An NMR Study of $H(\mu\text{-}H)Os_3(CO)_{11}$

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The title compound appears to be present in solution as one major (98%) and two minor (ca. 1% each) isomers. All three isomers contain one bridging and one terminal hydride ligand. However, they differ in the location of the terminal hydride. Proton T_1 measurements at variable temperature have allowed the determination of $H_T{-}H_B$ distances in each isomer. An estimation of the relative "hydridicity" of bridging and terminal hydrides has been gained by measuring the T_1 of $^2H(\mu\text{-}^2H)Os_3(CO)_{11}$, while insights into the terminal/bridging hydride exchange have been gained from ^1H variable-temperature NMR.

Introduction

In metal carbonyl cluster chemistry, the coordinatively unsaturated 46 e^- compound $(\mu\text{-}H)_2Os_3(CO)_{10}$ (**I**) represents the starting material for the synthesis of a variety of trinuclear osmium derivatives. This is due to its extraordinary ability to fill up its coordination vacancy by forming covalent adducts with a number of two-electron donor ligands L.[1−4] Upon reaction with L there is a rearrangement inside the hydride moiety with the formation of one terminal (H_T) and one bridging (H_B) hydride ligand (Chart 1).

In most $H(\mu\text{-}H)Os_3(CO)_{10}L$ (**II**) derivatives the ligand L is bound to $Os_{(2)}$ (see Chart 1), although there is evidence for derivatives containing L at the other two osmium atoms.[5,6] When the positions of the hydride ligands are kept "frozen" as in **II**, up to 11 structural isomers could be drawn for the different positions of L. It has been recently reported that when L is phosphine, 5 of the 11 possible isomers can be detected and characterized.[6]

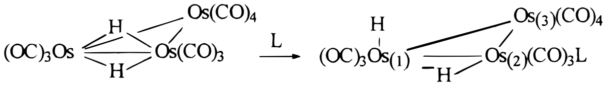
In principle, other isomers may arise following different layouts of the hydride ligands. The occurrence of isomers corresponding to arrangements of H_T and H_B, which differ from that in **II,** have been mentioned by Rosenberg et al. in the case of $H(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}C_4H_6N)Os_3(CO)_8(PPh_3)$.[7]

We thought it of interest to pursue a more accurate characterization of such types of isomers by choosing the $H(\mu\text{-}H)Os_3(CO)_{11}$ derivative, which is the simplest among the available species that show this type of isomerism.

Experimental Section.

$(\mu\text{-}H)_2Os_3(CO)_{10}$ was prepared according to the published procedure.[8] A specimen of $(\mu\text{-}^2H)_2Os_3(CO)_{10}$ was synthesized by bubbling D_2 (instead of H_2) in an octane solution of $Os_3(CO)_{12}$.

Chart 1



I **II**

The nonselective inversion recovery pulse sequence[9] was used to obtain the ^1H and ^2H T_1 values of previously degassed samples. Errors in the reported T_1 values were estimated to be in the range of 5%. Proton relaxation times were measured on JEOL EX-400, JEOL GX-270, and JEOL EX-90 instruments, operating at 399.65, 270.05, and 90.0 MHz, respectively. Deuterium relaxation times were measured on the JEOL EX-400 spectrometer operating at 61.64 MHz. The temperature calibration was carried out according to the method reported in ref 9.

Results and Discussion.

The synthesis of $H(\mu\text{-}H)Os_3(CO)_{11}$ was reported several years ago.[1,2] The positions of H_T and H_B in the solid-state structure, inferred by the isostructurality with $Os_3(CO)_{12}$, were shown to be as in **II**.[10] The maintainance of this structure also in solution was supported by the observation of two hydride resonances at -10.46 (H_T, $^2J_{H-H} = 2.3$ Hz) and -20.25 ppm (H_B, $^2J_{H-H} = 2.3$ Hz) in toluene-d_8 at 183 K. In agreement with the behavior of the entire series of $H(\mu\text{-}H)Os_3(CO)_{10}L$ derivatives, an averaging process of the hydride resonances takes place at higher temperatures.[2,3] However, 2D exchange spectroscopy (EXSY) ^{13}C NMR experiments showed that at temperatures only slightly higher than 183K (i.e., well below those required for detecting the $H_T{-}H_B$ exchange process), a concerted motion of the H_T and 10 of the 11 carbonyl groups leads to the enantiomerization of $H(\mu\text{-}H)Os_3(CO)_{11}$.[11]

