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Spin lattice relaxation measurements on osmium carbonyl hydrido clusters containing interstitial tetrahedral and octahedral hydrido ligands

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Abstract

The potential of the inversion recovery method for obtaining the values of spin-relaxation times (T_1) for a series of hydrido decaosmium clusters, containing interstitial hydrido ligands is presented. From the results on the hydridocarbonylosmium clusters studied, it appears that for a hydrido ligand in an interstitial tetrahedral site the T_1 value is 2.75 s, and for a hydrido ligand in an interstitial octahedral site one of 3.81 s.

Introduction

The characteristic splitting patterns observed in NMR spectroscopy from coupling to spin $\frac{1}{2}$ nuclei provide an important diagnostic aid in organometallic chemistry. Several values of $^1J(^{187}Os-^1H)$ have been reported at a natural abundance of ^{187}Os ($I = \frac{1}{2}$, 1.6% natural abundance) [1–4].

Use of spin-lattice relaxation times (T_1) has been shown to be a useful technique for the investigation of molecular dynamics in solution. Crabtree and coworkers [5] reported the measurement of proton relaxation times for a series of mononuclear hydrido complexes and showed that the relaxation rates for the hydrido ligands were very short. Aime [7] and Shapley [6] each independently investigated the relaxation rates of terminal and bridging hydrides in osmium and ruthenium clusters. We now report the first examples of the use of the inversion-recovery technique [8] for hydridocarbonyl clusters of osmium containing interstitial hydrido ligands (see Fig. 1 and Table 1) and present the relaxation times for hydrido ligands in tetrahedral and octahedral interstitial sites in osmium carbonyl clusters.

Results and discussion

All pulse NMR sequences for measuring T_1 either initialise the spin system and monitor its evolution or achieve a steady state in which the signal size depends on

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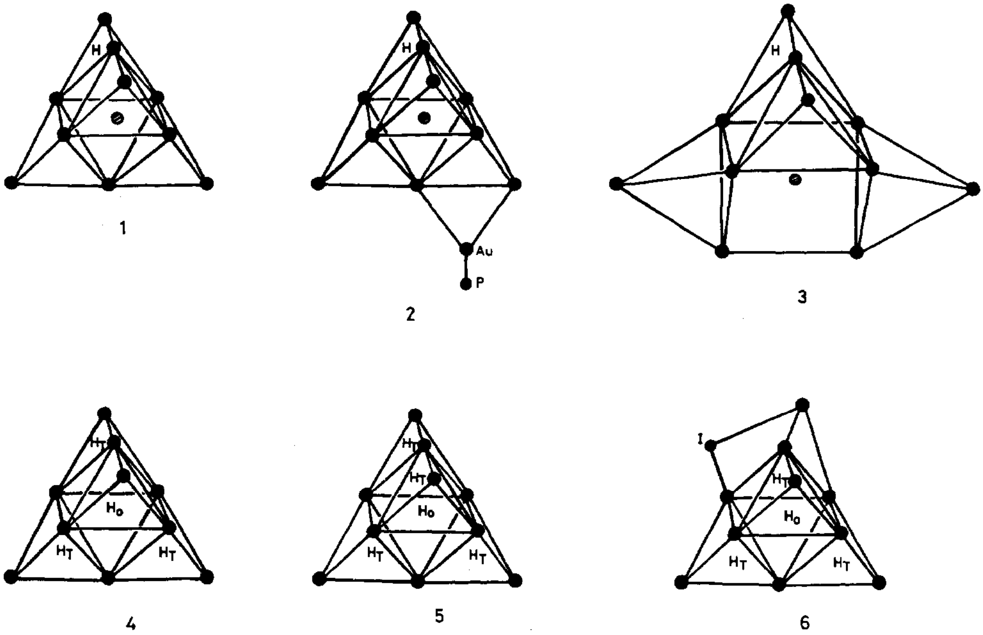

Fig. 1. Structures of the hydrido clusters, $[PPh_3Me][HOs_{10}C(CO)_{24}]$ (1), $[HOs_{10}C(CO)_{24}AuPPh_3]$ (2), $[PPh_3Me][HOs_{11}C(CO)_{27}]$ (3), $[N(PPh_3)_2]_2[H_4Os_{10}(CO)_{24}]$ (4), $[N(PPh_3)_2][H_5Os_{10}(CO)_{24}]$ (5), $[N(PPh_3)_2][H_4Os_{10}(CO)_{24}I]$ (6).

