[Os₂(CO)₈(μ_2-η^1,η^1-propene)] and Related Complexes as Vibrational Models for Alkenes Chemisorbed on Single-Crystal Metal Surfaces

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Abstract: The FTIR spectra of [Os₂(CO)₈(μ_2-η^1,η^1-C₂H₃CH₃)] and of its methyl-d_3 and d_6 isotopologues have been measured and assigned. Comparison of these vibrational data with previously published EELS and RAIRS studies of propene chemisorbed on Pt(111) and Ni(111) at low temperatures indicates that, on these surfaces, the propene species are chemisorbed *via* a (μ_2-η^1,η^1-C₂H₃CH₃) bonding mode. However, differences in the intensity patterns between the spectra of the adsorbed species compared with that of the model compound imply additional twisting or tilting with respect to the surface. Assignment of the FTIR spectra of the corresponding 1-butene and *trans*-2-butene complexes [Os₂(CO)₈(μ_2-η^1,η^1-C₂H₃C₂H₅)] and [Os₂(CO)₈(μ_2-η^1,η^1-CH₃C₂H₂CH₃)] indicates similar bonding modes for chemisorbed 1-butene and *trans*-2-butene on Pt(111). Infrared data for the mononuclear propene complex [Os(CO)₄(η^2-C₂H₃CH₃)], on the other hand, are in good agreement with published EEL data for propene on Ru(0001) and Rh(111), indicating that at low temperatures on these surfaces, propene is chemisorbed as a methyl-substituted "metallacyclopropane-like" species. These bonding modes are analogous to those established for low-temperature ethene chemisorption on these surfaces.

Introduction

There is now a very large number of papers in the literature describing the electron energy loss spectroscopy (EELS) or reflection-absorption infrared spectroscopy (RAIRS) of ethene chemisorbed on metal single-crystal surfaces.[1] In the large majority of cases, chemisorption at low temperatures (*T* < 200 K) was found to be nondissociative, without the breaking of any of the original C−C or C−H bonds. At these temperatures, the published EEL spectra have been grouped into three basic types, designated[1] Types I, I′, and II.

The structural identification of these surface species has been greatly facilitated by the comparison of the surface spectra with vibrational data from ethene ligands of known structures coordinated to metal complexes and clusters. For example, comparison of Type II EEL spectra with the vibrational spectra[2] of Zeise's salt, K[(η^2-C₂H₄)PtCl₃], and its deuteriologue led to the identification of ethene chemisorbed as a π-complex to a single metal atom, either on metal single-crystal surfaces[3a,b] or on finely divided metal catalysts.[3c,d] Similarly, we[4] have used the vibrational spectra of the bridging ethene complex [Os₂(CO)₈-(μ_2-η^1,η^1-C₂H₄)] (**1**) and its isotopologues to support the "1,2-

di-σ" or (μ_2-η^1,η^1-C₂H₄) structure that had been proposed[5,6] to give rise to Type I EEL spectra, such as those from the Pt(111) and Ni(111) surfaces. In this case, however, reasonable wavenumber agreements were accompanied by differences in intensity patterns between the spectrum of the model compound **1** and those of the surface species. These differences were considered to arise probably from more substantially twisted skeletal conformations for the adsorbed species. An alternative explanation of these differences has emerged from a recent diffuse LEED study of ethene on Pt(111) by Döll et al.,[7] which suggests that the "1,2-di-σ" species is bonded over a 3-fold site. In this structure, one of the PtC σ-bonds is proposed to be attached to a bridging Pt₂ site, leading to a modified bonding pattern with a C−C bond that is substantially tilted with respect to the surface. Such a less-symmetrical site would contribute to the high proportion of features with largely impact-scattering character in the EEL spectrum of ethene on Pt(111).[5b] We note, however, that a twisted "1,2-di-σ" structure was not one of the possible structures tested by Döll *et al.*; to avoid underdetermination in their analysis, only structures with mirror symmetry were considered.[7]

More recently, we[8] have assigned the vibrational spectra of the osmacyclopropane complex [Os(CO)₄(η^2-C₂H₄)] (**2**) and shown that at least some Type I′ EEL spectra, typified by those from the Ru(0001) and Rh(111) surfaces, may result from ethene chemisorbed as a metallocyclopropane species on the surface.

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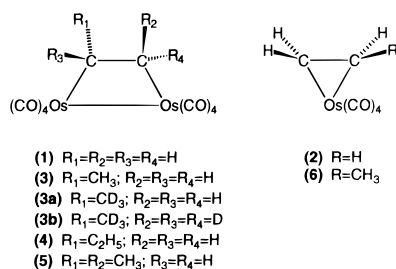(5) (a) Ibach, H.; Lehwald, S. *J. Vac. Sci. Technol.* **1978**, *15*, 407. (b) Steininger, H.; Ibach, H.; Lehwald, S. *Surf. Sci.* **1982**, *117*, 685.
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Scheme 1

(1) R$_1$=R$_2$=R$_3$=R$_4$=H
(3) R$_1$=CH$_3$; R$_2$=R$_3$=R$_4$=H
(3a) R$_1$=CD$_3$; R$_2$=R$_3$=R$_4$=H
(3b) R$_1$=CD$_3$; R$_2$=R$_3$=R$_4$=D
(4) R$_1$=C$_2$H$_5$; R$_2$=R$_3$=R$_4$=H
(5) R$_1$=R$_2$=CH$_3$; R$_3$=R$_4$=H

