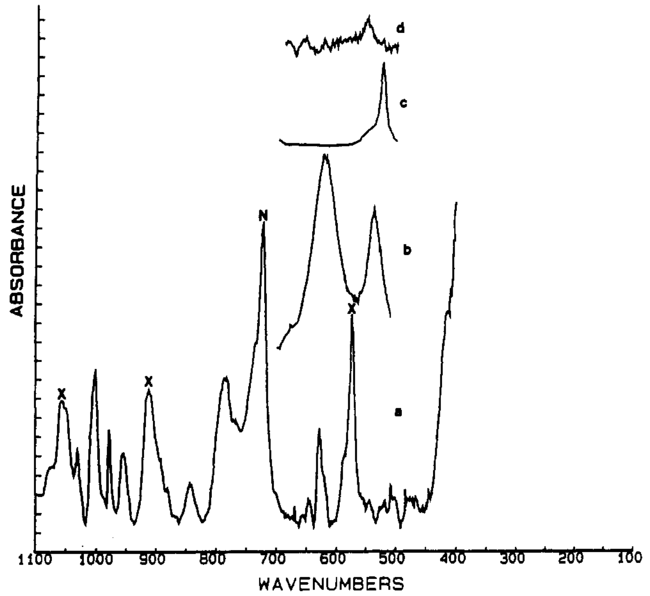

Figure 4. (a) Infrared spectrum of solid $(Et_4N)_2S_2O_4$. Peaks marked with an X are due to $S_2O_4^{2-}$. The peak labeled with N is due to Nujol. (b-d) Infrared spectra of (b) $Et_4NCl{\cdot}2H_2O$, (c) Et_4NBF_4, and (d) Et_4NI in the 500-700-cm^{-1} region.

constants for the internal coordinates for the $S_2O_4^{2-}$ and $S_2O_5^{2-}$ ions in aqueous solution (determined by Takahashi et al.) with those obtained for the dithionite ion in nonaqueous solvents and in solid $(Et_4N)_2S_2O_4$. The S-S bond stretch force constant is larger than that determined for the dithionite ion in aqueous solution but smaller than that for the metabisulfite ion. Previous investigators have assigned the band at 472[13] cm^{-1}, or alternatively the band at 208[6] cm^{-1}, as a "sulfur-sulfur" stretching frequency. The atom displacement vectors for these two vibrational modes suggest significant mixing of internal coordinates. The potential energy distributions for both normal modes indicate that each arises from approximately equal contributions from the sulfur-sulfur bond stretch and the S-S-O valence angle bends. There is therefore no vibrational mode which reflects an "independent" sulfur-sulfur stretching vibration. The torsion force constant is not included in the table, since the calculated frequency consists of a contribution from essentially one internal coordinate for which there are no observed data.

Concluding Remarks

Evidence for the existence of a centrosymmetric dithionite ion in aqueous solution[6,7] has been extended in this work to nonaqueous systems and the solid state. In all other known ionic crystal structures, the ion adopts a distorted eclipsed configuration, and we have hypothesized that this results from preferential orientation of the ion to maximize interaction with relatively small cations in the lattice. On the basis of this premise, it follows that the observed distortion of the ion results from crystallographic packing effects rather than intrinsic properties of the anion itself. The adoption of a "solution-like" conformation by the dithionite anion in an ionic solid that contains a cation large enough to minimize the effects of such preferential orientation provides strong support for this hypothesis.

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Registry No. $(Et_4N)_2S_2O_4$, 108563-02-6.

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(13) Simon, A.; Kuchler, H. *Z. Anorg. Chem.* **1949,** *260,* 161.

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^{1}H Spin-Lattice NMR Relaxation Studies of Hydride Carbonyl Clusters. A Method To Evaluate Distances Involving Hydrido Ligands

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Proton longitudinal relaxation rates of hydride resonances are dominated by the dipolar interaction with other ^{1}H nuclei in the same molecule and may provide relevant structural information once the molecular correlation times are determined by independent experiments. H-H distances were determined by this route in $HOs_3(CO)_{10}(O_2CH)$ (I), $HOs_3(CO)_9C_2H$ (II), and $HOs_3(CO)_{10}OH$ (III), whose resonances are well separated in their ^{1}H NMR spectra. When the proton NMR spectrum of compound III is recorded in acetone, it shows a mixture of two different isomers differing in the orientation of the lone pair on the μ-oxygen atom, as revealed by a marked difference in the relaxation times of the hydride ligands. Furthermore, an alternative procedure based on the comparison of the proton relaxation rates between H,H and H,D isotopomers has been applied for the dihydride species $H_2Os_3(CO)_{10}$ (IV), $H_2FeOs_3(CO)_{13}$ (V), and $H_2FeRu_3(CO)_{13}$ (VI), where the hydride ligands are chemically equivalent.

