

as indicated above,⁴ we are in the presence of d^{13} , d^{14} , and d^{15} species, respectively, but metal-oxygen triple bonding cannot be obviously proposed, for the closed-shell configuration of the metals is far from being obtained and involvement of oxygen d orbitals in bonding seems quite unrealistic. The magnetic and structural features in compounds of this type with the metals in octahedral environments have been often rationalized through qualitative MO pictures similar to that of Figure 2b.¹⁴ Notice that the HOMO e_g level is nonbonding and that the removal of two or four electrons from it (corresponding to d^{14} or d^{13} initial electron counts) does not alter the overall M-O-M bonding network.

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Appendix

All calculations were performed with use of the extended Hückel methods.¹⁵ The programs, kindly supplied by Professor Roald Hoffmann, were implemented and run on an SEL 32/70 computer. The parameters used for Co, Ni, and Cr were taken from ref 5b. P-H, N-H, and C-O distances were idealized at 1.40, 1.09, and 1.15 Å, respectively. The M-S, M-P, and M-C bond lengths were taken from the experimental values of related structures.

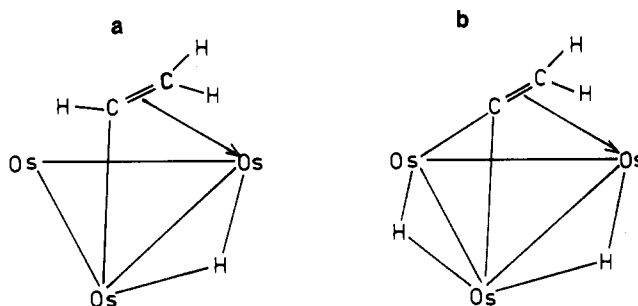


Figure 1. Structures of (a) $\text{HOs}_3(\text{CH}=\text{CH}_2)(\text{CO})_{10}$ and (b) $\text{H}_2\text{Os}_3(\text{C}=\text{CH}_2)(\text{CO})_9$.

surface species are contained in a number of recent publications (see, for example, ref 4).

In this paper we report the vibrational spectra and assignments of two metal cluster compounds, incorporating unusual olefinic groups, of formulas $\text{HOs}_3(\text{CH}=\text{CH}_2)(\text{CO})_{10}$ and $\text{H}_2\text{Os}_3(\text{C}=\text{CH}_2)(\text{CO})_9$,^{5,6} with the structures shown in Figure 1a,b. The spectra and the interpretation described here confirm previous suggestions, based on X-ray crystallographic data,⁶ that in these compounds the olefinic groups are both σ and π bonded. In metal surface studies of chemisorbed olefins, both σ and π bonding have been suggested, although not usually in conjunction. A third compound, $\text{H}_2\text{Os}_3(\text{CO})_{10}$,⁷ has also been studied in the present work to assist in the interpretation of the bands from hydride ligands in the spectra of the first two compounds.

For the vinyl and vinylidene compounds, only solution infrared spectra in the carbonyl stretching region have been reported previously.^{5,6} Our more complete investigation of the vibrational spectra of these compounds in the solid state has shown that the intensity of the peaks associated with the organic groups are almost 1 order of magnitude smaller than those from the carbonyl groups and that those associated with the bridging hydrogen atoms are even weaker. Fortunately, the motions of the olefinic, bridging hydrogen, and carbonyl groups are clearly largely uncoupled and the associated spectral features are therefore discussed separately.

Results

Bands Associated with Vibrations of CO Ligands. The study of metal carbonyls is well documented in the literature, and so bands due to carbonyl vibrations will not be discussed here except to point out that the bands occur in the usual regions,⁸ i.e., $\nu(\text{CO})$ near 2000, $\nu(\text{M}-\text{C})$ and $\delta(\text{MCO})$ at 600-400, and $\delta(\text{OC}-\text{M}-\text{CO})$ below 100 cm^{-1} .

The vibrations of the other ligands described here do not normally occur in these regions.

The results are considered in three sections: olefinic bands, metal-hydrogen bands, and skeletal modes involving the metal atoms.