(2) R=H
(6) R=CH$_3$

There have been far fewer reports of EELS data for chemisorbed higher alkenes, presumably as a consequence of the lower resolution of EEL spectrometers compared to infrared spectroscopy. Avery and Sheppard[9,10] have measured EEL spectra for propene, 1-butene, *cis-* and *trans*-2-butene, 1-pentene, and 2-methylpropene (isobutene) on Pt(111) in the temperature range 170−220 K, and proposed a "1,2-di-σ" or (μ_2-η^1,η^1-C$_2$H$_3$R) bonding mode. Somorjai *et al.*[11] measured the EEL spectra of propene on Pt(111) and Rh(111) at 100 K and found the two spectra to be rather dissimilar; this was taken to indicate "different degrees of rehybridization and possibly different bonding sites" on the two surfaces. Sakakini *et al.*[12] have obtained the EEL spectrum of propene on Ru(0001) and found it to resemble that from Rh(111). Recently, Raval has measured the RAIR spectra of propene on Pt(111)[13] and Ni(111).[14] The ν(CH) modes of propene on Pt(111) have also been studied by Cremer *et al.*[15] using sum frequency generation spectroscopy.

Following our rather successful use of vibrational data from ethene-osmium complexes to determine the natures of the different bonding modes of ethene chemisorbed on Pt(111) and Rh(111), it was decided to extend the study to propene and butene complexes to determine whether the higher alkenes are chemisorbed on metal surfaces with bonding modes similar to those for ethene. To this end, the infrared spectra of the binuclear propene complex [Os$_2$(CO)$_8$(μ_2-η^1,η^1-C$_2$H$_3$CH$_3$)][16] (3), its (3,3,3-d_3) and (d_6) deuterium-substituted isotopologues (3a and 3b), the analogous 1-butene and *trans*-2-butene complexes[16] (4 and 5), and the osmamethylcyclopropane complex [Os(CO)$_4$(η^2-C$_2$H$_3$CH$_3$)][16] (6) (Scheme 1) have been measured, and the vibrational modes of the alkene ligands have been assigned. The *cis*-2-butene and 2-methylpropene (isobutene) complexes proved insufficiently stable for shipping from Colorado to Norwich, and so were unfortunately not available for study. With recent increases in sensitivity for RAIR spectrometers and improvements in resolution for EEL spectrometers, it is to be anticipated that further vibrational studies on the chemisorption of these more complex organic molecules may be forthcoming; the interpretation of such studies may be facilitated by the assignments of the vibrational spectra presented in this paper.

Results and Discussion

(a) Assignment of Spectra of the Complexes. The infrared spectra of the bridging propene complex 3, as well as its partially

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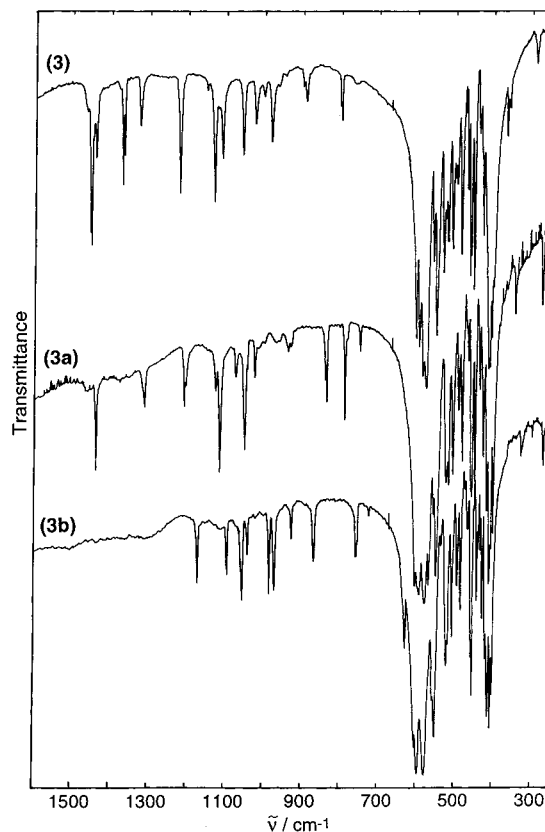

