Spectroscopic Studies on C_2 Hydrocarbon Fragments. Part 1. Vibrational Studies of Cluster-bound Vinyl and Vinylidene Ligands †

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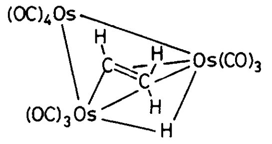
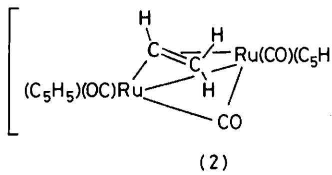
Vibrational assignments of the vinyl and vinylidene groups in $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)]$ (1) and $[Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)]$ (3) respectively have been made on the basis of normal co-ordinate analyses of the $Os_3(C_2H_n)$ (n = 2 or 3) fragments and [^{2}H] substitution. π-Co-ordination caused the lowering of the principal ν(C=C) vibration to 1 311 and 1 331 cm^{-1} in (1) and (3) respectively. The vinyl group frequencies could largely be transferred to assign partially the spectrum of another vinyl complex $[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}CH{=}CH_2)]BF_4$ (2) with the same co-ordination mode. The vinylidene frequencies in (3) were quite distinct from those of another complex, $[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}C{=}CH_2)]$ (4) which has a different co-ordination mode; a band at 1 586 cm^{-1} in (4) is assigned as consisting largely of the ν(C=C) mode. Analysis was also made of the Os(μ-H) group in (1) and showed strong mixing between the symmetric ν(Os–H) and out-of-plane bend giving rise to the i.r. active vibrations at 1 285 and 710 cm^{-1}; the asymmetric ν(Os–H) stretch occurs at 1 394 cm^{-1}.

Metal carbonyl clusters provide the types of co-ordination geometry which are also available to adsorbates on metal surfaces.[1] They therefore provide the best model complexes for obtaining a data bank for the interpretation of spectroscopic studies on metal surfaces.[2] An excellent example of this is that characterisation of a μ_3-ethylidyne on a Pt(111) surface by electron energy loss spectroscopy [3] was only possible following a corrected vibrational assignment for $[Co_3(CO)_9(\mu_3\text{-}CMe)]$.[4] In this paper, we report vibrational studies of two other C_2 moieties which might be encountered on metal surfaces. Two vinyl complexes with the same co-ordination mode were investigated to test the transferability of group frequencies *viz.* $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)]$ (1) and $[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}CH{=}CH_2)]BF_4$ (2). Secondly a pair of vinylidene complexes with different co-ordination modes were studied to test for differentiability *viz.* $[Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)]$ (3) and $[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}C{=}CH_2)]$ (4).



(1)



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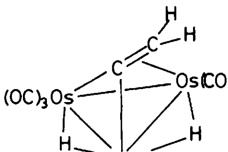

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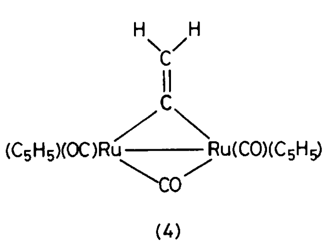

(4)

Experimental

Nuclear magnetic resonance, mass, i.r., and Raman spectra were recorded on Varian XL-100, AEI MS12, Perkin-Elmer 580B (with model 3500 Data Station), and Cary 82 instruments respectively.

The complexes $[Os_3(CO)_{12}]$,[5] $[Os_3(CO)_{10}H_2]$,[6] and $[Ru_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ [7] were prepared by published procedures. Compounds were characterised by their ν(CO) i.r. bands, mass spectrum, and ^{1}H n.m.r. and, unless otherwise stated, spectra were in agreement with those published previously.

Preparations.—$[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)]$ (1). Complex (1) was prepared from $[Os_3(CO)_{10}H_2]$ by the method of Deeming *et al.*[8] Purification was by thin layer chromatography on silica plates using hexane as solvent and subsequent recrystallisation from hexane. ^{13}C N.m.r. ($CDCl_3$): δ 68.7 (CH_2), 101.3 p.p.m. (CH). I.r. (excluding carbonyl bands) CCl_4: 3 048w, 3 018w, 2 990w, 2 916w, 1 476m, 1 311m, 990m cm^{-1}; CS_2: 3 045w, 3 016vw, 2 986vw, 2 911vw, 1 310m, 1 263w, 1 010w, 993m, 985m, 779w, 705s cm^{-1}; KBr disc at 298 K: 3 062w, 2 997w, 2 920w, 1 475s, 1 311s, 1 266ms, 1 009s, 990vs, 786s, 710vvs cm^{-1}; KBr disc at 77 K: additional bands at 1 394ms and 1 285m cm^{-1}.

