short time. Since $Ru_3(CO)_{12}$ and $(\mu\text{-H})_4Ru_4(CO)_{12}$ are the two major species recovered upon workup, these signals are most likely due to $[(\mu\text{-H})Ru_3(CO)_{12}]^+$ and $[(\mu\text{-H})_5Ru_4(CO)_{12}]^+$. The other signals observed at 5.81, 5.51, and 2.55 ppm are weak compared to the signals for toluene, and the species responsible for these were not identified. The species associated with the resonance at −14.22 ppm is stable for a few hours at −30 °C in neat acid solution but eventually decomposes to other species characterized by resonances at −7.59, −10.25, −18.00, and −20.53 ppm. These species are also stable for only a few hours before decomposing further to unidentified metal-containing species. The species associated with the resonance at −7.59 ppm is presumed to be $[HRu(CO)_5]^+$.

Addition of 1 drop of acid to a $CDCl_3$ solution of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CPh})(CO)_9$ produced only one signal in the hydride region at −13.79 (s) ppm, with the other signals attributed to toluene (6.69 (s, phenyl) and 1.84 (s, methyl) ppm), acid (11.06 (s) and 9.80 (s) ppm), an impurity in the acid (−0.30 (s) ppm), and unidentified resonances (4.10 (s), 3.47 (s), and −0.52 (s) ppm). The presence of toluene was confirmed by comparison with the $^1H$ NMR spectrum of toluene in $CDCl_3$ with $HSO_3CF_3$ added. The species associated with the −13.79 ppm signal in this spectrum is most likely the same as that associated with the −14.22 ppm signal when $(\mu\text{-H})_3Ru_3(\mu_3\text{-CPh})(CO)_9$ is dissolved in neat acid solution, the difference in chemical shift of the resonance being due to the change of solvents.

**Protonation of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CX})(CO)_9$ (X = H, Cl, Br).** Dissolution of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CX})(CO)_9$ (X = H, Cl, Br) in neat $HSO_3CF_3$ is followed by immediate gas evolution. $(\mu\text{-H})_3Ru_3(\mu_3\text{-CX})(CO)_9$ (X = H, Ph) are very soluble in $HSO_3CF_3$, but the chloro and bromo analogues are much less soluble. After 5 min of mixing (at room temperature) small (ca. 30 mg) samples of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CX})(CO)_9$ (X = Cl, Br) still had not completely dissolved in the acid solution. Consequently, much decomposition occurred during the preparation of these protonated clusters before their $^1H$ NMR spectra could be recorded. No starting cluster was recovered from any of these acid solutions.

A common feature of all these spectra, including that of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CPh})(CO)_9$ in $HSO_3CF_3$, is a resonance near −14 ppm (X = Ph (−14.22), H (−13.77), Cl (−14.60), Br (−13.83 ppm)). Since each of these spectra was referenced to the acid resonance (introducing an error of ca. ±0.5 ppm), it is possible that all four of these clusters decompose to a common metal-containing complex when dissolved in $HSO_3CF_3$.

These results are very similar to those reported by Shapley and co-workers for the protonation of $(\mu\text{-H})_3Os_3(CH)(CO)_9$.[17] Therefore, the species associated with the resonance at ca. −14 ppm is proposed to be the analogue of $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}O_3SO)$, $(\mu\text{-H})Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}O_3SCF_3)$, or possibly the protonated derivative $[(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}O_3SCF_3)]^+$.

The factors affecting the stability of protonated clusters are not well understood at this time. It is not known why

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stable, agostic bond-containing clusters are formed when M = Ru and R = Et or $CHPhCH_2Ph$ and when M = Os and R = Me but when M = Ru and R = H, Cl, Br, or Ph or when M = Os and R = H immediate cluster decomposition is observed. Clearly, tautomers having agostic M-H-C interactions may be implicated in many stoichiometric and catalytic reactions of hydrocarbons with polymetallic systems. The fundamental chemistry of such species remains an important area for investigatigation.

**Acknowledgment.** We thank T. P. Fehlner for preprints of research results and for many helpful comments. This work has been supported by the National Science Foundation through Grants CHE-8900921 and CHE-8520276. J.B.K. also thanks the Alfred P. Sloan Foundation for support.