A careful examination of the hydride region in the ^1H NMR spectrum of $H(\mu\text{-}H)Os_3(CO)_{11}$ at 183 K in toluene-d_8 revealed the presence of two low-intensity (∼1:100 with respect to the main signal) pairs of resonances at -12.53 (H_T, $^2J_{H-H} = 17.1$ Hz) and -18.40 (H_B, $^2J_{H-H} = 17.1$ Hz) and at -8.64 and -19.42 ppm (Figure 1).

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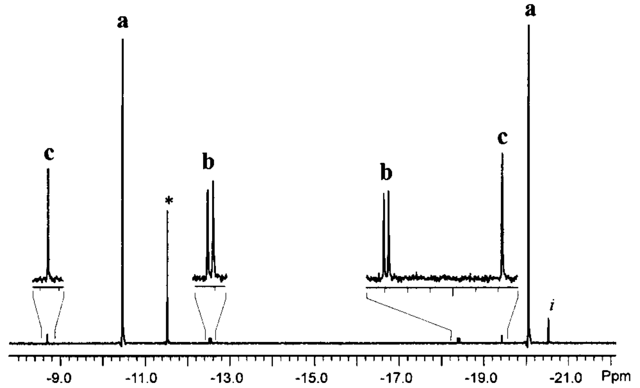
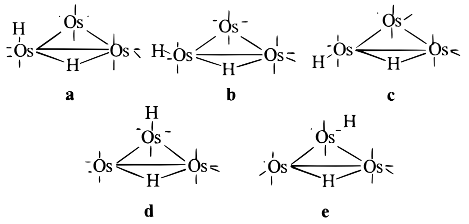


Figure 1. ^1H NMR spectrum of $H(\mu\text{-}H)Os_3(CO)_{11}$ (toluene-d_8, 183 K, 399.65 MHz). i denotes impurity, the signal marked with ∗ is assigned to $(\mu\text{-}H)_2Os_3(CO)_{10}$.

Chart 2



The possibility that these signals could be due to impurities was ruled out because of their persistence whatever preparative route was used (i.e., by reacting $(\mu\text{-}H)_2Os_3(CO)_{10}$ and CO both in the solid state and in solution and under different reaction conditions: temperature (323 and 353 K), CO pressure (200, 360, 760 Torr), reaction time, and solvent (toluene, chloroform, dichloromethane, acetone). Furthermore, no change in the ^1H NMR spectrum was observed even after submitting the starting material to repeated purification steps.

Unfortunately, all attempts to separate the mixture by thin-layer chromatography (TLC) were unsuccessful because this caused extensive decomposition of the specimen. On the other hand prolonged low-temperature removal of the solvent at the vacuum line caused the transformation of all the species that were present in the mixture into $Os_3(CO)_{12}$ and $(\mu\text{-}H)_2Os_3(CO)_{10}$, as clearly shown by ^1H and ^{13}C NMR spectroscopy.

These considerations were taken as an indication that $H(\mu\text{-}H)Os_3(CO)_{11}$ is actually a mixture of three isomeric species. As anticipated in the introduction, in the case of $H(\mu\text{-}H)Os_3(CO)_{11}$ isomers may only arise from a different layout of the hydride ligands. Therefore, one may envisage five possible structures for the three isomeric forms, as depicted in Chart 2.

Structure **a** is found in the solid state and corresponds to the major isomer in solution. By observation of Figure 1, a **b**-type structure may be envisaged because of the presence of a large $^2J_{H-H}$ coupling between the signals at −12.3 and −18.40 ppm.

^1H T_1 Measurements. A particularly useful and generalizable method for spectral assignments and for the determination of the structure of the third isomer from the three available possibilities, **c**, **d**, and **e**, was provided by the measurement of the longitudinal relaxation times (T_1) of the hydride resonances.