Olefinic Bands. When the spectra of $\text{HOs}_3(\text{CH}=\text{CH}_2)(\text{CO})_{10}$ and $\text{H}_2\text{Os}_3(\text{C}=\text{CH}_2)(\text{CO})_9$ are compared with that of the parent carbonyl cluster, $\text{Os}_3(\text{CO})_{12}$, at high concentrations (5-15% by weight) in pressed potassium bromide disks, the most striking difference is the appearance in the olefin complexes of bands between 1700 and 600 cm^{-1} , which are of fairly low intensity compared to the $\delta(\text{MCO})$ bands and of very low

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Infrared and Raman Spectra of $\text{HOs}_3(\text{CH}=\text{CH}_2)(\text{CO})_{10}$, $\text{H}_2\text{Os}_3(\text{C}=\text{CH}_2)(\text{CO})_9$, and $\text{H}_2\text{Os}_3(\text{CO})_{10}$: Wavenumbers Associated with Olefinic and Hydride Ligands and the Metal Skeleton

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We have recently been investigating the vibrational spectroscopy of metal cluster systems, particularly of osmium carbonyl derivatives. It has been suggested that some clusters may be catalytically important and that they may provide model compounds for the study of chemisorbed species on metal surfaces.¹⁻³ For this reason a detailed understanding of the vibrational spectra of such compounds should aid the interpretation of the spectra of chemisorbed species. Examples of the use of the infrared spectra of metal cluster compounds in interpreting the vibrational spectra obtained from metal

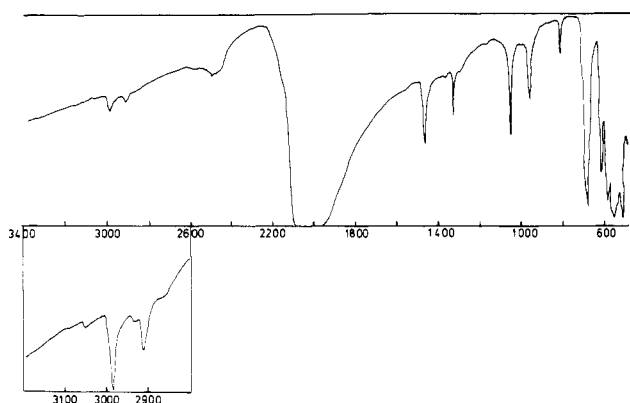
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Table I. Infrared and Raman Spectra (cm^{-1}) of $\text{HOs}_3(\text{CH}=\text{CH}_2)(\text{CO})_{10}$ and $\text{H}_2\text{Os}_3(\text{C}=\text{CH}_2)(\text{CO})_9$, Compared with Infrared Spectrum of $\text{GeH}_3(\text{CH}=\text{CH}_2)$ (Bands due to Carbonyl and Hydrogen Vibrations Omitted)

	$\text{HOs}_3(\text{CH}=\text{CH}_2)(\text{CO})_{10}$		$\text{GeH}_3(\text{CH}=\text{CH}_2)$	$\text{H}_2\text{Os}_3(\text{C}=\text{CH}_2)(\text{CO})_9$		
	assignt	IR		IR	IR	Raman
$\nu_{\text{asym}}(\text{CH}_2)$		3052 w	3066 m		3100 w bd	
$\nu_{\text{sym}}(\text{CH}_2)$		2998 w	3002 m		3055 m	
$\nu(\text{CH})$		2920 vw	2959 w		2995 m	
				2910 w	2916 m	overtone
				2860 vw		
coupled $\nu(\text{C}=\text{C})/\delta(\text{CH}_2)$ scissors	1476 m	1477 vw	(1595 Raman) ($\nu(\text{C}=\text{C})$)	1467 m	1470 w	coupled $\nu(\text{C}=\text{C})/\delta(\text{CH}_2)$ scissors
	1310 m	1314 w	1398 ms ($\delta(\text{CH}_2)$)	1328 m	1332 w	
$\delta(\text{CH})$ (in plane)	1266 m	1270 w	1268 m			
		1014 w				
CH_2 rock (in plane)	1005 m	1003 w	1007 m	1048 m		CH_2 rock
$\gamma(\text{CH}_2)$ wag ^a	990 s	990 w	950 m	959 ms	963 w	$\gamma(\text{CH}_2)$ wag
$\gamma(\text{CH}_2)$ twist ^a	987 s		887 m	808 m		$\gamma(\text{CH}_2)$ twist
$\gamma(\text{CH})^a$	782 m		524 m			
$\nu(\text{Os-olefin})$ str	332 s	336 w				$\gamma(\text{Os-olefin})$ str ^b
	309 vw			311 s	310 m	
	296 s	297 vw		311 s	310 m	
	191 m	193 w		255 s	254 m	
$\nu(\text{Os-Os})$ str ^b	166 m	168 s				$\nu(\text{Os-Os})$ str ^b
	129 m	126 vs		174 m	175 s	
	110 w	116 ms		147 w	150 m	
				112 m	115 s	
Os-CO def or lattice modes ^b	93 m	101 vs		90 m	94 vs	Os-CO def or lattice modes ^b
		88 vs			82 vs	
		59 s			77 m	
		48 s			60 w	
					41 s	

^a Denotes out-of-plane CH modes. ^b Key: str = stretching; def = deformations.

