3058 *J. Am. Chem. Soc.* **1994,** *116,* 3058–3062

Assignments of the Infrared and Raman Spectra of the $Os_2(\mu_2\text{-}CHCH_3)$ Group of $[(\mu_2\text{-}CHCH_3)Os_2(CO)_8]$ and of Its d^1 and d^4 Isotopologues as Models for the Spectra of Such Ethylidene Groups on Metal Surfaces

Christopher E. Anson,[†] Norman Sheppard,[*,†] Donald B. Powell,[†] Jack R. Norton,[*,‡] Wolfgang Fischer,[‡] Richard L. Keiter,[‡,∇] Brian F. G. Johnson,[§] Jack Lewis,[∥] Ashok K. Bhattacharyya,[⊥] Selby A. R. Knox,[#] and Michael L. Turner[#]

Contribution from the School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K., Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, Department of Chemistry, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh EH9 3JJ, U.K., University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW, U.K., Department of Engineering, University of Warwick, Coventry CV4 7AL, U.K., and Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS, U.K.

Received August 25, 1993[⊗]

Abstract: Procedures are described for the preparation of the d^1 ($CDCH_3$) and d^4 isotopologues of $[(\mu_2\text{-}CHCH_3)Os_2(CO)_8]$ (**1**). Infrared and Raman spectra for the d^0, d^1, and d^4 molecules are analyzed, in comparison with those of CH_3CHCl_2 and its deuterium-containing species, in order to characterize the vibrational spectrum of an ethylidene group bonded to metal atoms. Taking into account the effects of the metal-surface selection rule for species adsorbed on metal surfaces, a comparison is made between the interpreted spectra of **1** and a number of vibrational spectra in the literature which may reflect the presence of ethylidene groups. These include electron energy loss spectra (EELS) near 300 K from ethene adsorbed on Pt(111) with coadsorbed potassium or oxygen, and a vibrational inelastic tunneling spectrum (IETS) obtained by hydrogen reduction of CO adsorbed on Rh/Al_2O_3. Taking into account the limited resolution of the EELS data, the spectra on Pt(111)/K and Pt(111)/O can reasonably be attributed to the ethylidene surface species. A more definitive structural assignment requires higher resolution spectra from the adsorbed species. The agreement between the infrared spectrum of **1** and the IETS spectrum on Rh/Al_2O_3 is particularly good.

Introduction

In recent years, the presence of an ethylidene surface species on metal surfaces, $(CH_3CH)M_2$ (M = metal atom), has been postulated several times in connection with the chemisorption or hydrogenation of ethene. The first suggestion for such a species was made by Ibach and Lehwald,[1] who concluded from vibrational electron energy loss spectroscopy (VEELS) that a methyl-containing species resulted from ethene chemisorption on Pt(111) at 320 K. It was subsequently shown that the species actually present was of the ethylidyne type, $(CH_3C)M_3$, rather than ethylidene.[2–4] However, ethylidene has since been postulated as an intermediate species in hydrogenation reactions of the ethylidyne[5] and in the conversion of di-σ-adsorbed ethene to ethylidyne.[6] It has not yet been spectroscopically characterized on a clean metal surface, but a spectrum at 300 K from Pt(111) with 0.12 monolayers of potassium has been tentatively assigned to the species.[7]

It has become increasingly clear, since the successful identification of the unexpected ethylidyne surface species,[3] that recognizable spectroscopic "fingerprints" of chemisorbed hydrocarbon groupings can be derived from the vibrational spectra of the same type of species present as a ligand on metal coordination or cluster compounds of known structures. The preparation[8] of the compound $[(\mu_2\text{-}CHCH_3)Os_2(CO)_8]$ (**1**) gave us the opportunity to provide such a vibrational spectroscopic characterization of the ethylidene ligand/surface complex. For purposes of achieving reliable vibrational assignments, it was necessary to measure the infrared and Raman spectra of **1** in its ($CHCH_3$), ($CDCH_3$), and ($CDCD_3$) isotopologues, designated below as (**1**-d^0), (**1**-d^1), and (**1**-d^4), respectively. To this end a small-scale synthetic route to these deuterium-containing molecules was developed.

For comparative purposes, we have also measured the infrared spectrum of $[(\mu_2\text{-}CHCH_3)Fe_2(CO)_6(\mu_2\text{-}Ph_2PCH_2PPh_2)]$ (**2**).[9] Although a considerable proportion of this spectrum is dominated by the absorptions from the $Ph_2PCH_2PPh_2$ ligand, most of those from the μ_2-$CHCH_3$ ligand could be identified through comparison with the spectrum of the structurally-related $[(\mu_2\text{-}CO)Fe_2(CO)_6(\mu_2\text{-}Ph_2PCH_2PPh_2)]$[9] helped by the use of low temperature to improve the spectral resolution.

Although neither **1** nor **2** has yet had its crystal structure determined, this has been carried out for *cis*-$[(\mu_2\text{-}CHCH_3)(\pi\text{-}C_5H_5)_2Fe_2(CO)_3]$,[10,11] giving for the ethylidene ligand a C–C

[†] University of East Anglia.

[‡] Colorado State University.

[§] University of Edinburgh.

[∥] University Chemical Laboratories, Cambridge, U.K.

[⊥] University of Warwick.

[#] The University of Bristol.

[∇] On leave from Eastern Illinois University.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1994.

(1) Ibach, H.; Lehwald, S. *J. Vac. Sci. Technol.* **1978,** *15,* 407.

