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Vibrational characteristics of μ-bridging hydride ligands in triangulo rhenium metal cluster compounds

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Abstract

The metal–hydrogen vibrational frequencies of μ-bridging hydride ligands of the rhenium cluster hydride anions $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$, $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$, $[Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]^-$, $[Re_3(\mu\text{-}H)_3(\mu\text{-}O_2CH)(CO)_{10}]^-$ and $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}OEt)(CO)_9]^-$ are assigned in the infrared and in the Raman (of the first four compounds) and are shown to be characteristic of the bridge environment.

Introduction

The most commonly encountered hydride ligands in metal-cluster compounds are those bridging two metal atoms. A satisfactory explanation of their stretching frequencies, which span an unusually large wavenumber range (ca. 1750–800 cm^{-1}), has been provided [1] in terms of a relationship involving the wide variation of the M–H–M inter-bond angles involved. Difficulties were encountered in the detection [2] of these hydridic vibrational modes due to their inherently weak intensities and the large breadth in both the infrared and the Raman spectra. Making measurements at low temperatures overcame these difficulties to a great extent due to the preferential sharpening of these bands which assist in the detection and assignment of these vibrational modes [3,4].

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Structural details of the hydrogen atoms in metal cluster compounds are best determined by using neutron diffraction techniques. However, the need for relatively large single crystals, the expense and the lack of ready access to neutron sources make such measurements rather rare. With the more accessible X-ray diffraction technique the hydrogen atoms are seldom located directly because the scattering is dominated by the heavy metal atom contribution. X-ray crystallography therefore depends on a variety of useful indirect methods [5] which rely mainly on metal–metal bond lengths and the geometries of the neighbouring groups on the molecule, or on potential energy calculations for the location of the hydrogen positions. ^{1}H NMR has been a particularly useful technique for establishing the presence of hydride ligands in metal cluster compounds [6], and in favourable cases, when metal nuclei with $I = 1/2$, for example, ^{103}Rh or ^{187}Os are present, their coupling to the proton may provide clues to its exact location [7]. This is not possible with quadrupolar nuclei such as rhenium. Therefore there is a need for reliable and relatively quick methods of locating these hydrogen positions.

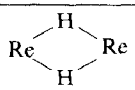
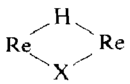
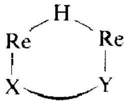
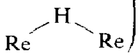
It is the purpose of the present communication to investigate such a possibility, of using the group frequency concept in vibrational spectroscopy to characterise the different μ-bridging hydride environments in rhenium cluster hydrides.

Results and discussion

All complexes investigated have their structures determined using X-ray diffraction, however the hydride positions were not directly observed but inferred from NMR data, metal–metal bond lengths and M–C=O geometries. Three types of ReHRe bridging environments are recognised, and their geometrical characteristics are given in Table 1. The type A environment consists of two hydride ligands bridging a Re–Re formal "double bond", analogous to the situation in the unsaturated triosmium cluster $[Os_3(CO)_{10}(\mu\text{-}H)_2]$. In the type **B** environment there is a single hydride bridge between two rhenium atoms that are also linked by a non-hydride ligand (either edge- or face-bridging). The type **C** environment involves

Table 1

The hydride bridging environments and the appropriate Rhenium–Rhenium distances

	Environment	Re–Re distance (Å)
A		2.78–2.90
B	 (X = 3e donor)	2.95–3.11
B′		3.03–3.35
C		

a single hydride bridging a Re–Re bond otherwise unsupported by ligands. If the "other ligand" in a type **B** environment is bidentate with the two coordinating atoms separated in the ligand molecule by a third atom, for example, bidentate carbonylate [μ^2-η^2-*O*,*O*′-O_2CR], then sterically the coordination is similar to 1,2-diaxial substitution by two monodentate ligands. Accordingly, this environment is designated type **B**′.

