Infrared spectra of C sub 2 hydrocarbon ligands coordinated to a triosmium framework: The effect of high pressure as a tool for assignment

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= 0.71 and ΔE_{tun} = –0.38 kcal/mol for H/Ru(0001). For comparison we find that D_{tun} = 0.64, 0.64, and 0.62 and ΔE_{tun} = –0.48, –0.45, –0.54 kcal/mol for potentials A, S, and M, respectively, for the same temperature range, in very good agreement. However we predict a significantly greater role of tunneling at lower *T*, e.g., ΔE_{tun} = –1.85, –1.43, and –2.01 kcal/mol for potentials A, S, and M, respectively, for the temperature range from 100 to 140 K.

The present dynamical calculations have not included the effect of metal motions. However, from our previous studies of H on Cu(100),[33–35] this effect further enhances the tunneling rate and also increases the KIE. The effect is very large at temperatures near 100 K, but smaller near 200 K. For instance, as the temperature decreases from 300 to 200 K, the effect of metal motions increases the KIE for H/Cu(100) by 4% to 13%.[35] Because the diffusion barrier for H on Ru(0001) is more than a factor of 2.5 smaller than that of H on Cu(100), the enhancement factor would be expected to be much smaller in the present study. If we take the result for H on Cu(100)[35] at 200 K as an approximate upper bound for the effect of metal motions on the KIE in the present case, the resulting D^H/D^D ratio may increase up to no more than 2.6 at 260 K.

In previous work,[6] the adsorption energy at a number of subsurface sites was also determined. Thus, it may be possible to generate a subsurface potential which could be used to study the kinetics of H diffusing to or between subsurface sites. Penetration of H and D adsorbed on Ru(0001) into interior sites has been postulated to retard the thermal desorption of H₂ and HD,[47] and

it would be very interesting to study this process theoretically.

5. Summary

We have calculated the adsorption energy of hydrogen on Ru(0001) at various sites as a function of height above the surface plane using ab initio electronic structure calculations of the total energy based on ab initio pseudopotentials and the local density approximation. The results were used to construct a classical potential energy function for the H–Ru(0001) interaction energy. Using this potential surface, we calculated the minimum-energy path for adatom surface diffusion, and we calculated diffusion rates for H and D by variational transition state theory with semiclassical tunneling approximations.

The classical diffusion barrier predicted from the ab initio potential energy function is 5.75 kcal/mol which results in an activation energy about 1 kcal/mol larger than the experimental value. We also presented dynamical results where the classical energy along the minimum energy path of the ab initio potential energy function is scaled by a factor of 0.9 and for another case with an empirically modified global potential. In both cases the potential function is modified so that the calculated activation energy is in reasonably good agreement with experiment. The calculated kinetic isotope effect for the temperature range from 260 to 300 K is similar for all three cases and is within the experimental error.

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Infrared Spectra of C₂ Hydrocarbon Ligands Coordinated to a Triosmium Framework: The Effect of High Pressure as a Tool for Assignment

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The effect of high pressure on the vibrational frequencies of a set of triosmium clusters (Os₃(CO)₁₀(μ₃,η²-C₂H₂) (**1**), HOs₃(CO)₉(μ₃,η²-CCH) (**2**), H₂Os₃(CO)₉(μ₃,η²-CCH₂) (**3**), H₃Os₃(CO)₉(μ₃-CCH₃) (**4**)) has been measured in the range 0–96 kbar. The pressure shifts observed for various infrared bands are used to assign previously uncharacterized bands and to confirm other existing assignments. For clusters **2** and **4**, the effect of deuteration on the hydrocarbon vibrations is reported in addition. In general, the pressure dependencies of the vibrational bands in terms of dν/d*P* follow the order C–H stretch > C–C stretch > C–H bend, with all bands typically shifting to higher energy with increasing pressure. For **2**, **3**, and **4**, this order changes to C–C stretch > C–H stretch > C–H bend, if the shifts are formulated in terms of a percent change $\Delta\nu/\nu_0$. For the C–C stretch, the magnitude of its shift to higher energy with increasing pressure is proportional to the initial value at atmospheric pressure.

Introduction

One important feature of organometallic carbonyl clusters is their use as structural models for adsorbed organic species on metal surfaces.[1] A number of infrared studies of the hydrocarbon vibrations for organometallic clusters of known structure have been undertaken, and these studies provide characteristic absorption profiles useful for the interpretation of high-resolution electron energy loss spectroscopic (HREELS) data of chemisorbed species on metal surfaces.[2,3] The value of this approach is exemplified

by Sheppard's pioneering use of a detailed vibrational assignment of Co₃(CO)₉(μ₃-CCH₃) to correctly identify a μ₃-ethylidyne moiety as the surface species derived from chemisorbed ethylene on Pt(111) above 300 K.[2a,3] This approach has also been extended

(1) Muetteries, E. L.; Rodin, T. N.; Band, E.; Pretzer, W. R. *Chem. Rev.* **1979,** *79,* 81.