**Registry No.** $(\mu\text{-H})_3Ru_3(\mu_3\text{-CEt})(CO)_9$, 98799-10-1; $[(\mu\text{-H})_3Ru_3(\mu_3\text{-HCEt})(CO)_9]SO_3CF_3$, 109672-64-2; $(\mu\text{-H})_3Os_3(\mu_3\text{-CMe})(CO)_9$, 51158-87-3; $[(\mu\text{-H})_3Os_3(\mu_3\text{-HCMe})(CO)_9]SO_3CF_3$, 109701-89-5; $[(\mu\text{-H})_3Os_3(\mu_3\text{-HCMe})(CO)_9]SO_3F$, 127972-69-4; $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCHPhCH}_2Ph)(CO)_9$, 86409-47-4; $[(\mu\text{-H})_3Ru_3(\mu_3\text{-HCCHPhCH}_2Ph)(CO)_9]SO_3CF_3$, 127972-67-2; $(\mu\text{-D})_3Ru_3(\mu_3\text{-CCDPhCHDPh})(CO)_9$, 127972-68-3; $H_3Ru_3(CPh)(CO)_9$, 73746-99-3; $(\mu\text{-H})_4Ru_4(CO)_{12}$, 34438-91-0; $(\mu\text{-H})_3Ru_3(\mu_3\text{-CH})(CO)_9$, 63280-43-3; $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCl})(CO)_9$, 73746-97-1; $(\mu\text{-H})_3Ru_3(\mu_3\text{-CBr})(CO)_9$, 73746-95-9; $Ru_3(CO)_{12}$, 15243-33-1; $[HRu(CO)_5]SO_3CF_3$, 127972-70-7; $CH_3CHPhCH_2Ph$, 5814-85-7; $CH_3Ph$, 108-88-3; $[Ph_3PCH_2Ph]Cl$, 1100-88-5; $[Ph_3PCH_3]Br$, 1779-49-3; acetophenone, 98-86-2; *cis*-1,2-diphenylpropene, 1017-22-7; *trans*-1,2-diphenylpropene, 833-81-8; 2,3-diphenylpropene, 948-97-0; deoxybenzoin, 451-40-1.

**Supplementary Material Available:** Descriptions of syntheses and listings of $^1H$ and $^{13}C$ NMR data for 1,2-diphenylpropane, 1,2-diphenylpropene, and 2,3-diphenylpropene standards used for comparison with products of decomposition of $[(\mu\text{-H})_3Ru_3(\mu_3\text{-}\eta^2\text{-HCCHPhCH}_2Ph)(CO)_9]^+$ (3 pages). Ordering information is given on any current masthead page.

# Metallacarboranes in Catalysis. 9. Catalytic Hydrosilanolysis of Alkenyl Acetates by Triethylsilane

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*Received January 23, 1990*

Reaction of an alkenyl acetate, $[CH_3CO_2CR{=}CH_2]$ (R = $CH_3$, $C_6H_5$), with triethylsilane in the presence of either the *closo*-rhodacarborane [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (I) or the *exo-nido*-rhodacarborane [*exo-nido*-$(PPh_3)_2$Rh-7,8-$(\mu\text{-}(CH_2)_3)$-7,8-$C_2B_9H_{10}$] (II) as catalyst precursors in $CH_2Cl_2$ at 40 °C for 42 h yielded triethylsilyl acetate and the alkene derived from the alkenyl acetate rather than the hydrosilylation product. The closo complex I was shown to be a superior catalyst precursor, giving over 80 turnovers, which corresponds to 80% conversion of alkenyl acetate to trialkylsilyl acetate under experimental conditions. The exo-nido complex II, however, showed limited catalytic activity and formed the closo bidentate acetato complex [*closo*-3-$(PPh_3)$-3,3-$(\eta^2\text{-}CH_3CO_2)$-1,2-$(\mu\text{-}(CH_2)_3)$-3,1,2-$RhC_2B_9H_9$] (III) as a detectable reaction intermediate. Under mild conditions, tris(triphenylphosphine)chlororhodium, $[(PPh_3)_3RhCl]$ (IV), was found to catalyze the hydrosilanolysis as well as the hydrosilylation of isopropenyl acetate. However, hydrosilanolysis predominated over hydrosilylation in a ratio of 20:1. Reaction of III with triethylsilane gave triethylsilyl acetate and the *exo-nido*-rhodacarborane II in the presence of triphenylphosphine. The mechanisms of the hydrosilanolysis and related reactions of alkenyl acetates are discussed.

## Introduction

The *closo*-rhodacarborane [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (I)[1] and the *exo-nido*-rhodacarborane [*exo-nido*-$(PPh_3)_2$Rh-7,8-$(\mu\text{-}(CH_2)_3)$-7,8-$C_2B_9H_{10}$] (II)[2] have been shown to be effective alkene hydrogenation and isomerization catalysts, and detailed kinetic and mechanistic studies of these systems have been presented.[3] During the course of our investigation of the further potential of rhodacarboranes in catalytic processes, it was discovered that when alkenyl acetates were employed as substrates for catalytic hydrogenation, the expected saturated esters were not obtained. Instead, quantitative hydrogenolysis of the ester C-O bond occurred to produce acetic acid and alkene.[4] The mechanism of these catalytic hydrogenolyses has been examined in detail.[3c] The cleavage of C-O bonds of alkenyl acetates such as vinyl acetate and allyl acetate, which was promoted by transition-metal complexes, has been previously reported in the literature. Zerovalent Mo,[5] Ni,[6] and Pd[7] complexes afforded the corresponding ($\eta^3$-

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