$[Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)]$ (3). Complex (3) was prepared by refluxing complex (1) in n-octane for 25 min.[7] ^{1}H N.m.r. ($CDCl_3$): δ 6.50 (s), 5.96 (s), −18.03 (s), −21.65 p.p.m. (s). ^{13}C N.m.r. ($CDCl_3$): δ 65.3 (CH_2), 160.4, 166.7, 168.1, 169.0, 169.7, 171.2, 173.3, 175.0, 176.5 (all CO), and 210.9 p.p.m. (*C*=CH_2). I.r. (excluding carbonyl bands) CCl_4: 3 019vw, 2 974w, 2 926w, 2 898w, 2 855vvw, 1 468m, 1 324m, 1 055m cm^{-1}; CS_2: 1 324w, 1 054m, 951w, 805w, 673m, 616m cm^{-1}; KBr disc: 3 047vw, 2 986w, 2 907w, 2 854vw, 1 470m, 1 331m, 1 051sm, 963s, 811m, 691s, 680s cm^{-1}.

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† *Non-S.I. unit employed:* dyn = 10^{-5} N.

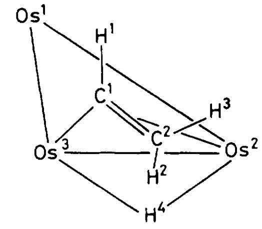

Figure 1. The $Os_3H(C_2H_3)$ fragment used in the partial normal co-ordinate analyses of (1). Bond lengths (Å): Os^1–Os^2 2.917, Os^1–Os^3 2.857, Os^2–Os^3 2.845, Os^3–C^1 2.107, Os^2–C^1 2.273, Os^2–C^2 2.362, C^1–C^2 1.396, C^1–H^1 1.078, C^2–H^2 1.093, C^2–H^3 1.077, Os^2–H^4 1.813, and Os^3–H^4 1.857

$[Ru_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (5). I.r. (excluding carbonyl bands) CCl_4: 3 115w, 1 415w, 1 348.5w, 1 107w, 1 056w, 1 010w, 997w cm^{-1}; KBr disc: 3 122(sh), 3 113m, 3 090(sh), 1 426m, 1 409s, 1 349(sh), 1 345s, 1 255w, 1 147w, 1 127w, 1 107s, 1 053s, 1 010vs, 992vs, 922w, 912w, 852m, 834vs,br, 810vs,br cm^{-1}.

$[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}CH{=}CH_2)]BF_4$ (2). Complex (2) was prepared by reacting $[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CHMe)]$ (6) with $[CPh_3]BF_4$ in CH_2Cl_2 under N_2.[9] The yellow salt was precipitated out by the addition of light petroleum (b.p. 60—80 °C). I.r. (excluding carbonyl bands) hexachlorobutadiene: 3 115m, 3 055(sh)vw, 2 988vw, 2 906vw, 1 468s, 1 433s(sh), 1 421s, 1 356w, 1 301s, 1 285m, 1 220m, 1 150—1 000br,s, 615m, 583m, 570w cm^{-1}; CsI disc: 3 118m, 3 041w, 2 981vvw,br, 2 939vw, 2 904vw, 1 469s, 1 421s, 1 412(sh)s, 1 355w, 1 301s, 1 286m, 1 222m, 1 150—1 000s,br, 970m, 865vs, 844s, 831m, 801w, 780m, 590s, 573vs, 535s, 521m, 501vs, 486vs, 471s, 413m cm^{-1}.