(2) (a) Skinner, P.; Howard, M. W.; Oxton, I. A.; Kettle, S. F. A.; Powell, D. P.; Sheppard, N. *J. Chem. Soc., Faraday Trans. 2* **1981,** *77,* 1203. (b) Anson, C. E.; Keiller, B. T.; Oxton, I. A.; Powell, D. B.; Sheppard, N. *J. Chem. Soc., Chem. Commun.* **1983,** 470. (c) Andrews, J. R.; Kettle, S. F. A.; Powell, D. B.; Sheppard, N. *Inorg. Chem.* **1982,** *21,* 2174. (d) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1983,** 639. (e) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1984,** 79.
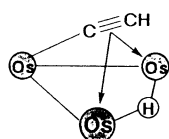
(3) Sheppard, N. *Annu. Rev. Phys. Chem.* **1988,** *39,* 589.

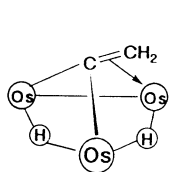to other types of hydrocarbon coordination on metal surfaces.[4]

In this work, we exploit the effect of high pressure on the vibrations of cluster-bound hydrocarbon ligands as an aid in spectroscopic assignments. The following set of triosmium clusters have been examined:
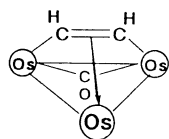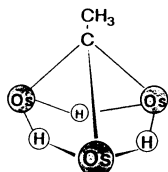

$Os_3(CO)_{10}(C_2H_2)$ (1)

$HOs_3(CO)_9(CCH)$ (2)

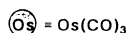$H_2Os_3(CO)_9(CCH_2)$ (3)

$H_3Os_3(CO)_9(CCH_3)$ (4)

⊙s = Os(CO)₃

Each of these clusters has been utilized previously for comparison with the appropriate organic species on a metal surface.[3] However, we report a corrected spectrum for **2** as well as new data for the deuterated versions of **2** and **4**.

It has been noted that high-pressure vibrational spectroscopy can serve as a complementary method to isotopic substitution experiments.[5] Pressure affects internuclear distances and perturbs the valence electron density throughout the molecule (i.e., "pressure tuning")[6] but it does not affect the nuclear masses. Isotopic substitution, on the other hand, changes the mass but leaves the other parameters unaffected. The effect of increasing pressure on a molecular vibration is dependent upon its force constant and the nature of the vibration (bend, stretch, etc.) as well as the interaction with its surroundings.[7] The first-order effect of compression on a vibration is typically a "stiffening" of the force constant and a subsequent shift to higher energy; however, the magnitude of this shift can be lessened by an attractive van der Waals interaction with the surroundings.

We analyze the pressure dependencies of the hydrocarbon ligand vibrations of these triosmium clusters by the magnitudes of $d\nu/dP$ observed as well as by the percent change ($\Delta\nu/\nu_0$) in a given pressure range. The trends observed are explained on the basis of both intra- and intermolecular effects. The observed pressure effects are used to assign several uncharacterized bands and also to verify other previous assignments.

Experimental Section

The compounds **1–4** were prepared by literature methods or minor variations thereof and were purified by thin-layer chromatography and/or crystallization until free of hydrocarbon contaminants. In particular, $Os_3(CO)_{10}(\mu_3,\eta^2-C_2H_2)$ (**1**)[8a] was obtained from $Os_3(CO)_{10}(NCCH_3)_2$ and acetylene and $HOs_3(CO)_9(\mu_3,\eta^2-CCH)$ (**2**)[8a] from pyrolyzing **1** in boiling n-octane. $H_2Os_3(CO)_9(\mu_3,\eta^2-CCH_2)$ (**3**)[8b] was obtained from pyrolyzing $HOs_3(CO)_{10}(\mu,\eta^2-CHCH_2)$ [from $H_2Os_3(CO)_{10}$ and C_2H_2] in n-octane, and $H_3Os_3(CO)_9(\mu_3-CCH_3)$ (**4**)[8b] was prepared by

(4) (a) Somorjai, G. A. *Pure Appl. Chem.* **1988**, *60*, 1499. (b) Grassian, V. H.; Muetterties, E. L. *J. Phys. Chem.* **1986**, *90*, 5900.

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(7) (a) Benson, A. M., Jr.; Drickamer, H. G. *J. Chem. Phys.* **1957**, *27*, 1164. (b) Moon, S. H.; Drickamer, H. G. *J. Chem. Phys.* **1974**, *61*, 48. (c) Roginski, R. T.; Shapley, J. R.; Drickamer, H. G. *J. Phys. Chem.* **1988**, *92*, 4316.

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TABLE I: Infrared Data for the Hydrocarbon Ligand Vibrations of $Os_3(CO)_{10}(\mu_3,\eta^2-C_2H_2)$ (1)

	$Os_3(CO)_{10}(HCCH)$			$Os_3(CO)_{10}(DCCD)$	
assignment	$\nu_0,^a$ cm^{-1}	$d\nu/dP,^b$ cm^{-1}/kbar	$\Delta\nu/\nu_0{}^c$	$\nu_0,^a$ cm^{-1}	$\nu(H)/\nu(D)$
ν(C–H) (sym)	2996 w	+1.14	+2.40	2180 w	1.37
ν(C–H) (asym)	2945 w	+1.80	+3.70	2140 w	1.38
ν(C–C) (sym)	1301 m	+0.48	+2.30	1282 m	1.01
δ(C–H) (asym)^d	1035 m	−0.11^e	−0.50	760 m	1.36
δ(C–H) (sym)^d	978 w	−0.01^e	−0.60	742 w	1.32
γ(C–H) (sym)^d	848 s	+0.04^e	+0.50	605 s	1.40
combination bands	1208 w	−0.06	−0.30	986 vw	1.23
	1234 w	+0.11	+0.80	998 w	1.24

