^{1}H and ^{13}C NMR Study of the Solid-State Dynamics of $H_4Ru_4(CO)_{12}$

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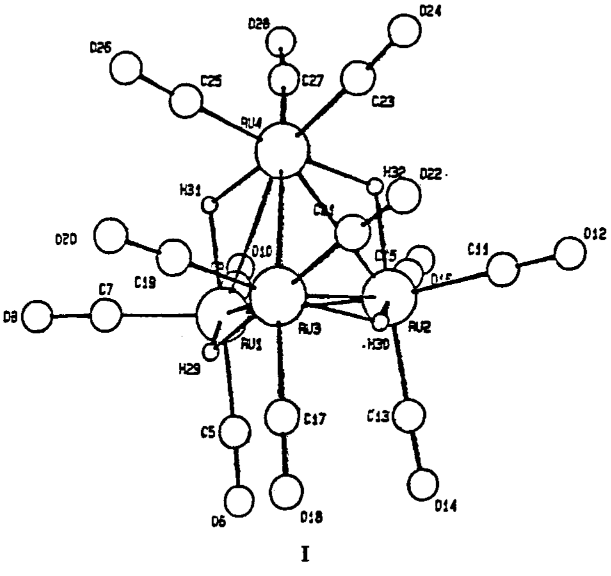
Variable temperature $^{13}C\text{-}\{^1H\}$ CP/MAS, ^{1}H MAS and ^{1}H wide-line NMR spectra of $H_4Ru_4(CO)_{12}$ are interpreted in terms of a dynamic process involving either the H_4Ru_4 moiety as a whole or the motion of the hydrides over the surface of the metallic core. The temperature dependence of the ^{1}H spin-lattice relaxation time (T_1) values over the range 298–360 K and the temperature dependence of the line width of the static ^{1}H spectrum over the range 153–380 K together give an activation energy for this motional process of 67.2 ± 8.0 kJ mol^{-1}. The rigidity of the carbonyl polyhedron is demonstrated by the fact that the ^{13}C chemical shift tensor components are typical for those in a nonfluxional molecule and are invariant between 200 and 360 K.

Introduction

With the techniques of solid-state NMR spectroscopy it is possible to obtain structural and dynamic information on organometallic carbonyl complexes which is not available from solution studies.[1] Following the early work of Anderson,[2] who analyzed the low-resolution proton spectra of a number of solid-state metallocenes at variable temperture, it is now well established that the measurement of ^{1}H spin–lattice relaxation times (T_1) provides a reliable tool for the determination of reorientational rates for a variety of ligands in the solid state.[3] In the context of high resolution applications of particular note are the ^{13}C MAS spectra of $Fe_3(CO)_{12}$. In solution exchange between bridging and terminal CO groups is rapid, even at the lowest attainable temperature (123 K), resulting in a single ^{13}C resonance.[4] In the solid state the asymmetric unit, as determined by X-ray structural analysis,[5] is one molecule and therefore a maximum of 12 ^{13}C resonances is expected. In fact six resonances are resolved at ambient temperature[6,7] and subsequent lower temperature ^{13}C MAS NMR spectra, reported by Hanson *et al.*,[8] were interpreted in terms of rotation of the Fe_3 triangle within the icosahedral ligand polyhedron. Such rapid motion was proposed as the reason for the reduction in the number of resonances from 12 to 6. Later Anson *et al.*[9] interpreted the dynamic behavior of solid $Fe_3(CO)_{12}$ in terms of small librations of the Fe_3 triangle about the molecular pseudo-2-fold axis sufficient to change the molecular geometry from C_2 to pseudo-D_3 symmetry. We report here our observations on the solid state dynamics of the ruthenium cluster $H_4Ru_4(CO)_{12}$ (**I**). In solution there is[10] just one ^{13}C resonance and one ^{1}H resonance down to 153 K. The X-ray structure showed[11] the asymmetric unit to be one molecule having a distorted tetrahedral arrangement for the Ru_4 core (see structure) with two shorter intermetal distances (Ru_1–Ru_2 and Ru_3–Ru_4) and four longer Ru–Ru distances.