**Figure 2.** Top: infrared spectrum (cm^{-1}) of $\text{H}_2\text{Os}_3(\text{C}=\text{CH}_2)(\text{CO})_9$ at room temperature. Bottom: expanded spectrum of Digilab FT IR.

intensity compared with the $\nu(\text{CO})$ absorption (Figure 2). These are mostly relatively very sharp at room temperature ($\Delta\nu_{1/2} = 5 \text{ cm}^{-1}$) and must clearly be assigned to vibrations of the olefinic groupings. The CH stretching modes in the 3000-cm^{-1} region are even weaker than the bands in the $1200\text{-}600\text{-cm}^{-1}$ region, and in order to study this region, it was necessary to use the spectral accumulation and other facilities offered by a Digilab FT IR spectrometer.

$\text{HOs}_3(\text{CH}=\text{CH}_2)(\text{CO})_{10}$. Infrared and Raman spectra were obtained, but for the latter, the 3000-cm^{-1} region was obscured either by fluorescence or by sample decomposition for all laser lines. The vinyl group vibrations can be assigned by comparison with other organometallic compounds containing this group. One such molecule where a full assignment has been made is $\text{GeH}_3(\text{CH}=\text{CH}_2)$, which, however, differs from the

present cluster complex in that there is no possibility of the σ -bonded vinyl group also forming a π bond with another metal atom.⁹ Comparison of the spectra of the two compounds, and the probable assignment of the observed features to particular modes of vibration, is given in Table I.

The π complexing of an olefin such as ethylene to a transition metal, as in Zeise's salt $\text{KPtCl}_3(\text{C}_2\text{H}_4)$, causes notable reduction in the wavenumbers associated with coupled $\nu(\text{C}=\text{C})$ and $\delta(\text{CH}_2)$ scissors modes (from 1623 to 1515 and from 1342 to 1243 cm^{-1} , respectively) and a raising of the out-of-plane CH_2 modes from 949 to 1010 cm^{-1} .¹⁰ When these factors are taken into account, there is very good correlation between the wavenumbers associated with the solely σ -bonded vinyl group in $\text{GeH}_3(\text{CH}=\text{CH}_2)$ and the σ - and π -bonded group in $\text{HOs}_3(\text{CH}=\text{CH}_2)(\text{CO})_{10}$ as shown in Table I. The infrared and Raman data for the latter compound thus provide support for the concept of σ and π bonding. For example, the $\nu(\text{C}=\text{C})$ and $\delta(\text{CH}_2)$ wavenumbers are more readily accounted for in these terms since if there were no π bond, frequencies closer to these found for $\text{GeH}_3(\text{CH}=\text{CH}_2)$ would be expected. All the $\nu(\text{CH})$ and $\nu(\text{CH}_2)$ stretching modes are also characteristically ethylenic in nature, the wavenumbers of the bands being similar to those observed for Zeise's salt.¹⁰

$\text{H}_2\text{Os}_3(\text{C}=\text{CH}_2)(\text{CO})_9$. Raman as well as infrared spectra of this compound were obtained over the whole frequency range. The bands assigned to the vinylidene group follow a similar pattern to those found for the vinyl group in $\text{HOs}_3(\text{CH}=\text{CH}_2)(\text{CO})_{10}$. No suitable organometallic derivative is available for comparison, but the spectrum of the vinylidene group is generally similar to that of the vinyl group, with bands due to the lone CH group missing. The bands in the CH stretching region were again very weak and were obtained with

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a Digilab interferometric spectrometer. The suggested assignment of the bands to particular modes of vibration is given in Table I. The frequencies of the bands assigned to $\nu(\text{C}=\text{C})$ and $\delta(\text{CH}_2)$ scissors again give clear evidence of coordination of the vinylidene group to the third osmium atom of the cluster through a π bond.

