Table II. Wavenumbers (cm^{-1}) Associated with Metal–Hydrogen Vibrations

	$HOs_3(CH{=}CH_2)(CO)_{10}$		$H_2Os_3(C{=}CH_2)(CO)_9$		$H_2Os_3(CO)_{10}$	$D_2Os_3(CO)_{10}$	
assignt	IR	Raman	IR	Raman	IR	IR	$\nu(H)/\nu(D)$
Os-H-Os[a] (asym)	1392 w	1390 w	1398 m	1401 w			
			1375 vvw	1373 vvw	1245 w	905 w	1.38
			1349 w	1352 w	1225 s	890 s	1.38
					1216 sh	887 sh	1.37
Os-H-Os[a] (sym)	1286 w	1285 w	1302 w	1308 w	1194 m	880 m	1.36
			1288 vw	1292 vw	1160 w	875 w	1.34
Os-H-Os	706 s		686 s		730 ms	obscured by CO bands	
			664 s				

[a] See text for comments on these assignments.

change on its half-width than the stretching modes.

The observed wavenumbers of hydrogenic vibrations are given in Table II.

Skeletal Modes Involving Metal Atoms. Metal–metal stretching modes have been identified in several compounds containing the Os_3 triangle. These modes usually appear as weak bands in the infrared but as relatively strong bands in the Raman spectra. In $Os_3(CO)_{12}$, where the osmium atoms form an equilateral triangle, two bands are found in the Raman at 158 cm^{-1} (a_1') and 117 cm^{-1} (e'); the band at 117 cm^{-1} also occurs in the infrared spectrum.[14] In the compound $Os_3(OEt)_2(CO)_{10}$, where the OEt groups bridge pairs of osmium atoms, the osmium triangle is isoceles and the lowering of symmetry results in a splitting of the e mode, and all three bands appear in both infrared and Raman spectra. The observed wavenumbers (Raman) are 172 (a_1), 136 (a_1), and 119 (b_2) cm^{-1}. The compounds $HOs_3(SMe)(CO)_{10}$, which has a hydrogen and a SMe group bridging the same pair of osmium atoms, has similar symmetry and also gives three bands with coincidence in the infrared and Raman spectra at 164, 125, and 104 cm^{-1}.

In the vinyl and vinylidene complexes, all three[12a] osmium atoms are different, but the observed bands, given in Table I, from a frequency pattern very similar to those described above.

Conclusions

For even a simple cluster compound, the number of infrared- and/or Raman-active modes is in principle very large. However, evidence is accumulating that the spectra are often more straightforward than might be expected because the vibration frequencies of molecular fragments appear at or near their characteristic frequencies in simpler compounds. The main objective of the present study was to investigate whether this situation holds for the present compounds. In this paper we have shown this to be the case for olefin-associated features and have also studied other spectral regions and shown that they too present no particularly unusual features which can be attributed to unexpected coupling of modes of other groups with those of the olefinic groups. The spectra confirm the σ and π bonding of the olefinic groups to metal atoms of the cluster as previously proposed on the basis of X-ray crystallography. Extension of the present work to complexes containing other novel organic ligands should serve to provide reasonable models for the interpretation of vibrational spectra of such species adsorbed on metal surfaces. The ν(CH) bands above 2980 cm^{-1} and the strong $\gamma(CH_2)$ bands between 800 and 1000 cm^{-1} are characteristic of olefinic groupings, and the low-wavenumber ν(C=C)modes between 1310 and 1480 cm^{-1} are only explicable in terms of π as well as σ bonding. However, it should be noted that individual band frequencies should be supplemented by comparing the overall band pattern of the observed spectra of an adsorbed species with that of the relevent cluster molecule, taking into account the effect of the metal–surface selection rule on the relative ntensities.

Experimental Section

We are very grateful to Dr. D. Pippard of the University of Cambridge for preparing pure samples of the three compounds.

Infrared spectra were run as pressed disks at high concentration (5–15%) in potassium bromide and cesium iodide. The mid-infrared spectra were recorded on a Perkin-Elmer 325 spectrophotometer, and extra sensitivity in the ν(CH) region was obtained by the use of the Digilab FTS14 interferometer. Far-infrared spectra were run as Nujol mulls supported on wedge-shaped polythene disks on a Beckman RIIC IR720M interferometer.