The temperature dependence of the relaxation times of the bridging and terminal hydrides at 2.1 T in the temperature range 188−253 K was determined for the **a** isomer (toluene-d_8). At this low magnetic field the proton relaxation rate can be considered to be dependent only on the $^1H-^1H$ dipolar term according to the following equation:[12]

$$\frac{1}{T_1} = \frac{3}{10}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2 \gamma_H{}^4 \tau_c}{r_{H-H}{}^6}\left(\frac{1}{1+\omega_0{}^2\tau_c{}^2} + \frac{4}{1+4\omega_0{}^2\tau_c{}^2}\right) \tag{1}$$

where μ_0 is the magnetic susceptibility in the vacuum, γ_H is the gyromagnetic ratio value for the proton, ω_0 is the experimental resonance frequency, and τ_c is the molecular reorientational time for the molecule. The latter parameter depends on the temperature according to

$$\tau_c = \tau_0\, e^{E_a/(RT)} \tag{2}$$

where R is the Boltzmann constant in J mol^{-1} K^{-1} and E_a is the activation energy for the reorientational motion.

The T_1 minimum observed at 207 K allowed the calculation of the molecular reorientational time at this temperature by the equation

$$\tau_c = \frac{0.6158}{\omega_0} \tag{3}$$

(i.e., $\tau_c(207\ K) = 977$ ps). The knowledge of τ_c was then exploited to obtain an estimation of the interproton distance from the T_1 value at 207 K (eq 1). The values of r_{H-H} and τ_c could subsequently be used as the starting parameters to fit, by successive iterative runs, the $1/T_1$ vs $1/T$ curves of the terminal and bridging hydrides to the theoretical values determined by eqs 1 and 2. The following values have been obtained: $r_{H-H} = 2.46 \pm 0.04$ Å, $E_a = 18.62 \pm 0.5$ kJ mol^{-1} K^{-1}, $\tau_0 = (1.92 \pm 0.2) \times 10^{-14}$ s.

The activation energy for the reorientational motion is significantly higher than the corresponding values previously reported for other hydride metal complexes.[13,14] Such a difference can be accounted for in terms of either the larger size of $H(\mu\text{-}H)Os_3(CO)_{11}$ with respect to mono- or binuclear derivatives or the higher viscosity of toluene-d_8 with respect to chlorinated solvents ($CDCl_3$ or CD_2Cl_2).[15,16] (The effect of solvent viscosity on E_a has been assessed for the parent $(\mu\text{-}H)_2Os_3(CO)_{10}$ derivative. In $CDCl_3$ E_a is 9.3 kJ/mol, whereas in toluene-d_8 it becomes 14.5 kJ/mol (unpublished results).)

When the hydride relaxation times at higher magnetic field strengths (6.34 and 9.4 T) are measured, the chemical shift anisotropy (CSA) contribution to the relaxation rate is no longer negligible and the following extended equation must therefore be considered:[12]

$$\frac{1}{T_1} = \frac{1}{T_1^{DD}} + \frac{1}{T_1^{CSA}} = \frac{3}{10}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2 \gamma_H{}^4 \tau_c}{r_{H-H}{}^6}\left(\frac{1}{1+\omega_0{}^2\tau_c{}^2} + \frac{4}{1+4\omega_0{}^2\tau_c{}^2}\right) + \frac{2}{15}\gamma_H{}^2 B_0{}^2 \Delta\sigma^2 \tau_c \left(\frac{1}{1+\omega_0{}^2\tau_c{}^2}\right) \tag{4}$$

where B_0 is the operating magnetic field and $\Delta\sigma$ is the CSA.

The values determined at 2.1 T for τ_0, E_a, and r_{H-H} were used to fit the experimental T_1 vs $1/T$ curves obtained at 6.34 and 9.4 T (eq 4). This allowed us to determine the CSA values for the bridging and the terminal hydrides, which are 22.6 ± 2.0 and 20.0 ± 1.9 ppm, respectively.

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Table 1: Hydride Chemical Shifts and Calculated H−H Distances for the Three Isomers of $H(\mu\text{-}H)Os_3(CO)_{11}$

	δ	r_{H-H} (Å)
a	H_T: −10.46; H_B: −20.05	2.46 ± 0.04
b	H_T: −12.53; H_B: −18.40	3.34 ± 0.07
c	H_T: −8.68; H_B: −19.42	2.12 ± 0.06

The obtained CSA values are very similar to those obtained by Nicol and Vaughan[17] for bridging hydride ligands in $(\mu\text{-}H)_2Os_3(CO)_{10}$ and $(\mu\text{-}H)_4Ru_4(CO)_{12}$ from solid-state ^1H NMR measurements. It is worth noting that the solution ^1H T_1 measurements at variable magnetic field provide a reliable route to an accurate determination of such relatively small CSA values.