(2) Kesmodel, L. L.; Dubois, L. H.; Somorjai, G. A. *J. Chem. Phys.* **1979,** *70,* 2180.

(3) Skinner, P.; Howard, M. W.; Oxton, I. A.; Kettle, S. F. A.; Powell, D. B.; Sheppard, N. *J. Chem. Soc., Faraday Trans. 2* **1981,** *77,* 1203.

(4) Steininger, H.; Ibach, H.; Lehwald, S., *Surf. Sci.* **1982,** *117,* 685.

(5) Zaera, F.; Somorjai, G. A. *J. Am. Chem. Soc.* **1984,** *106,* 2288.

(6) Zhou, X.-L.; Zhu, X.-Y.; White, J. M. *Surf. Sci.* **1988,** *193,* 387.

(7) Windham, R. G.; Koel, B. E. *J. Phys. Chem.* **1990,** *94,* 1489.

(8) Bullock, R. M.; Hembre, R. T.; Norton, J. R. *J. Am. Chem. Soc.* **1988,** *110,* 7868.

(9) Hogarth, G.; Knox, S. A. R.; Turner, M. L. *J. Chem. Soc., Chem. Commun.* **1990,** 145.

(10) Meyer, B. B.; Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1981,** *20,* 3024.

(11) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1983,** 1427.

0002-7863/94/1516-3058$04.50/0

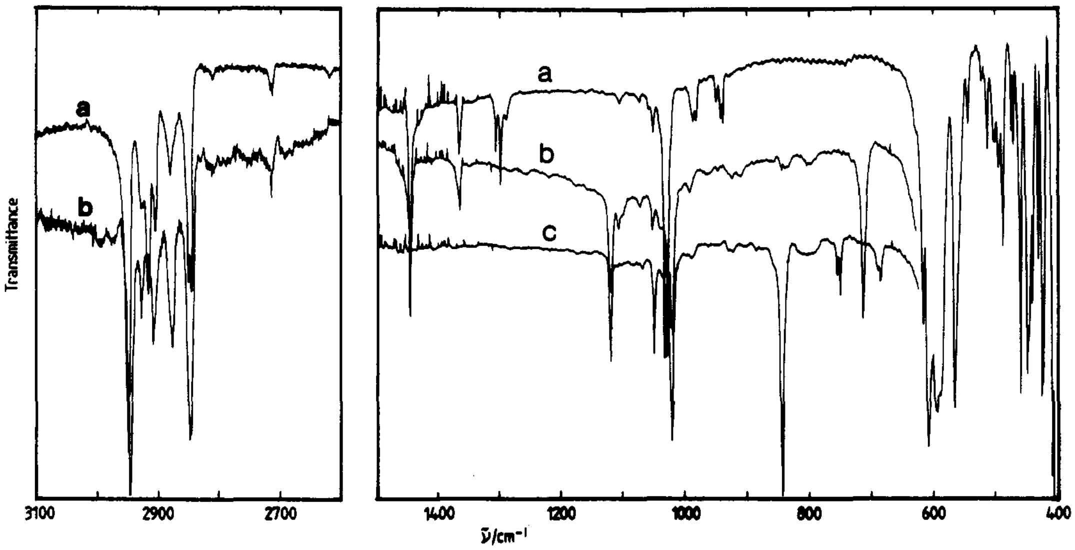


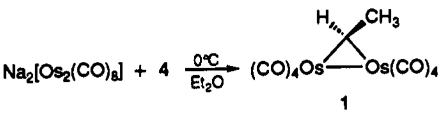
Figure 1. Infrared spectra of $[(\mu_2\text{-CH}_3CH)Os_2(CO)_8]$ (**1**) (a) d^0, (b) d^1, and (c) d^4 isotopologues taken as powdered solids in Nujol at 100 K.

bond length of 1.517 Å and an H–C–CH_3 angle of 108.9. These values imply close to sp³ hybridization and a C–C bond order close to unity.

Results and Discussion

(a) Synthesis of the Isotopologues of 1. Our published preparation of unlabeled **1** had involved the reaction of CH_3CHI_2 (**3**) with AgOTf (OTf = trifluoromethanesulphonate) to make $CH_3CH(OTf)_2$ (**4**) (eq 1), followed by use of the latter to prepare **1** from $Na_2[Os_2(CO)_8]$[12–15] (eq 2).[8]

$$\underset{\mathbf{3}}{CH_3CHI_2} + 2AgOTF \xrightarrow[CH_2Cl_2]{-23\,°C} \underset{\mathbf{4}}{CH_3CH(OTf)_2} \qquad (1)$$



1 (2)

The preparation of deuterated isotopologues of **1** such as **1**-d^1 and **1**-d^4 thus required the preparation of deuterated isotopologues of **3** and **4**. The commercial availability of CH_3CDO and CD_3CDO suggested them as starting materials. However, in our hands (and those of others[16]), the procedure reported by Friederich and co-workers for preparing **3** from acetaldehyde (iodination of the hydrazone in the presence of Et_3N)[17] gave low yields of **3**-d^1 from CH_3CDO. We thus converted CH_3CDO and CD_3CDO to the 1,1-dichlorides **5**-d^1 and **5**-d^4 with PCl_5 (eqs 3a,b).[18] Conversion of these to **3** by the standard procedure[19] for the conversion of CH_3CHCl_2 to CH_3CHI_2 (EtI in the presence of $AlCl_3$) proved to be unsatisfactory on a small scale; we found a better method (eqs 4a,b) to be treatment with AlI_3 in CS_2, reported in 1874 by Gustavson.[20] Conversion of **3**-d^1 and **3**-d^4 to **4**-d^1 and **4**-d^4 with AgOTf (eq 5), and reaction with $[Os_2(CO)_8]^{2-}$ (eq 6), gave **1**-d^1 and **1**-d^4.