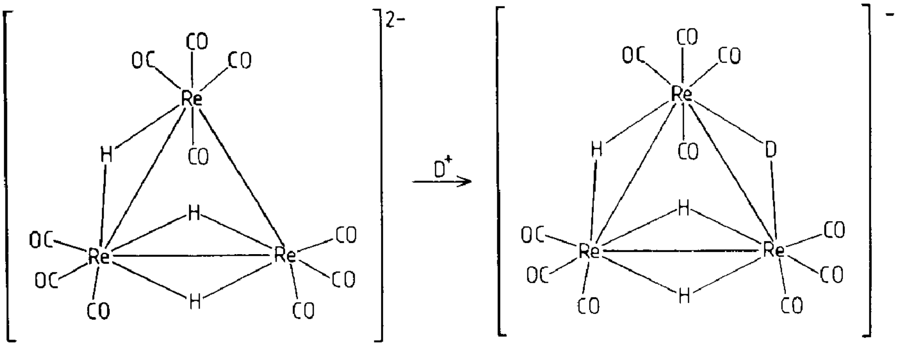
From Table 1, it can be seen that Re–Re separations are shortest in type **A** environments, as might be expected. There is a slight overlap between Re–Re separations of **B** and **C** environments, but in general the presence of the bridging ligand in **B** environments results in a shortening of the Re–Re distance relative to the **C** environment. The exception to this occurs with the **B**′ environment, where the "1,2-diaxial" coordination of the other ligand does not result in Re-Re bond shortening, and the Re–Re distance is thus typical of the **C** and not **B** environment.

The most detailed vibrational analysis so far for a μ-hydride bridging rhenium complex is that for $H_3Re_3(CO)_{12}$ [8]. This complex has all hydrides in **C**-type environments, as defined in Table 1, but probably with differing M–H–M bond angles. The antisymmetric stretches are assigned to frequencies from ca. 1635 to 1700 cm^{-1}, and the symmetric stretches to frequencies from ca. 1025 to 1110 cm^{-1}. The out-of-plane deformation of the Re–H–Re bridges are assigned a frequency of 624 cm^{-1}. Other literature data on rhenium hydride systems involve the tetrametallic $[H_6Re_4(CO)_{12}]^{2-}$ ion,where all the hydride bridges are in (pseudo)-**B**′-type environments with the frequencies of ca. 1745 to 1670, ca. 1125 and ca. 630 cm^{-1} assigned to $\nu(MH_{as})$, $\nu(MH_{sym})$ and $\gamma(MHM)$ vibrational modes, respectively [9], and the bimetallic compound $H_2Re_2(CO)_8$ where the frequencies of ca. 1382 and 1272 cm^{-1} are assigned to the stretching modes of the pseudo-*A*-type bridging hydrides [10].

$[NEt_4][Re_3(\mu\text{-}H)_4(CO)_{10}]$

The hydride environments in this complex, though not determined directly by diffraction techniques, were inferred from the cluster geometry and the arrangement of the carbonyl groups to involve two **C**-types and an **A**-type [11]. It was possible to prepare the partially deuteriated complex by the treatment of the dianion $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$ with CF_3COOD.

As shown in Scheme 1, the deuterium atom would be expected to occupy a



Scheme 1.

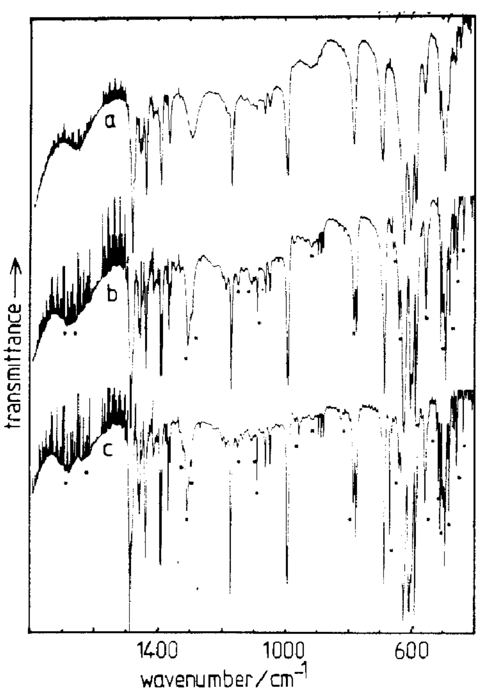


Fig. 1. Infrared spectra of (a) $[NEt_4][Re_3(\mu\text{-}H)_4(CO)_{10}]$ run at room temperature; (b) that at ca. 100 K and (c) $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}D)(CO)_{10}]$ run at ca. 100 K. The temperature sensitive bands are indicated with asterisks. (There is only one more band in the spectrum down to 200 cm^{-1}, and that is at 380 cm^{-1}.)

