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Preliminary communication

ON THE POSSIBILITY OF A CARBENIUM ION STRUCTURE FOR THE COMPLEXES $[Os_3H_3(CO)_9CCR_2]^+$. FURTHER APPLICATION OF THE ^{187}Os NUCLEUS

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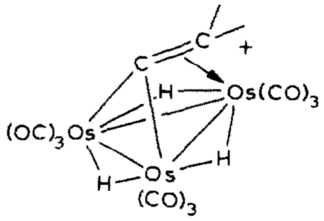
Summary

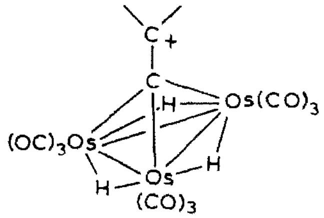
In the ^1H NMR spectrum of the complex $[Os_3H_3(CO)_9C\overline{C(CH_2)_2C}H_2]^+$ at 30°C, under conditions of rapid exchange, the single hydride resonance has two sets of satellites of equal intensity (separated by 32.0 and 28.8 Hz) caused by $^{187}Os—^1H$ spin—spin coupling. The spectral data rule out the upright carbenium ion structure for the complex, and are consistent with the fluxional process involving hydrocarbon ligand rotation about the $C—\overline{C(CH_2)_2C}H_2$ axis in a tilted structure, with concomitant rotation of the $Os_3H_3(CO)_9$ moiety.

The $Co_3(CO)_9C$ cluster [1,2] and the closely related $Os_3H_3(CO)_9C$ cluster [3] represent organometallic groups which effectively delocalize a positive charge. The ^1H NMR spectrum obtained at −10°C for the complex $[Os_3H_3(CO)_9CCH_2]^+$ indicates that the tilted structure I is the most stable, but the temperature dependence of the spectrum may be interpreted either in terms of hydride migration around the Os_3 triangle, or alternatively via an intermediate of carbenium ion structure II [3]. Very recently, Mislow and coworkers [4] presented ^{13}C NMR evidence for the tilted structure of $[Co_3(CO)_9CCHCHMe_2]^+$ at −65°C. Coalescence of the isopropyl-methyl ^{13}C resonances takes place at higher temperatures, presumably by disrotatory correlated rotation about the $Co_3(CO)_9—C$ and $C—CHCHMe_2$ axes, in accord with the theoretical predictions of Schilling and Hoffmann [2]. However, the NMR data do not rule out uncorrelated rotation (i.e. rotation of the $CHCHMe_2$ fragment without concomitant rotation of the $Co_3(CO)_9$ moiety), or the realization of the carbenium ion upright structure at higher temperatures.

Our interest in organometallic substituted carbocations has led to an examination of the possibility of carbenium ion structure II for the complexes $[Os_3H_3(CO)_9CCR_2]^+$.



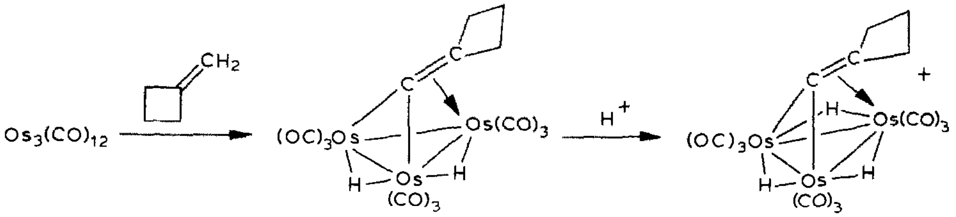
(I)



(II)

In principle, one would expect that application of ^{187}Os enrichment may resolve the question of structure and bonding in the complexes $[Os_3H_3(CO)_9CCR_2]^+$, on the basis of the ^{187}Os—^{13}C coupling constants observed [5] in the ^{13}C NMR spectra. By using ^{57}Fe enrichment, ^{57}Fe—^{13}C coupling constants have been observed in the ^{13}C NMR spectra of α-ferrocenylcarbocations, providing evidence for Fe—C$_\alpha$ bonding [6a,b]. However, the possibility of observing ^{187}Os,^{1}H satellites for the complexes $[Os_3H_3(CO)_9CCR_2]^+$ allow us to exclude the necessity of enrichment with the expensive metal isotope.