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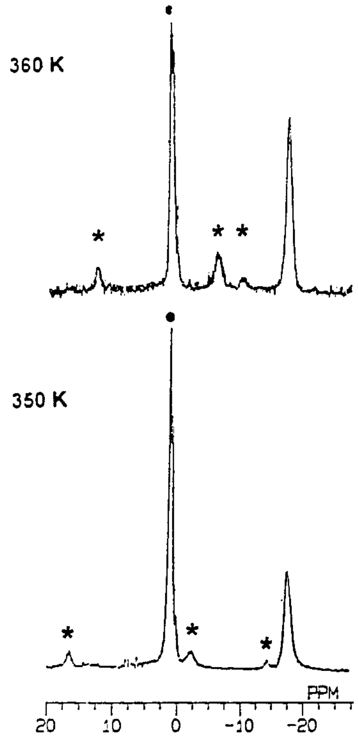

Figure 1. High temperature ^1H MAS spectra of $H_4Ru_4(CO)_{12}$. An asterisk indicates spinning side bands, and a solid dot indicates an impurity arising from residual solvent or silicone grease. The strong intensity of the impurity signal is the result of its much shorter relaxation time in respect to that of $H_4Ru_4(CO)_{12}$.

Although the evidence was not conclusive the hydrogen atoms were believed to be bridging the four long edges. The carbonyl ligands are staggered with respect to the Ru–Ru bonds.

Experimental Section

$H_4Ru_4(CO)_{12}$ (**I**) was prepared by hydrogenation of $Ru_3(CO)_{12}$ as described[12] in the literature, and the product was recrystallized from cyclohexane. ^{13}C-enriched **I** was prepared from ^{13}C-enriched $Ru_3(CO)_{12}$ as described by Aime *et al.*[13] Wide-line ^1H spin–lattice relaxation times (T_1) for **I** were measured using the inversion recovery pulse sequence with a JEOL GSE-270 spectrometer operating at 270 MHz. High-resolution ^1H and ^{13}C magic angle spinning (MAS) NMR spectra were measured with a Bruker MSL-300 spectrometer operating at 300 and 75.5 MHz respectively. In addition ^{13}C spectra were recorded on ^{13}C-enriched **I** using $^{13}C\{^1H\}$ cross polarization (CP) and high power ^1H decoupling. In a typical experiment the CP contact time was 1 ms, the recycle times were 90 s at 200 K, 60 s at 296 K, and 30 s at 360 K, and the spinning speeds were around 4.3–6.2 kHz.

Results and Discussion

^{1}H Spectra. The solid-state ^1H MAS spectrum of **I** at 297 K show one resolved signal at −18 ppm with a width ($\Delta\nu$) ca. 480 Hz, and this width did not decrease with an increase in the temperature (Figure 1). This chemical shift is in very good agreement with that found[10b] in solution (−17.6 ppm) and suggests that the solvation/crystal packing effects have a negligible influence on these hydride ligands. Since the asymmetric unit is one molecule, it was expected that up to four signals would be resolved—in this context we have observed[10c] resolution of two ^1H chemical shifts in the solid-state spectrum of the complex $H_2Os_3(CO)_{10}$ which again has one molecule as the asymmetric unit, in contrast to the solution-state spectrum where the protons are equivalent. The observation of just one ^1H resonance for **I** could therefore be due to accidental overlap of the resonances or to some motional process. Nicol and Vaughan[14] measured the ^1H multiple pulse spectrum of **I**, found just one resonance and suggested the possibility of there being a motional process involving the hydrides. To gain further insight into the possible dynamic behavior of **I** the temperature dependence of the static ^1H spin–lattice relaxation time (T_1) and the static ^1H line shape were measured. The T_1 value, measured by the inversion–recovery technique, is strongly temperature dependent and we have analysed these data on the basis of dominant interproton dipole–dipole interactions, according to the expression proposed by Kubo and Tomita[15] (eq 1), where τ_c is a correlation time describing the dynamic

$$T_1^{-1} = C[\tau_c/(1 + \omega^2\tau_c^2) + 4\tau_c/(1 + \omega^2\tau_c^2)] \qquad (1)$$

process, and is assumed to follow the simple activation law[16] (eq 2). The rate of the dynamic process is given by

$$\tau_c = \tau_o \exp(E/RT) \qquad (2)$$

$k = (2\pi\tau_c)^{-1}$, ω is the ^1H resonance frequency (here $2\,\pi\,270 \times 10^6$ rad s^{-1}), and the dipole–dipole relaxation constant, C, between a proton and its neighbours, is given by eq 3.