$[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}C{=}CH_2)]$ (4). Complex (4) was a gift from Dr. S. A. R. Knox. I.r. (CH_2Cl_2): 1 994vs, 1 953m, 1 790s cm^{-1}; CsI disc (excluding carbonyl bands): 3 112s, 3 094s, 3 032m, 3 019mw(sh), 2 964w, 2 927vw, 1 586s, 1 581s(sh), 1 427w, 1 414m, 1 351w, 1 106vw, 1 059w, 1 010m, 995m, 988m, 973ms, 915vw, 850w, 835m, 809s, 801s, 596vs,br, 557s, 528ms, 506ms, 495m, 463w, 445w, 417m, 383w, 344w, 317w, 261vw, 221vw cm^{-1}. Raman (solid): 3 118s, 3 095m, 3 022w, 3 013w, 2 967w, 2 922vvw, 1 964w, 1 927w, 1 778w, 1 578vw, 1 415w, 1 357w, 1 107s, 1 056w, 814w,br, 571vw, 524w, 494w, 460m, 442m, 417vw, 380m, 340m, 319s, 257w, 220vs, 121vs, 87vs, 30vs cm^{-1}.

Deuteriation of (1) *and* (3).—D_2 and DCCD were prepared by treating sodium and CaC_2 respectively with D_2O. Different levels of deuteriation were achieved by using D_2O–H_2O mixtures. Deuterium enriched $[Os_3(CO)_{10}H_2]$ was prepared from $[Os_3(CO)_{12}]$ and enriched hydrogen, (1) from its reaction with labelled acetylene, and (3) by subsequent pyrolysis of (1). The degree of enrichment was determined by matching calculated and observed mass spectral isotope patterns.

Results

$[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)]$ (1).—Although (1) is vibrationally complex, and has C_1 symmetry, investigation of the vibrations of the vinyl group is simplified by the narrow frequency ranges of the other modes within the complex. The carbonyl groups cover the 2 100—1 900 and 400—600 cm^{-1} regions, and ν(MM) and low frequency carbonyl group deformations are all below ~200 cm^{-1}. Outside these ranges, both vinyl and hydride vibrations are observable. These results agree closely with those of Sheppard and co-workers,[10] who also identified ν(Os–vinyl) stretching modes at 332 and 296 cm^{-1} and ν(MM) stretches at 168, 126, and 116 cm^{-1}. The marked sharpening of the absorptions at 1 394 and 1 285 cm^{-1} at low temperature indicate that these are ν(M–H) in character.[11] However the detailed assignment remains uncertain and so the $Os_3(CHCH_2)$ and Os_3H moieties were the subject of a normal co-ordinate analysis (the vinyl group vibrations are unlikely to mix strongly with carbonyl modes) using the molecular geometry established for (1) by neutron diffraction (Figure 1).[12] A version of SOTONVIB [13] was used for this analysis, but was modified for interactive use. The initial force field was taken from that developed for $BF_2CH{=}CH_2$.[14] Five sets of spectra were recorded in KBr and/or CsI discs *viz.* (1), 40% [^{2}H] (1), 65% [^{2}H] (1), and 80% [^{2}H] (1) at room temperature and (1) and 80% [^{2}H] (1) at 77 K. From comparisons of these spectra, bands due to different isotopomers, Figure 2, could be tentatively assigned and described by the force fields shown in Table 1. These force fields allowed an essentially complete assignment of the observed vinyl bands (Table 2). Unfortunately no ν(CD) stretches were unambiguously detectable because of their close proximity to the more intense ν(CO) absorptions. The vibrations of the Os_3H moiety could also be fitted on the basis of the force field in Table

Table 1. Force fields (mdyn Å^{-1}) used for the $Os_3(C_2H_3)$ and Os_3H moieties in (1); R = stretching, α = bending constants

(*a*) $Os_3(C_2H_3)$		
	R_{CH}	4.873
	R_{CC}	6.680
	R_{Os-Os}	1.084
	α_{HCH}	0.390
	R_{Os-C}	0.868
	α_{OsOsC}	2.60
	$\alpha_{CCH_2\ and\ 3}$	0.54
	α_{OsCH}	0.3
	α_{CCH_1}	0.81
	ρ_w	0.194
	ρ_τ	0.180
	α_{OsCC}	1.805
	$R_{CH}R_{CH}$	−0.074
	$R_{CC}\alpha_{HCH}$	−0.245
	$R_{OsOs}R_{OsOs}$	0.049
	$R_{CC}\alpha_{CCH}$	0.4
	$\alpha_{OsCH_1}\rho_\tau$	0.117
(*b*) Os_3H		
	R_{OsOs}	0.9580
	R_{OsH}	0.7674
	α_{OsOsH}	1.4867
	$R_{OsOs}R_{OsOs}$	0.0386
	$R_{OsOs}\alpha_{OsOsH}$	−0.0815