^{a} Bands recorded at atmospheric pressure in CsI from ref 2b. ^{b} Pressure shifts observed in nujol. ^{c} Percent change in ca. 60 kbar. ^{d} The designation of δ(C–H) (in-plane) or γ(C–H) (out-of-plane) refers to the nature of the vibration with respect to the plane containing the atoms H–C–C–H. ^{e} At approximately 49 kbar, these bands change slope to the following values (cm^{-1}/kbar): δ(C–H) (sym) = +0.03/0.22 (split sym mode); δ(C–H) (asym) = +0.36; γ(C–H) (sym) = +0.37.
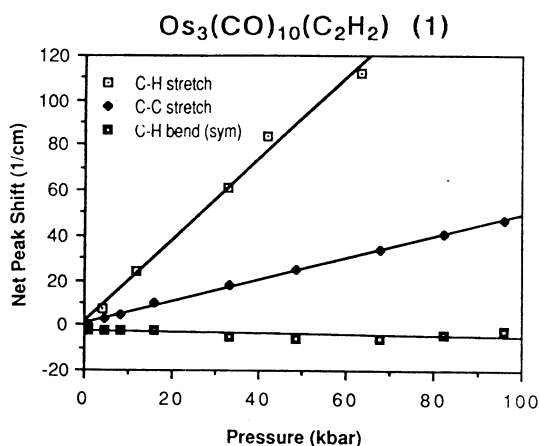

Figure 1. Pressure dependencies of selected hydrocarbon ligand vibrations for $Os_3(CO)_{10}(\mu_3,\eta^2-C_2H_2)$ (**1**).

treating **3** with hydrogen in boiling n-octane. The deuterated compounds were prepared analogously with D_2 and C_2D_2 as deuterium sources.

Infrared absorption spectra were taken in a gasketed diamond anvil cell (DAC) employing type IIA diamonds. Nujol, CsCl, and fluorolube were utilized as pressure-transmitting media, with no significant differences discerned in the pressure effects. Spectra were obtained on a Nicolet 7199 FT IR with an 800-cm^{-1} HgCdTe detector and a Perkin-Elmer 4X beam condenser. An *XYZ* mount was used to position the DAC at the focus. Pressure was calibrated by the ruby fluorescence method. All runs were both reversible and reproducible. For $H_3Os_3(CO)_9(\mu_3-CCH_3)$, cluster fluorescence interfered with the ruby pressure calibration. The observed pressure values for this cluster were calibrated against the pressure shift of the 1377-cm^{-1} band of nujol, which was independently calibrated in a blank run with a sample containing a ruby chip.

Results

$Os_3(CO)_{10}(\mu_3,\eta^2-C_2H_2)$ (**1**). This compound contains a simple hydrocarbon ligand in a relatively symmetrical environment and therefore seemed a good point to start our study. Furthermore, Sheppard and co-workers have reported a detailed study of both **1** and its fully deuterated analogue.[2b] These infrared data and suggested assignments are shown in Table I. Table I also lists the pressure dependencies for the vibrations in **1** that were accessible to us. Both the initial slope ($d\nu/dP$) and the percent change in 60 kbar ($\Delta\nu/\nu_0$) are given. For three representative vibrations ν(C–H) (asym), ν(CC), and δ(C–H) (sym)) of $Os_3(CO)_{10}(\mu_3,\eta^2-C_2H_2)$, the effect of increasing pressure is graphically represented in Figure 1. From an examination of both the graphical and tabular results, it is apparent that the ν(C–H) bands show the greatest pressure dependence, with the symmetric and antisymmetric bands shifting to higher wavenumbers at rates of

TABLE II: Infrared Data for the Hydrocarbon Ligand Vibrations of $HOs_3(CO)_9(\mu_3,\eta^2$-CCH) (2)

vibration	$HOs_3(CO)_9(CCH)$ $\nu_0,{}^a$ cm^{-1}	$d\nu/dP,{}^b$ cm^{-1}/kbar	$\Delta\nu/\nu_0{}^c$	$DOs_3(CO)_9(CCD)$ $\nu_0,{}^a$ cm^{-1}	$\nu(H)/\nu(D)$
ν(C–H)	3157 s	+1.20	+2.40	2377 s	1.33
ν(C–C)	1534 s	+0.81	+2.92	1496 ms	1.03
ν(Os–H)	1402 vw			1115 vw	1.26
ν(Os–H)	1344 w			1020 w	1.32
δ(CCH)^d	864 s	+0.41	+3.36	714 m	1.21
	855 s	+0.10	+0.88	709 m	1.20
γ(CCH)^d	762 s	−0.05	−0.13		
ν(Os–H)	680 vs				

^{a} Bands recorded at atmospheric pressure in KBr. ^{b} Pressure shifts observed in nujol. ^{c} Percent change in ca. 60 kbar. ^{d} The designation δ(CCH) (in-plane) and γ(CCH) (out-of-plane) refers to the nature of the vibration with respect to the plane containing the atoms C–C–H.