Introduction

NMR spectroscopy has become one of the most successful analytical techniques for transition-metal carbonyl hydrides, since ^{1}H resonances of these ligands fall in a characteristic region (-5/-20 ppm) upfield of TMS,[1] allowing their rapid and unambiguous characterization. Few exceptions to this general rule have been reported until now, and their observation is consistent with an early theoretical treatment of δ_H forwarded by Buckingham and Stephens.[2]

Couplings too are very useful in the assignment of stereochemical properties of hydride complexes both with nuclei on other ligands and with magnetically active metals.[3]

Relaxation properties have not been deeply investigated, yet nevertheless their determination can be of high potential value in the elucidation of the structural and dynamic features of these species.[4]

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(1) See, for example: Kaesz, H. D.; Saillant, P. B. *Chem. Rev.* **1972,** *72,* 231. Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979,** *25,* 145.

(2) Buckingham, A. D.; Stephens, P. J. *J. Chem. Soc.* **1964,** 2747; **1964,** 4583.

(3) (a) Mann, B. E.; Masters, C.; Shaw, B. L. *Chem. Commun.* **1970,** 1041. (b) Vander Velde, D. G.; Holmgren, J. S.; Shapley, J. R. *Inorg. Chem.* **1987,** *26,* 3077. (c) Koridze, A. A.; Kizas, O. A.; Kolobova, N. E.; Petroskii, P. V.; Fedin, E. I. *J. Organomet. Chem.* **1984,** *265,* C33. (d) Holmgren, J. S.; Shapley, J. R.; Belmonte, P. A. *J. Organomet. Chem.* **1985,** *284,* C5. (e) Constable, E. C.; Johnson, B. F. G.; Lewis, J.; Pain, G. N.; Taylor, H. J. *J. Chem. Soc., Chem. Commun.* **1982,** 754. (f) Cabeza, J. A.; Mann, B. E.; Brevard, C.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1985,** 65. (g) Cabeza, J. A.; Mann, B. E.; Maitlis, P.; Brevard, C. *J. Chem. Soc., Dalton Trans.* **1988,** 629.

Table I. ^1H and ^{13}C Spin–Lattice Relaxation Times (Solvent $CDCl_3$; 298 K) and Calculated Reorientatioinal Correlation Times τ_c

		^1H T_1, s			
no.	compd	hydride	other H	^{13}C T_1^{DD}, s	τ_c, ps
I	$HOs_3(CO)_{10}(O_2CH)$	82	98.5	2.2	22.4
II	$HOs_3(CO)_9C_2H$	39	41	2.1	23.4
III	$HOs_3(CO)_{10}OH$	22.9	14.8		

Actually, there is still the need for a spectroscopic approach to obtain a better understanding of the bonding scheme involving hydrides although both direct and indirect localization of hydrides may be performed in the X-ray structural determination, avoiding the annoying problems often associated with neutron diffraction analysis.[5]

On the other hand, results obtained by NMR spectroscopy refer to the solution state, which could be different from the situation occurring at the solid state, where packing forces may be responsible for the found spatial arrangements.

The work presented in this paper deals with the evaluation of distances between ^1H nuclei obtained via the measurement of proton spin–lattice relaxation times together with the determination of correlation times for molecular tumbling obtained by T_1 nOe studies of a rigid C–H fragment or through the Stokes–Debye formula.

Results and Discussion

In Table I the proton spin–lattice relaxation times and the homonuclear Overhauser effects of three triosmium derivatives are presented, which show the common feature of having a μ^2-bridging hydride and another ^1H nucleus situated on the ligand on the same Os–Os edge. In all three cases, the homonuclear nOe's give the maximum values (=0.5), indicating that the only relaxation mechanism occurring in these systems is the ^1H–^1H dipole–dipole one.