Thermal reaction of $Os_3(CO)_{12}$ with methylenecyclobutane at 145°C gave the complex $Os_3H_2(CO)_9C{=}\overline{C(CH_2)_2C}H_2$ (III). According to the spectral data, this complex has a structure similar to $Os_3H_2(CO)_9C{=}CH_2$ [7]. The ^{1}H NMR spectrum of complex III at −35°C in $CDCl_3$ solution shows two doublets at δ −18.71 and −21.16 ppm, both with coupling constants of 1.6 Hz; methylene hydrogens are observed as two multiplet resonances at δ 3.06 and 2.87 ppm (α-CH$_2$ groups), and as a weakly resolved quintet at 2.19 ppm (β-CH$_2$ group).



(III) (IV)

In $CF_3COOH/CDCl_3$ (1/1 v/v), complex III undergoes protonation to yield the cationic complex IV. The ^{1}H NMR spectrum of complex IV at 30°C shows a triplet at 3.11 (4H, J 7.3 Hz) and a quintet at 2.45 ppm (2H, J 7.3 Hz) due to methylene protons, and a single hydride resonance at −19.63 ppm, with two sets of ^{187}Os,^{1}H satellites of equal intensity, separated by 32.0 and 28.8 Hz (Fig. 1).

The observed spectral pattern of the CH$_2$ protons at 30°C is consistent with the carbenium ion structure as well as with the rapid fluxional process including rotation about the $C{-}\overline{C(CH_2)_2C}H_2$ axis in a tilted structure with concomitant rotation of the $Os_3H_3(CO)_9$ moiety, but contradicts the migration of hydride ligands around the Os$_3$ triangle.

The stereochemical rigidity of the hydride ligands unambiguously indicates the values of the ^{187}Os—^{1}H coupling constants. As can be seen from Table 1, for saturated osmium complexes with stereochemical rigid (bridging) hydride ligands,

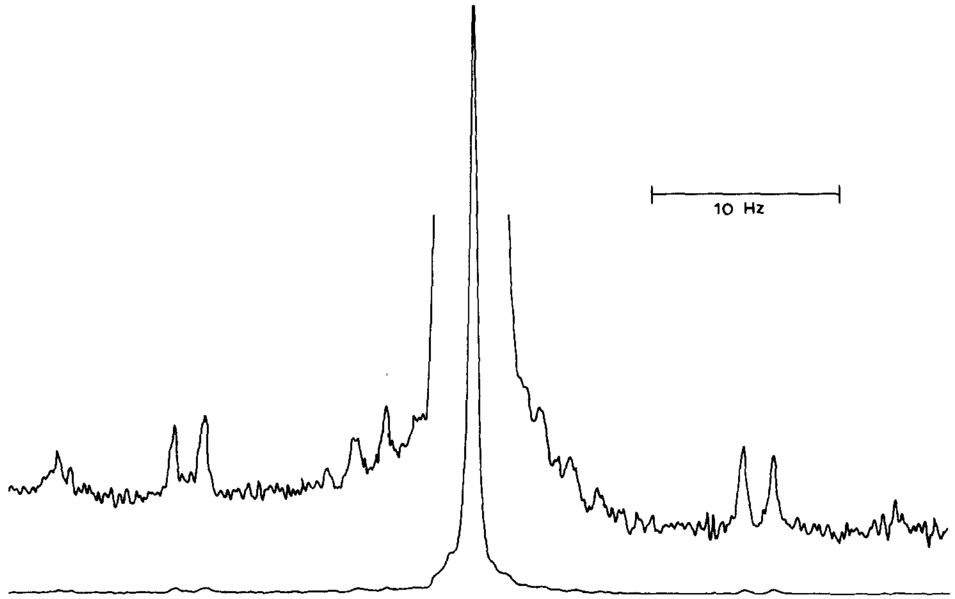


Fig. 1. ^{187}Os,^{1}H satellites in the ^{1}H NMR spectrum of compound IV at 30°C.