Figure 1. IR spectra (CsBr disks, 100 K) of [Os$_2$(CO)$_8$(C$_2$H$_3$CH$_3$)] (3), [Os$_2$(CO)$_8$(C$_2$H$_3$CD$_3$)] (3a), and [Os$_2$(CO)$_8$(C$_2$D$_3$CD$_3$)] (3b)
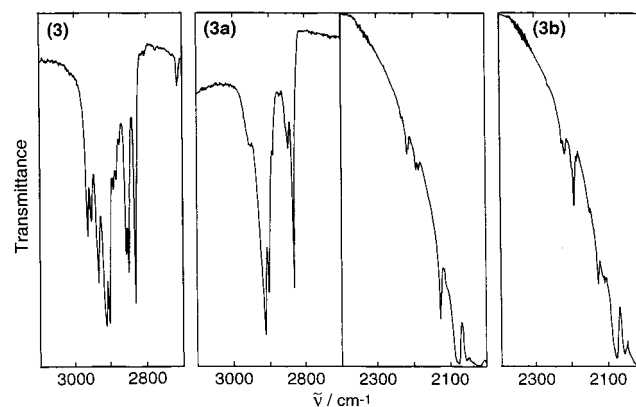
Figure 2. IR Spectra (CsBr disks, 100 K) of [Os$_2$(CO)$_8$(C$_2$H$_3$CH$_3$)] (3), [Os$_2$(CO)$_8$(C$_2$H$_3$CD$_3$)] (3a), and [Os$_2$(CO)$_8$(C$_2$D$_3$CD$_3$)] (3b). Because the ν(CD) modes occur on a highly sloping baseline resulting from the very intense ν(CO) absorptions, the 2400−2000 cm^{-1} regions are plotted with a different transmittance scale to that for the 3100−2700 cm^{-1} regions.

and fully deuterium-substituted isotopologues 3a and 3b, are shown in Figures 1 and 2. The propene ligand in complex 3 has no symmetry and is vibrationally complex, and the assignment of the spectra was only made possible by the availability of the three isotopologues; reference to our assignment[4] for 1 was also helpful. Comparison of the spectra of 3 and 3a clearly identified the vibrational modes associated with the methyl group. In general, these modes seem fairly well vibrationally localized; the H/D ratios are typical for a methyl group, with the rocks showing lower ratios than the other deuterium-sensitive modes.

Careful study of the deuteration shifts of the remaining bands in the 1500−600 cm^{-1} region allowed assignment of the modes of the metal-bound H$_2$CCH moiety. Comparison of the three spectra enables the two ν(OsC) modes to be picked out from

[Os₂(CO)₈(μ₂-η¹,η¹-propene)] and Related Complexes

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Table 1. Vibrational Assignments for **3**, **3a**, and **3b**[a,b]

mode	3	3a	H/D	3b	H/D (rel. to 3)
$\nu_{as}(CH_3)$	2964/2953 m	2218/2214 mw	1.34	2223/2216 mw	1.33
$\nu_s(CH_3)/2\delta_{as}(CH_3)$	2932 ms	2193/2186 w	1.34	2195 vw	1.34
$\nu_{as}(CH_2)$	2911 s	2913 s	1.00	2190 m	1.33
$\nu(CH)$	2902 s	2902 ms	1.00	2183 w	1.33
$2\delta_{as}(CH_3)$ (E)	2890/2883 vw	n.o.		n.o.	
$2\delta(CH_2)$	2854 m	2848 mw	1.00	n.o.	
$2\delta_{as}(CH_3)/\nu_s(CH_3)$	2848 ms	2109 vw	1.35	2108 vw	1.35
$\nu_s(CH_2)$	2832 s	2832 ms	1.00	2150 w	1.32
$\delta_{as}(CH_3) + \delta_s(CH_3)$	2806 vw	n.o.		n.o.	
$2\delta_s(CH_3)$	2715 w	n.o.		n.o.	
$\delta_{as}(CH_3)$	1454/1452 s	1052/1050 s	1.38	1057/1052 s	1.38
$\delta(CH_2)$	1439 m	1439 ms	1.00	1094/1092 m	1.32
$\delta_s(CH_3)$	1370/1366 m	1026 mw$	1.33	1040/1038 m$	1.32
$\delta(CH)$	1326 mw	1318/1313 mw	1.01	981 s	1.35
$\omega(CH_2)$	1223 ms	1210/1207 mw	1.01	970/967 s	1.26
$\gamma(CH)$	1131 ms	1116 ms	0.98	866 m	1.31
$\nu(C-CH_3)$	1110 m	1128 mw$	0.98	1168 ms$	0.95
$\tau(CH_2)$	1057 mw	1075 mw$	0.95	752 w,sh*	1.41
$\rho(CH_3)$	1022 m*	842/839 m	1.26	756/754 m*	1.35
$\rho(CH_3)$	982 m*	792 m*	1.24	721 mw*	1.36
$\nu(CC)$	901/893 w*	940 w*	0.96	924 m*	0.97
$\rho(CH_2)$	803/800 w	752 w*	1.07	627 m	1.28
$\nu_{as}(OsC)$	528 s	523 s	1.01	520 s	1.02
$\nu_s(OsC)$	459 s	456 ms	1.01	438 ms	1.05
$\delta(Os_2C_2)$	363/357 mw	343 m	1.05	321 mw	1.12
$\delta(CCC)$	289 w	271 m	1.07	264 m	1.09

[a] All measurements in cm^{-1}. s, strong; m, medium; w, weak; v, very; sh, shoulder. [b] $, *: − groups of strongly coupled modes.
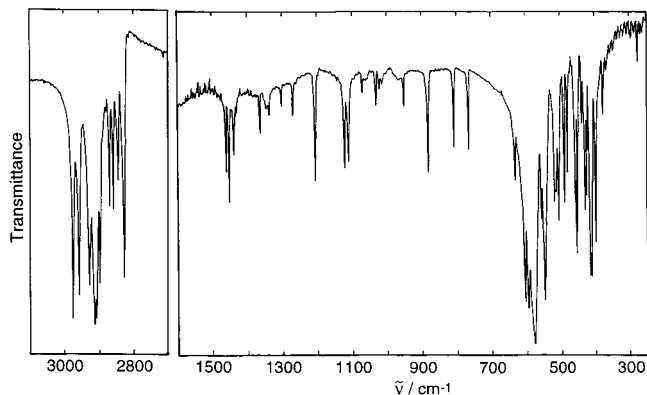

Figure 3. IR spectrum (CsBr disk, 100 K) of [Os₂(CO)₈(C₂H₃CH₂-CH₃)] (**4**). For clarity, the ν(CH) region is plotted with an expanded transmittance scale.