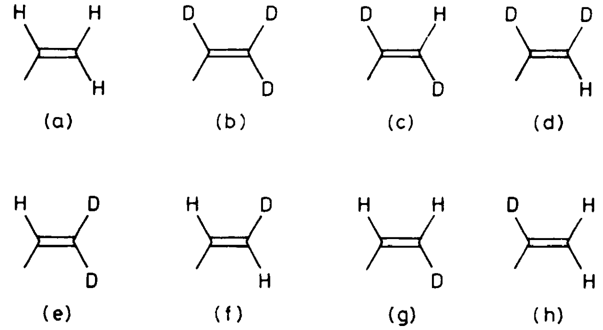

Figure 2. The eight hydrogen isotopomers (a)—(h) for the vinyl group in (1)

Table 2. Observed bands (cm^{-1}) and assignments of the vinyl group in (1)

80% [^{2}H]	65% [^{2}H]	40% [^{2}H]	(1)	Assignment of principal component (isotopomer and calculated frequency/cm^{-1})
			3 062w	$\nu_{asym}(CH_2)$ (1a, 3 064)
			2 997w	$\nu(CH)$ (1a, 2 993)
			2 920w	$\nu_{sym}(CH_2)$ (1a, 2 922)
1 476w	1 478w	1 476s	1 475s	$\delta(CH_2)$, $\nu(CC)$, ρ_r (1a, 1 474)
1 393s	1 393s	1 393ms		$\nu(CC)$ (1c, 1d, 1 388)
1 354w	1 354w	1 352w		$\nu(CC)$ (1e, 1 358)
1 345s	1 345m	1 345vw		$\nu(CC)$ (1b, 1 347)
	1 310vw	1 311m	1 311s	$\nu(CC)$ (1a, 1 312)
1 294vw	1 294w	1 294w		$\nu(CC)$ (1h, 1 304)
			1 266ms	$\delta(CH)$ (1a, 1 263)
1 262w(sh)	1 262w	1 264m		$\delta(CH)$ (1f, 1 265)
1 259m	1 258w	1 260mw(sh)		
1 247w	1 247vw	1 247vw		$\rho_r(CHD)$, $\nu(CC)$ (1c, 1 250)
1 235w	1 235w	1 235w		$\rho_r(CHD)$, $\nu(CC)$ (1d, 1 238), $\delta(CH)$ (1e, 1 235)
1 192vw	1 192vw	1 192mw		$\delta(CH)$ (1g, 1 190)
1 046m, br	1 046m, br			$\delta(CD)$, (1b, 1 050)
1 030m, br	1 030m, br	1 030vw		$\delta(CH)$, $\rho_r(CHD)$ (1c, 1 032)
		1 009w	1 009s	ρ_τ, ρ_w (1a, 1 012)
		990s, br	990vs	ρ_r (1a, 992)
990m	990m			$\delta(CD_2)$, $\rho_r(CD_2)$ (1b, 1 004)
951w	951w	951w		$\rho_w(CHD)$, $\rho_\tau(CHD)$ (1d, 945)
		907w		ρ_τ, ρ_r (1g, 909)
		857w		$\rho_r(CHD)$ (1f, 853), ρ_r (1g, 859)
840w	840w	840m		$\rho_w(CHD)$ (1c, 833), $\delta(CD)$ (1h, 844)
803w	803vw	803vw		
791s (sh)	791s	791m		$\rho_r(CHD)$, $\delta(CD)$ (1c, 785)
787s	787m (sh)	787m		$\rho_w(CD_2)$, $\rho_\tau(CD_2)$ (1b, 785)
			786s	$\delta(OsCH)$, ρ_w (1a, 786)
753vs				$\rho_r(CHD)$, $\delta(CD)$ (1d, 751)
	750	750m		$\delta(OsCH)$, $\rho_w(CHD)$ (1g, 753)
730vs	738m	730mw		$\rho_r(CD_2)$, $\delta(CD)$ (1b, 732)
			332 *	$\nu(OsC)$, $\delta(OsOsC)$, (1a, 329)
			309 *	$\nu(Os{-}C)$, $\delta(OsOsC)$, (1a, 313)
			296 *	$\nu(Os{-}C)$, ρ_w (1a, 283)

* Ref. 10.