bridging location on a C-type edge of the triangle. Previous NMR studies have already shown that the two types of H present in $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ do not exchange, so the ^{1}H NMR spectrum of this sample should exhibit two hydridic resonances in the ratio 1/2. The ratio observed for this sample is however 1/1.54 and this could be due to, (a) incomplete deuteriation, resulting from the presence of traces of water during the reaction with acid; (b) incomplete selectivity, that is in the protonation stage some exchange between the H (or D) ligands bridging the lateral edges and those bridging the base could have occurred (ca. 20%) [12]. The second hypothesis is favoured on the basis of the integrations with respect to the cationic signals in the NMR (which confirm the presence of three hydridic H atoms) and also on the basis of the care with which the reaction was performed in order to avoid contamination. The H's of the A-type bridges would therefore be only 1.8, while those of the C-type bridges would be 1.2. Using these estimates of the degree of deuteriation one arrives at the following distribution for species present in the partially deuteriated sample: ca. 80 and 20% of A-type, H_2 and HD containing molecules, respectively, giving ca. 10% each of isolated H and D bridges of A-type; and ca. 20 and 80% of C-type, H_2 and HD containing molecules respectively giving ca. 40% each of isolated H and D bridges of C-type. These estimates are used later in this manuscript for assignment purposes.

The infrared and Raman spectra of these compounds are shown in Figs. 1 and 3 with the hydride frequency assignments in Table 2. Relative temperature dependence of band intensities is used as an assignment criterion together with the partial deuteriation information. The bands due to the cation are relatively easily identified

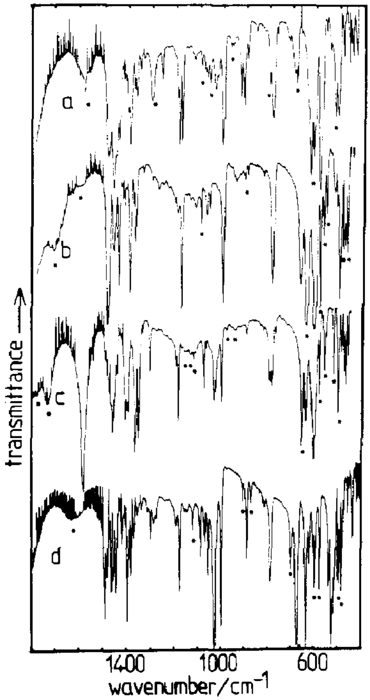


Fig. 2. Infrared spectra of (a) $[NEt_4]_2[Re_3(\mu\text{-}H)_3(CO)_{10}]$; (b) $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]$; (c) $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}O_2CH)(CO)_{10}]$ and (d) $[NEt_4][Re_3(\mu\text{-}H)_3(\mu_3\text{-}OC_2H_5)(CO)_{10}]$ all run at ca. 100 K. The temperature sensitive bands are indicated by asterisks.