$$CH_3CDO + PCl_5 \rightarrow \underset{\mathbf{5}\text{-}d^1}{CH_3CDCl_2} + Cl_3P{=}O \qquad (3a)$$

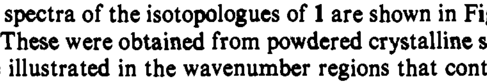
$$CD_3CDO + PCl_5 \rightarrow \underset{\mathbf{5}\text{-}d^4}{CD_3CDCl_2} + Cl_3P{=}O \qquad (3b)$$

$$3\ \mathbf{5}\text{-}d^1 + 2AlI_3 \xrightarrow{CS_2} \underset{\mathbf{3}\text{-}d^1}{3CH_3CDI_2} + 2AlCl_3 \qquad (4a)$$

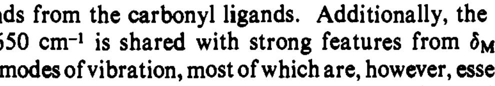
$$3\ \mathbf{5}\text{-}d^4 + 2AlI_3 \xrightarrow{CS_2} \underset{\mathbf{3}\text{-}d^4}{3CD_3CDI_2} + 2AlCl_3 \qquad (4b)$$

$$\mathbf{3}\text{-}d^1 + 2AgOTf \rightarrow \underset{\mathbf{4}\text{-}d^1}{CH_3CD(OTf)_2} + 2AgI \qquad (5a)$$

$$\mathbf{3}\text{-}d^4 + 2AgOTf \rightarrow \underset{\mathbf{4}\text{-}d^4}{CD_3CD(OTf)_2} + 2AgI \qquad (5b)$$



1-d^1 (6a)



1-d^4 (6b)

(b) Assignment of the Vibrational Spectra. The infrared and Raman spectra of the isotopologues of **1** are shown in Figures 1 and 2. These were obtained from powdered crystalline samples and are illustrated in the wavenumber regions that contain the vibrations of the hydrocarbon ligand. Some of the lower-wavenumber ν_{CD} features are unfortunately overlapped by strong ν_{CO} bands from the carbonyl ligands. Additionally, the region below 650 cm⁻¹ is shared with strong features from $\delta_{M\text{–}CO}$ or $\nu_{M\text{–}(CO)}$ modes of vibration, most of which are, however, essentially invariant in the spectra from the different isotopic species.

---

[12] $[Os_2(CO)_8]^{2-}$ has been prepared by Na/Hg reduction of $Os_2(CO)_8I_2$,[13] by the reductive disproportionation of CO_2 in its reaction with $[Os(CO)_4]^{2-}$,[14] and by the Na/Ph_2CO reduction of $(\mu\text{-}C_2H_4)Os_2(CO)_8$.[15]

[13] Motyl, K. M.; Norton, J. R.; Schauer, C. K.; Anderson, O. P. *J. Am. Chem. Soc.* **1982**, *104*, 7325.

[14] Bhattacharyya, N. K.; Coffy, T. J.; Quintana, W.; Salupo, T. A.; Bricker, J. C.; Shay, T. B.; Payne, M.; Shore, S. G. *Organometallics* **1990**, *9*, 2368 and ref 11 therein.

[15] Bender, R. B. Ph.D. Thesis, Colorado State University, 1990.

[16] Getty, S. J.; Berson, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 4607.

[17] Friederich, E. C.; Falling, S. N.; Lyons, D. E. *Synth. Commun.* **1975**, *5*, 33.

[18] For the procedure, see: Geuther, A. *Justus Liebigs Ann. Chem.* **1858**, *105*, 321. Also: *Beilstein*, 4th ed. Springer: Berlin, 1918; Vol. 1, p 83 (System #8).

[19] Letsinger, R. L.; Kammeyer, C. W. *J. Am. Chem. Soc.* **1951**, *73*, 4476.

[20] For the procedure of G. Gustavson, see: Kuhlberg, A. *Ber. Dtsch. Chem. Ges.* **1874**, *7*, 728 (procedure quoted on p 731).

Table 1. Comparison of Vibrational Assignments (cm^{-1}) and Infrared Intensities for the CH_3CH/CD_3CD Groups in $[(CH_3CH)Os_2(CO)_8]$ (d^0 and d^4) and in CH_3CHCl_2 (d^0 and d^4)[a]

symmetry	CH_3CHCl_2	$[(CH_3CH)Os_2(CO)_8]$	CD_3CDCl_2	$[(CD_3CD)Os_2(CO)_8]$	assignments
a′, a″	2995 (s)	2950 (s)	2248 (m)	2206 (ms)	ν_{CH_3/CD_3} (as)
a′	(3015) (ms)	(2916) (ms)	(2256) (m)[b]	(2185) (m)	$\nu_{CH/CD}$
a′	2946/2876 (m/m)[c]	2905/2850 (m/ms)[c]	2125 (w)	obs (–)	ν_{CH_3/CD_3} (s)
a′	1446 (ms)	1447 (ms)	1151 (s)	1123 (ms)	δ_{CH_3/CD_3} (as)[d]
a″	1446 (ms)	1447 (ms)	1047 (m)	1052 (m)	δ_{CH_3/CD_3} (as)
a′	1381 (ms)	1369 (m)	1045 (–)	1037 (w)	δ_{CH_3/CD_3} (s)[d]
a′	(1280) (ms)	(1302) (ms)	(933) (–)	(928) (w)	$\delta_{CH/CD}$ (ip)[d]
a′	1091 (w)	1053 (mw)	1014 (m)	1023 (m)	CH_3 (rock)/ν_{CC}[d]
a″	1058 (s)	1030 (s)	829 (m)	845 (s)	CH_3/CD_3 (rock)
a′	982 (ms)	989 (m)	775 (m)	754 (mw)	ν_{CC}/CD_3 (rock)[d]
a″	(1229) (s)	(945) (m)	(964) (vs)	(689) (mw)	$\gamma_{CH/CD}$ (oop)