Table 3. Observed and calculated bands (cm^{-1}) for the Os_3H group in (1)

Obs.	Calc.	Assignment
1 394	1 394	$\nu_{asym}(OsH)$
1 285	1 285	$\delta(OsOsH)$, $\nu_{sym}(OsH)$
995	989	$\nu_{asym}(OsD)$
931	910	$\delta(OsOsD)$, $\nu_{sym}(OsD)$
710	710	$\delta(OsOsH)$, $\nu_{sym}(OsH)$
—	508	$\delta(OsOsD)$, $\nu_{sym}(OsD)$
166 *	166	$\nu(OsOs)$
129 *	128	$\nu(OsOs)$
110 *	111	$\nu(OsOs)$

* Ref. 10.

1(*b*) (Table 3). Generally no differentiation between non-symmetry related force constants of the same type *e.g.* R_{CH} was made to restrict the number of independent variables. Some differences are noted between our assignments and those made qualitatively by Sheppard and co-workers.[10] Using our isotopic data, we have identified the major components of the coupled motions in the fingerprint region.

$[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}CH{=}CH_2)]BF_4$ (2).—Infrared spectra of (2) were recorded in an hexachlorobutadiene mull and a CsI disc. In addition to the CO bands, these spectra also contained a prominent $\nu(B{-}F)$ band covering the 1 150—1 000 cm^{-1} range which masked any other absorptions in that region. The vibrations of the bridging vinyl group (Table 4) were identified from the remaining bands on comparison with the spectra of $NaBF_4$ and $[Ru_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (5) (Figure 3).

Table 4. $\mu\text{-}\eta^2$-Vinyl group vibrations in $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)]$ (1) and $[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}CH{=}CH_2)]BF_4$

Frequencies (cm^{-1})		Assignment (principal component)
(1)	(2)	
3 062	3 041	$\nu_{asym}(CH_2)$
2 997	2 981	$\nu(CH)$
2 920	2 904	$\nu_{sym}(CH_2)$
1 475	1 469	$\delta(CH_2)$
1 311	1 301	$\nu(CC)$
1 266	1 286, 1 222	$\delta(CH)$
1 009	970	ρ_τ
990	865	ρ_r
786	780	$\delta(OsCH)$, ρ_w

$[Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)]$ (3).—Solution and solid state spectra were obtained for (3) to ascertain the vinylidene group vibrations. More than the expected two $\nu(CH)$ absorptions were observed and it is likely that the lower frequency bands (2 907 and 2 854 cm^{-1}) emanate from overtone or combination bands involving the fundamental at 1 470 cm^{-1}. A normal co-ordinate analysis was carried out on the $Os_3(C{=}CH_2)$ moiety using the structural data reported for (3)[15] (Figure 4). Spectra were recorded on (3) and also for two samples at different deuteriation levels. As with (1) the metal hydride