Figure 4. IR spectrum (CsBr disk, 100 K) of [Os₂(CO)₈(*trans*-CH₃C₂H₂CH₃)] (**5**). For clarity, the ν(CH) region is plotted with an expanded transmittance scale.

among the multiple bands in the 600−400 cm^{-1} region associated with the carbonyl ligands; these two modes (at 528 and 459 cm^{-1} in **3**) occur at similar but slightly lower wavenumbers than for **1**, as might be expected. The two low-wavenumber modes, at 363/357 and 289 cm^{-1} in **3**, are assigned to the in-plane ring deformation and the C−C−C angle-bending modes, respectively; the former band shows greater sensitivity to deuteration at the coordinated carbons, the latter to deuteration of the methyl group. Overall, despite the lack of molecular symmetry, and the consequent coupling of the vibrational modes, the assignment of the spectra of the three isotopologues seems rather satisfactory, and the assignments are listed in Table 1.

The infrared spectra of the 1-butene and *trans*-2-butene complexes **4** and **5** are shown in Figures 3 and 4, respectively, and the assignments are also reasonably straightforward. It was assumed that modes associated with the methyl groups in **3** and **5** will occur at similar wavenumbers, and a corresponding vibrational analogy holds between the Os₂C₂H₃ moieties in **3** and **4**. These assumptions are justified, in view of the lack of significant coupling between the methyl modes
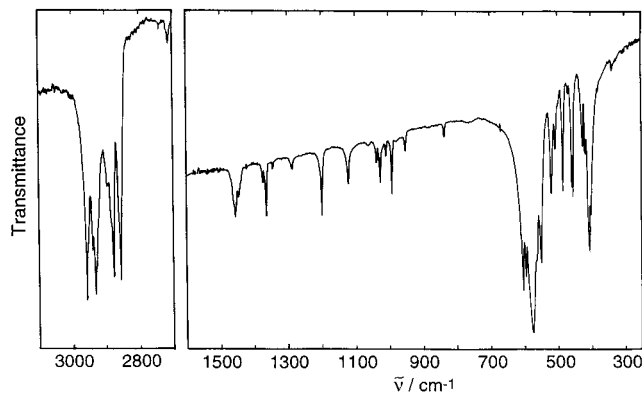
and those of the Os₂C₂H₃ unit seen in the spectra of **3** and **3a**. Care must be taken with the ν_{CC} modes, however, as these may show significant changes in wavenumber between **3**, **4**, and **5**, through coupling with CH₃ or CH₂ rocking modes. Comparison of the spectra of **1** and **3**−**5** again allows identification of the ν(OsC) modes; these are shifted in wavenumber relative to **3** as a result of coupling to additional δ(CCC) modes. However, assignment of the low-wavenumber modes is not problematic. The assignments for **4** and **5** are listed in Tables 2 and 3.

A vapor-phase infrared spectrum of the mononuclear propene complex **6** was obtained (Figure 5). The corresponding spectra of the deuterium-substituted isotopologues were not available. However, comparison with our assignment[8] of the spectrum of the ethene complex **2**, together with knowledge of the vibrational data of the methyl modes in **3** and **5**, allowed assignment of the spectrum of **6** with a reasonable degree of confidence, and particularly where the modes that are likely to dominate EEL or RAIR spectra are concerned.

(b) Comparison with Chemisorbed Propene on Pt(111) and Ni(111). The vibrational assignment for **3** is compared with

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Table 2. Vibrational Assignment for **4** and Comparison with EELS Data[9] for 1-Butene Chemisorbed on Pt(111) at 170 K