+1.14 and +1.80 cm^{-1}/kbar, respectively. These are followed in magnitude by a strong shift to higher energy of +0.48 cm^{-1}/kbar for the C=C stretch.

The remaining vibrations, primarily C–H bend in character, demonstrate more complex behavior. The symmetric and antisymmetric in-plane bending motions (δ(C–H)) shift initially to lower energy with increasing pressure (−0.01 and −0.11 cm^{-1}/kbar, respectively), but after ca. 49 kbar both modes show shifts to higher energy (+0.13 cm^{-1}/kbar (av split sym mode) and +0.36 cm^{-1}/kbar (asym mode)). The symmetric out-of-plane bend, γ(C–H), shows initially a slight shift to higher energy with increasing pressure of +0.04 cm^{-1}/kbar, but after ca. 49 kbar it shifts substantially faster at a rate of +0.37 cm^{-1}/kbar. These changes in slope suggest that at pressures of 50 kbar and above intramolecular interactions tend to dominate intermolecular effects for these bending modes.

For **1**, consideration of the pressure effects on peak position in terms of their fractional behavior $\Delta\nu/\nu_0$ leads to the same order as for $d\nu/dP$, i.e., ν(C–H) > ν(CC) > δ(C–H) or γ(C–H). The percent change in the pressure range studied is 3.0 (average) for ν(C–H) and 2.3 for ν(CC), while those for δ(C–H) or γ(C–H) are significantly smaller and variable in sign.

An additional point worth mentioning is the behavior of the combination bands at 1208 and 1234 cm^{-1} with increasing pressure. Although the exact composition of these bands is presently unclear, their differing behavior with increasing pressure suggests that at least one of the two parent modes which contribute to each band is substantially different in character. A number of low-frequency bands in the 200–700-cm^{-1} region have been observed for this cluster by both Sheppard and co-workers[2b] and by Evans and McNulty.[2e] One possible assignment for the 1234-cm^{-1} band is a combination of the vibrations at 665 cm^{-1} (symmetric bridging CO bend[2c]) and 570 cm^{-1} (symmetric stretch of the Os–C σ bonds[2c]). We are unable to identify specific combinations appropriate for the 1208-cm^{-1} band.

$HOs_3(CO)_9(\mu_3,\eta^2$-CCH) (2). This compound is derived from the acetylene complex (**1**) and contains an even simpler acetylide ligand. Infrared data for a sample of **2** have been reported by Evans and McNulty,[2e] but they were unable to provide a definitive assignment for three bands observed at 1259, 858, and 762 cm^{-1}. Thus, this compound appeared to be a good candidate for examination by the pressure technique. Our sample of **2**, however, did not show a band at 1259 cm^{-1}, and we attribute this peak to an impurity in the previous sample. The IR spectrum of the previously unreported deuterated analogue $DOs_3(CO)_9(CCD)$ also does not show a band near 1259 cm^{-1} or near 899 cm^{-1} (1259/1.4). However, both of the remaining bands, now assigned as bending modes, show large shifts upon deuteration (Table II).

The results for all vibrations studied are given in Table II, with the pressure dependencies of three representative vibrations (ν-(C–H), ν(CC), and γ(C–H)) of this cluster shown in Figure 2. The pressure dependencies in terms of $d\nu/dP$ of the acetylide cluster (**2**) follow the trend observed above for the acetylene derivative (**1**), with ν(C–H) > ν(C–C) > δ(C–H) or γ(C–H). The single ν(C–H) frequency observed at 3166 cm^{-1} exhibits the largest
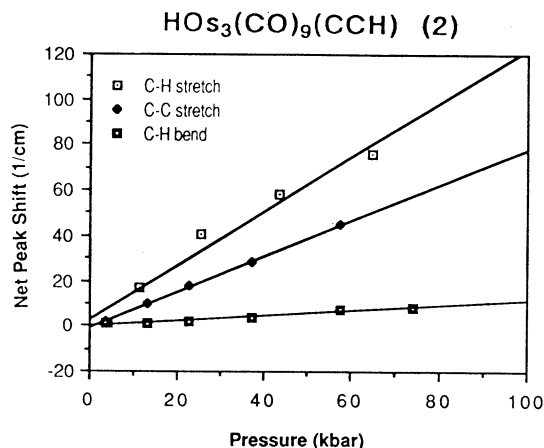
Figure 2. Pressure dependencies of selected hydrocarbon ligand vibrations for $HOs_3(CO)_9(\mu_3,\eta^2$-CCH) (**2**).

shift to higher energy in this cluster, a rate of +1.20 cm^{-1}/kbar. This is followed by the C–C stretch with a value of $d\nu/dP$ = +0.81 cm^{-1}/kbar. If the shifts with pressure are viewed in terms of percent change $\Delta\nu/\nu_0$, however, this order is reversed. $\Delta\nu/\nu_0$ for ν(CC) is 2.9% in ca. 60 kbar while that of ν(C–H) is 2.4%.