[a] The vibrational symmetry classes were determined by the Raman polarizations and gas-phase infrared contours for the dichloride.[21] The wavenumbers in parentheses denote modes of the lone CH group which are most dependent on the non-hydrocarbon substituents. The abbreviation used are as follows: obs, obscured (this region obscured by ν_{CO} bands); as, antisymmetric; s, symmetric; ip, in-plane; oop, out-of-plane; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; b, broad; vb, very broad. [b] This mode was assigned differently in the spectra of CD_3CDCl_2[21] and CD_3CDBr_2;[22] we have adopted the latter assignment as more consistent with the infrared band contours for the dichloride. [c] Fermi resonance doublets involving ν_{CH_3} (s) and 2 × δ_{CH_3} (as). [d] These group modes are strongly coupled in the CD_3CD spectra.

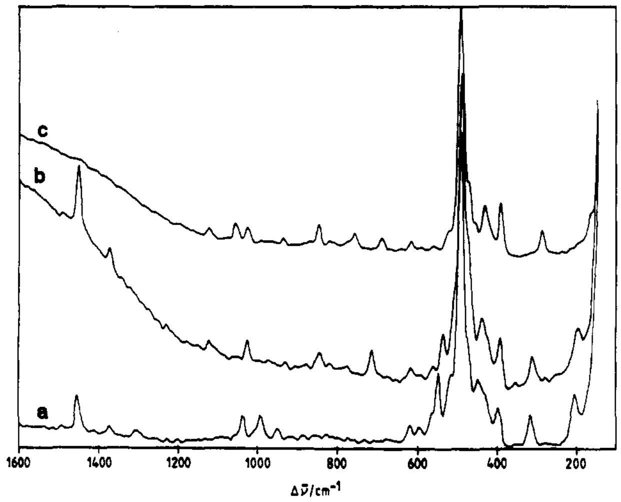


Figure 2. Raman spectra of $[(\mu_2\text{-}CH_3CH)Os_2(CO)_8]$ (**1**) (a) d^0, (b) d^1, and (c) d^4 isotopologues as powdered solids.

The wavenumbers and relative intensities of the features observed in the spectra of the three isotopically-related molecules are listed in Table 1, together with our proposed vibrational assignments. The spectral interpretations are based on an assumed C_s symmetry for the $(CH_3CH)M_2$ group, which gives rise to the vibrational symmetry classifications a′ and a″, i.e. vibrations symmetric or antisymmetric with respect to the single plane of symmetry.

Considerable aids in achieving consistent assignments were derived from the infrared and Raman spectra of the 1,1-dihaloethanes, CH_3CHX_2 (X = Cl or Br), which have been analyzed in detail[21,22] using infrared band contours and Raman polarizations. The polarizations of the Raman lines from these liquids were of particular help in enabling unequivocal identifications to be made to the a′ and a″ symmetries of the complete set of fundamentals in the 1500–600-cm^{-1} region. The latter region is of particular use for "fingerprint" purposes. Unfortunately, it did not prove to be possible to obtain solution Raman spectra with polarizations for **1**. However, with the exception only of the modes associated with the CH group adjacent to the different X atoms in CH_3CHX_2 (X = Os and Cl), there is a close correlation between the wavenumbers of the CH_3CH modes in the fingerprint region for **1**-d^0 and **1**-d^4 and for 1,1-dichloroethane and its d^4 equivalent.[21] These are listed in Table 1 and assigned according to the established vibrational symmetries for the dichloride.

The 1280- and 1229-cm^{-1} bands in the CH_3CHCl_2 spectrum have been convincingly assigned to the δ_{CH} in-plane and δ_{CH} out-of-plane modes, respectively;[21] in CH_3CHBr_2, these are shifted to 1260 and 1172 cm^{-1}.[22] In the spectra of **1**-d^0 and **1**-d^1, it is clear from the shifts of the 1302- and 945-cm^{-1} bands to 1120 and 713 cm^{-1}, respectively, that these are the corresponding δ_{CH} (δ_{CD}) modes. In the overall infrared spectra of the two d^0 compounds, even the relative intensities of the corresponding bands are similar. It is clear, for example, that of the two CH_3 rocking modes, ρ_{CH_3} (Table 1), it is the lower-wavenumber out-of-plane one that has much the greater intensity. Also, as expected, the bands at 989 and 982 cm^{-1} assigned to the ν_{CC} modes of **1**-d^0 and CH_3CHCl_2 are strong in both Raman spectra. Overall, therefore, the assignments in Table 2 for the CH_3CH and CH_3CD variants of **1** are very satisfactory.