$$C = (3/10)(\mu_o/4\pi)^2\gamma_H^4\, h^2 \sum\nolimits_{i=1,n} r_i^{-6} \qquad (3)$$

With neglect of intermolecular interactions and ^1H–^{99}Ru and ^1H–^{101}Ru interactions, the summation in eq 3 has $n = 3$. In the low temperature limit when $\omega^2\,\tau_c^2 \gg 1$, and combination of eqs 1 and 2 gives eq 4. A plot of our

$$T_1 = (\omega^2\tau_o/2C)\exp(E/RT) \qquad (4)$$

experimental data ln T_1 vs T^{-1} is linear (Figure 2), as predicted from eq 4, and the slope and intercept yield values for (E/R) and ln $(\omega^2\tau_o/2C)$, respectively. The value for E thus obtained is 59.2 kJ mol^{-1}. In order to obtain rate information it is necessary to evaluate k *via* τ_c, which in turn can be obtained from the intercept of Figure 2 and eq 2, if an independent estimate for C is available. With the evidence[11] that the hydrides symmetrically bridge two ruthenium atoms with a Ru–H distance of 1.76 Å the four protons form an essentially rectangular (near square) planar arrangement with sides 2.752 and 2.745 Å (estimated using MOLDRAW[17]). These distances are close to the 2.79 Å estimated by Nicol.[14c] We therefore calculate a value for $C = 8.437 \times 10^8$ s^{-2} which gives a value for $\tau_o = 2.76 \times 10^{-17}$ s.

The measurement of T_1 at temperatures lower than 298 K is made difficult by their very long values, and therefore

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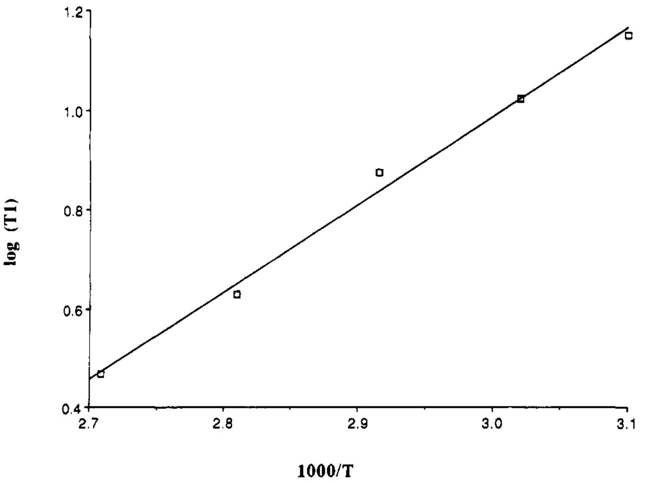

Figure 2. Plot of ^1H static spin-lattice relaxation times (log T_1) of $H_4Ru_4(CO)_{12}$ as a function of temperature.

the dynamic process was explored over a wider temperature range by analysis of the static ^1H line shape. The ^1H spectrum was recorded in the temperature range 150–380 K and the line shape at all temperatures was best fitted (using the program NMRi[18]) to a single Lorentzian function rather than a Gaussian. As described by Abragam[19] the second moment of the Lorentz shape is not defined and therefore, following the work of Gutowsky and Pake,[20] we use the full width at half-height ($\Delta\nu$) as an "unambiguous parameter of the observed resonance curve".[21] The experimental data are plotted in Figure 3, and these were fitted to eq 5 (given by Gutowsky and Pake[20]). The

$$(\Delta\nu)^2 = B^2 + D^2(2/\pi)\tan^{-1}[\alpha(\Delta\nu/k)] \qquad (5)$$

coefficient α is assumed to be unity. The rigid lattice width (low-temperature limit) is A, and B is the width in the high-temperature limit.