T_1. The former approach involves a pulse (or a group of pulses) to prepare the nuclear spins in some non-equilibrium configuration, and then, after a waiting period during which the spins are allowed to relax, a pulse monitors the state of the

Table 1

Spin-lattice relaxation values (T_1) for the series of compounds studied

Complex	Temperature (±1° C)	δ (ppm) [a]	T_1 (s^{-1})	Interstitial site
$[HOs_{10}C(CO)_{24}]^-$	+20	−15.3	2.76	tetrahedral
(1)	−60	−15.3	2.10	tetrahedral
$[HOs_{10}C(CO)_{24}AuPPh_3]$	+20	−20.4	2.75	tetrahedral
(2)	−60	−20.4	2.14	tetrahedral
$[HOs_{11}C(CO)_{27}]^-$	+20	−19.1	2.73	tetrahedral
(3)	−60	−19.1	2.18	tetrahedral
$[H_4Os_{10}(CO)_{24}]^{2-}$	+20	−16.5	2.98	[b]
(4)	−80	−14.7	2.84	[c]
		−19.1	3.25	[c]
$[H_5Os_{10}(CO)_{24}]^-$	+21	−15.9	2.79	tetrahedral
(5)		−16.2	3.80	octahedral
	−60	−15.9	2.08	tetrahedral
		−16.2	3.44	octahedral
$[H_4Os_{10}(CO)_{24}I]^-$	+20	−16.05	2.78	tetrahedral
(6)		−17.14	3.82	octahedral

[a] Measured at 400.13 MHz in CD_2Cl_2. [b] Assignment of interstitial site is not possible, since the hydrides are fluxional at room temperature, see text. [c] For discussion of these two T_1 relaxation-times, see text.

spins. The recovery of the nuclear spin population is monitored as a function of the waiting time. After perturbation of the equilibrium magnetisation by an external magnetic field, magnetisation growth back towards the equilibrium is given by Curie's Law and defined as spin-lattice relaxation. Assuming that this process is exponential, the magnetisation will have recovered to within a factor $[1-(1/e)]$, 63% of the equilibrium value at a time T_1, the spin lattice relaxation time.

The observed relaxation times may best be understood in terms of two parameters, the proximity of other ^1H nuclei and molecular mobility and/or if T_1 is temperature dependent. The T_1 values for a series of μ_2 bridging hydrides were determined by Aime et al. [7] and found to be in the region of 4 s at +20 °C and 1 s at −60 °C, showing a clear temperature dependence at a field of 270 MHz.

The clusters $[HOs_{10}C(CO)_{24}]^-$ (**1**) [8], $[HOs_{10}C(CO)_{24}AuPPh_3]$ (**2**) [9] and $[HOs_{11}(CO)_{27}]^-$ (**3**) [10] represent a series of related hydrido clusters. Clusters **1** and **2** have similar structures consisting of a tetracapped octahedron, whereas in **3** the essential unit is a capped trigonal prism (see Fig. 1). The hydride ligands were not located directly in the X-ray studies of **1** and **3**, but in each case it was suggested from elongation of Os–Os metal bonds that they occupied interstitial tetrahedral sites. This is in agreement with out ^1H NMR data, which revealed ^{187}Os–^1H satellites and also the use of the inversion-recovery method to obtain spin lattice relaxation times, (T_1). The T_1 values were all very similar, with a mean value of 2.75 s at +20 °C, which changed on cooling to −60 °C (see Table 1).

The ^1H NMR spectrum of $[H_4Os_{10}(CO)_{24}]^{2-}$ (**4**) (as its $[N(PPh_3)_2]^+$ salt) [12] in CD_2Cl_2 at room temperature exhibits one resonance at δ −16.48, but no ^{187}Os–^1H satellites could be detected because the signal is too broad. The dianion

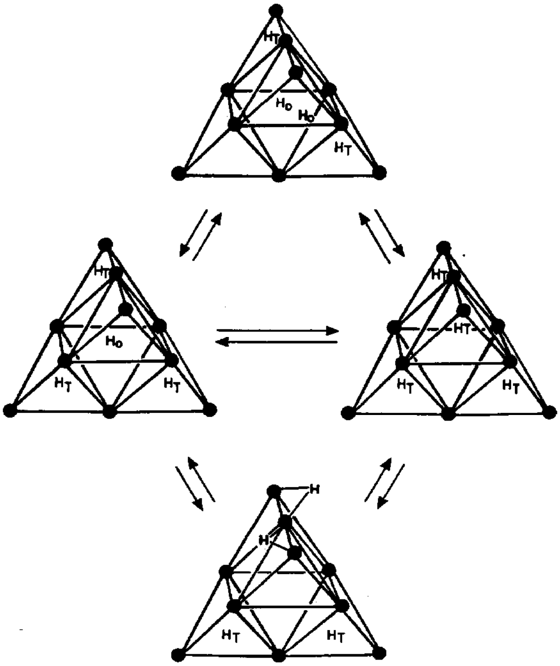

Fig. 2. Proposed exchange mechanism for $[H_4Os_{10}(CO)_{24}]^{2-}$ (4).

$[H_4Os_{10}(CO)_{24}]^{2-}$ (**4**) is considered to be fluxional, with hydrides moving from octahedral to tetrahedral sites (see Fig. 2). This process is similar to that suggested for $[Rh_{13}(CO)_{24}H_2]^{3-}$ in solution [13,14]. Polyhedral rearrangements in cluster units are well documented [15], but in **4** this mechanism seems to be unlikely to occur. On slow cooling of a solution of **4** to 193 K in CD_2Cl_2, the resonance at δ -16.48 ppm gradually broadens and slowly disappears, with the appearance of two new broad signals at δ -14.70 and -19.08 ppm in the ratio of 1/1 (signal width at half height is 12 Hz). The signals are still too broad to observe ^{187}Os-^{1}H satellites.