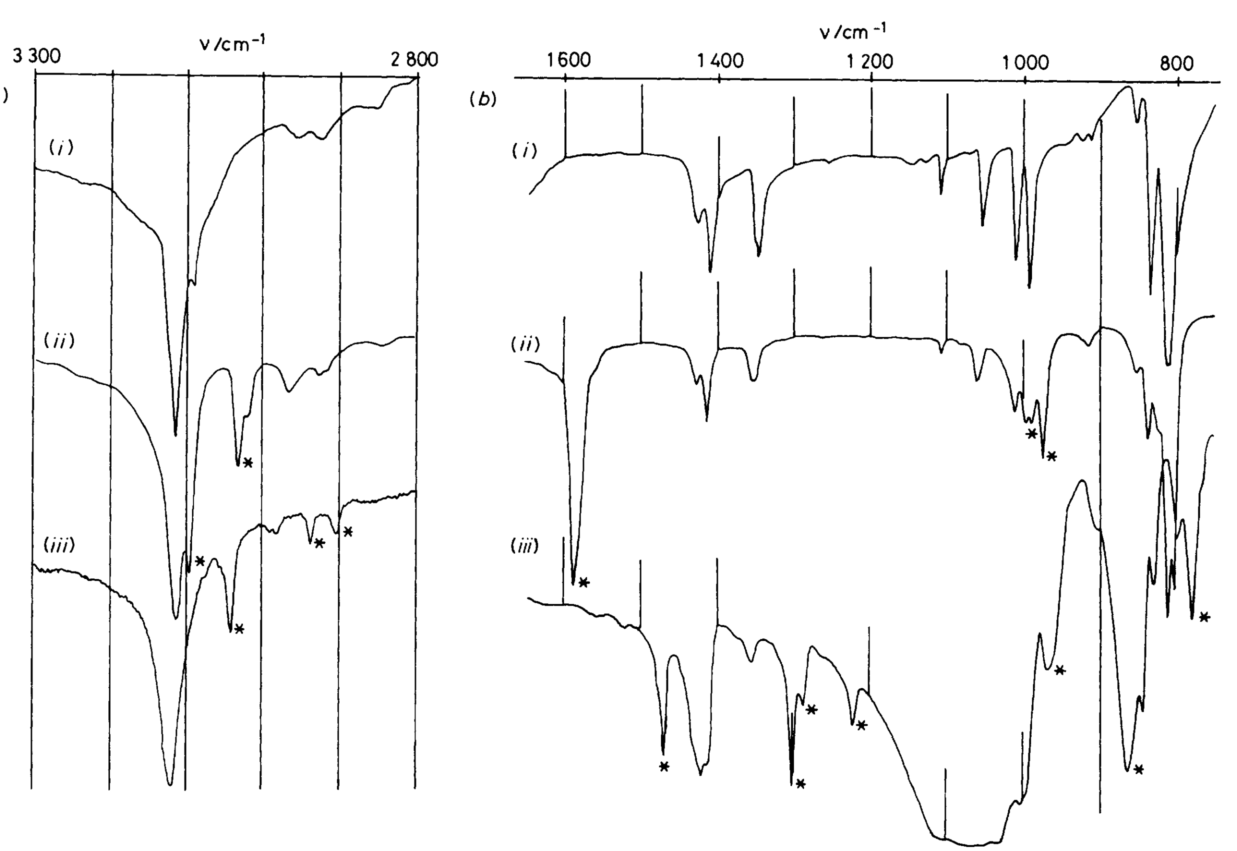

Figure 3. I.r. spectra of (*i*) $[Ru_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (5), (*ii*) $[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}C{=}CH_2)]$ (4), and (*iii*) $[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}CH{=}CH_2)]BF_4$ (2) between (*a*) 3 300—2 800 cm^{-1} and (*b*) 1 650—750 cm^{-1}. Marked peaks are assigned to the C_2 fragments

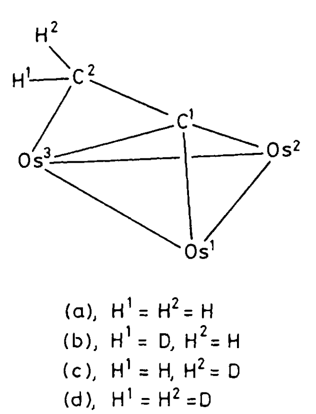

Figure 4. The $Os_3(C{=}CH_2)$ fragment used in the normal co-ordinate analysis of (3) and the four hydrogen isotopomers (a)—(d). Bond lengths (Å): $Os^1\text{–}Os^2$ 2.890, $Os^1\text{–}Os^3$ 2.795, $Os^2\text{–}Os^3$ 2.916, $Os^1\text{–}C^1$ 2.046, $Os^2\text{–}C^1$ 2.035, $Os^3\text{–}C^1$ 2.180, $Os^3\text{–}C^2$ 2.345, $C^1\text{–}C^2$ 1.384, and $C^1\text{–}H$ 1.09. Bond angles: H–C–H 118.3°, C–C–H 118.4°, and $Os^3\text{–}C^2\text{–}H$ 111.7°

stretching vibrations were only prominent at 77 K,[10] and the strong absorptions near 700 cm^{-1} (691 and 680 cm^{-1}) were assigned to the hydride deformations. Slightly different force fields were developed for the different isotopomers (3a)—(3d) and these are presented in Table 5. Their close similarity indicates that these force fields provide good semi-quantitative descriptions. The observed bands and their assignments are in Table 6; they are very similar to those of Sheppard and co-workers.[10]