by comparison with the spectrum of $(NEt_4)Br$. A comparison of the IR spectra between ambient and liquid nitrogen sample temperatures (Fig. 1a and 1b) of the fully protonated compound shows distinct relative increase of intensity at the lower temperature of the following bands in the metal–hydride stretching regions. These are at ca. 1685, 1309, 1297, 1153, 1110, 1092 and 921 cm^{-1}. From a consideration of the metal–metal bond lengths and data on other systems it is clear that the M–H–M interbond angles for the A-type hydrides are narrower than those of the C-type. Therefore the broad band showing features at 1309 and 1297 cm^{-1} is assigned to overlapping asymmetric and symmetric stretching modes of the A-type bridges. In $[Os_3(CO)_{10}(\mu\text{-}H)_2]$, which, contains an analogous A-type double bridge, the ν(OsH) similarly all occur in a fairly narrow frequency range (1245–1194 cm^{-1}) [13]. The bands at ca. 1685 and 1660 cm^{-1} are assignable to the asymmetric modes of the C-type bridges with the other four lower frequencies to the corresponding symmetric stretches. Now a comparison with the spectra of the partially deuteriated complex (Fig. 1c) shows the stretching modes assigned to the A-type bridges (ca. 1300 cm^{-1}) to be almost unaffected by deuterium substitution, as expected, vide supra. There is a new weak band at ca. 960 cm^{-1}, which is assignable to the stretching modes of the ca. 10% of the type A deuterium bridges present in this partially deuteriated sample when compared in intensity with the band at ca. 1309 cm^{-1}. This assignment gives a very reasonable deuterium isotopic shift ratio of ca. 1.36 for these modes [8,14]. There is a definite loss of intensity of the band at ca. 1640 cm^{-1} which is assigned to an asymmetric stretch of a C-type bridge. Further, the loss of intensity of the bands assigned to the C-type symmetric stretches at ca.

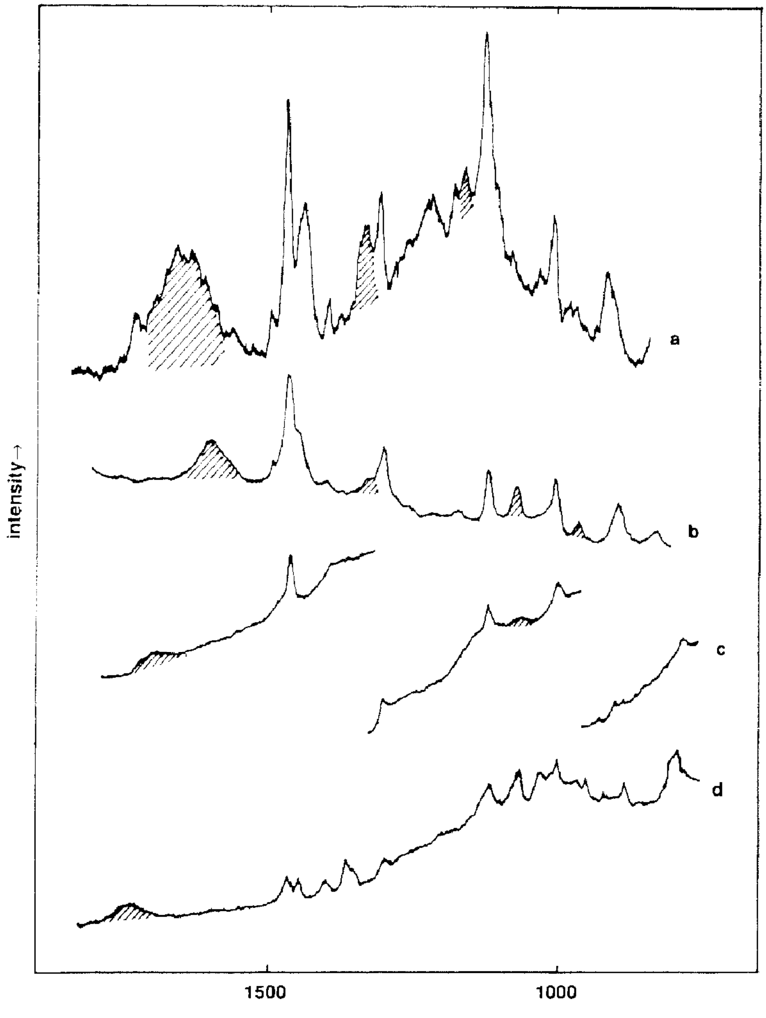


Fig. 3. Raman spectra of (a) $[NEt_4][Re_3(\mu\text{-}H)_4(CO)_{10}]$; (b) $[NEt_4]_2[Re_3(\mu\text{-}H)_3(CO)_{10}]$; (c) $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]$ and (d) $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}O_2CH)(CO)_{10}]$ in the metal–hydrogen stretching region run at room temperature. The bands assigned to hydridic modes are shaded for clarity.