The spin lattice relaxation data for **4** at +20 °C indicates that all the hydrides are fluxional, with a T_1 value of 2.95 s. On cooling a CD_2Cl_2 solution of **4** to −80 °C, two T_1 values are obtained, of 2.84 and 3.25 s. These two values are intermediate between those obtained for protons in either tetrahedral or octahedral environments (see Table 1), the T_1 (tetrahedral and octahedral) values both show temperature dependence. It has been noted that there are large variations in activation energies for hydrogen migration in metals [16–18] and this may be related to the jump distances involved [13].

For the body centred cubic cluster **4**, hydrogen migration may occur via two processes, either by tetrahedral–tetrahedral jumps or octahedral–tetrahedral jumps at all the temperatures studied. A third possible explanation of the low temperature T_1 results is that there may be tetrahedral and μ_2-bridging protons in a 1/1 ratio.

Attempts to prepare $[H_3DOs_{10}(CO)_{24}]^{2-}$ or $[H_4DOs_{10}(CO)_{24}]^{-}$ have so far been unsuccessful, and this has prevented determination of the molecular correlation time.

A calibration experiment for a cluster with a hydride in an octahedral site was attempted for $[HRu_6(CO)_{18}]^{-}$. Unfortunately the experiment failed because a pulse delay of 30 seconds was necessary to obtain the metal-hydride signal in this cluster, which is indicative of a much longer relaxation time (T_1) than in the species under study here.

The ^{1}H NMR and spin lattice relaxation data for $[H_5Os_{10}(CO)_{24}]^{-}$ (**5**) (as its $[N(PPh_3)_2]^{+}$ salt) at +20 °C suggests that this monoanion is not fluxional at room temperature with a T_1 (tetrahedral) of 2.79 s and a T_1 (octahedral) of 3.80 s. The T_1 (tetrahedral) value of **5** is very close to that observed for the monohydridoosmium cluster systems **1**, **2** and **3** where T_1(tetrahedral)$_{ave}$ is 2.75 s at ambient temperature. On cooling a solution of **5** to −60 °C the spin-lattice relaxation of the four equivalent tetrahedral protons are decreased, whilst the octahedral proton is barely affected (see Table 1).

The room temperature ^{1}H NMR spectrum of $[H_4Os_{10}(CO)_{24}I]^{-}$ (**6**) (as its $[N(PPh_3)_2]^{+}$ salt) (in CD_2Cl_2) shows two broad signals in a ratio of 3/1, and the spectrum obtained was also found to be temperature independent [2]. The corresponding carbido derivative $[Os_{10}C(CO)_{24}I]^{-}$ [19] has the iodine atom bridging an Os_4 butterfly, but, with one osmium cap opened. There is no further reaction of **6** with iodine, which is as expected if three of the hydrogen atoms are in tetrahedral sites. As for **4** and **5** no ^{187}Os-^{1}H satellites are observed in **6**.

The spin lattice relaxation time of **6** at +20 °C shows that this monoanion has a T_1(tetrahedral) of 2.78 s in good agreement with the T_1(tetrahedral)$_{ave.}$(2.75 s) for the monohydridoosmium clusters **1**, **2** and **3**, whilst the T_1(octahedral) value of **6** (3.82 s) is in close agreement with that observed for $[H_5Os_{10}(CO)_{24}]^{-}$ (**5**) (3.80 s).

The T_1's of the tetrahedral protons for the **5** and **6** are consistent with those observed for the mono-hydrido clusters **1**, **2** and **3**, with T_1(average tetrahedral) 2.791 s. The T_1's of the hydrido ligands in the octahedral environments are, as expected, much longer, T_1(average octahedral) 3.80 s.

Experimental

Compounds **1**, **2**, **3**, **4**, **5**, and **6** were made by published methods [2,9–12] and their purities checked by mass spectrometry, IR, ^{1}H and ^{187}Os-^{1}H NMR spectroscopy.

NMR measurements were carried out on a Brucker WH 400 spectrometer. The samples were all prepared by use of Schlenk tube techniques and oxygen-free CD_2Cl_2. Where ^{1}H–^{1}H dipolar coupling from different protons contributes to relaxation, non-exponential relaxation may give rise to errors in T_1's obtained. The relaxation was found experimentally to be exponential over 5 T_1's. All relaxation times are the result of a computer fitting of ca. 20 observations over the range 0.1 $T_1 - 5\ T_1$, and allowing 30 s recovery time between acquisition. In all cases strict first order behaviour was observed in the recovery of the magnetisation. The nonselective inversion–recovery pulse sequence was used to obtain T_1 values, and errors are estimated to be $\pm 10\%$.

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