mode	4	1-butene/Pt(111) at 170 K EELS data (ref 9)
$\nu_{as}(CH_3)$	2974/2957 s	
$\nu_{as}(CH_2)$ (ethyl CH_2)	2928 ms	
$\nu_s(CH_2)$ (ethyl CH_2)	2915 m,sh	
$\nu_s(CH_3)/2\delta_{as}(CH_3)$ (A_1)	2912 s	2950 m, br
$\nu_{as}(CH_2)$	2907 s	
$\nu(CH)$	2898 ms	
$2\delta_{as}(CH_3)$ (E)	2889/2882 vw	
$2\delta_{as}(CH_3)$ $(A_1)/\nu_s(CH_3)$	2870 m	
$2\delta(CH_2)$ (ethyl CH_2)	2859 m	
$2\delta(CH_2)$	2845 mw	
$\nu_s(CH_2)$	2827 s	
$\delta_{as}(CH_3)$	1461/1452 ms	1465 mw
$\delta(CH_2)$	1439 m	
$\delta(CH_2)$ (ethyl CH_2)	1431 w	
$\delta_s(CH_3)$	1363 m	1385 s
$\delta(CH)$	1338 w	
$\omega(CH_2)$ (ethyl CH_2)	1302 w	1280 w
$\tau(CH_2)$ (ethyl CH_2)	1270 mw	
$\omega(CH_2)$	1206 s	
$\gamma(CH)$	1122 s	1120 ms
$\nu(C\text{-}CH_3)$	1111 ms	1120 ms
$\tau(CH_2)$	1070 w	1055 m
$\rho(CH_3)$	1031 mw	
$\rho(CH_3)$	1023 w	
$\nu(CC)$	952 m	955 s
$\nu(CC)$	883 s	870 ms
$\rho(CH_2)$	808 s	790 m
$\rho(CH_2)$ (ethyl CH_2)	766 s	730 w
$\nu_{as}(OsC)$	630 ms	630 m
$\nu_s(OsC)$	490 mw	525 s
$\delta(C\text{-}C\text{-}CH_3)$	429ms	
$\delta(Os_2C_2)$	374 m	
$\delta(CCC)$	272 mw	250 m

Table 3. Vibrational Assignment for **5** and Comparison with EELS Data[10] for *trans*-2-Butene Chemisorbed on Pt(111) at 170 K

mode [and symmetry under C_2]	5	*trans*-2-butene/Pt(111) at 170 K EELS Data (ref 10)
$\nu_{as}(CH_3)$ $[a + a + b + b]$	2955 m	2960 sh
$\nu_s(CH_3)/2\delta_{as}(CH_3)$	2937 mw	
$\nu_{as}(CH_3)$ $[b]$	2929 m	
$2\delta_{as}(CH_3)$	2920, 2892 vw	2900 m, br
$\nu_s(CH)$ $[a]$	2876 m	
$2\delta_{as}(CH_3)/\nu_s(CH_3)$	2855 m	
$\delta_{as}(CH_3) + \delta_s(CH_3)$	2806 vw	
$2\delta_s(CH_3)$	2739,2709 w	
$\delta_{as}(CH_3)$ $[a + a + b + b]$	1459, 1456, 1453, 1444 ms	1445 m
$\delta_s(CH_3)$ $[b]$	1372 m	
$\delta_s(CH_3)$ $[a]$	1363 ms	1365 mw
$\delta(CH)$ $[a]$	1343 w	
$\delta(CH)$ $[b]$	1286 m	
$\gamma(CH)$ $[b]$	1198 vs	
$\gamma(CH)$ $[a]$	1121 ms	1125 m
$\nu(C\text{-}CH_3)$ $[a]$	1038 m	1040 s
$\rho(CH_3)$ $[b]$	1026 ms	
$\rho(CH_3)$ $[a]$	1009 m	ca. 1000 sh
$\rho(CH_3)$ $[b]$	993 s	
$\rho(CH_3)$ $[a]$	980 vw	
$\nu(C\text{-}CH_3)$ $[b]$	952 m	
$\nu(CC)$ $[a]$	837 m	840 s
$\nu_{as}(OsC)$ $[b]$	585 m,sh	
$\nu_s(OsC)$ $[a]$	518 ms	540 s
$\delta(CCC)$ $[a]$	380 mw	375 s
$\delta(Os_2C_2)$ $[b]$	339 mw	

the EEL data[9] for propene on Pt(111) and RAIR data[13,14] for propene on Pt(111) and Ni(111) in Table 4. The weak peak at ca. 710 cm^{-1} in the EEL spectrum[9] of propene on Pt-
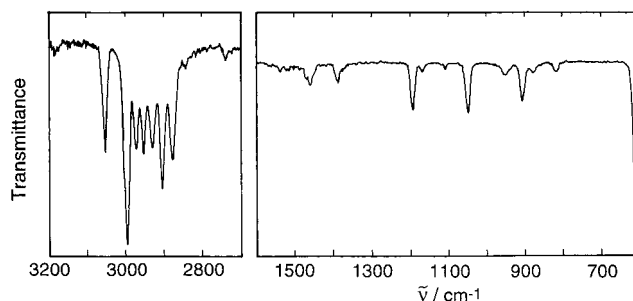
Figure 5. Vapor-phase IR spectrum of $[Os(CO)_4(C_2H_3CH_3)]$ (**5**). For clarity, the $\nu(CH)$ region is plotted with an expanded transmittance scale.

(111) has no counterpart in the spectrum of **3**, and may result from a different minority species on the surface.

When comparing relative intensities between the spectrum of **3** and the surface spectra, consideration must be taken of the metal-surface selection rule[17] (MSSR). Although for a surface species with no formal symmetry all modes are allowed under the MSSR, it is the component of the dipole-moment change normal to the surface that determines the intensities of the observed bands in EELS or RAIRS spectra. Account must therefore be taken of the anticipated angle between the surface normal and the dipole associated with each of the modes.