TABLE 1

^{1}H NMR SPECTRAL DATA FOR THE HYDRIDOOSMIUM COMPLEXES

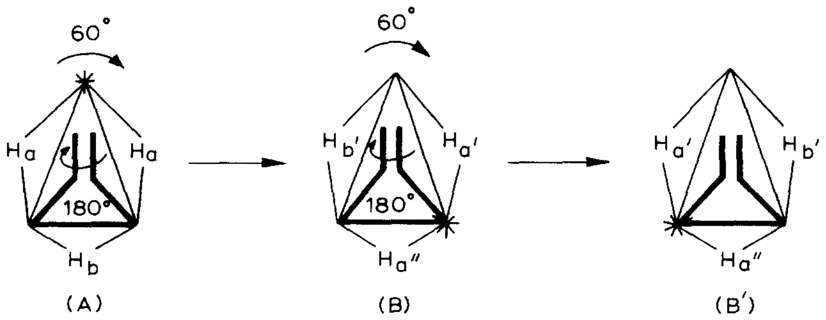
Complex	Solvent	Chemical shift (δ)[a]	Coupling constant $^1J(^{187}Os—^1H)$ (Hz)
$[Os_3H_3(CO)_9C\overline{C(CH_2)_2C}H_2]^+$	$CF_3COOH/CDCl_3$	–19.63	32.0, 28.8
$[Os_3H(CO)_{12}]^+$	H_2SO_4	–20.07	30.5
$[Os_2RuH(CO)_{12}]^+$	H_2SO_4	–19.03	29.1
$^{187}Os_3H_2(CO)_{10}$	$CDCl_3$	–11.73	47.0[b]
$Os_3ReH(CO)_{16}$	CD_2Cl_2	–18.99	34.9, 27.0
$Os_3Re_2H_2(CO)_{20}$	CD_2Cl_2	–17.02	29.3, 27.8
		–18.11	33.7, 30.6
$Os_3H(CO)_{10}C_2C_6H_5$	$CDCl_3$	–16.39	33.5[c]
$^{187}Os_4H_4(CO)_{12}$	$CDCl_3$	–20.50	14.6[d]

[a] Measured at 200 MHz and 30°C. [b] $^2J(^{187}Os—^1H)$ coupling was also observed as 1.0 Hz. [c] The complex $Os_3H(CO)_{10}C_2C_6H_5$ is fluxional: the σ- and π-bonds binding the bridging $C{\equiv}C_6H_5$ group are rapidly interchanged between two osmium atoms. [d] The hydride resonance at 30°C was observed as a quintet, implying rapid exchange of hydride ligands. The fluxionality of $Os_4H_4(CO)_{12}$ has also been mentioned by Lewis and coworkers [8].

coupling constants are observed in the range 27.0—35.0 Hz; only for complex $Os_3H_2(CO)_{10}$ with a metal—metal double bond [9] is $^1J(^{187}Os—^1H)$ 47.0 Hz.

The observation of two ^{187}Os—^{1}H coupling constants in the ^{1}H NMR spectrum of complex IV shows conclusively that the osmium atoms are non-equivalent. In other words, this observation rules out the possibility of carbenium ion structure II for the complexes $[Os_3H_3(CO)_9CCR_2]^+$.

In order to understand the presence of two sets of satellites of equal intensity in the ^{1}H NMR spectrum of complex IV, it is necessary to consider the interconversion of isotopomers containing one ^{187}Os isotope: at 1.64% abundance of ^{187}Os, our experiment detects only these molecules, whereas doubly and triply



SCHEME 1

labelled molecules would be unobservable. There are three such isotopomers, A, B and B′, two of them being enantiomers (Scheme 1; an asterisk indicates the ^{187}Os atom).

In the ^{1}H NMR spectrum of complex IV only the hydrogen atoms H^{a}, $H^{a'}$ and $H^{a''}$, directly bonded to the ^{187}Os atom, should experience spin—spin coupling with values of $^{1}J(^{187}Os—^{1}H)$ in the range 27—35 Hz. The rapid interconversion of A, B and B′ at 30°C leads to equilibration of all the hydride ligands in the NMR time scale. At the same time, this process leads to pairwise equilibration among the $^{1}J(^{187}Os—^{1}H^{a})/^{1}J(^{187}Os—^{1}H^{a'})$ and $^{1}J(^{187}Os—^{1}H^{a})/^{1}J(^{187}Os—^{1}H^{a''})$ coupling constants. As a result, two sets of ^{187}Os,^{1}H satellites of equal intensity are observed.

In the light of our results on the osmium cluster it seems very probable that under conditions of rapid exchange the tilted structure is retained as well as for the related cobaltous clusters $[Co_3(CO)_9CCR_2]^+$ [2—4].

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