Despite a large difference in their isotropic chemical shifts, the CSA values of the bridging and terminal hydrides in $H(\mu\text{-}H)Os_3(CO)_{11}$ are very similar. This is an unexpected result, expecially when compared with the CSA variation of about 10 ppm, which is observed upon hydrogen bond formation in organic systems.[18]

Since the three isomers have the same molecular weight and essentially the same overall shape, the τ_c values determined for isomer **a** at the various temperatures (by using eq 2) can be assumed to be the same for **b** and **c** isomers as well. On this basis, from the relaxation times of the minor isomers measured at 217 K (9.4 T) it has been possible to calculate r_{H-H} for both derivatives by using eq 4 (Table 1).

The trans arrangement proposed for **b** is confirmed by an H−H distance of 3.34 Å. Moreover, the H−H distance of 2.12 Å allowed us to assign the third set of resonances to the cisoid structure **c**. It is then possible to conclude that the structures (**a**−**c**) containing the bridging and terminal hydrides bound to the same Os center are preferred to those (**d**−**e**) in which the two hydrides are kept distant on the surface of the metallic cluster.

It is worth noting that the short H−H distance found in isomer **c** may suggest the occurrence of some interaction between the two hydride ligands. In fact, in several organometallic systems, such short H−H distances have been recently associated with the presence of nonconventional hydrogen bonds.[19−22] However, no example has yet been reported for the occurrence of such an interaction between two hydride ligands. The hypothesis that a different polarization of the metal−hydrogen bonds causes the upsurge of different polarities on the hydride ligands such that an H···H interaction may take place is suggestive. One may envisage such an interaction scheme as a situation between classical and nonclassical hydride bonding modes.

There is no observable effect of solvent polarity on the relative isomers populations. This is in accordance with the occurrence of structures of approximatively the same polarity, as it is reasonable to assume, since they differ only in the position of an H atom on the same Os center.

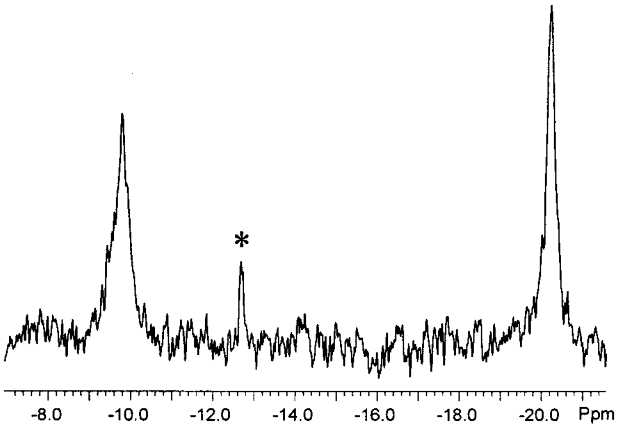

Figure 2. ^2H NMR spectrum of $^2H(\mu\text{-}^2H)Os_3(CO)_{11}$ (toluene-d_8, 183 K, 61.64 MHz). The signal marked with * is assigned to $(\mu\text{-}^2H)_2Os_3(CO)_{10}$.

Furthermore, no change in their relative populations was observed when the temperature was varied. This is indicative of a large energy difference between **a** and **b**/**c.** The greater stability of **a** with respect to **b**/**c** can be explained on the basis of the CO back-donation. In fact electron−acceptor ligands such as carbonyl groups prefer positions trans to the hydride ligands for minor competition for the metal d orbitals.[23]