Raman spectra were obtained from solid samples in capillary tubes with use of the 90° scattering mode of a Spex 1401 monochromator Spectra-Physics Ar/Kr laser being used to provide the exciting lines. The Raman frequencies recorded are based on spectra obtained with several exciting lines. In some cases the best spectra were obtained with the red line at 799 nm. No changes were observed that could be attributed to sample decomposition in the time taken to run the spectra. In all cases the power output of the laser was kept to a minimum consistent with an acceptable signal-to-noise ratio. It was not possible to obtain sufficiently concentrated solutions to enable solution spectra to be obtained in the Raman or far-infrared regions.

Registry No. $HOS_3(CH{=}CH_2)(CO)_{10}$, 55072-96-3; $H_2Os_3(C{=}CH_2)(CO)_9$, 42765-74-2; $H_2Os_3(CO)_{10}$, 41766-80-7.

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[14] Quicksell, C. O.; Spiro, I. G. *Inorg. Chem.* **1968**, *7*, 2365.

[15] Hartley, D.; Kilty, P. A.; Ware, M. J. *Chem. Commun.* **1968**, 493.

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On the Infrared Spectrum of $(\mu\text{-}H)(\mu\text{-}D)Os_3(CO)_{10}$

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The Os–H and Os–D stretching vibrations of the metal cluster complexes $(\mu\text{-}H)_2Os_3(CO)_{10}$ and $(\mu\text{-}D)_2Os_3(CO)_{10}$, respectively, are described in a companion work.[1] It appears to be worthwhile to draw attention to additional spectral information available from a minor constituent in the latter complex which gives rise to two sharp bands of *equal* intensity in the Os_2H deformation (out-of-plane rocking) region and two bands of *unequal* intensity in the Os–H stretching region of the infrared spectrum. We attribute these weak absorptions to the presence of the $(\mu\text{-}H)(\mu\text{-}D)Os_3(CO)_{10}$ species as a *dilute*

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[1] J. R. Andrews, S. F. A. Kettle, D. B. Powell, and N. Sheppard, *Inorg. Chem.*, preceding paper in this issue.

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(ca. 5%) isotopic impurity in $(\mu\text{-D})_2Os_3(CO)_{10}$.[1] The usefulness of vibrational data of this type lies in the decoupling which must occur between the motions of equivalent, or very similar, molecular groupings. The vibrations of the isotopically dilute $(\mu\text{-H})(\mu\text{-D})Os_3(CO)_{10}$ species will be subject to neither the correlation-field (factor-group) coupling which may occur in the crystal nor the intramolecular coupling between two similar H (or D) atoms of the isotopically pure species.

The infrared spectrum of $(\mu\text{-D})_2Os_3(CO)_{10}$[1] contains two weak, but well-defined, absorptions in the Os–H stretching region, with the lower frequency band (1222 cm^{-1}) being 4–5 times *more* intense than that at higher frequency (1242 cm^{-1}). Two bands are also observed in the Os_2H rocking region, at 710.0 cm^{-1} and 701.5 cm^{-1}, whereas $(\mu\text{-H})_2Os_3(CO)_{10}$ absorbs at 730 cm^{-1}.

Interpretation of these observations leads to two conclusions. (i) The two μ-bridging hydrido atoms in $(\mu\text{-H})_2Os_3(CO)_{10}$ are symmetrically disposed with respect to Os–H bond length and Os–H–Os bond angle but are nonetheless inequivalent, as evidenced by the dissimilarity of the Os_2H rocking frequencies associated with the two protons. This description differs from the results of neutron[2] and combined X-ray/neutron[3] diffraction studies only in the disparity of the two Os–H–Os angles determined in the former work.[2] (ii) The symmetric Os–H stretching mode is at higher wavenumber than the antisymmetric mode in $(\mu\text{-H})(\mu\text{-D})Os_3(CO)_{10}$ if, as is generally assumed,[4,5] the infrared intensity associated with the antisymmetric mode is the greater.

The second conclusion provides an insight into the accuracy of the model proposed to describe the vibrations of μ-bridging hydride ligands in metal cluster complexes,[5] in that the Os–H stretching frequencies of the isotopically dilute $(\mu\text{-H})(\mu\text{-D})Os_3(CO)_{10}$ species, on that model, lead to a calculated interbond angle of 89°, 4–5° less than that determined by neutron diffraction.[2,3] The limitations of this model have been outlined with respect to high-angle hydrido bridges,[5] but the data described here permit an assessment of the predictive accuracy of the model in the case of lower angle systems. In the simple treatment presented by Howard et al.,[5] the metal–hydride stretching frequencies are related to the interbond angle, θ, by expression 1. It is, however, apparent from the plot of