The infrared bands observed for the two bending vibrations display markedly different behavior with increasing pressure. The higher energy feature is observed as a single band in CCl_4 solution at 858 cm^{-1}. In a solid-state environment (KBr, nujol, or CsCl) this mode is observed as two bands at 855 and 864 cm^{-1}, due presumably to inequivalent sites in the crystal lattice. This split band shifts significantly to higher wavenumbers at rates of +0.41 cm^{-1}/kbar for the 864-cm^{-1} peak and +0.10 cm^{-1}/kbar for the 855-cm^{-1} peak. The markedly larger value of $d\nu/dP$ for the 864-cm^{-1} peak is attributed to its coupling to another mode with a stronger pressure dependence. A possible candidate for this unidentified mode is a low-frequency metal–carbon stretch, which should have a larger $d\nu/dP$ value than that of a bending vibration.

The lower energy bending vibration is observed at 762 cm^{-1}. In contrast to the behavior of the split 858-cm^{-1} band, this peak shifts slightly to lower wavenumber at a rate of −0.05 cm^{-1}/kbar. Evans and McNulty have suggested one possible assignment of these bands, with the 858-cm^{-1} peak as an in-plane C–H bending mode (δ(C–H)) while the 762-cm^{-1} band is the corresponding out-of-plane C–H bend (γ(C–H)).[2e] This assignment was based in analogy to an assignment for cluster **1** by Sheppard and co-workers, where δ(C–H) is assigned at a higher frequency than γ(C–H).[2b] If we adopt Evans and McNulty's assignment of the these bands in **2**, then the initial effect of pressure on δ(C–H) and γ(C–H) is reversed in comparison to cluster **1**. That is, at modest pressures for **1** both δ(C–H) modes shift to lower energy (−0.11 cm^{-1}/kbar for δ(C–H) (asym) and −0.01 cm^{-1}/kbar δ(C–H) (sym)) and γ(C–H) shifts slightly to higher energy (+0.04 cm^{-1}/kbar). In contrast, for **2** δ(C–H) shifts significantly to higher energy (+0.40/0.10 cm^{-1}/kbar) and γ(C–H) shifts slightly to lower energy (−0.05 cm^{-1}/kbar).

Although the magnitudes of these initial pressure shifts in **1** are small, there are two possible explanations for the difference with respect to **2**: (a) the suggested assignment for δ and γ(C–H) by Evans and McNulty for **2** is incorrect and should be reversed or (b) the pressure shift of the 864-cm^{-1} peak is modified in both sign and magnitude by its selective coupling with a low-frequency mode. Given the general observation that δ(C–H) is at a higher frequency than γ(C–H) in coordinated acetylene complexes,[3] the latter explanation is the more plausible.

$H_2Os_3(CO)_9(\mu_3,\eta^2$-$CCH_2$) (3). Infrared data for this compound have been reported both by Sheppard[2c] and by Evans and McNulty.[2d] The latter also reported values for derivatives of **3** at various levels of deuteration. One of the intriguing features of this cluster is the bands observed at 1332 and 1468 cm^{-1}, which are attributed to coupled C–C stretch and C–H bending (scissor) vibrations. Force constant analyses and the effect of deuteration have suggested that the 1332-cm^{-1} band is largely the "CC" stretch

TABLE III: Infrared Data of the Hydrocarbon Ligand Vibrations of $H_2Os_3(CO)_9(\mu_3,\eta^2$-CCH$_2$) (3)

| | $H_2Os_3(CO)_9(CCH_2)$ | | | | $D_2Os_3(CO)_9(CCD_2)$ | |
vibration	$\nu_0,^a$ cm^{-1}	$d\nu/dP,^B$ cm^{-1}/kbar	$\Delta\nu/\nu_0^c$	ν_0^a cm^{-1}	$\nu(H)/\nu(D)$
ν(C–H) (sym)	2990 w	+0.70	+1.40		
ν(C–H) (asym)	3052 vw	+0.92	+2.00		
δ(CH$_2$) (asym)^d	1468 m	+0.23	+0.95	943 m	1.56
ν(C–C)	1332 m	+0.57	+2.60	1363 m	0.98
δ(CH$_2$) (sym)^d	1048 m	+0.23	+1.43	877 m	1.19
γ(CH$_2$) (sym)^d	959 ms	+0.08	+0.40	752 s	1.28
γ(CH$_2$) (asym)^d	808 m	+0.32	+2.09		

^{a} Bands recorded at atmospheric pressure in KBr from ref 2d. ^{b} Pressure shifts observed in CsCl. ^{c} Percent change in ca. 60 kbar. ^{d} These bending modes are defined with respect to the plane containing the atoms C–CH$_2$. δ(C–H) (asym) and δ(C–H) (sym) are also known as scissor and rock modes, respectively. γ(C–H) (asym) and γ(C–H) (sym) are also known as twist and wag, respectively.
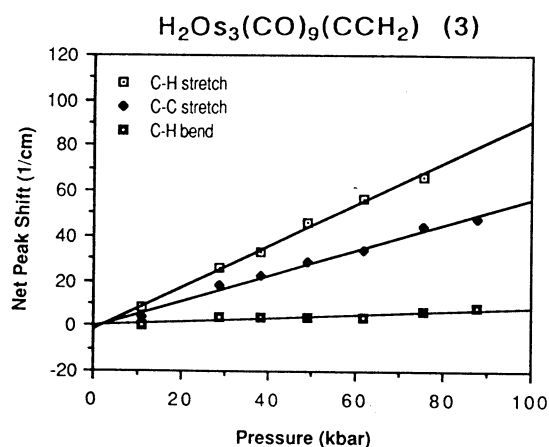
Figure 3. Pressure dependencies of selected hydrocarbon ligand vibrations for $H_2Os_3(CO)_9(\mu_3,\eta^2$-CCH$_2$) (3).