The minor differences between the relaxation times of the two different ^1H resonances in the same compound might be attributed both to the anisotropic components in the molecular motion and/or to the presence of intermolecular interactions with the solvent or dissolved O_2 molecules, which show a certain degree of specificity. In these cases, we choose the longest value of T_1.

For our purpose, we have assumed that in all three cases the molecular tumbling is isotropic. The molecular correlation times τ_c for I and II have been computed from T_1 and nOe measurements of the C–H fragment (Table I) through the usual equation for dipolar interaction[6]

$$1/(T_1^{DD})_{^{13}C} = n_H(2.0325 \times 10^{10}\tau_c) \qquad (1)$$

by using $r_{C-H} = 1.1$ Å.

The almost identical τ_c values found for I and II (which are also quite similar to those already reported for $H_2Os_3(CO)_{10}$, $HOs_3(CO)_9CH{=}CH_2$, and $H_2Os_3(CO)_9C{=}CH_2$)[7] suggest that the molecular tumbling of triosmium clusters is determined mainly by the metallic moiety whereas the differences in polarity and in the overall geometry induced by other ligands seem to affect in a negligible way the motion of these species.

The proton T_1 shown by the hydride ligand in I is, to our knowledge, the longest proton T_1 measured in solution, and it calls for great care for the search of a hydride resonance when no other magnetically active nucleus with a high gyromagnetic ratio is present in proximity.

Table II. ^1H NMR Data for $HOs_3(CO)_9(C_6H_7)$ (VII) (Solvent $CDCl_3$; 295 K)

	^1H				
	A	B	C	D	E
δ, ppm	5.79	4.65	2.83	5.35	2.63
T_1, s	2.15	2.34	1.91	0.428	0.558
J, Hz	5	8 5	8	16 4	16

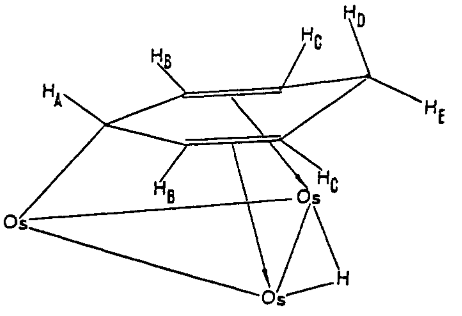
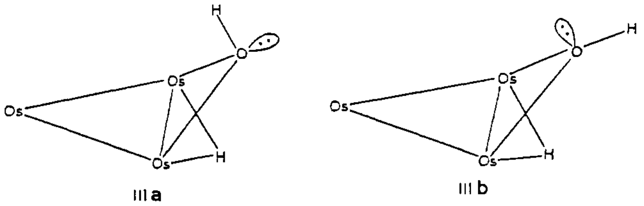


Figure 1. Schematic representation of $HOs_3(CO)_9C_6H_7$ (carbonyl groups omitted for clarity).



IIIa IIIb

Figure 2. Schematic structures of the two isomers of $HOs_3(CO)_{10}OH$ (III).

Osmium shows two magnetically active isotopes, ^{187}Os and ^{189}Os in natural abundances of 1.64% and 16.1%, respectively, but no detectable contribution to T_1 through dipolar or scalar mechanism has been observed.

Now using the τ_c values found in the ^{13}C experiments for I and II and assigning an analogous τ_c value (25 ps) to III, we can evaluate the proton–proton distance by applying

$$1/T_1^{DD} = {}^3/_2\gamma_H{}^4\hbar^2\tau_c(1/r_{HH}{}^6) \qquad (2)$$

In I we found a value of 3.28 Å, which is in good agreement with the value of 3.25 Å obtained from the X-ray structure[8] (assuming a C–H distance equal to 1.1 Å). For II we found a H–H distance of 2.85 Å; a comparison with the structural data obtained in the neutron diffraction study[9] of the analogous $HRu_3(CO)_9$(TBA) suggests that the H—C≡C— framework is linear rather than bent as found for the bulky *tert*-butyl substituent. Otherwise an unlikely upshift of the hydride from the bottom of the Os_3 plane is required. Support of this suggestion arises from the lack of the spin–spin coupling between these protons: although not yet systematically shown, such long-range J_{H-H} coupling seems strongly stereodependent. To this end, we report in Table II the ^1H spectrum of the closely related $HOs_3(CO)_9(C_6H_7)$ (VII) (Figure 1), where the two geminal protons of the methylene group show opposite steric relationships to the hydride: as shown in 2D COSY and NOESY experiments, only H_D is scalar-coupled to the hydride whereas H_E is dipolar-coupled.