The assignments for **1**-d^4 were more difficult to establish, doubtless because of stronger coupling that occurs between the δ_{CD} mode and the δ_{CD_3} (as), δ_{CD_3} (s), CD_3 (rock), and ν_{CC} modes, all of symmetry a′. For **1**-d^0, the situation is simpler because δ_{CH_3} (as), δ_{CH_3} (s), and δ_{CH} are separately identifiable as group vibration modes. Nevertheless, comparison of the spectra from CD_3CDCl_2 and **1**-d^4 once again gives a satisfactory pattern as shown in Table 1, the symmetry classes once again being determined from Raman polarizations of the chloride.

Table 2 lists the isotopic ratios for individual normal modes for the CH_3CH/CH_3CD and CH_3CH/CD_3CD pairs of **1**. The main unexpected feature is the low d^0/d^4 isotopic ratio for the 1030/845-cm^{-1} bands (ρ_{CH_3} and ρ_{CD_3}), although this is in part compensated by the substantial value for the isotopic ratio for the ν_{OsC} (as) modes.

Because of anharmonicity effects, "pure" modes involving H → D replacement tend to have isotopic ratios of 1.36 ± 0.02 rather than $\sqrt{2}$. For the collected a′ modes in the 1600–400-cm^{-1} region, the product ratio is equal to $(1.350)^4$, which satisfactorily reflects the fact that four out of the six modes are H → D dependent. The a″ product ratio is $(1.339)^3$, reflecting three out of four H → D sensitive components. There seems to be a general tendency for such product ratios to be scaled down for antisymmetric relative to symmetric modes for CH_3-containing compounds.[23]

Table 3 summarizes the assignments of the fundamentals of **1**-d^0 and for comparison purposes also includes those ethylidene fundamentals that are free of overlap from the bands from the more complex ligands in **2** and in *cis*-$[(\mu_2\text{-}CHCH_3)Ru_2(CO)_3(\pi\text{-}C_5H_5)_2]$ (**6**). The infrared spectrum of the latter had been

---

(21) Durig, J. R.; Sloan, A. E.; Witt, J. D. *J. Phys. Chem.* **1972**, *76*, 3591.

(22) Durig, J. R.; Sloan, A. E.; Thompson, J. W.; Witt, J. D. *J. Chem. Phys.* **1974**, *60*, 2260.

(23) See, for example, the methyl halides and methyl acetylenes: Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand: New York, 1945.

Table 2. Positions (cm^{-1}), Relative Infrared Intensities, Isotopic Ratios, and Vibration/Symmetry Assignments for the Infrared and Raman Bands of $[(\mu_2\text{-}CHCH_3)Os_2(CO)_8]$ d^0, d^1, and d^4 Isotopologues[a]

						isotopic ratios			
CH_3CH		CH_3CD		CD_3CD		CH_3CH/ CH_3CD	CH_3CH/ CD_3CD	assignment	symmetry
IR	Ra	IR	Ra	IR	Ra				
					2242 (w)			$2 \times \delta_{CD_3}$ (as)	A″
2950 (s)	2950 (mw)	2945 (s)	2948 (mw)	2206 (ms)	2207 (m)	1.00	1.337	ν_{CH_3/CD_3} (as)	a′, a″
2926 (w)		2926 (w)						$2 \times \delta_{CH_3}$ (as) (FR)	A′
2916 (ms)	2919 (s)	2184 (m)	*ca.* 2190 (ms)	2187/3 (m)	2186 (m)	1.335	1.334	$\nu_{CH/CD}$	a′
2905 (m)	*ca.* 2910 (sh)	2907 (m)	2911 (ms,sh)			1.00		$2 \times \delta_{CH_3/CD_3}$ (as) (FR)	A′
2878 (w)	2883 (mw)	2877 (m)	2878 (m)	2170 (w)	obs	1.00	1.328	$2 \times \delta_{CH_3/CD_3}$ (as)	A″
2850/48 (ms)	2860/52 (m)	2847 (s)	2847 (s)	obs	obs	1.00		ν_{CH_3/CD_3} (s) (FR)	a′
2714 (w)	2715 (w)	2715 (w)	2714 (w)	obs	2062 (mw)	1.00	1.317	$2 \times \delta_{CH_3/CD_3}$ (s)	A′
1447 (ms)	1450 (m)	1447 (ms)	1449 (m)	1123 (ms)	1121 (m)	1.00	1.291	δ_{CH_3/CD_3} (as)[b]	a′
1447 (ms)	1450 (m)	1447 (ms)	1449 (m)	1052 (ms)	1054 (m)	1.00	1.375	δ_{CH_3/CD_3} (as)	a″
1369 (m)	1371 (w)	1368 (m)	1370 (w)	1037 (w)		1.00	1.338	δ_{CH_3/CD_3} (s)[b]	a′
1302 (ms)	1303 (w)	1120 (ms)	1121 (w)	932/24 (vw)	928 (w)	1.163	1.403	δ_{CH}/δ_{CD}[b]	a′
1053 (mw)		1054 (w)		1023 (m)	1023 (m)	1.00	1.029	CH_3 (rock)/ν_{CC}[b]	a′
1030 (s)	1035 (m)	1024/1 (s)	1023 (mw)	845 (s)	845 (s)	1.006	1.219	CH_3/CD_3 (rock)	a″
989/4 (m)	989 (m)	846/37 (vw)	841 (mw)	757/51 (mw)	757 (ms)	1.175	1.306	ν_{CC/CD_3} (rock)[b]	a′
952/45 (m)	945 (w)	713 (m)	712 (m)	691/87 (mw)	689 (mw)	1.331	1.377	$\gamma_{CH/CD}$	a″
545 (w)	545 (ms)	537 (ms)	535 (ms)	525 (m)	*ca.* 520 (m,sh)	1.017	1.038	ν_{OsC} (as)	a″
448 (s)	445 (ms)	432 (ms)	438 (ms)	434 (ms)	431 (ms)	1.028	1.032	ν_{OsC} (s)	a′
	312 (m)		309 (m)		286 (m)	1.010	1.091	$\delta_{Os_2C_2}$ (s)	a′
	196 (m)		195 (m)		*ca.* 176 (sh)	1.005	1.115	$\delta_{Os_2C_2}$ (as)	a″
	155 (vs)		155 (vs)		155 (vs)	1.000	1.000	ν_{OsOs}	a′