$$A = (B^2 + D^2)^{1/2} \qquad (6)$$

The rate of the process, k, is assumed to be of the form (*cf.* eq 2)

$$k = k_o \exp(-E/RT) \qquad (7)$$

The data in Figure 3 were fitted to eqs 5–7 by using the parameters $A = 12045$ Hz, $B = 4849$ Hz, $E = 75.1$ kJ mol^{-1}, and $k_o = 4.93 \times 10^{15}$ s^{-1}. Therefore $\tau_o = 3.23 \times 10^{-17}$ s, and this value together with the value for E are in very good agreement with the values found from the relaxation time measurements. Average values from the two methods are then $\tau_o = 3.0 \times 10^{-17}$ s and $E = 67.2 \pm 8.0$ kJ mol^{-1}.

^{13}C Spectra. The solid-state ^{13}C CP-MAS spectrum of (**I**) at 297 K shows 11 resonances (Figure 4b) with isotropic chemical shifts 193.5, 192.9, 192.7, 192.2, 191.9, 190.9, 188.3, 187.9, 187.2, 186.7, and 184.6 ppm. It was our observation[22] that the solid state ^{13}C spectra of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$, both of which crystallize[23,24] with one molecule as the

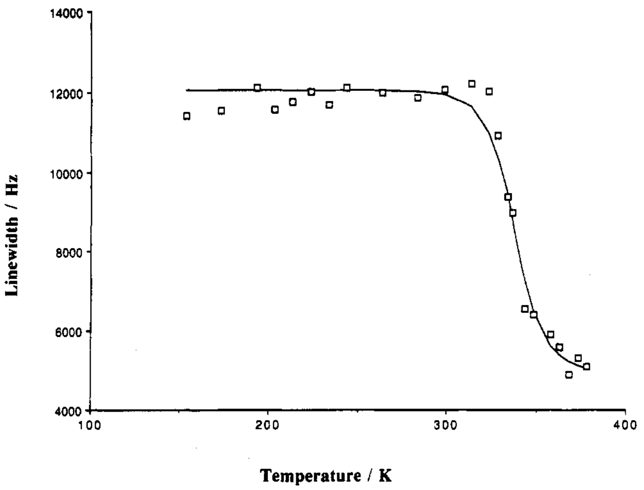

Figure 3. Temperature dependence of the ^1H static line width of $H_4Ru_4(CO)_{12}$. An open square indicates experimental values, and the solid line is calculated using the best fit values for the parameters as described in the text.