No diffraction study has been reported yet for III although its structure can be assumed analogous to that found for $HOs_3(CO)_{10}OMe$;[10] however, for the sp^3-hybridized oxygen two possibilities IIIa and IIIb can be visualized (Figure 2). On the basis of the single hydride resonance reported for III in $CDCl_3$ solution,

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(4) (a) Crabtree, R. H.; Segmuller, B. E.; Uriarte, R. J. *Inorg. Chem.* **1985**, *24*, 1929. (b) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124. (c) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032. (d) Aime, S.; Botta, M.; Gobetto, R.; Osella, D. *Inorg. Chem.* **1987**, *26*, 2551. (e) Drake, S. R.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1988**, *346*, 105. (f) Ammann, C.; Isaia, F.; Pregosin, P. S. *Magn. Reson. Chem.* **1988**, *26*, 236.

(5) Teller, R. G.; Bau, R. *Struct. Bonding* (*Berlin*) **1981**, *44*, 1.

(6) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, 1983.

(7) Aime, S.; Osella, D.; Hawkes, G. E. In *Topics in Physical Organometallic Chemistry*; Gielen, M., Ed.; Freund Publishing House: London, 1987; Vol. 2.

(8) Shapley, J. R.; George, G. M. S.; Churchill, M. R.; Kollander, F. J. *Inorg. Chem.* **1982**, *21*, 3295.

(9) Catti, M.; Gervasio, G.; Mason, S. A. *J. Chem. Soc., Dalton Trans.* **1977**, 2261.

(10) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1980**, *19*, 2391.

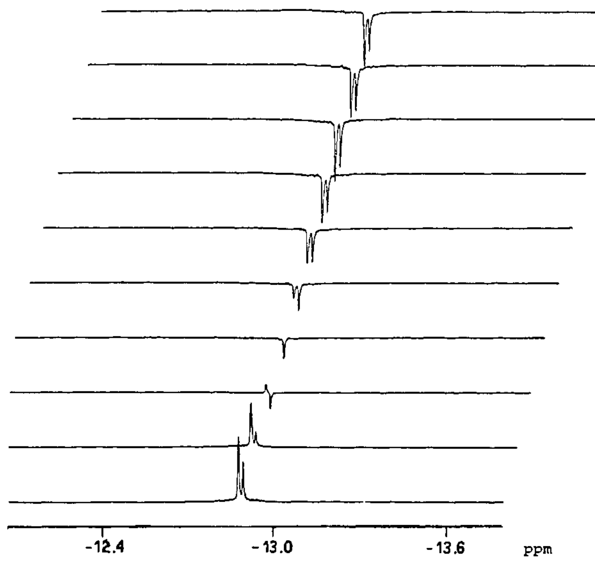

Figure 3. Inversion recovery T_1 measurement for the two $HOs_3(CO)_{10}OH$ (III) isomers in $(CD_3)_2CO$.

it is not possible to unequivocally determine if only one isomer is present or if a rapid IIIa–IIIb interconversion process is occurring. However, by the use of acetone as solvent, both the hydroxyl and hydride resonances are split to confirm the existence of the two proposed isomers in the ratio of 3:2.

As the temperature is raised to +56 °C, no change occurred in the hydride region to indicate that no interconversion is occurring between the two isomers; at this temperature however the hydroxyl resonances actually appear as a single peak, which may be interpreted on the basis of a differential temperature-dependent shift of the two resonances following differential interactions with the solvent molecules. In this mixture the proton T_1 measurement at room temperature has proved to be very useful to assign the resonances of the two isomers, since we obtained values of 28.8 and 56.1 s for the lower and higher field hydride resonances, respectively (Figure 3). By applying eq 2 (and using a τ_c value of 25 ps), we obtained r_{H-H} values of 3.26 and 2.90 Å for IIIa and IIIb, respectively.

