

Preliminary communication

PROTONATION OF $(\mu\text{-H})_3\text{Ru}_3(\mu_3\text{-CR})(\text{CO})_9$. EVIDENCE FOR THE FORMATION OF AN AGOSTIC METAL–HYDROGEN–CARBON BOND

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Summary

Protonation of $(\mu\text{-H})_3\text{M}_3(\mu_3\text{-CR})(\text{CO})_9$ ($\text{M} = \text{Ru}$, $\text{R} = \text{Et}$ or $\text{M} = \text{Os}$, $\text{R} = \text{Me}$) by dissolution in HSO_3CF_3 yields $\text{H}_3\text{M}_3(\text{HCR})(\text{CO})_9^+$, containing a $\text{M}\text{-H}\text{-C}$ bridge. The products were characterized by ^1H and ^{13}C NMR spectroscopy. Decompositions of other protonated methylidyne clusters form CH_3R and a variety of metal-containing products.

Recently the importance of the three-center metal–hydrogen–carbon interaction, the so-called “agostic” bond, in organometallic chemistry has become widely recognized [1]. We have proposed that reversible formation of an agostic hydrogen precedes reductive elimination of CH_3R from $(\mu\text{-H})_3\text{Ru}_3(\mu_3\text{-CR})(\text{CO})_9$ [2], and were therefore interested in the structures and dynamics of Ru_3C clusters having agostic hydrogens. Very recently Fehlner and co-workers reported that deprotonation of $(\mu\text{-H})_3\text{Fe}_3(\mu_3\text{-CH})(\text{CO})_9$ yields $(\mu\text{-H})\text{Fe}_3(\mu_3\text{-HCH})(\text{CO})_9^-$, which was shown by NMR spectroscopy to contain an agostic hydrogen [3]. Although deprotonation does not induce the formation of agostic interactions in the ruthenium clusters [4], we considered it likely that protonation would lead to an agostic hydrogen since calculations [5] indicate that the HOMOs of these molecules are metal–carbon bonding in character. In 1976 Johnson and co-workers had reported that dissolution of $(\mu\text{-H})_3\text{Os}_3(\mu_3\text{-CMe})(\text{CO})_9$ in HSO_3F formed “ $\text{H}_4\text{Os}_3(\text{CMe})(\text{CO})_9^+$ ” by protonation at the metal–metal vector [7]. However, since it is now recognized that the chemical shifts of metal hydrides and agostic hydrogens are similar, we decided to re-investigate the nature of the protonated clusters.

Dissolution of $(\mu\text{-H})_3\text{Ru}_3(\mu_3\text{-CEt})(\text{CO})_9$ in HSO_3CF_3 yields a yellow solution with no gas evolution. The ^1H NMR spectrum of this solution contains, in addition to the resonance due to the acid, the following resonances: 3.25 (q, 2H_a), 1.28 (t, 3H_b , J_{ab} 6Hz), -9.45 (s, 1H), and -18.37 (s, 3H) ppm. The resonance at highest field is assigned to three bridging hydrides, since the chemical shift is very close to

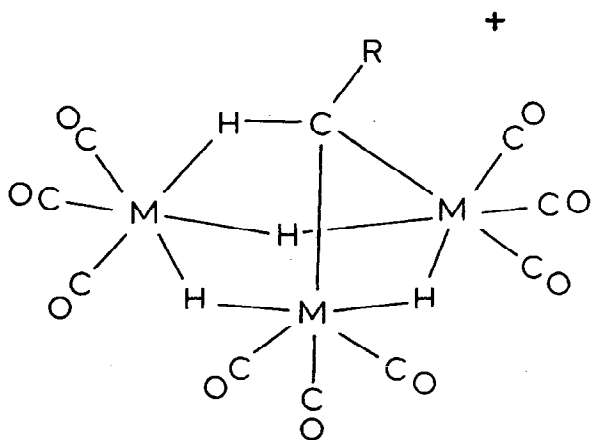


Fig. 1. Structure proposed for $\text{H}_3\text{M}_3(\text{HCR})(\text{CO})_9^+$ ($\text{M} = \text{Ru}$, $\text{R} = \text{Et}$; $\text{M} = \text{Os}$, $\text{R} = \text{Me}$).

that of the hydrides of $(\mu\text{-H})_3\text{Ru}_3(\mu_3\text{-CEt})(\text{CO})_9$. The chemical shift at -9.45 ppm might be assigned to either a terminal hydride ligand (cf. $\text{H}(\mu\text{-H})\text{Ru}_3(\text{CO})_{11}$, -11.98 ppm [8]) or to an agostic hydrogen (cf. $(\mu\text{-H})\text{Fe}_3(\text{HCH})(\text{CO})_9^-$, -10.1 ppm [3]). To resolve this question the ^{13}C NMR spectrum was recorded. The spectrum at -20°C consists of the following resonances: 184.1 (s, 3C, axial CO ligands), 182.2 (d, 6C, $J(\text{CH})$ 12 Hz, equatorial CO ligands), 143.3 (d, 1C, $J(\text{CH})$ 58 Hz), 45.1 (t, 1C, $J(\text{CH})$ 137 Hz, methylene), and 22.2 (q, 1C, $J(\text{CH})$ 127 Hz, methyl) ppm, in addition to the resonance due to HSO_3CF_3 . Assignments of the resonances due to the CO ligands are analogous to those of the neutral precursor [9], which is static on the NMR timescale at 25°C . The signal at 143.3 ppm is clearly indicative of a carbon involved in an agostic bond; thus the chemical shift is 89.5 ppm upfield from that of the methylidyne carbon resonance of the precursor cluster [9] and the C–H coupling constant, verified by selective decoupling to be due to the proton resonating at -9.45 ppm, is very similar to that found for $(\mu\text{-H})\text{Fe}_3(\text{HCH})(\text{CO})_9^-$ (118.5 ppm, $J(\text{CH})$ 65 Hz) [3]. Treatment of the acid solution with ice, extraction with dichloromethane, and chromatography allowed the recovery of $(\mu\text{-H})_3\text{Ru}_3(\mu_3\text{-CEt})(\text{CO})_9$ (32%) and $\text{Ru}_3(\text{CO})_{12}$ (22%) as the major products. The latter product must be formed during work-up because there is no hydride resonance due to $\text{HRu}_3(\text{CO})_{12}^+$ in the spectrum of the acid solution [10].