[a] Abbreviations used in the table are as follows: FR, Fermi Resonance of $2 \times \delta_{CH_3/CD_3}$ (as) with ν_{CH_3/CD_3} (s); obs, band obscured by strong carbonyl ν_{CO} bands; IR, infrared; Ra, Raman. Additional IR/Ra bands that are virtually unaffected by isotopic substitution are assumed to be carbonyl $\delta_{M\text{-}CO}$ and $\nu_{M\text{-}CO}$ bands, *viz.* 616 (m, IR; w, Ra); 605 (vs, IR); 592 (vs, IR; w, Ra); 583 (s, IR); 562 (s, IR; w, Ra); 495/90 (m, IR; vs, Ra); (470, m, sh, Ra); 455 (s, IR); 423 (s, IR; w, Ra); 390 (m, Ra). Other very weak features are assumed to be $\delta_{M\text{-}CO}/\nu_{M\text{-}CO}$ overtones or combinations, *viz.* CH_3CH 1110, 1070; CH_3CD 1108, 1065, 1041, 992; CD_3CD 1070, 991. [b] These group modes of the CD_3CD compound are strongly coupled.

Table 3. Assigned Fundamentals (cm^{-1}) for the Ethylidene Groups in Several Metal Coordination Compounds and for Possible Ethylidene Species on Metal Surfaces[a]

	3	2	1-d^0 [b]	$CO/H_2/Rh/Al_2O_3$[c]	C_2H_4/Pt(111)/K[d] (300 K)	C_2H_4/Pt(111)/O[e] (325 K)
a′ modes						
ν_{CH_3} (as)	2947	2954	2950 (s)	2964 (s, b)	2955 (w)	2980 (ms, b)
ν_{CH}	2903	2917	2918 (ms)	2916 (s, b)		
ν_{CH_3} (s)	2835	2832	2849 (ms)		2855 (vw)	
δ_{CH_3} (as)	1445	1449	1449 (ms)	1463 (ms)	1435 (s, bd)	1420 (s, vb)
δ_{CH_3} (s)		1366	1369 (m)	1378 (m)		
δ_{CH} (ip)	1264	1313	1302 (ms)	1256 (m)		
ρ_{CH_3}		1056	1053 (mw)	1058 (m)	1110 (w)	
ν_{CC}	968	971	989 (m)	940 (mw)	900 (mw)	940 (m)
ν_{OsC} (s)		505	448 (s)		415 (s)	480 (vs)
δ_{CCOs} (s)			312			300 (m)
ν_{OsOs}			155			
a″ modes						
ν_{CH_3} (as)			(2950)			
δ_{CH_3} (as)	(1445)	(1449)	(1449)			
ρ_{CH_3}		1026	1030 (s)			
δ_{CH} (oop)	(968)	938	945 (m)			
ν_{OsC} (as)		629	545 (w)	594 (ms)		
δ_{CCOs} (oop)			196			

[a] **1**-d^0 = $[(\mu_2\text{-}CHCH_3)Os_2(CO)_8]$; (**2**) = $[(\mu_2\text{-}CHCH_3)\ Fe_2(CO)_6\ (\mu_2\text{-}Ph_2PCH_2PPh_2)]$; (**3**) = *cis*-$[(\mu_2\text{-}CHCH_3)Ru_2(CO)_3(\pi\text{-}C_5H_5)_2]$. [b] Intensities as in the infrared spectrum (Table 2). [c] Reference 28. [d] Reference 7. [e] Reference 4.

measured and assigned previously.[24] Some modifications of the previous assignments for **6** have been made for reasons of consistency with our assignments for **1**-d^0. Overall rather satisfactory assignments have been achieved for the fundamentals of the $(CH_3CH)Os_2$ group and of its d^1 and d^4 isotopologues.

Identification Criteria for Surface Ethylidene Species

The use of these results in order to anticipate spectra from ethylidene species on metal surfaces requires an additional account to be taken of the intensity changes resulting from the operation of the metal-surface selection rule (MSSR).[25,26]

For reflection–absorption infrared (RAIR) spectroscopy and on-specular VEELS, this requires that only the squares of the components of vibrational dipole moments that are perpendicular to the metal surface contribute to band intensities. With the plane of symmetry of the $(CH_3CH)M_2$ group assumed to be perpendicular to the metal surface, the only active modes in this criterion should be those of a′ symmetry. Furthermore, because the directions of the CC and lone CH bonds are at *ca.* 50° with respect to the surface normal,[10,11] the group vibrations giving dipole changes in those directions will be relatively weaker than in the infrared spectrum of **1** (where the MSSR does not apply) whereas those perpendicular to the metal surface (in this case only the symmetric ν_{OsC} mode) will be relatively enhanced. A RAIR spectrum of a surface ethylidene complex can therefore be expected to show at least the more prominent of the following features. The wavenumbers have been rounded off to the nearest 10 as variations of several tens of cm^{-1} are to be expected due to the metal-surface species having other metal atoms replacing the