The expected H–H distance for the IIIb isomer on the basis of the structural data from $HOs_3(CO)_{10}OMe$ (assuming r_{O-H} = 0.96 Å) is 3.09 Å. The difference with our value (IIIb isomer) may be ascribed to an overestimation of the efficiency of the dipole–dipole relaxation process although structural changes occurring in solution may not be ruled out. The T_1 measurement of III in $CDCl_3$ solution gives an r_{H-H} value of 2.87 Å, which unambiguously supports the view that only the IIIb species is present in this solvent.

Until now we have considered only species containing two hydrogens per molecule, giving rise to well-separated resonances where the homonuclear nOe (and then T_1^{DD}) can be easily evaluated; in the following we will deal with molecules containing two chemically and magnetically equivalent hydrides to show that it is still possible to extract structural distances from proton T_1 measurements.

The method consists of determining the differences in the relaxation rates of the two isotopomers H,H and H,D, which can be assigned to the dipolar contribution in the relaxation of a given hydride; the distances can be evaluated if τ_c is known by an independent experiment. This procedure was already presented in a previous note;[4d] here we present an improvement of the method that consists of the detection of the relaxation times T_1 of the two isotopomers in the same experiment by making use of the small isotopic shift between the hydrido resonances of the two isotopomers.

The ^1H hydrido resonance of the H,D isotopomers is shifted to high field with respect to that of the H,H isotopomers, as expected from the theory developed for simple molecules: in $H_2Os_3(CO)_{10}$ (IV) this shift is equal to 0.0068 ppm. Interestingly,

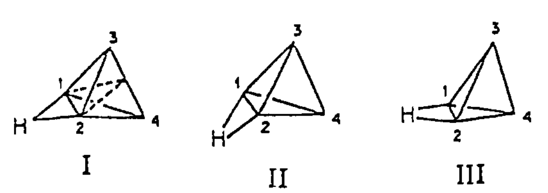

Figure 4. Different dispositions of μ_2-hydrides in tetrahedral clusters.

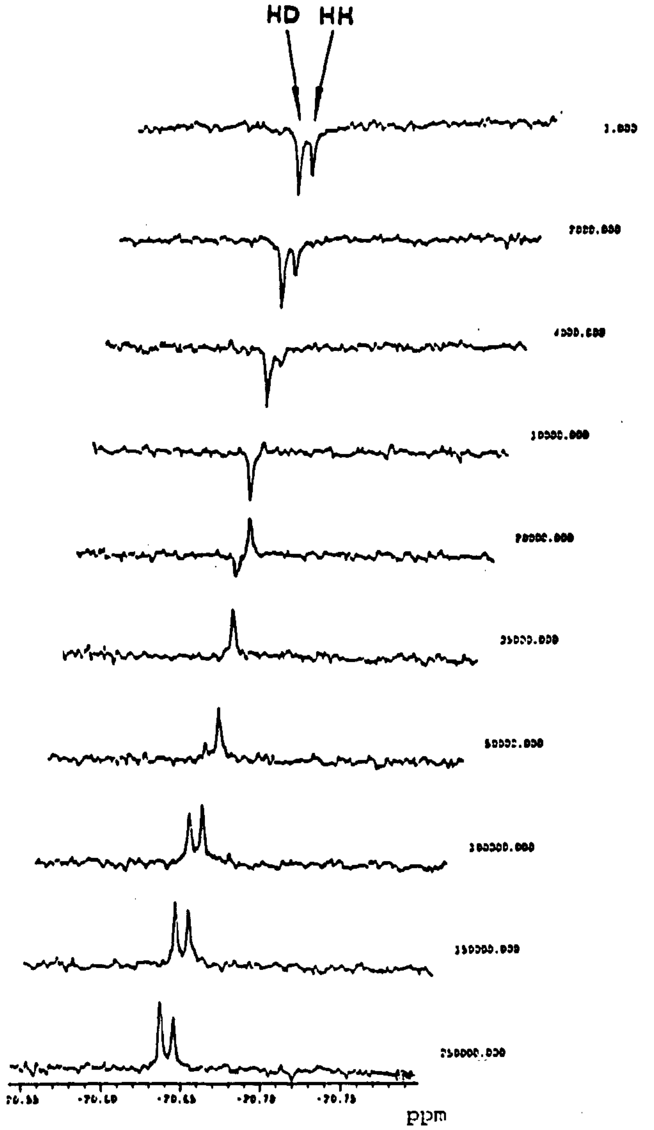

Figure 5. Inversion recovery T_1 measurement for the two $H_2FeOs(CO)_{13}$ isotopomers.

the isotopic substitution also affects the value of ^1J between ^{187}Os and ^1H, which increases by 0.3 Hz in the isotopomer containing deuterium; likely this may be a result of a larger vibrational amplitude of Os–H bonds over Os–D.