1153, 1110, 1092 and 921 cm^{-1} are apparent in spite of their inherent weak intensities. This multiplicity of bands shown by the C-type bridges in the symmetric stretching region has been shown to be due to Fermi resonance with the overtone/combination bands of ν(M–C) and δ(M–C–O) modes, in the case of the compounds $H_3Mn_3(CO)_{12}$ [14], and $H_3Re_3(CO)_{12}$ [8]. It was also shown that the deuterium bridges give much simpler spectra for this mode. The new band at ca. 830 cm^{-1} in the partially deuteriated sample is therefore assigned to the symmetric stretching mode of a deuteriated C-type bridging environment.

The spectral region where the γ(HReH) modes are expected to appear is generally crowded with δ(MCO) and ν(MC) modes. Relatively little work is reported in the literature regarding this frequency region, when, for example, compared to the ν(CO) region. Nevertheless, some important generalisations could

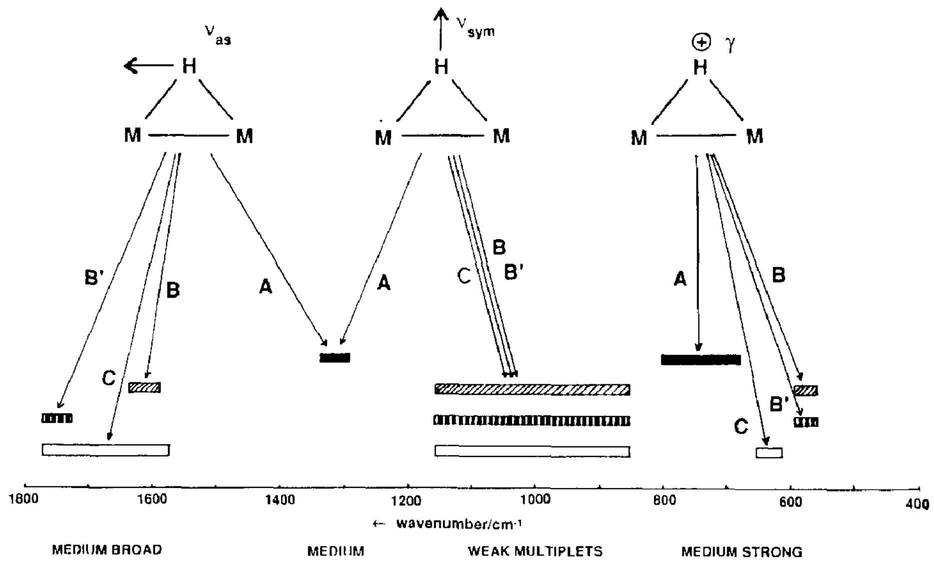


Fig. 4. A structure-vibrational frequency correlation for hydrogen bridging environments in the rhenium cluster hydrides. Relative infrared intensities are indicated at the bottom of the diagram as medium broad, medium, weak multiplets and medium strong, and rectangles with different degrees of shading show the characteristic frequency ranges.

be drawn from the available literature regarding the δ(MCO) and ν(MC) vibrational modes [15–19]. First, that the δ(MCO) vibrations occur at higher frequencies (ca. 650–500 cm^{-1}) than the ν(MC) vibrations (ca. 500–350 cm^{-1}), with some overlap between the two regions [15,16]. Second, that the vibrational coupling amongst these modes is generally of a low enough magnitude, for this frequency region to be conducive to assignment, to a good first approximation, using an isolated-metal model [18], where only the groups attached to one metal atom are considered. Further, there appears negligible coupling between the axial and equatorial vibrations in this spectral region, and even between ν(MC) and δ(MCO) with a common carbon atom [19]. These observations together with a detailed examination of the molecular structure of this compound shows that a qualitative understanding of the IR intensities in this spectral region should be viable.