Wavenumber (cm^{-1})

Figure 4. IR spectra for $H_2Os_3(CO)_9(\mu_3,\eta^2$-CCH$_2$) (3) in the range 1500–950 cm^{-1} at several pressures. An arrow indicates the region of peak growth (ca. 1270 cm^{-1}).

while the 1468-cm^{-1} absorption is largely C–H bend.[2d] Thus, we were interested in the effect of pressure specifically on these bands.

Table III lists values of $d\nu/dP$ and $\Delta\nu/\nu_0$ for all vibrations measured on crystalline samples of **3** dispersed in CsCl, and plots of the peak shift versus pressure for ν(C–H), ν(CC), and γ(CH$_2$) are illustrated in Figure 3. As in the case of the previous two clusters, there is a distinct order in the pressure dependencies of the vibrational absorptions in terms of $d\nu/dP$, namely, ν(C–H) > ν(C–C) > δ(C–H) or γ(C–H). With increasing pressure the ν(C–H) bands at 2990 (sym) and 3052 cm^{-1} (asym) shift to higher wavenumbers at the greatest rates for any of the vibrations; $d\nu/dP$ = +0.70 and +0.92 cm^{-1}/kbar, respectively.

As noted above, one of the intriguing vibrational features of this cluster is the pair of bands initially at 1332 and 1468 cm^{-1}. The 1332-cm^{-1} band is observed to shift to higher wavenumbers at a rate greater than twice that of the 1468-cm^{-1} band (+0.57 cm^{-1}/kbar vs +0.23 cm^{-1}/kbar). The higher energy band is also split into two bands in CsCl with ν_0 = 1465 and 1473 cm^{-1}, with both features shifting at the same rate. The relative pressure dependencies observed for the two vibrations confirms that the 1332-cm^{-1} band with its larger pressure dependence is due to the C–C stretch, while the 1468-cm^{-1} band is largely due to a C–H bending mode (scissor).

Note that in the deuterated compound (see Table III) the shift of the 1468-cm^{-1} band to 943 cm^{-1} is the basis of its assignment as a CH$_2$ (CD$_2$) scissor, whereas the shift of the C=C stretch to *higher* frequency (1363 cm^{-1}) is consistent with it being coupled in the protonated compound.

Interestingly, with increasing pressure (in either CsCl or nujol) a new band appears at ca. 1270 cm^{-1}, grows in intensity, and shifts slightly to lower wavenumber (Figure 4). Vibrational modes associated with the bridging hydrogen ligands have been located in this region (e.g., ν(Os–H–Os) (sym) at 1302 (w) and 1288 (vw) cm^{-1} for **3**). These bands are broad and weak at room temperature but sharpen and grow dramatically at lower temperatures.[2c]
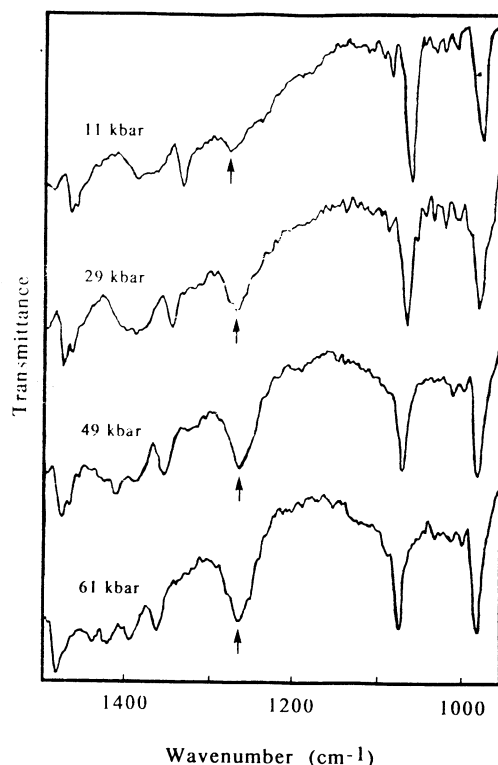
However, we do not think that the new band is directly due to a bridging hydrogen mode for the following reasons: (a) the observed location of the new band is appreciably different from the location of the hydride modes for **3** and its pressure shift is in the wrong direction for a fundamental stretching frequency; and (b) similar effects have not been observed for compounds **2** and **4**, which also contain bridging hydrogen ligands. We suggest that this new band is a combination mode involving the CH$_2$ wagging motion at 959 cm^{-1} and a symmetric osmium–methylenic carbon stretch at 311 cm^{-1}.[2c,2d] The pressure-induced growth of new vibrational bands have been observed to occur at the expense of other peak(s),[9] but we see no appreciable loss of intensity in any of the C–H modes in this region. However, the Os–H–Os (sym) stretching mode involves an appropriate motion to couple with the combined CH$_2$ bend/Os–CH$_2$ stretch (959 and 311 cm^{-1}, respectively). Although the bridging hydrogen modes appear weak at room temperature, they contain appreciable intensity and therefore may serve as the source of intensity borrowing for the growth of the 1270-cm^{-1} band.