Table 5. Force constants (mdyn Å^{-1}) used for the $Os_3(C{=}CH_2)$ fragment of $[Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)]$ (3)

	(3a)	(3b)—(3d)
R_{CH}	4.96	4.96
R_{CC}	6.17	6.17
R_{OsC}	2.0	2.0
R_{OsOs}	1.178	1.178
α_{HCH}	0.454	0.51 ± 0.01
α_{CCH}	0.541	0.36 ± 0.03
α_{OsCC}	1.1	1.1
α_{OsCH}	0.498	0.57 ± 0.02
$R_{OsOs}R_{OsOs}$	0.011 68	0.011 68
$R_{CH}R_{CH}$	0.0775	0.0775
$R_{CC}\alpha_{HCH}$	0.2257	0.225 ± 0.001
$\alpha_{CCH}\alpha_{OsCH}$	−0.208	−0.192

$[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}C{=}CH_2)]$ (4).—Comparisons of the partial i.r. spectra of (4) and (5) in alkali halide discs are given in Figure 3. Establishing the fundamentals associated with the vinylidene group is less clear than for the vinyl complex (2). The two most prominent differences in the ν(CH) region are bands at 3 094 and 3 032 cm^{-1} with weaker features at 3 019, 2 964, and 2 927 cm^{-1} [also observed in the spectrum of (5)]. Some difficulty was encountered in completely removing hydrocarbon impurities from these hydrophobic complexes which gave rise to absorptions at ~2 855, ~2 925, and ~2 960 cm^{-1}. Hence the two vinylidene ν(CH) stretches are tentatively assigned to the bands at 3 094, 3 032, and 3 019 cm^{-1}, with the splitting due to solid state effects. Clear additions to the i.r. spectrum of (5) in the fingerprint region only occur at

Table 6. Observed spectra (cm^{-1}) of the $Os_3(CCH_2)$ moiety in $[Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)]$ (3) and their assignments

80% [^{2}H]	45% [^{2}H]	(3)	Assignment of principal component (isotopomer and calculated frequency/cm^{-1})
		3 047w	$\nu_{asym}(CH_2)$ (3a, 3 047)
		2 986w	$\nu_{sym}(CH_2)$ (3a, 2 986)
1 506w			
1 471w, br	1 471ms	1 470m	δ(HCH), ν(CC), ρ_r (3a, 1 471)
1 456w, br			
1 398m	1 398ms		ν(CC) (3c, 1 396; 3b, 1 395)
1 375 (sh)			
1 363ms			ν(CC) (3d, 1 359)
	1 332mw	1 331m	ν(CC) (3a, 1 329)
1 270vw	1 270vw		δ(HCD), δ(OsCH) (3b, 3c, 1 272)
1 260vw	1 260vw		
1 052vw, br	1 052ms	1 051s	ρ_r (3a, 1 051)
1 040w, br			δ(DCD) (3d, 1 041)
	963m	963s	ρ_w (3a, 963)
	957w (sh)		ρ_r, ρ_w (3b, 960)
943vw	943w		ρ_r, ρ_w (3c, 938)
932w	932m		
896w	896m		ρ_w, ρ_r (3c, 888)
877vs	877ms		ρ_r (3d, 879)
	874m (sh)		ρ_w, ρ_r (3b, 870)
	812w	811m	ρ_τ (3a, 811)
778vw			
752vs			ρ_w (3d, 750)
		311s *	ν(OsC) (3a, 326)
		255s *	ν(OsC), δ(OsCC) (3a, 243)
		174m *	ν(OsOs) (3a, 174)
		147w *	ν(OsOs) (3a, 135)
		137vw *	
		112m *	ν(Os–Os) (3a, 119)

* Ref. 10.