The T_1's measured in the mixture of the two isotopomers agree quite well with those reported from independent measurements on the two species, and therefore, they will not be discussed any further in this work.

We then considered another dihydrido species, $H_2FeOs_3(CO)_{13}$ (V), where the X-ray diffraction study was unable to locate the H atoms accurately. As pointed out by Churchill and co-workers[11] in tetrahedral clusters, μ^2-bridging hydrides may assume three

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(11) (a) Churchill, M. R.; Bueno, C.; Hsu, W. L.; Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 1958. (b) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1979**, *18*, 161. (c) Churchill, M. R.; Bueno, C.; Kennedy, S.; Bricker, J. C.; Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 627.

different positions (Figure 4): (i) the M_1–H–M_2 plane bisects the angle formed by the M_1–M_2–M_3 and M_1–M_2–M_4 planes; (ii) the M_1–H–M_2 plane is coplanar with the M_1–M_2–M_3 triangle; (iii) the M_1–H–M_2 plane is coplanar with the M_1–M_2–M_4 triangle.

The T_1 measurement of the mixture of $H_2FeOs_3(CO)_{13}$ and $HDFeOs_3(CO)_{13}$ isotopomers (Figure 5) afforded values of 11.2 and 43.5 s, respectively, the isotopic shift being equal to 0.0081 ppm. The molecular correlation time τ_c was evaluated by applying the Stokes–Debye equation as modified by Gierer–Wiertz[12]

$$\tau_c = \eta V f / kT \qquad (3)$$

η = viscosity
V = molecular volume
f = microviscosity factor
k = Boltzmann's constant
T = absolute temperature

and a value of 10.5 ps was found when V was set equal to 496 Å^3 and a microviscosity factor of 0.16 was employed. It is clear by comparison of this value with those obtained by nOe measurements on the C–H fragment of the molecule that the Stokes–Debye equation leads to an underestimation of the correlation times. By introducing a more reasonable value of 30 ps into eq 2, a value similar to those found in other organometallic derivatives via the measurement of T_1 and nOe values of a rigid C–H fragment, we found an r distance of 2.67 Å. We checked the effect of changes in τ_c (from 20 to 40 ps) on the calculated H–H distances, concluding that eventual errors in this range introduced through τ_c are not dramatic (about 0.1 Å).

In order to establish whether the hydrides were involved in a chemical exchange process, we observed their spin–spin coupling with ^{187}Os; since its value (32 Hz) is in the expected range for μ^2-hydrides in coordinatively saturated osmium clusters and furthermore it does not change on lowering the temperature from room temperature to −50 °C, we decided that no intermetallic motion of these ligands is occurring on the surface of this tetrametallic cluster; otherwise only fractions of the one-bond coupling value would be detectable. The lack of 2:1 splitting in the ^{187}Os satellite subspectrum in the hydride region may be accounted for in terms of a localized oscillation of these ligands that averages the minor differences of the H–Os interactions associated with the slight chemical differences of the two osmium atoms or by an intermetallic motion of the type described by Geoffroy and Gladfelter[13] in the related tetrahedral clusters.

Simple trigonometric calculations based on metal–metal and metal–hydrogen distances taken from ref 11 suggest that the hydrides lie in situation ii, as depicted in Figure 5; conversely by use of an Os–H distance equal to 1.83 Å (which represents the average value obtained from diffraction studies of analogous systems containing μ^2-hydrides bridging Os atoms), the position of the hydride becomes consistent with situation i.