In the structure of **1**[18] the Os_2C_2 ring is twisted such that the molecular symmetry is reduced from C_{2v} to C_2; the OsCCOs torsional angle is close to 20°. A consequence of this twist is that in **1**, the four hydrogens can be divided into two pairs, with the two members of each pair (one on each of the carbons) related by the molecular C_2 symmetry. One pair of hydrogens lie with their C−H vectors projecting out from, and nearly perpendicular to, the molecular 2-fold axis, while the other pair have their C−H vectors pointing "upward" and closely coparallel to the 2-fold axis. Although we do not have crystallographic structural data for **3**, **4**, and **5**, analysis of the NMR *J*-couplings indicates that the methyl and ethyl substituents replace one of the latter pair of hydrogens (i.e. those with C−H closely coparallel to the 2-fold axis) and are enough to "lock" the conformation. $[Os_2(CO)_8(\mu_2\text{-}\eta^1,\eta^1\text{-}C_2H_3CH_3)]$ (**3**) and $[Os_2(CO)_8(\mu_2\text{-}\eta^1,\eta^1\text{-}C_2H_3C_2H_5)]$ (**4**) have ^3J values of $^3J_{cis} = 7.6(2)$ Hz and $^3J_{trans} = 13.2(2)$ Hz and $^3J_{cis} = 7.4(2)$ Hz and $^3J_{trans} = 12.6(2)$ Hz, respectively. The vicinal coupling constant in the *trans*-2-butene complex **5** has $^3J_{trans} = 12.2(8)$ Hz. The structures of the complexes are depicted in Scheme 1. The crystallographically determined structures of the methyl acrylate[19] and dimethyl fumarate[19b] analogues of **1**, which have a twisted structure like that of the parent complex, similarly show the ester substituents replacing the latter (coparallel) type of hydrogens, occupying the sterically less demanding sites displaced away from the "surface" represented by the osmium atoms and six of their carbonyl ligands. It is therefore likely that if a $(\mu_2\text{-}\eta^1,\eta^1\text{-}C_2H_3R)$ surface species also has such a twisted structure, the alkyl substituent will be oriented so that the C−R bond is directed well away from the surface, rather than parallel to it, and that the complexes **3**, **4**, and **5** will be good models for such a species. In summary, then, a good match between vibrational

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[Os₂(CO)₈(μ₂-η¹,η¹-propene)] and Related Complexes

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Table 4. Comparison of Vibrational Assignment for **3** with EELS[9] and RAIRS[13,14] Data for Chemisorbed Propene on Pt(111) and Ni(111)

mode	3	propene/Pt(111) at 170 K EELS data (ref 9)	propene/Pt(111) at 90 K, 0.4 L RAIRS data (ref 13)	propene/Ni(111) at 110 K, 0.1 L RAIRS data (ref 14)
$\nu_{as}(CH_3)$	2964/2953 m			
$\nu_s(CH_3)/2\delta_{as}(CH_3)$	2932 ms		2916 ms	2906 s
$\nu_{as}(CH_2)$	2911 s	} 2925 br	2902 w	
$\nu(CH)$	2902 s		2883 m	
$2\delta(CH_2)$	2854 m			
$2\delta_{as}(CH_3)/\nu_s(CH_3)$	2848 ms		2859 mw	2860 mw
$\nu_s(CH_2)$	2832 s		2836 mw	
$\delta_{as}(CH_3)$	1454/1452 s			
$\delta(CH_2)$	1439 m	1440 m	1438 m	1445 w
$\delta_s(CH_3)$	1370/1366 m	n. res.	1370 mw	1353 w
$\delta(CH)$	1326 mw	1335 mw	1310 vw	
$\omega(CH_2)$	1223 ms	n. res.	1217 w	1164 vw
$\gamma(CH)$	1131 ms	} 1095 ms, sh	1130 vw	
$\nu(C-CH_3)$	1110 m		1088 ms	1142 w
$\tau(CH_2)$	1057 mw		1038 m	
$\rho(CH_3)$	1022 m		1015 s	1029 s
$\rho(CH_3)$	982 m			
$\nu(CC)$	901/893 w	880 s	862 s	871 m
$\rho(CH_2)$	803/800 w			
$\nu_{as}(OsC)$	528 s			
$\nu_s(OsC)$	459 s	455 s		
$\delta(Os_2C_2)$	363/357 mw	395 w, sh		
$\delta(CCC)$	289 w	*ca.* 250 mw		

data for the surface species and those for the model compounds must involve not only the wavenumbers of the vibrational modes but also the relative intensities of the bands after making suitable allowance for the MSSR, given the likely geometry of the surface species.

In general, there is good wavenumber agreement between the data[9,13] for the surface species on Pt(111) and the assignment for **3**. The relative intensities are also largely as might be expected (*vide supra*) for a surface species with a twisted structure to that described above for the model complex, taking into account the effects of the MSSR. The most pronounced difference between the spectrum of **3** and that of the surface species is the absence in the EEL spectrum[9] of a feature, other than some very weak and unresolved intensity between the 1335 and 1095 cm⁻¹ peaks, corresponding to the CH₂ wagging mode, which gives rise to a medium-strong band at 1223 cm⁻¹ in the spectrum of **3**. The situation has now been partially clarified by RAIR spectra[13] of low coverages (0.4−1.0 L) of propene on this surface, which show a weak but reproducible peak at 1217 cm⁻¹. The low intensity for $\omega(CH_2)$, and also for $\gamma(CH)$, in the EEL and RAIR spectra probably result in the propene species on Pt(111) having a more twisted structure than the model complex, such that the dipole moment vectors for these modes now subtend a rather larger angle to the surface normal. Similar conclusions were reached for ethene on Pt(111).[4] Consideration of the relative intensities of the symmetric and antisymmetric methyl modes (in particular those that should not be substantially coupled to other non-methyl modes) in the EEL and RAIR spectra (Table 4) suggests that the direction of the local C_3 axis of the methyl group is close to perpendicular to the surface, again indicating that the surface species shows a similar or greater twisting to that found in the metal complexes.