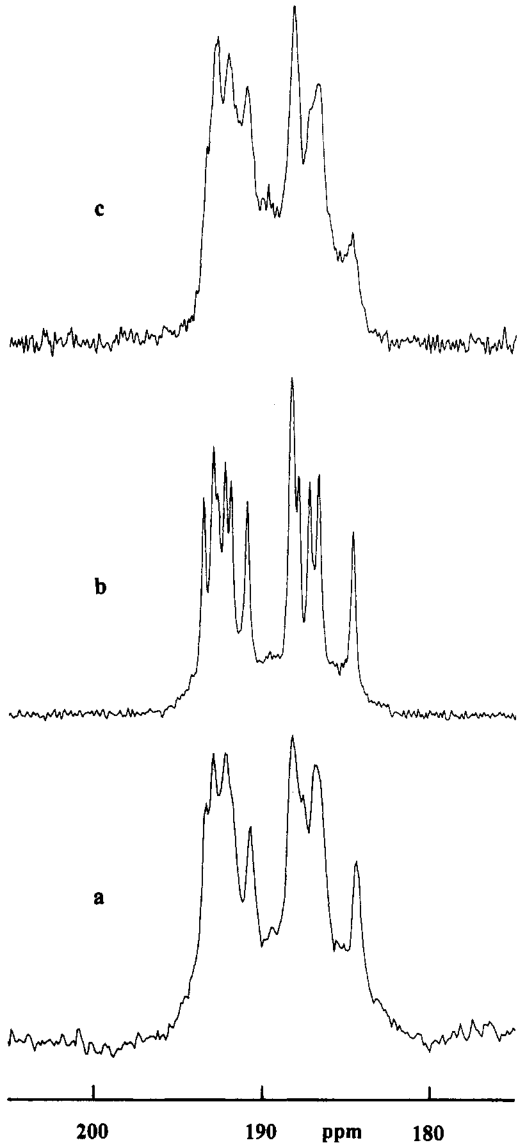

Figure 4. ^{13}C CP/MAS center band resonances of $H_4Ru_4(CO)_{12}$: (a) at 200 K, spinning speed 4320 Hz, 272 scans in 2.3 h; (b) at 296 K, spinning speed 6190 Hz, 1088 scans in 8.2 h; (c) at 360 K, spinning speed 6207 Hz, 1072 scans in 26.8 h.

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asymmetric unit show 11 and 9 resolved resonances respectively. Since the asymmetric unit of **I** is also one molecule, a maximum of 12 resonances is expected and the resonance at 188.3 ppm appears to have greater intensity than the others. The spectrum was repeated at 200 and 360 K (Figure 4a,c), and while there is some loss in resolution at these extremes of temperature, particularly at the higher temperature, there is no significant change in the overall bandwidths and therefore no conclusive evidence for a dynamic process influencing the ^{13}C spectrum. This point is discussed in more detail below. The spectrum at 360 K was accumulated over 26 h, and after this, the measurement was repeated at 296 K. The resulting spectrum showed essentially the same features as the original spectrum at 296 K, but superimposed upon some broad resonances. It is probable therefore that maintaining the sample at the elevated temperature for such a long period of time resulted in partial decomposition.

The full spinning side-band manifolds for the ^{13}C CP-MAS spectra at 200, 296, and 360 K are shown in Figure 5. In the spectrum at 200 K it is evident that there is some loss of resolution in the side bands, and this is due to an instability in the spinning speed at this temperature. However, as discussed by us[7] this does not affect the accuracy of the following analysis. This pattern of side-band groups of resonances is typical[7,22,25,26] of organometallic carbonyl groups and is due to the relatively high values for the ^{13}C chemical shift anisotropies of the resolved resonances. The relative intensities of the partially resolved resonances within each side-band group are effectively constant throughout the full set of groups, which means that the chemical shift anisotropies for the partially resolved center-band resonances are the same as each other (within experimental error), as are the chemical shift asymmetry parameters. Therefore the spinning side-band manifold was analyzed, using our adaptation[7,25,26] of the Herzfeld and Berger method,[27] to give average values for the principal elements of the *nuclear shielding* tensor (σ_{11}, σ_{22}, σ_{33}, with the convention $\sigma_{33} > \sigma_{22} > \sigma_{11}$), the *average* chemical shift anisotropy ($\Delta\delta$), and the *average* asymmetry parameter (η) for the partially resolved resonances by taking the integrated intensity of each side-band group as a whole as input data. The isotropic shielding is given by

$$\sigma_{\text{iso}} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3 \qquad (8)$$