Conclusions on Olefinic Bands. It is clear that the patterns of bands observed for the vinyl and vinylidene groups in these clusters are rather characteristic, sufficiently so for them to be used for the identifications of these groups in the spectra of olefinic species chemisorbed on metal surfaces providing account is taken of the possibility of π bonding as well as δ bonding on the surface species. In a recent publication,¹¹ data on these compounds were used in interpreting the spectra obtained when ethylene is adsorbed on the Pt(III) face.

Metal-Hydrogen Bands. As the structures in Figure 1 show, both compounds contain bridged hydrogen atoms. These give rise to bands in the infrared spectra which are very weak, even compared with the bands due to the organic groups. However, on cooling to liquid-nitrogen temperatures, the bands show a marked sharpening and become readily resolved. The degree of band sharpening is much greater than for the organic groups. This temperature sensitivity of the metal-hydrogen modes is of considerable importance since not only does it enable these weak bands to be detected but also does it provide a well-established and reliable means of assigning these modes. The use of this method of identifying metal-hydrogen vibrations has been shown in recent studies¹² where parallel deuterium substitution experiments have been carried out on the same compounds. No such data are available for the vinyl and vinylidene complexes, but the data presented here on a hydride derivative of the osmium triangle, $\text{H}_2\text{Os}_3(\text{CO})_{10}$, which contains a double hydrogen bridge, illustrates the equivalence of the two methods. In Figure 3 the temperature sensitivity of the expected four main ($\mu\text{-H}$)($\mu\text{-D}$) bands for this compound is shown by comparison of spectra a and b, and in spectra c, the low-temperature spectra of $\text{D}_2\text{Os}_3(\text{CO})_{10}$, a similar cluster of four main bands is observed at lower frequencies, giving ratios of $\nu(\text{H})/\nu(\text{D})$ of 1.38, 1.38, 1.36, and 1.34. It is of interest to observe that for these compounds the wavenumbers of the four bands expected for the asymmetric and symmetric $\mu\text{-H}$ stretching modes are very close so that they form one group of bands. This is a consequence of the small M-H-M bond angle of 92.6° based on a neutron diffraction study.⁶ It has been shown that an approximate theoretical linear relationship between the ratio of $\nu_{\text{asym}}(\text{MH})$ to $\nu_{\text{sym}}(\text{M-H})$ and $\tan(\theta/2)$, where θ is the M-H-M angle. This relationship is well obeyed experimentally except at large θ values.¹³ It follows that, to this first approximation, for a value of θ of 90° the asymmetric and symmetric frequencies should be identical.

In the case of the single $\mu\text{-H}$ bridge of the compound $\text{HOs}_3(\text{C}=\text{CH}_2)(\text{CO})_{10}$, two main bands are observed at 1392 and 1286 cm^{-1} in the infrared (1390 and 1285 in Raman) and, with use of the relationship given in ref 10 and with the assumption that the high wavenumber band is $\nu_{\text{asym}}(\text{Os-H-Os})$, this would lead to a predicted value for the M-H-M bond angle of 100° , compared with the observed value of 101.5° . In the case of the vinylidene derivative, the two hydrogen bridges are nonequivalent, and as expected four main bands