An analogous study has been undertaken for the isostructural $H_2FeRu_3(CO)_{13}$ (VI) derivative whose variable-temperature ^{13}C NMR spectra showed that at room temperature the hydrido ligands are jumping on the edges of the ruthenium triangle to accompany an oscillatory motion of the iron atom over the plane containing the ruthenium atoms.[13]

Although we are considering a dynamic system, our measurements deal with the hydrogen position in the ground state; i.e., the frequency of the hydride jumps does not affect the relaxation rates of these resonances whose dipolar interaction is modulated only by the molecular reorientation time τ_c. The spectral data obtained are the following: δ_H = −18.6 ppm (the isotopic shift for the $HDFeRu_3(CO)_{13}$ isotopomer is 0.011 ppm) and T_1 = 17.1 and 50.7 s for H_2- and $HDFeRu_3(CO)_{13}$, respectively. Following the same approach used for V (r_{Ru-H} = 1.79 Å; τ_c = 25 ps), a type I structure (with a dihedral angle between the Ru_1–H–Ru_2 and Ru_1–Ru_2–Ru_3 planes of 42.5°) is assigned to this cluster.

Table III. ^{1}H Spin–Lattice Relaxation Times for Oxygen-Free Samples in $CDCl_3$ and in the Presence of $Cr(acac)_3$ in a Molar Ratio 1:10 Compared to Cluster Concentration

compd	T_1 of hydride, s	T_1 with $Cr(acac)_3$,[a] s
$H_2Os_3(CO)_{10}$	6.5	0.344
$HOs_3(CO)_9C_2H$	39.0	0.835
$HOs_3(CO)_{10}(O_2CH)$	82.0	0.634
$HOs_3(CO)_{10}OH$	22.9	0.265

[a] Molar ratio 1:10.

In conclusion, the body of these results confirms that proton relaxation measurements may provide further insight into the molecular structure when the relaxation path of a given hydride resonance is accurately determined. Furthermore, the exceedingly long T_1 values often found in these systems may give rise to problems when their spectra are acquired under normal experimental conditions with not enough delay between pulses. This problem (common to ^{13}C resonance of CO groups, especially at low magnetic fields) may be overcome by adding to the solution small amounts of paramagnetic relaxation agents such as $Cr(acac)_3$ (Table III).

The enhancement of relaxation rates in presence of the paramagnetic agents depends on several electronic, structural, and dynamic parameters, and we are currently investigating the possibility of their use as probes for molecular structure and dynamics.

Experimental Section

Compounds I–VI were prepared by the published methods,[14–19] and their purities were checked by IR and proton NMR spectroscopy.

$H_2FeOs_3(CO)_{13}$ and its mono- and bideuterated isomers in the relative ratio 2:8:90 were obtained by the reaction of $Fe(CO)_5$ with $D_2Os_3(CO)_{10}$, the latter prepared by bubbling D_2 in a refluxing octane solution of $Os_3(CO)_{12}$ (150 mg, 0.165 mmol) for 2 h.

The syntheses of the mixtures H_2-, HD-, and $D_2FeRu_3(CO)_{13}$ were performed by starting with $D_4Ru_4(CO)_{12}$ previously obtained by bubbling D_2 gas in a refluxing cyclohexane solution of $Ru_3(CO)_{12}$ for 3 h.

NMR measurements were carried out on a Jeol GX 270/89 spectrometer. The samples were prepared by using Schlenk-tube techniques and oxygen-free $CDCl_3$ (20–30 mg of compound in 0.5 mL of solvent) and were degassed via the freeze–thaw methodology. The nonselective inversion recovery pulse sequence was used to obtain T_1 values; the spin-lattice relaxation times were measured at 298 K on sealed samples, and for all measurements a waiting time of more than $5T_1$ between the pulses was used.

Nuclear Overhauser effects were measured by allowing a delay time of $10T_1$ between the pulses. Errors are estimated to be ±2%.

Registry No. I, 64443-52-3; II, 122658-61-1; III, 63373-90-0; IV, 41766-80-7; V, 12563-74-5; VI, 55073-02-4; D_2, 7782-39-0.

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(12) Gierer, A.; Wiertz, K. *Z. Naturforsch.* **1953**, *A8*, 532.

(13) Gladfelter, W. L.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 2579.

(14) Bryan, E. G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 1328.

(15) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614.

(16) Andrews, M. A.; Kirtley, S. W.; Kaesz, H. D. *Inorg. Chem.* **1977**, *16*, 1556.

(17) Plotkin, J. S.; Alway, D. G.; Weinsenberger, C. R.; Shore, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 6156.

(18) Yawney, D. B. W.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 502.

(19) Bryan, E. G.; Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1976**, 254.