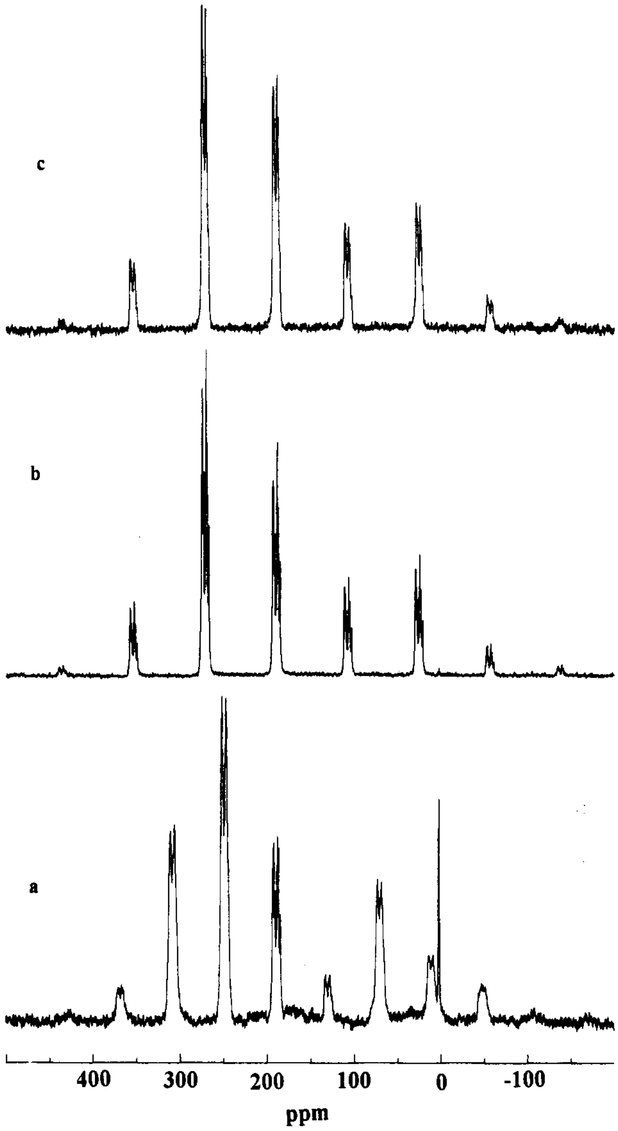

Figure 5. Full ^{13}C CP/MAS spectra of $H_4Ru_4(CO)_{12}$: (a) at 200 K; (b) at 296 K, (c) at 360 K. Acquisition conditions were as for the spectra of Figure 4. At 200 K, the peak at around 0 ppm is assigned to silicone grease, which appears to be sufficiently immobilized to give a sharp cross-polarized ^{13}C signal.

Table 1. ^{13}C Chemical Shift Tensor Components, Anisotropies, and Asymmetries for $H_4Ru_4(CO)_{12}$

temp/K	δ_{iso}[a]	δ_{11}[a]	δ_{22}[a]	δ_{33}[a]	$\Delta\delta$	η
200	188	344	294	−73	392	0.2
297	188	348	294	−79	400	0.2
360	188	349	294	−79	401	0.2

[a] Chemical shift values in ppm to high frequency of tetramethylsilane (TMS).

For the compounds studied here these shielding components happen to agree with the Haeberlen convention:[28] $|\sigma_{33} - \sigma_{\text{iso}}| > |\sigma_{11} - \sigma_{\text{iso}}| > |\sigma_{22} - \sigma_{\text{iso}}|$. We here use the normal chemical convention and quote chemical shifts, ($\delta_{ii} = -\sigma_{ii}$; $\delta_{\text{iso}} = -\sigma_{\text{iso}}$). The chemical shift anisotropy, $\Delta\delta$, and asymmetry, η, are given by

$$\Delta\delta = \delta_{33} - (\delta_{11} + \delta_{22})/2 \qquad (9)$$

$$\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{\text{iso}}) \qquad (10)$$

The results for the spectra at 200, 296, and 360 K are given in Table 1, and it can be seen that the values of the chemical shift tensor components, and chemical shift anisotropy and asymmetry do not change significantly over this temperature interval. The values in Table 1 are typical for terminal bonded carbonyl groups in a range of organometallic complexes[7,25,26,29] which are not involved in any dynamic process. It is important at this point to consider if the dynamic process which influences the ^{1}H spectra might also be expected to affect the ^{13}C spectra. The average values for E and for τ_0, obtained from the ^{1}H