---

(24) Evans, J.; McNulty, G. *J. Chem. Soc., Dalton Trans.* **1984**, 79.
(25) Greenler, R. G. *J. Chem. Phys.* **1966**, *44*, 310.
(26) Pearce, H. A.; Sheppard, N. *Surf. Sci.* **1976**, *59*, 205.

carbonyl groups of **1**. CH_3CH: 2950 (s), 2920 (m), 2850 (m), 1450 (s), 1370 (w), 1300 (m), 1050 (mw), 990 (mw), 450 (s), and 310 (m). CD_3CD: 2210 (s), 2185 (mw), *ca.* 2060 (m), 1120 (s), 1040 (w), 1020 (w), 930 (w), 760 (m), and 430 (s). The estimated intensities are appropriate for a RAIR spectrum. VEEL spectra show losses that are systematically stronger at lower wavenumbers and weaker at higher wavenumbers; dipole-excited ν_{CH} features can be particularly weak.[27]

A vibrational spectrum at 300 K from ethene adsorbed on a Pt(111) metal surface with 0.12 monolayers of potassium has recently been tentatively assigned to an ethylidyne surface species. A comparison was made with our then-unpublished data on the infrared spectrum of **1**.[7] It was shown that the coadsorbed potassium increased the activation energy for CH dissociation of the adsorbed ethene leading to ethylidyne. This process normally occurs at *ca.* 300 K but was retarded to *ca.* 400 K in the presence of potassium. The changed spectrum at 300 K was attributed to the ethylidene as an intermediate. The spectral data are listed in Table 3. Another possible case of ethylidene is that obtained from adsorption of ethene on Pt(111), with 0.23 of a monolayer of preadsorbed oxygen, taken after annealing to 325 K.[4] The features in these spectra are also listed in Table 3.

In the discussion[7] of the C_2H_4/Pt(111)/K system, it was considered that the coadsorbed potassium could raise the activation energy for C–H dissociation in two alternative ways. The potassium atoms could either alter the electronic properties of the surface or physically block the sites that would otherwise be available for a hydrogen-atom dissociation from ethylidene. The same alternatives apply in the Pt(111)/O case. However, the extreme opposite electronegativities of the two coadsorbates would be expected to cause electronic effects also in opposite directions, whereas a site-blocking mechanism could, as is observed, have the same effect in both cases.

More surprisingly it has already been pointed out that the heating in hydrogen of CO adsorbed on Rh/Al_2O_3 leads to an inelastic electron tunneling spectrum that results from a hydrocarbon species that is possibly ethylidene.[28] These relatively high resolution data are also listed in Table 3 and are indeed in best agreement with the predictions derived from the analysis of the spectrum of **1**.

Taking into account the limited resolution of the EEL spectra from Pt(111)/K and Pt(111)/O (in particular the expected *ca.* 1300-cm^{-1} band may not be resolved from the very broad 1435/1420-cm^{-1} features) and the effects of the other ligands in the spectra of the model compounds, it is concluded that the species involved might well be ethylidene. Better resolved RAIR spectra would be of value for a more certain structural identification. The agreement between the higher resolution spectrum from CO/$H_2/Rh/Al_2O_3$ and the infrared spectrum of **1** is remarkably good.

Finally we note the much greater complexity and different wavenumber/intensity patterns expected from ethylidene compared with those well-established for ethylidyne.[29] The higher C_{3v} symmetry for the latter causes the MSSR to be correspondingly much more effective in limiting the number of the active a_1 modes. CH_3C: 2880 (s), 1350 (s), 1150 (s), and 450 (ms). CD_3C: 2080 (ms), 1170 (s), 1000 (w), and 420 (ms).

Experimental Section

General. Unless otherwise stated, all chemistry was performed in an inert-atmosphere box. Solvents used inside the box were prepared as follows: THF was distilled from Na/Ph_2CO under N_2 and stored over freshly cut Na for at least 24 h before use, while CH_2Cl_2 was distilled from CaH_2 under N_2 and stored over additional CaH_2 in the box. Solvents used outside the box were prepared as follows: Et_2O was freshly distilled from Na/Ph_2CO, while CS_2, was spectrograde without further treatment.

CD_3CDO and CH_3CDO were both purchased from Aldrich. AlI_3 (95%) from Aldrich proved unsatisfactory for reaction 4; the yields reported below are with the 99.9% material from Cerac.

CH_3CDCl_2 (5-d^1) and CD_3CDCl_2 (5-d^4) were prepared from the corresponding acetaldehydes by the traditional procedure.[18] PCl_5 (26 g, 0.125 mol) was loaded into a 50-mL flask inside the inert-atmosphere box and cooled to −78 °C under N_2 outside the box (the color of the PCl_5 changed from yellow to white). CH_3CDO or CD_3CDO (5 g, 0.11 mol) was added *slowly* dropwise (about 1 h) with the cooling bath still present. The reaction was warmed slowly with stirring, then heated to 70 °C for 2 h. Distillation gave 5.0 g (45%) of crude **5**-d^1, and 56% of crude **5**-d^4. The product was washed with H_2O, dried over $CaCl_2$, and redistilled. ^1H NMR of **5**-d^1 ($CDCl_3$): δ 2.05. ^2H NMR of **5**-d^1 ($CDCl_3$): δ 5.88.