Similarly good agreements are obtained between the vibrational data for **4** and the EELS data for 1-butene on Pt(111)[10] (Table 2), and for **5** and the EELS data for *trans*-2-butene on Pt(111)[10] (Table 3). As was the case for propene, comparison with the data from the two model complexes leads to assignment of the EEL features to vibrational modes of the surface butene species that would be predicted to have significant EEL intensities if the surface species again have a twisted structure.

The consistency of the results over the three alkenes increases confidence in our vibrational assignments and structural model for the chemisorbed propene and butene species, and it is very likely that the 1,2-di-σ structure for ethene on Pt(111) is twisted to a similar extent.

The RAIR spectra[13,14] from propene on Pt(111) and on Ni(111) (Table 4) show a basic "family resemblance", although the relative intensities of the bands are somewhat different, and the 1038 cm⁻¹ band in the Pt(111) spectrum is either missing or coincident with and obscured by the dominant 1029 cm⁻¹ band in the Ni(111) spectrum. Consideration of the changes in relative intensities of the vibrational modes between the spectra, taking account of the MSSR, tends to suggest that the propene species on Ni(111) is flatter or less twisted than that on Pt(111), with the C−CH₃ bond vector subtending a larger angle to the surface normal. The metal−metal distance on Ni(111) is less than that for Pt(111), so that if the propene undergoes a similar degree of rehybridization to 1,2-di-σ as on Pt(111), then on geometrical grounds the propene might be expected to be more twisted, rather than less, on Ni(111).

The flatter geometry on the Ni(111) surface can be explained by a lower degree of rehybridization of the propene from sp² to sp³ on this surface, compared to Pt(111). This would also be consistent with higher wavenumbers for the $\nu(CC)$ and $\delta(CH_2)$ modes, and a lower value for $\omega(CH_2)$. The same pattern of differences in wavenumbers and relative intensities occurs in the spectra of the 1,2-di-σ surface species from ethene on the same surfaces.[1b]

We therefore conclude that for ethene and propene, and presumably for the higher alkenes, the same 1,2-di-σ bonding pattern occurs on both Ni(111) and Pt(111), but with a more complete rehybridization of the surface-bound carbon atoms from sp² to sp³ on the latter surface, with a concomitant increase in the degree of twisting within the connectivity of the 1,2-di-σ structure.

(c) Comparison with Chemisorbed Propene on Rh(111) and Ru(0001). The vibrational assignments for **6** and the EELS data for propene chemisorbed on Rh(111) at 100 K,[11] and on Ru(0001) at 153 K,[12] are compared in Table 5. If a (η^2-C₂H₃R) species on a metal surface has a geometry basically similar to

Table 5. Vibrational Assignment for **6** and Comparison with EELS Data[11,12] for Chemisorbed Propene

mode	6	propene/Rh(111) at 100 K EELS Data (ref 11)	propene/Ru(0001) at 153 K EELS Data (ref 12)
$\nu_{as}(CH_2)$	3051 m		
$\nu(CH)$	2997 s		
$\nu_s(CH_2)$	2971 m		
$\nu_{as}(CH_3)$	2952/2928 m	2960 s, br	2928 s
$\nu_s(CH_3)/2\delta_{as}(CH_3)$	2902 ms		
$2\delta_{as}(CH_3)/\nu_s(CH_3)$	2874 m		
$\delta(CH_2)$	1470 w, sh		
$\delta_{as}(CH_3)$	1457 m	1380–1460	1444 ms
$\delta_s(CH_3)$	1386 m		1383 m
$\nu(CC)$	1191 s	1200 m	1234 mw
$\delta(CH)$	1171 mw		
$\tau(CH_2)$	1106 vw		
$\omega(CH_2)$	1049 s	1050 m	1024 ms
$\rho(CH_3)$	954 mw		
$\gamma(CH)$	906 ms	925 s	932 m
$\nu(C-CH_3)$	876 w		
$\rho(CH_2)$	816 w		815 w

that of the alkene ligands in **2** and **6**, then under the MSSR[17] it is again necessary to take into account the anticipated angle between the surface normal and the dipole change associated with each of the modes. The CH_2 planes in **2** are bent away from the $Os(CO)_4$ unit; they each subtend an angle $\alpha/2$ of 32.5° to the plane perpendicular to the molecular 2-fold axis.[20] By analogy, the following modes of the propene surface species, $\nu_{as}(CH_3)$ (one component), $\delta_{as}(CH_3)$ (one component), $\nu(CC)$, $\omega(CH_2)$, $\rho(CH_3)$ (one component), and $\gamma(CH)$, are likely to subtend angles of less than ca. 35° between the vectors of their respective dipole moment changes and the surface normal; the intensities of the other modes will, to a greater or lesser extent, be attenuated by the MSSR. Taking this into account, inspection of Table 5 shows close agreement between the spectrum of **6** and the EEL spectra, strongly indicating that the chemisorbed propene forms a metallomethylcyclopropane species on these surfaces, a structure analogous to that established[8] for ethene.