Using the molecular symmetry C_{2v} for the isolated cluster ion, the vibrations expected in the region ca. 800–300 cm^{-1} are the following with only a_1, b_1 and b_2 symmetries being IR active:

γ(MHM) $a_1 + a_2 + 2b_2$
δ(MCO) $5a_1 + 5b_1 + 5a_2 + 5b_2$
ν(MC) $4a_1 + 3b_1 + a_2 + 2b_2$

Twenty seven vibrations are therefore expected to appear in the IR but only about 19 bands are observed with any reasonable intensity (Fig. 1) even at liquid nitrogen temperatures. A detailed examination of the molecular structure [11] shows that the dipole vectors of the internal coordinates of relevance to this frequency range are approximately either parallel or perpendicular to each other (hydride coordinates and metal–carbonyl coordinates to be considered separately). A simple examination of the relevant symmetry coordinates therefore shows that many involve zero or

Table 2

The rhenium–hydrogen vibrational mode frequencies assigned during this investigation

$[NEt_4][Re_3(\mu\text{-}H)_4(CO)_{10}]$		$[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}D)(CO)_{10}]$	$[NEt_4]_2[Re_3(\mu\text{-}H)_3(CO)_{10}]$		$[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]$		$[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}O_2CH)(CO)_{10}]$		$[NEt_4][Re_3(\mu\text{-}H)_3(\mu_3\text{-}OC_2H_5)(CO)_{10}]$	Assignment
IR	Ra	IR	IR	Ra	IR	Ra	IR	Ra	IR	
							1776			$\nu(MH_{as})$; C and B′ types
								1750		
							1736			
					1722					
					1709					
						1700				
1685										
		1680								
1660	1660									
	1630									
				1600						
			1582							
									1628	$\nu(MH_{as})$; B type
					1590					
	1330			1325						$\nu(MH_{as/sym})$; A type
1309		1310								
			1304							
1297		1297								
	1160						1159			$\nu(MH_{sym})$; C, B and B′ types
1153		1153								
							1137			
							1122		1120	

1110	1110							
1092	1091	1095		1094				
			1075		1075			
		1060						
						990		
		958	960					
						945		
921	920							
				903			903	
							869	
	960							$\nu(MD_{as/sym})$; A type
	830							$\nu(MD_{sym})$; C type
		802						$\gamma(MHM)$; A type
788	788							
		689						
		683						
	671							$\gamma(MHM)$; (isolated) C type
						656		$\gamma(MHM)$; C type
644	644			641				
		622						
							595	$\gamma(MHM)$; B and B′ types
						585		
							574	
				567				
	527							$\gamma(MDM)$; (isolated) A type
	520							$\gamma(MDM)$; (isolated) C type

nearly zero net dipole moment changes, thus giving the following prediction of only 18 modes to show any appreciable IR intensity in this spectral region.

γ(MHM) a_1(A-type) + b_2(C-type)
δ(MCO) $3a_1 + 4b_1 + 3b_2$
ν(MC) $2a_1 + 2b_1 + 2b_2$

Now if one were to impose the added restriction that a metal–carbonyl vibration, (ν(MC) and δ(MCO)), would couple to a metal–hydrogen deformation only when these units have a metal–atom in common, one arrives at the prediction of only the following 9 modes to possess any hydridic character.

γ(MHM) a_1(A-type) + b_2(C-type)
δ(MCO) $a_1 + 3b_2$
ν(MC) $a_1 + 2b_2$

This is almost exactly what is observed (when the cation absorption at ca. 780 cm^{-1} is ignored) with 18 to 19 bands, out of which about 9 show definite temperature sensitivity characteristic of hydride involvement in the normal mode.

In spite of this extensive vibrational coupling of the metal–hydrogen out-of-plane deformations to other modes in this system, it is possible to identify the bands to which the MHM deformation coordinates mainly contribute, and the following is such an assignment. Guided by the estimated isotopomer distribution and the intensity predictions, the bands at 788 and 644 cm^{-1} are assigned respectively to the a_1 mode of **A**-type bridges and the b_2 mode of the **C**-type bridges. These two bands show the most temperature sensitivity in this region and partial deuteriation produces the expected major decrease in intensity of the 644 cm^{-1} band (Fig. 1). Partial deuteriation has produced three new bands in this spectral region at 671, 527 and 520 cm^{-1} which are assigned respectively to the H and D bridges of **C**-type in "**C**-type HD molecular species", giving a deuterium shift ratio of ca. 1.29 which is in very good agreement with such ratios found for similar systems elsewhere [8,14]. The weakest new band at 527 cm^{-1} is assigned to the deuterium bridges of **A**-type in "**A**-type HD molecular species". The corresponding band due to the H-bridges is not detected probably due to overlap.