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Table 2. Correlation Times and Rates for the Hydrogen Ligand Motion in $H_4Ru_4(CO)_{12}$

temp/K	τ_c/s	k/s^{-1}
200	10.7	0.015
296	21.7×10^{-6}	7.4×10^3
360	1.7×10^{-7}	9.4×10^5

data, give values for the correlation time, τ_c (eq 2), and the rate, k, at the three temperatures as shown in Table 2. The values for the rates, k, at 296 and 360 K are significantly greater than the isotropic bandwidth (8.9 ppm = 4222 rad s^{-1}), and therefore if the CO groups were involved in this motion, it would be expected that the spectra at 296 and 360 K should be collapsed into fewer resonances than observed (Figure 4). A second window into the possible involvement of the CO groups in a motional process would be the effect of the process on the chemical shift tensor components. The effect of molecular motion on powder spectra line shapes for axially symmetric tensors has been considered in detail by Spiess *et al.*[30] They calculated line shapes for a range of values of $\Delta\omega\ \tau_c$, where $\Delta\omega$ is the frequency width of the spectrum. The details of the line shapes in the presence of the motion were also shown to depend on the nature of the jumping motion, but it was clear that significant deviations from line shapes without motion occurred when $\Delta\omega\ \tau_c \leq 30$. The frequency width of the spectra here are $\delta_{11} - \delta_{33}$ (417 ppm = 1.98×10^5 rad s^{-1} at 200 K), and $\Delta\omega\ \tau_c$ has the values 4.3 and 0.03 at 296 and 360 K respectively. Clearly the CO groups for **I** are not involved in the same motional process determined by the ^{1}H spectra. It is possible however that the broadening of the ^{13}C spectrum at 360 K (Figure 4c) may be due to the onset of some other dynamic process involving the CO groups, but this could not be investigated further because of the tendency for the sample to decompose on being kept for extended periods of time at higher temperatures. Thus the rigid cloud of carbonyl ligands gives the number of ^{13}CO resonances determined only by their crystallographic inequivalencies. The "freezing-out" of the hydride exchange at low temperature induces only a limited broadening of the ^{13}C resonances. This is unexpected in view of the high sensitivity of solid state ^{13}C chemical shifts to minor changes in the structure. Therefore we draw the conclusion that the hydride exchange process is independent of the CO groups and has to occur between equivalent positions, thereby ruling out both bridge/facial exchange as well as involvement of the shorter Ru_1–Ru_2 and Ru_3–Ru_4 bonds.

Conclusion

The ^{1}H spectra reveal motion of the hydride ligands in solid state (**I**), but this dynamic process does not involve the CO ligands. There are two possible processes which account for our observations.

(i) The Ru_4 core rotates as a whole, together with the edge-bridging hydrides, about the approximate C_2 axis passing through the mid-points of the Ru(1)–Ru(2) and Ru(3)–Ru(4) bonds (see the structure above).

(ii) The ligand hydrides move over the Ru_4 cluster through jumps between the four equivalent positions in a concerted manner.

There is some evidence that case (ii) may occur in hydrido carbonyl complexes. In the related complex $H_4Os_4(CO)_{12}$ in solution, osmium–hydrogen coupling constants of 14.4 Hz at 300 K and 30.5 Hz at 168 K were measured.[31] This was interpreted as arising from a static four-edges-bridged structure at low temperature and a fast migration of the hydrides over all six Os–Os edges at the higher temperature. With the evidence available on **I** in the solid state, we are unable to choose[32] between the two cases.

Acknowledgment. We thank the Science and Engineering Research Council for a studentship (to M.D.M.), Dr. P. J. Barrie of the University of London Intercollegiate Research Service (ULIRS) in solid-state NMR (now at University College, London) for some of the ^{13}C spectra, and Dr. Hans Foerster (Bruker Analytische Messtechnik GMBH) for his valiant attempts to observe the ^{99}Ru spectrum of **I**.

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[32] It was suggested by a reviewer that a distinction between cases (i) and (ii) might be made by observing the temperature dependence of the ^{99}Ru spectrum. We are not aware of any reports of solid state ^{99}Ru (natural abundance 12.7%, spin $I = {}^5/_2$) spectra in the literature, but in solution the ^{99}Ru resonance from $Ru_3(CO)_{12}$ has been reported[33] at −1208 ppm from the $Ru(CN)_6^{4-}$ reference. We were able to measure the solid-state MAS ^{99}Ru spectrum from a sample of $K_4Ru(CN)_6$ at 23.1 MHz (11.75 T), but were not successful in observing a resonance from (I) presumably because of excessive broadening of the resonance.

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