With respect to percent changes, once again the order between ν(C–H) and ν(CC) is reversed from the $d\nu/dP$ trends, with $\Delta\nu/\nu_0$ for ν(CC) = 2.6% while that of ν(C–H) is 1.7%. These values are still larger than those for δ or γ(C–H), as $\Delta\nu/\nu_0$ = 1.43% (average).

Finally, it should be noted for this cluster that bands attributed to CH$_2$ bending motions shift with a range of values, depending on the nature of the vibration. The out-of-plane antisymmetric CH$_2$ band (γ(CH$_2$), twist) shifts at the largest rate of these bends, +0.32 cm^{-1}/kbar, followed by the symmetric and antisymmetric in-plane CH$_2$ bends (δ(CH$_2$), rock and scissor, respectively) each shifting to higher energy at a rate of +0.23 cm^{-1}/kbar. The out-of-plane symmetric CH$_2$ bend (γ(CH$_2$), wag) at 959 cm^{-1} shifts only slightly to higher energy with increasing pressure at a rate of +0.08 cm^{-1}/kbar.

$H_3Os_3(CO)_9(\mu_3$-CCH$_3$) (**4**). The ethylidyne ligand contained in this cluster is now the paradigm for connections between hy-

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TABLE IV: Infrared Data for the Hydrocarbon Ligand Vibrations of $H_3Os_3(CO)_9(\mu_3\text{-}CCH_3)$ (4)

	$H_3Os_3(CO)_9(CCH_3)$			$D_3Os_3(CO)_9(CCD_3)$	
vibration	ν_0,[a] cm⁻¹	$d\nu/dP$,[b] cm⁻¹/kbar	$\Delta\nu/\nu_0$[c]	ν_0[a] cm⁻¹	$\nu(H)/\nu(D)$
$\nu(C\text{-}H)$ (asym)[d]	2918 m	+0.73	+2.05	2182 m	1.34
$\nu(C\text{-}H)$ (sym)[d]	2894 m	+0.97	+2.80		
$\delta(CH_3)$ (asym)[d]	1438 m			1028 w	1.40
$\delta(CH_3)$ (sym)[d]	1361 m			1002 w	1.36
$\nu(C\text{-}C)$	1147 m	+0.43	+3.30	1169 m	0.98
$\rho(CH_3)$[d]	1037 w	+0.30	+2.02	848 s	1.22
overtones	2701 w	+0.46	+1.07		
	2833 w	+0.72	+1.48		
	2863 w	+0.71	+1.53		

[a] Bands recorded at atmospheric pressure in KBr. [b] Pressure shifts observed in nujol. [c] Percent change in ca. 60 kbar. [d] $\rho(CH_3)$ is a methyl rocking motion parallel to the Os_3 plane. The designations (sym) and (asym) refer to the nature of $\nu(C\text{-}H)$ or $\delta(C\text{-}H)$ relative to the C_3 axis.
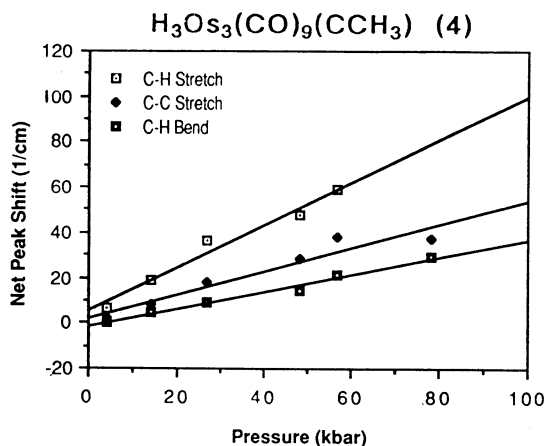
Figure 5. Pressure dependencies of selected hydrocarbon ligand vibrations for $H_3Os_3(CO)_9(\mu_3\text{-}CCH_3)$ (4).

drocarbon moieties on clusters and on surfaces due in large part to the seminal work of Sheppard and co-workers on the compound $Co_3(CO)_9(CCH_3)$.[2a,3] Infrared data for the triosmium compound **4** have been reported previously by Evans and McNulty.[2e] Our measurements for **4**, along with values for the previously unreported deuterated analogue $D_3Os_3(CO)_9(CCD_3)$, are given in Table IV. Attention for this cluster centers on the vibrations observed at 1147 and 1037 cm⁻¹, as assignment of these modes for the osmium ethylidyne cluster have been made in analogy with the cobalt case.[2e] The fact that the 1037-cm⁻¹ band is substantially affected by deuteration (shifted to 848 cm⁻¹; Table IV) while the 1147-cm⁻¹ band is perturbed only slightly (shifted to *higher* frequency, 1169 cm⁻¹) supports the assignment that the lower energy absorption is a methyl rocking mode ($\rho(CH_3)$) and the higher energy band is $\nu(CC)$.