A very important outcome of this partial deuteriation experiment is the observation of the new band at 671 cm^{-1} assignable to an isolated H-bridge in a **C**-type environment. The appreciable difference of this frequency from the **C**-type bridge frequency of 644 cm^{-1} of the fully protonated compound is evidence for a considerable strength of vibrational coupling between the two **C**-type hydride bridges in the fully protonated compound.

The Raman spectrum of the fully protonated compound is given in Fig. 3 with the assigned metal-hydrogen frequencies reported in Table 2. After accounting for the cationic modes, the bands at ca. 1660, 1630, 1330 and 1160 cm^{-1} are assignable to the hydridic modes and these are in good agreement with the infrared data.

$[NEt_4]_2[Re_3(\mu\text{-}H)_3(CO)_{10}]$

This complex is of some interest because in its crystal structure, it lies at the intersection of two perpendicular mirror planes [20]. However, sound crystallographic reasoning has been put forward to show the presence of disorder in the solid state with the mirror plane normal to the metal triangle being only statistical. Therefore two **A**-type and one **C**-type bridges are assigned. Fig. 2a shows the infrared spectrum at liquid nitrogen temperatures with a tentative assignment of hydridic frequencies given in Table 2. From the temperature dependence of intensities the bands at 1582 and 1304 cm^{-1} appear as definite candidates for stretching modes. Also some sharpening is observed of the peaks from 1050 to 1150 cm^{-1} with the band at 1095 cm^{-1} perhaps being the most hydridic. There is also a distinct weak peak at 958 cm^{-1} at low temperatures which is absent in the room temperature spectrum. Therefore these two bands at 1095 and 958 cm^{-1} together with the very broad band peaking at ca. 1582 cm^{-1} are assigned to the disordered **C**-type bridging environments. The band at ca. 1304 cm^{-1} is clearly due to the **A**-type bridges present in this compound and is very close in frequency to that found for such a bridging environment in the previous compound discussed in this manuscript.

The low frequency region of this compound shows some similarities to the previous compound with respect to the number and temperature sensitivity of the observed bands, as would be expected from the similarities of their molecular structures. From a comparison of the spectra between these compounds and the temperature sensitivities, it is possible to assign the bands at 802 and 689/683 cm^{-1} to the a_1 and b_2 vibrations of the **A**-type hydride bridges while the disordered **C**-type bridging environments are assigned to a deformation frequency of 622 cm^{-1}.

The Raman spectrum is shown in Fig. 3 with the bands at ca. 1600, 1325, 1075 and 960 cm^{-1} assignable to the hydridic modes (Table 2).

$[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]$

Two **C**-type and one **B**-type hydride bridges were assigned to this complex [21]. Using similar criteria to those used earlier, a frequency of ca. 1709 cm^{-1} and probably another of ca. 1590 cm^{-1} are assigned to the asymmetric stretching modes of these hydride bridges. The infrared spectrum of this compound is given in Fig. 2b with a tentative assignment of hydridic frequencies in Table 2. A band at ca. 1094 cm^{-1} appears to be the most probable candidate for the symmetric stretching modes. The a' mode (under C_s molecular symmetry) of the deformation of **C**-type bridges is assignable to a band at 641 cm^{-1} in agreement with the assignments given for the previous compounds. This leaves the band at ca. 567 cm^{-1} to be assigned mainly to the out-of-plane deformation of the **B**-type hydrogen bridge. These modes are well mixed with many δ(MCO) and ν(MC) modes and those showing temperature sensitivity are indicated in Fig. 2b.

The Raman spectrum is shown in Fig. 3, and in spite of this compound being a very weak scatterer the bands observed at ca. 1700 and 1075 cm^{-1} are assignable to hydridic modes and are in agreement with the infrared assignments.