$$\nu_{\text{asym}}/\nu_{\text{sym}} = \tan(\theta/2) \tag{1}$$

$\nu_{\text{asym}}/\nu_{\text{sym}}$ vs. $\tan(\theta/2)$ in ref 5 that there is a systematic deviation from this relationship. When the interaction force constant associated with the stretching of the two M–H bonds, f_{rr}, is incorporated into eq 1, one obtains expression 2 in which

$$\nu_{\text{asym}}/\nu_{\text{sym}} = [(k_r - f_{rr})/(k_r + f_{rr})]^{1/2} \tan(\theta/2) \tag{2}$$

k_r is the primary M–H stretching force constant. The direction of the deviation between the experimental data and eq 1 is consistent with a small, positive value of f_{rr}. In the case of $(\mu\text{-H})_2Os_3(CO)_{10}$, we may derive values of +90 N m^{-1} and +5 N m^{-1} for k_r and f_{rr}, respectively,[6] utilizing the Os–H stretching frequencies of the $(\mu\text{-H})(\mu\text{-D})Os_3(CO)_{10}$ species and the mean value of θ determined by Orpen et al.[3] (92.9°).

While the predictive value of the simple model remains valid, it would appear that the M–H–M angles estimated in this way will be underestimated by at least 4–5°. This implication will be examined in more detail when spectroscopic data from a wider selection of metal hydrido cluster complexes have been obtained.

Use of vibrational data from isotopic "impurities", of the type discussed here, might be expected to prove worthwhile in the study of other metal cluster complexes containing more than one μ-bridging hydrido ligand such as $(\mu\text{-H})_3Mn_3(CO)_{12}$[7,8] or in cases where the presence of inequivalent bridged-hydride locations is suspected.

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Registry No. $(\mu\text{-H})(\mu\text{-D})Os_3(CO)_{10}$, 81293-87-0.

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(2) R. W. Broach and J. M. Williams, *Inorg. Chem.*, **18**, 314 (1979).

(3) A. G. Orpen, A. V. Rivera, E. G. Bryan, D. Pippard, G. M. Sheldrick, and K. D. Rouse, *J. Chem. Soc., Chem. Commun.*, 723 (1978).

(4) V. Katkovič and R. E. McCarley, *Inorg. Chem.*, **17**, 1268 (1978).

(5) M. W. Howard, U. A. Jayasooriya, S. F. A. Kettle, D. B. Powell, and N. Sheppard, *J. Chem. Soc., Chem. Commun.*, 18 (1979).

(6) While it is possible that the value of f_{rr} is angle dependent, it would appear from the data given in ref 5 that the ratio f_{rr}/k_r is approximately constant.

(7) S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Am. Chem. Soc.*, **95**, 4532 (1973).

(8) M. W. Howard, U. A. Jayasooriya, D. B. Powell, and N. Sheppard, to be submitted for publication.

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INEPT ^{109}Ag NMR Evidence for Direct Pt-to-Ag Bonding in Dinuclear $[[2,6\text{-}(Me_2NCH_2)_2C_6H_3][p\text{-}tolNC(H)NR]PtAgBr]$

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Recently, it was shown that application of the INEPT technique (insensitive nuclei enhancement by polarization transfer[1a]) results in a considerable intrinsic experimental time saving for the recording of ^{109}Ag NMR spectra. This allowed for the first time the study of the structure of a series of silver complexes by means of ^{109}Ag NMR.[1b] A prerequisite for the application of the INEPT technique is the presence of a spin–spin coupling to a sensitive nucleus (e.g., ^{1}H[1b]) with the insensitive nuclei to be measured. The same requirement holds equally for FT-INDOR-like experiments as recently shown for $[(EtO)_3P]_nAg^+$ complexes.[2] However, so far Ag–H couplings have been reported for only a restricted number of silver complexes.[3–8] This is due to the fact that silver complexes are very prone to intra- and intermolecular exchange processes.[1b–9]

In the course of a study directed to the synthesis of stable heterodinuclear metal complexes, we synthesized a series of Pt–Hg and Pt–Ag complexes.[10–13] For the Pt–Hg complexes two distinctly different molecular geometries have been established, containing either (a) a five-coordinate platinum with a Pt-to-Hg donor interaction (type 1) or (b) a six-coordinate platinum with a covalent Pt–Hg bond (type 2). Structures of two representative examples, determined by X-ray analysis,[9–12] are shown in Figure 1.

A series of Pt–Ag complexes $[[2,6\text{-}(Me_2NCH_2)_2C_6H_3](p\text{-}tolNYNR)PtAgBr]$ (Y = CH, N; tol = tolyl) had also been

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