We propose the structure in Fig. 1 for $(\mu\text{-H})_3\text{Ru}_3(\text{HCEt})(\text{CO})_9^+$. This structure, having only C_s symmetry, should give rise to two hydride resonances and five carbonyl resonances, but migration of the agostic hydrogen to each of the three Ru–CEt vectors at a rate fast on the NMR timescale would generate apparent C_{3v} symmetry. Although no broadening of the resonances due to the hydrides or to the carbonyls is observed at -65°C , fluxional processes have been observed in both ^1H and ^{13}C spectra of $(\mu\text{-H})\text{Fe}_3(\text{HCH})(\text{CO})_9^-$. A structure containing a face-capping agostic proton (i.e. $(\mu_3\text{-H})\text{Ru}_2\text{CEt}$) is also consistent with our spectral data, but is at this time without precedent. However, such a species may represent the intermediate in the edge-hopping process.

Since the rates of fluxional exchanges on Os clusters are usually much slower than for the Ru analogs, we re-investigated the spectroscopic characterization of the

protonated Os cluster. Johnson and co-workers reported the ^1H NMR spectrum of " $\text{H}_4\text{Os}_3(\text{CMe})(\text{CO})_9^+$ " at 35°C in HSO_3F to consist of three resonances, -12.85 (br s), -16.62 (s), and -16.81 (br s) ppm, in a 1:2:1 ratio, in addition to the methyl resonance at 5.35 ppm, consistent with the symmetry of the structure in Fig. 1. In our hands, dissolution of $(\mu\text{-H})_3\text{Os}_3(\mu_3\text{-CMe})(\text{CO})_9$ in either HSO_3F or HSO_3CF_3 at 22°C produced a species having only two high field resonances in a 1:3 ratio, entirely analogous to the Ru analog [11]. The NMR spectrum was unchanged at -65°C . The starting cluster was recovered in 87% yield after the experiment.

The ^1H NMR spectrum of $(\mu\text{-H})_3\text{Ru}_3(\mu_3\text{-CPh})(\text{CO})_9$ in HSO_3CF_3 at -20°C displays high-field resonances at -10.25 (s), -14.27 (s), and -20.53 (s) ppm in relative ratios of 3:9:1, respectively; ^1H and ^{13}C resonances due to toluene were also identified. From the spectra of several experiments we know that the -10.25 ppm signal is due to a decomposition product of the species associated with the -14.27 ppm resonance. Although we have not been able to characterize the initial product, it must be very different than that formed by protonation of the ethyl analog, and the ^{13}C spectrum, too complex to permit structural characterization at this time, rules out protonation of the phenyl ring.

In acid solution all of these clusters decompose at varying rates. Over a period of several hours at 25°C decomposition of $\text{H}_3\text{Ru}_3(\text{HCe}t)(\text{CO})_9^+$ in HSO_3CF_3 gives a new species characterized by a ^1H NMR signal at -7.59 ppm and ^{13}C NMR signals at 179.0 (br, 4C) and 178.8 (sh, 1C) ppm; we attribute these spectra to $\text{HRu}(\text{CO})_5^+$ [12]. Decomposition of $\text{H}_3\text{Os}_3(\text{HCMe})(\text{CO})_9^+$ occurs overnight, forming a species characterized by a hydride resonance at -12.20 ppm, which we believe to be $\text{HOs}_3(\text{O}_3\text{SCF}_3)(\text{CO})_9$ [13]. Dissolution of $(\mu\text{-H})_3\text{M}_3(\mu_3\text{-CR})(\text{CO})_9$ ($\text{M} = \text{Ru}$, $\text{R} = \text{H}$ or Br , or $\text{M} = \text{Os}$, $\text{R} = \text{H}$) in HSO_3CF_3 leads to immediate gas evolution; ^1H NMR spectra of these solutions show several signals in the hydride region, none of which may be attributed to the corresponding $(\mu\text{-H})_3\text{M}_3(\text{HCR})(\text{CO})_9^+$. Decomposition of $(\mu\text{-H})_3\text{Ru}_3(\mu_3\text{-CPh})(\text{CO})_9$ in HSO_3CF_3 gives toluene, $\text{HRu}(\text{CO})_5^+$, and a number of other hydride-containing species. Shapley and co-workers, independently studying the protonation of $(\mu\text{-H})_3\text{Os}_3(\mu_3\text{-CH})(\text{CO})_9$, were able to characterize the products of decomposition in H_2SO_4 as $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-O}_3\text{SO})$ and methane; they also studied the decomposition in HSO_3CF_3 , although the cluster product was not identified [13].

In conclusion, protonation of $(\mu\text{-H})_3\text{M}_3(\mu_3\text{-CR})(\text{CO})_9$ in strong acids occurs at the metal-carbon bond when R is alkyl, but the nature of the protonated species appears to differ for the phenyl derivative. Elimination of CH_3R is more facile from these protonated clusters in strong acid media than from the neutral precursors [2], a factor which may be due to the presence of an agostic hydrogen.

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