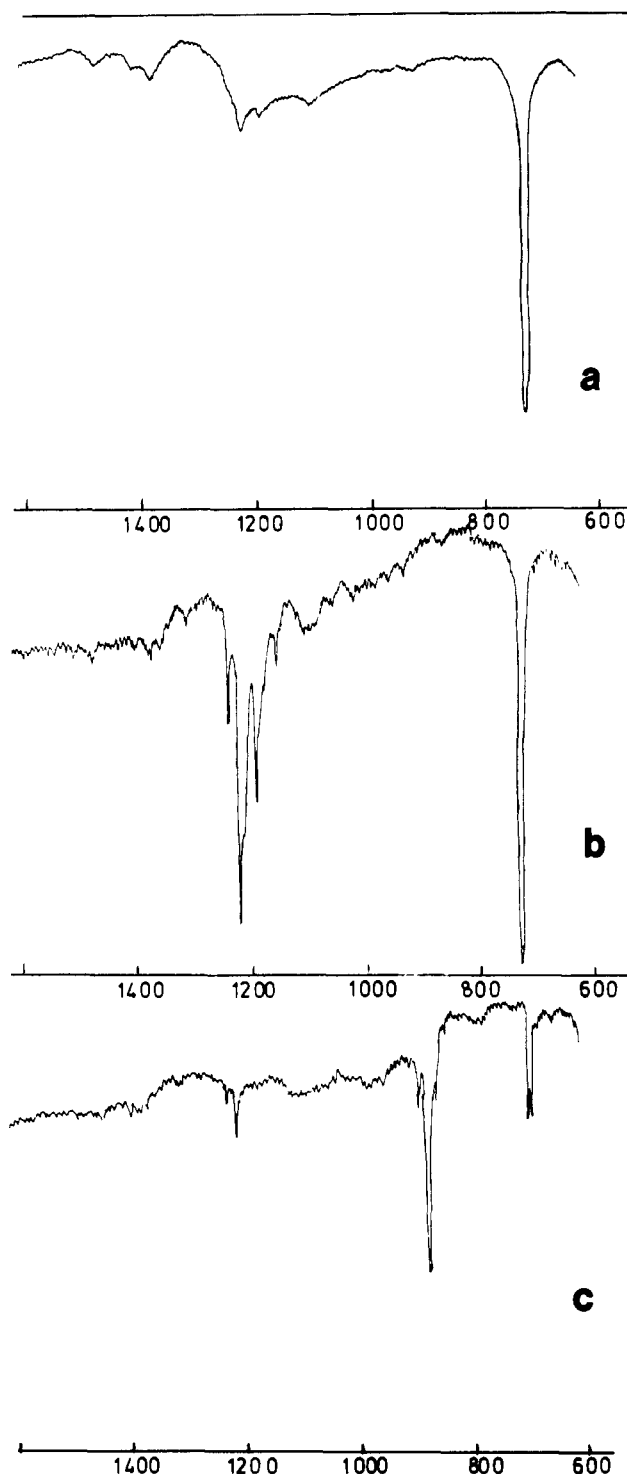


Figure 3. Infrared spectra (cm^{-1}) of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ at room temperature (a) and liquid-air temperature (b) and of $\text{D}_2\text{Os}_3(\text{CO})_{10}$ at liquid-air temperature (c).

are once again observed. By analogy we assign the two asymmetric stretching modes at 1398 and 1349 and the two symmetric stretching modes at 1302 and 1288 cm^{-1} . However, there is no way of determining which pairs of asymmetric and symmetric stretching bands go together, so no reliable estimation can be made of the bond angles on this basis, except to suggest that they fall in the range $98\text{--}103^\circ$.

In each case the deformation vibrations of the hydrogen bridge corresponding to a pair of stretching modes gives rise to bands near 700 cm^{-1} . This is higher in wavenumbers than the $\nu(\text{M-CO})$ and $\delta(\text{CO})$ modes and occurs as a relatively strong band which is less sensitive to the effect of temperature

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Table II. Wavenumbers (cm⁻¹) Associated with Metal-Hydrogen Vibrations

assignt	HOs ₃ (CH=CH ₂)(CO) ₁₀		H ₂ O ₃ (C=CH ₂)(CO) ₉		H ₂ O ₃ (CO) ₁₀	D ₂ O ₃ (CO) ₁₀	ν(H)/ν(D)
	IR	Raman	IR	Raman	IR	IR	
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 Os₃ triangle. These modes usually appear as weak bands in the infrared but as relatively strong bands in the Raman spectra. In Os₃(CO)₁₂, where the osmium atoms form an equilateral triangle, two bands are found in the Raman at 158 cm⁻¹ (a₁') and 117 cm⁻¹ (e'); the band at 117 cm⁻¹ also occurs in the infrared spectrum.¹⁴ In the compound Os₃(OEt)₂(CO)₁₀, where the OEt groups bridge pairs of osmium atoms, the osmium triangle is isocenes 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 (a₁), 136 (a₁), and 119 (b₂) cm⁻¹. The compounds HOs₃(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 γ(CH₂) 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 relevant cluster molecule, taking into account the effect of the metal-surface selection rule on the relative intensities.

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. HOs₃(CH=CH₂)(CO)₁₀, 55072-96-3; H₂O₃(C=CH₂)(CO)₉, 42765-74-2; H₂O₃(CO)₁₀, 41766-80-7.

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On the Infrared Spectrum of (μ-H)(μ-D)Os₃(CO)₁₀

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The Os-H and Os-D stretching vibrations of the metal cluster complexes (μ-H)₂Os₃(CO)₁₀ and (μ-D)₂Os₃(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 Os₂H 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 (μ-H)(μ-D)Os₃(CO)₁₀ species as a dilute

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