CH_3CDCl_2 (3-d^1) and CD_3CDI_2 (3-d^4) were prepared by a modern adaptation of the 1874 procedure of Gastavson.[20] AlI_3 (99.9%) (12.5 g, 30.7 mmol) was loaded into a 100-mL flask inside the inert-atmosphere box; 35 mL of CS_2 was added outside the box, and the mixture was cooled to −78 °C. (It is essential that this reaction be initiated at low temperature!) A solution of the **5**-d^1 prepared above (2.94 g 29.5 mmol) in 25 mL of CS_2 was added dropwise over 60 min to the chilled reaction mixture, which was then allowed to room temperature and stirred overnight. The solution was then added to 200 mL of saturated aqueous $NaHSO_3$, which discharged the I_2 color. After filtration, the CS_2 layer was dried with $MgSO_4$ overnight. Most of the solvent was removed with a water aspirator; the remainder was removed at 10^{-2} mmHg while the product was kept at 0 °C. The product (4.75 g, 57%) was distilled at that pressure into a receiving flask cooled to −15 °C. ^1H NMR ($CDCl_3$): δ 2.87. ^2H NMR ($CDCl_3$): δ 5.22. ^{13}C NMR ($CDCl_3$) of **4**-d^1: δ 38.7 ($J(^{13}C-^1H)$ = 131.4 Hz), −38.3 ($J(^{13}C-^2H)$ = 26.9 Hz). ^{13}C NMR ($CDCl_3$) of **4**-d^4: δ 37.8 ($J(^{13}C-^2H)$ = 20.1 Hz), −38.6 ($J(^{13}C-^2H)$ = 26.3 Hz).

$CH_3CD(OTf)_2$ (4-d^1) and $CD_3CD(OTf)_2$ (4-d^4) were prepared by the procedure reported[8] for unlabeled **4**, although the products were purified by transfer on a high-vacuum line rather than a Kugelrohr apparatus. ^1H NMR of **4**-d^1 (CD_2Cl_2): δ 1.90. IR (Et_2O): 1222 (vs), 1254 (s), 1430 (vs) cm^{-1}.

(μ_2-$CH_3CD)Os_2(CO)_8$ (1-d^1) and (μ_2-$CD_3CD)Os_2(CO)_8$ (1-d^4). The $[Os_2(CO)_8]^{2-}$ dianion was prepared in the inert-atmosphere box by dropwise reduction of $(\mu_2\text{-}C_2H_4)Os_2(CO)_8$ in THF with a THF solution of Na/Ph_2CO. The persistence of the blue color of the ketyl indicated that reduction was complete and that proton sources were absent. IR (THF): ν_{CO} 1947, 1877 cm^{-1}. Outside the box, the dianion (0.37 mmol, assuming complete reduction of the $(\mu\text{-}C_2H_4)Os_2(CO)_8$ above) was dried by removing the THF in vacuo. Et_2O (20 mL) was added and the suspension cooled to 0 °C. A prechilled ether solution of $CH_3CD(OTf)_2$ (**4**-d^1) (0.72 mmol in 3 mL) or **4**-d^4 was added to the reaction mixture at that temperature. (The use of too large an excess of **4** causes difficulty in the purification of **1**, as the large amount of **3** that arises from the $[Bu_4N]I$ treatment below is difficult to remove from **1**.) Formation of the product was monitored by the appearance of the characteristic ν_{CO} of **1**[8] at 2079 cm^{-1}. After 1 h, $[Bu_4N]I$ (1.03 g, 2.8 mmol) was added to destroy excess **4** by converting it back to **3**, and the solution was stirred for 2.5 h while it was warmed to room temperature. (The IR should show no remaining **4**.) The Et_2O was removed in vacuo and the residual solid extracted four times with 20 mL of pentane. Concentration of the extract (≈1 mL) and application to a silica gel chromatotron plate (EM Science, Silica Gel 60 PF_{254} containing gypsum) permitted easy purification of the product. The first band eluted with pentane contained 39 mg (17%) of labeled **1**. Both **1**-d^1 and **1**-d^4 were purified by transfer on a high-vacuum line prior to spectroscopic studies.

Infrared spectra of **1** and its isotopologues were obtained on CsI and CsCl discs cooled to *ca.* 100 K, using a Beckmann Research and Industrial Instruments Co. low-temperature cell, in order to improve resolution. The spectra were measured on a Digilab FTS-20V FTIR spectrometer. FT near-infrared Raman spectra of the polycrystalline particles were obtained at room temperature using a Bruker IFS 66/FRA106 spectrometer.

Acknowledgment. C.E.A. thanks the Emission Project of the A.R.G. at the University of Warwick for a Research Fellowship. We thank Dr. R. T. Hembre for preliminary results on the synthesis of isotopologues of **1**. Work of Colorado State University was supported by U.S. Department of Energy Grant DE-FG02-841 3299.AOO5.

---

(27) Chesters, M. A.; Sheppard, N. *Spectroscopy of Surfaces*; Clark, R. J. H., Hester, R. E., Eds.; Wiley: Chichester and New York, **1988**; pp 406–410.

(28) Kroeker, R. M.; Kaska, W. C.; Hansma, P. K. *J. Catal.* **1980**, *61*, 87.

(29) Sheppard, N. *Ann. Rep. Phys. Chem.* **1988**, *39*, 589.