^{2}H T_1 Measurements. For better insight into the minor electronic differences between terminal and bridging hydrides of the title compound, a ^2H NMR study was undertaken. The ^2H NMR spectrum of $^2H(\mu\text{-}^2H)Os_3(CO)_{11}$ (Figure 2) shows that the terminal hydride signal is significantly broader than that of the bridging hydride (unfortunately, the larger line width and the smaller frequency separation of the ^2H resonances prevented the observation of the minor isomers **b** and **c**). In the presence of isotropic molecular motion the observation of different broadening for the two resonances is an indication of the difference in the deuterium quadrupolar coupling constants (QCC) for the two hydride ligands. The accurate determination of the latter parameter is possible by measuring the longitudinal relaxation time T_1 of the two ^2H resonances and by applying the following:[24]

$$\frac{1}{T_1} = \frac{3}{50}\pi^2 \frac{2I+3}{I^2(2I+1)}(\mathrm{QCC}(^2\mathrm{H}))^2\left(1+\frac{\eta^2}{3}\right)\left(\frac{\tau_c}{1+\omega_0^2\tau_c^2}+\frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right) \qquad (5)$$

where

$$\mathrm{QCC}(^2\mathrm{H}) = \frac{e^2 q_{zz} Q}{h}$$

By assuming that the asymmetry factor η is equal to zero and by using the τ_c values obtained from the ^1H T_1 measurements, the QCC(^{2}H) values of 86.4 ± 1.5 kHz and 60.1 ± 2.0 kHz for H_T and H_B, respectively, were obtained by fitting the experimental T_1 vs $1/T$ data against eq 5.

Deuterium QCCs have been reported for several metallic hydrides.[24−26] The smallest value (33 kHz) has been found for

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LiD, getting close to the ionic limit of a M−D bond with a zero QCC(^{2}H).[24] The pure covalent end of the scale is reported for the HD molecule, whose QCC(^{2}H) is 277 kHz. In the field of metal carbonyl hydrides, the QCC(^{2}H) values have been measured for a terminal hydride in $^2HMn(CO)_5$[26] (68.1 kHz) and for bridging hydrides in six binuclear derivatives of formula $[(\mu\text{-}^2H)M_2(CO)_{10}]^-X^+$ (M = Cr, Mo) (with values ranging from 54.8 to 90.4 kHz, depending on the metal ion and on the counterion X^+).[25] Thus, although the values found for $^2H(\mu\text{-}^2H)Os_3(CO)_{11}$ fall in the range of the literature data, it appears difficult to draw an overall rationalization of the relationship between the QCC(^{2}H) values and the hydride bonding scheme in metal complexes. However, it seems reasonable to compare the deuterium QCCs for related classes of compounds and even more for different hydrides in the same molecule, as in $H(\mu\text{-}H)Os_3(CO)_{11}$. Of course, the assumption of the same η (equal to zero) for both the terminal and the bridging hydrides in the latter compound may introduce an error in the determination of their QCC(^{2}H)s. Anyway, it is clear that the asymmetry should be larger for the bridging than for the terminally bound hydride. Thus, the difference between the deuterium QCCs of the two hydrides calculated in this work represents a low-limit value.

Some further considerations can be made on the basis of the suggestion that the ionicity of the M−D bonds in metal hydrides can be estimated by applying the following equation:[24]

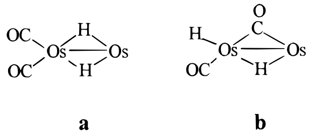
$$i = 1 - \frac{\mathrm{QCC}(^2\mathrm{H})}{227} \qquad (6)$$

Upon introducing the QCC(^{2}H) values calculated for $^2H(\mu\text{-}^2H)Os_3(CO)_{11}$, i values of 0.736 and 0.620 have been obtained for H_B and H_T, respectively. This finding supports the occurrence of a different “hydridicity” for bridging and terminal hydrides in the title molecule, H_T being less negatively charged than H_B. One may further speculate that H_T in isomer **c** might have an even reduced “hydridicity” (because it is trans to an Os−Os bond) to make more acceptable the idea of some H···H interaction, as the H distance would suggest.

Terminal/Bridging Hydride Exchange. Keister et al. showed that isomer **a**, in analogy with the other $H(\mu\text{-}H)Os_3(CO)_{10}(L)$ species, undergoes a bridging/terminal hydride exchange process via rotation around an Os−Os bond of the rigid plane formed by two hydrides and two equatorial carbonyl groups.[2,3] The temperature-dependent ^{1}H NMR spectra recorded for the **b** isomer are consistent with the occurrence of the same exchange mechanism. Conversely, no temperature effect was observed in the ^{1}H NMR spectra of isomer **c** up to 353 K. This is reasonable because in this isomer the terminal hydride is perpendicular to the rotation plane, thus preventing the terminal/bridging hydride exchange process found in the other isomers.