$[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}O_2CH)(CO)_{10}]$

This compound was inferred to possess two **C**-type and one **B**-type hydride bridges [22]. Its infrared spectra are given in Fig. 2c and a tentative assignment of the hydridic modes are given in Table 2. The asymmetric stretching modes in this case are found at ca. 1776 and 1736 cm^{-1}. Symmetric stretching modes are weak as expected and the probable candidates are around 1122 and 945 cm^{-1}. Out-of-plane deformations of the **C**-type bridges are assignable to a band at 656 cm^{-1} and the **B**′-type bridge mainly to a band at 583 cm^{-1}. Bands with hydridic character are all indicated in Fig. 2. The Raman spectrum shown in Fig. 3 provides an assignment of only a broad band at ca. 1750 cm^{-1} to a hydridic mode.

$[NEt_4][Re_3(\mu\text{-}H)_3(\mu_3\text{-}OC_2H_5)(CO)_{10}]$

The hydride positions in this compound have been inferred to be of **B**-type for all the hydrides using NMR and X-ray diffraction techniques [23]. The infrared spectra of this compound are given in Fig. 2d together with a tentative assignment of hydrogenous modes in Table 2. From the temperature sensitivity and elimination of the cationic vibrational bands the hydride asymmetric stretching vibrations are assigned a frequency of ca. 1628 cm^{-1}. The spread of hydrogenous frequencies in the symmetric stretching region is similar to that observed for other similar complexes [9] with candidates at 1120, 903 and 869 cm^{-1} assignable to the symmetric stretches. This assignment implies two bridges with similar interbond angles while the third is fairly different. The out-of-plane deformation region has two bands showing the most temperature sensitivity at frequencies of 595 and 574 cm^{-1} assignable to these **B**-type bridging environments.

Experimental

All compounds were prepared from literature methods [11,20–23]. The partially deuteriated derivative was made by treating the dianion $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{2-}$ with CF_3COOD (Scheme 1). All infrared spectra were run as CsI discs on a Digilab FTS-20 spectrophotometer. Raman spectra of polycrystalline samples were run using a Spex 1401 Raman spectrophotometer equipped with a Spectra Physics Model 156 ion laser. The 647 nm Laser line was used.

Conclusion

This investigation has shown that hydride ligands in rhenium clusters display characteristic vibrational frequencies that are diagnostic of the ligand environment (Table 2, Fig. 4). For the asymmetric stretching modes, types **C** and **B** give rise to bands in the frequency range of ca. 1800 to 1550 cm^{-1} with **C**-type towards the higher frequency end and the **B**-type towards the lower frequency end with a fair amount of overlap. This is not surprising as the **B**-type would be expected to show a greater variation depending on the group X and therefore a **B′**-type is defined to bridge this gap. **A**-type bridges seem to show much lower frequencies, around ca 1300 cm^{-1}. These observations are in agreement with the reported correlation between these modes and the MHM bond angles [1], when the Re–Re distance is taken as an approximate indicator of the magnitude of this angle.

Symmetrical stretching vibrations generally tend to give rise to a large number of weak features and do not appear to be useful as a diagnostic. Surprisingly, the out-of-plane deformation vibrations, in spite of their location within the forest of δ(MCO) and ν(MC) frequencies, appear quite characteristic of the bridging environment. **A**-type bridging environments giving rise to a medium intensity band around 790 cm^{-1} while the **C**-type environments give medium intensity bands in the range ca. 620 to 660 cm^{-1}. The **B**-type bridge appears lowest in frequency in the range of ca. 565 to 600 cm^{-1}, with **B′** towards the higher frequency edge of this range.

The most intense hydridic vibrations in the Raman spectra of these complexes, irrespective of the bridge type, are found to be the asymmetric stretching modes. Symmetric stretches are sometimes observed but appear weak. However, the out-of-plane deformations are not observable in the Raman [9].

This investigation has demonstrated the use of vibrational spectroscopy as a tool in the elucidation of bridging hydride environments in metal cluster compounds (Fig. 4).

Partial isotopic substitution work has provided good evidence, for the first time, to show that γ(MHM) vibrators are strongly coupled to each other, unlike the metal–hydride stretching modes at higher frequencies. Note that this is in contrast to the behavior shown by the carbonyl vibrations, where it is the C–O stretching modes which show strong coupling.

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