The effect of increasing pressure on the infrared spectrum of the ethylidyne cluster $H_3Os_3(CO)_9(\mu_3\text{-}CCH_3)$ is shown in Figure 5 and Table IV. Once again, the vibrations follow the order $\nu(C\text{-}H) > \nu(C\text{-}C) > \delta(C\text{-}H)$ or $\gamma(C\text{-}H)$ in terms of their absolute rate of shift ($d\nu/dP$) to higher energy with increasing pressure. The stretching vibrations $\nu(C\text{-}H)$ (sym) and $\nu(C\text{-}H)$ (antisym) shift with the largest rates. With regard to percent changes, $\Delta\nu/\nu_0$ of $\nu(CC)$ is greater than that of $\nu(C\text{-}H)$, 3.3% vs 2.4% (average), in the pressure range studied.

The differing pressure behavior of the vibrations assigned as $\nu(CC)$ and $\rho(CH_3)$ (sym, rock) is a point worth elaborating here. In our experiments, the 1147-cm⁻¹ band is observed to shift to higher wavenumbers at a greater rate (+0.42 cm⁻¹/kbar) than the 1037-cm⁻¹ band (+0.36 cm⁻¹/kbar). Thus, the correlation observed throughout this work, that $d\nu/dP$ of C–H stretching modes is greater than that of C–H bending modes, is in this instance reflected in the observation of a larger pressure shift for

TABLE V: $\nu(CC)$ and $d(C\text{-}C)$ for 1-4 at Atmospheric Pressure and the Corresponding Value of $d\nu/dP$

cluster	ν_0, cm⁻¹	$d\nu/dP$,[a] cm⁻¹/kbar	$d(C\text{-}C)$, Å
$HOs_3(CO)_9(\mu_3,\eta^2\text{-}CCH)$	1538	+0.81	1.315[b]
$H_2Os_3(CO)_9(\mu_3,\eta^2\text{-}CCH_2)$	1329	+0.64	1.384[c]
$Os_3(CO)_{10}(\mu_3,\eta^2\text{-}C_2H_2)$	1297	+0.49	1.439[d]
$H_3Os_3(CO)_9(\mu_3\text{-}CCH_3)$	1150	+0.43	1.511[e]

[a] Pressure shifts recorded in nujol. [b] Value for $HRu_3(CO)_9(\mu_3,\eta^2\text{-}CCR)$ (R = *tert*-butyl) (ref 10); a value for $HOs_3(CO)_9(\mu_3,\eta^2\text{-}CCCF_3)$ also lies within this trend $d(C\text{-}C) = 1.331$ Å (ref 11). [c] Reference 12. [d] Value for $Os_3(CO)_{10}(\mu_3,\eta^2\text{-}C_2Ph_2)$ (ref 13). [e] Value for $H_3Ru_3(CO)_9(\mu_3\text{-}CCH_3)$ (ref 14).

a C–C stretching mode than for a C–C bending mode.

For the remaining vibrations, the importance of examining their pressure shifts in terms of fractional changes can be seen. Bands at 2701, 2833, and 2863 cm⁻¹, assigned by Evans and McNulty[2e] as overtones of $\delta(C\text{-}H)$ bands at 1438 and 1361 cm⁻¹, all shift significantly to higher wavenumbers with increasing pressure at rates of +0.46, +0.72, and +0.71 cm⁻¹/kbar, respectively. Although the absolute magnitude(s) of these rates are greater than those of $\nu(CC)$, in terms of percent change ($\Delta\nu/\nu_0$) they are far less, since $\Delta\nu/\nu_0$ for $\nu(CC)$ = 3.3% while that for the overtones is 1.36% (average in ca. 60 kbar).

Discussion

From an examination of the pressure effects on the hydrocarbon ligand vibrations of clusters **1-4**, several trends may be noted. The first involves the relative ordering of the pressure dependencies within a cluster in terms of $d\nu/dP$. Typically, $d\nu/dP$ of $\nu(C\text{-}H)$ is greater than that of $\nu(CC)$, which is then followed by $\delta(C\text{-}H)$ or $\gamma(C\text{-}H)$. However, consideration of these shifts in terms of percent change ($\Delta\nu/\nu_0$) for a vibration in a given pressure range leads to the conclusion that $\nu(CC)$ is greater than $\nu(C\text{-}H)$ for three out of the four clusters (**2, 3,** and **4**). These trends are useful in providing support for spectroscopic assignments.

Another interesting trend derived from these studies is the correlation between $d\nu/dP$ of the C–C stretch with other properties of the C_2 fragment. Table V lists values of $\nu(CC)$ at atmospheric pressure for **1-4** as well as C–C bond lengths. A greater value of $d\nu/dP$ is associated with a shorter $d(CC)$ and a larger value of $\nu(CC)$. Thus the shape of the potential well of the C–C stretching mode appears to be quite sensitive to the external perturbation of pressure.

In summary, we have shown that the effect of high pressure on the infrared spectra of a set of organotriosmium clusters reveals distinct trends based on the type of vibrational mode for the C_2 hydrocarbon ligands. The observed trends provide useful information with regard to vibrational assignment. This is particularly applicable in distinguishing modes appearing in energetically similar regions of the spectrum, e.g., in separating C–C stretching modes from C–H bending vibrations. The pressure shift as a tool is clearly complementary to the use of deuterium substitution. However, given the time required to obtain clean samples of fully deuterated compounds, the pressure-tuning approach may have some general utility.

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