The rate constant values for the exchange processes at different temperatures were obtained by simulating the variable-temperature (VT) NMR spectra of **a** and **b**, and the activation parameters were calculated from the Eyring plot of $\ln[kh/(k_BT)]$ vs $1/T$. $\Delta G^‡$, $\Delta H^‡$, and $\Delta S^‡$ are similar for the two species ($\Delta G^‡(\mathbf{a}) = 12.6 \pm 1.3$ kcal/mol, $\Delta G^‡(\mathbf{b}) = 11.0 \pm 0.9$ kcal/mol; $\Delta H^‡(\mathbf{a}) = 13.4 \pm 1.0$ kcal/mol; $\Delta H^‡(\mathbf{b}) = 12.2 \pm 1.1$ kcal/mol; $\Delta S^‡(\mathbf{a}) = 3.0 \pm 3.6$ cal mol^{-1} K^{-1}; $\Delta S^‡(\mathbf{b}) = 4.7 \pm 1.3$ cal mol^{-1} K^{-1}), supporting the view that the same exchange mechanism can be invoked for both isomers. The fact that isomer **b** exchanges slightly more quickly than isomer **a** suggests that the energy difference between the transition states of **a** and **b** is smaller than the energy difference between their ground states. This could be due to the fact that in isomer **a** the transition state should contain two bridging hydrides, whereas in isomer **b** a bridging hydride and a bridging carbonyl should be observed, as shown in Chart 3.

Chart 3



No evidence of exchange among **a**, **b**, and **c** on the NMR time scale was observed up to 353 K.

Conclusions

The results reported above show that two more isomers are present for the previously reported $H(\mu\text{-}H)Os_3(CO)_{11}$ derivative, which differ for a different layout of the terminal hydride ligand. It seems likely that the three arrangements of the hydride moieties found in $H(\mu\text{-}H)Os_3(CO)_{11}$ may occur in the whole series of $H(\mu\text{-}H)Os_3(CO)_{10}(L)$ derivatives. The number of isomers possible for the $H(\mu\text{-}H)Os_3(CO)_{10}(L)$ adducts can therefore be high because the 11 structures based on the different coordination sites for L have to be multiplied by 3 to account for the possible arrangements of the hydride moiety.

Moreover, the short H_T−H_B distance found in isomer **c** of $H(\mu\text{-}H)Os_3(CO)_{11}$ suggests a possible pathway for the elimination of molecular hydrogen, which is a process associated with this compound. In fact, some years ago Pöe et al. reported that the first-order loss of H_2 from $H(\mu\text{-}H)Os_3(CO)_{11}$ is somewhat analogous to the release of H_2 in the nonclassical $(Cy_3P)(CO)_3W(\eta\text{-}H_2)$.[27] Our observation of the occurrence of isomer **c**, with a relatively short H−H distance (likely also as a consequence of a reduced hydridicity of H_T trans to the Os−Os bond), may be taken as an indication that this structure could represent an important step in the loss of hydrogen (i.e., the formation of molecular hydrogen should be easier from **c** than from **a** and **b**).

Finally, the analogy in the VT-NMR spectra of isomers **a** and **b** confirms that at high temperature, the stereochemical nonrigidity of these systems is based on a simple rotation of the equatorial plane at the octahedral osmium bearing the terminal hydride. Nothing can be said about the occurrence of an analogous process in isomer **c**. Such a process would be easily elucidated by ^{13}C VT-NMR spectroscopy, but the very low amount of this species prevents its observation.

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Supporting Information Available: ^{1}H T_1 vs temperature data at 2.1, 6.34, and 9.4 T for the hydrides of the main isomer of $H(\mu\text{-}H)Os_3(CO)_{11}$, ^{1}H T_1 values measured at 217 K and 9.4 T for the two minor isomers of $H(\mu\text{-}H)Os_3(CO)_{11}$, and ^{2}H T_1 vs temperature data at 9.4 T for the hydrides of the main isomer of $H(\mu\text{-}H)Os_3(CO)_{11}$ (toluene-d_8). This material is available free of charge via the Internet at http://pubs.acs.org.

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