Conclusions

The vibrational modes of the propene ligands in complexes **3** and **6** have been assigned. Comparison of these assignments with EELS data for propene chemisorbed at low temperature on Rh(111)[11] and Ru(0001)[12] indicates that the propene species on these surfaces can best be described as a methyl-substituted metallacyclopropane. This is consistent with the structure established[8] for ethene on the same surfaces.

In contrast, similar comparison with EELS and RAIRS data from Pt(111)[9,13] and Ni(111)[14] indicates that, on these surfaces, propene is chemisorbed as a 1,2-di-σ species, with a greater degree of rehybridization toward sp^2 on Pt(111). As a consequence of these rehybridizations, on Pt(111) the propene is skeletally twisted so that the methyl group is oriented nearly perpendicular to the surface, while on Ni(111) the propene is

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flatter with a lesser degree of twisting. Ethene on these two surfaces[4] is likely to show a similarly twisted 1,2-di-σ structure.

Experimental Section

FTIR spectra of **3**, **3a**, **3b**, **4**, and **5** were measured as CsBr disks with use of a Perkin-Elmer 1700 spectrometer equipped with a conventional liquid-nitrogen-cooled low-temperature cell. The vapor-phase infrared spectrum of **6** was measured with a Perkin-Elmer 983 spectrometer and a 10 cm path length gas cell with KCl windows.

Propene (CP grade, Phillips 66 Co.), *trans*-2-butene (Union Carbide, Linde Division), and 1-butene, (99+%, Aldrich Chemical) were used as received. Isotopically labeled gases, propene-d_6 (98% D, Cambridge Isotopes) and propene-3,3,3-d_3 (99% D, Cambridge Isotopes), were received in break-seal flasks and transferred to gas storage bulbs. Unused labeled gases were recollected after preparation of osmium complexes and checked by gas-phase IR.

The preparations of **3**, **5**, and **6** have been described elsewhere.[16] **3a** and **3b** were prepared by a similar method but on a smaller scale. $Os_3(CO)_{12}$ (50 mg, 0.056 mmol) was slurried in approximately 15 mL of freshly distilled CH_2Cl_2 in two heavy-walled vacuum bulbs of approximately 35 mL volume. Each bulb was thoroughly degassed and then the appropriately labeled propene (100 mL, 1 atm) was vacuum transferred into the bulb. The contents were thawed and photolyzed[16] for approximately 96 h to give clear, colorless solutions. The mononuclear and dinuclear products were separated chromatographically as previously described.[16]

The preparation of the 1-butene complex (μ-η^1,η^1-$CH_2CHCH_2CH_3$)-$Os_2(CO)_8$ (**4**) has not been previously described, and is given here. The 1-butene adduct was prepared in the same way as for the propene adduct **3**,[16] but because of the greater solubility and lower vapor pressure of 1-butene, the photoreaction was carried out at ambient pressure. A slurry of 300 mg of $Os_3(CO)_{12}$ in 250 mL of CH_2Cl_2 was freeze–pump–thaw degassed on a vacuum manifold, and 1-butene was introduced into the manifold to give a saturated solution at ambient pressure. The slurry was then stirred and irradiated[16] overnight to give a colorless solution. Workup identical to that described[16] for the propene adduct yielded approximately 50–70% yields of (μ-η^1,η^1-CH_2CHCH_2-CH_3)$Os_2(CO)_8$. IR (pentane) $\nu(CO)/cm^{-1}$ 2120 (vw), 2075 (s), 2036 (m), 2030 (vs), 2020 (m), 2008 (s), 1992 (m br). ^1H NMR (200 MHz, CD_2Cl_2, −20 °C): δ 0.78 t, 3H, $^3J_{HH}$ = 7.2 Hz (CH_3); δ 1.05 dd, 1H, $^3J_{trans}$ = 12.6 Hz, $^2J_{gem}$ = 9.7 Hz (HCH); δ 1.59 "quintet", 2H, $^3J_{HH}$ = 7.2(3) Hz, $^3J_{HH}$ = 6.8 Hz (ethyl CH_2); δ 1.74 m, 1H, $^3J_{trans}$ = 12.6 Hz, $^3J_{cis}$ = 7.4 Hz, $^3J_{HH}$ = 6.8 Hz (CH); δ 2.25 dd, 1H, $^3J_{HH}$ = 7.4 Hz, $^2J_{gem}$ = 9.7 Hz (HCH). The mononuclear 1-butene adduct (η^2-CH_2-$CHCH_2CH_3$)$Os(CO)_4$ was isolated by high-vacuum fractionation, but no yield was determined.

Concentrated solutions of the dinuclear products **3**, **3a**, **3b**, **4**, and **5** (each pure by solution IR) were syringed into 5 mL ampules attached to a vacuum manifold. The pentane solvent was removed under high vacuum, and each sample was then flame-sealed under approximately 1 atm of the appropriate alkene for transportation from Fort Collins to Norwich.