Table 7. Assignments of the vinylidene group vibrations (cm^{-1}) in $[Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)]$ (3) and $[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}C{=}CH_2)]$

(3)	(4)		
I.r.	I.r.	Raman	Assignment
3 047	3 094	3 095	$\nu_{asym}(CH_2)$
2 986	3 032	3 022	$\nu_{sym}(CH_2)$
1 470	—	—	$\delta(CH_2)$, ν(CC), ρ_r
1 331	1 586	1 578	ν(CC)
1 051	988	—	ρ_r
963	973	—	ρ_w
811	—	—	ρ_τ

1 586 (with a shoulder at 1 581 cm^{-1}), 988, and 973 cm^{-1} with the region between 810 and 850 cm^{-1} being dominated by bands common to (5). Two bands would be anticipated between ~1 300 and ~1 600 cm^{-1} due to mixtures of the ν(CC) and $\delta(CH_2)$ modes, and a Raman spectrum was therefore recorded to identify a possible second band. Although this was rich in detail, only one signal was obtained in this region which might not be assigned to the dimer. At 1 578 cm^{-1}, that is essentially coincident with an i.r. band. A tentative assignment for these vibrations is given in Table 7.

Discussion

The frequencies of the vibrational modes of the vinyl moieties of (1) and (2) above ~1 000 cm^{-1} agree within 20 cm^{-1}. Below that figure, the assignments become difficult due to the fact that $[Ru_2(CO)_4(C_5H_5)_2]$ (5) also has bands in the 750—850 cm^{-1} region. The identification of the band at 780 cm^{-1} as being due to the vinyl group is tentative, as is the assignment of the 865 cm^{-1} absorption. Both (2) and (4) exist in isomeric forms;[9,16] this may contribute to the changing profiles of the non-C_2 fragment vibrations and splittings and shoulders in modes which are associated with these fragments. However, the μ-η^2 vinyl group frequencies differ markedly from those of simple σ bonded vinyl ligands as in $BF_2CH{=}CH_2$,[14] $GeH_3CH{=}CH_2$,[17] and $GeBr_3CH{=}CH_2$.[17] Hence these frequencies are largely transferable between two complexes of the same co-ordination mode (μ-η^2) and are distinguishable from those of the groups alternative method of co-ordination (σ). In vinyl chloride, the three ν(CH) modes all absorb above 3 000 cm^{-1} [18] and σ co-ordination of the vinyl group to a GeH_3 moiety leaves these in the range 2 959—3 066 cm^{-1}.[17] Co-ordination of the olefinic band evidently lowers one of these vibrations to ~2 910 cm^{-1}. The effect is similar to that observed in $[Fe(CO)_4(C_2H_4)]$,[19] and more marked than in Zeise's salt.[20] The most satisfactory fit was obtained for (1) if this low frequency band was assigned as the symmetric (CH_2) stretch. Three modes are observed in the 1 250—1 600 cm^{-1} region arising from the ν(CC), $\delta(CH_2)$, and δ(CH, in plane) modes. The last of these is relatively unshifted [1 279, 1 268, and 1 266 cm^{-1} in $ClCH{=}CH_2$, $GeH_3CH{=}CH_2$, and (1) respectively]. The major effect of π-co-ordination is to lower the vibration predominantly due to the C=C stretching mode from ~1 600 cm^{-1} to ~1 310 cm^{-1}. Concomitant with this is an increase in the frequency of the remaining band from 1 369 cm^{-1} in $ClCH{=}CH_2$ and 1 395 cm^{-1} in $GeH_3CH{=}CH_2$ to ~1 470 cm^{-1} in (1) and (2). Vinyl chloride exhibits four vibrations between 600 and 1 050 cm^{-1} which consist largely of vinyl group deformation modes. There is no clear frequency order for four modes [ρ_r, ρ_w, ρ_τ, and δ(CCH) out-of-plane] within the series $XCH{=}CH_2$ (X = Cl, BF_2, GeH_3, and $GeBr_3$).[14,17,18] However, like $BF_2CH{=}CH_2$ and $GeBr_3CH{=}CH_2$, two of the modes, ρ_τ and ρ_r, resonate near 1 000 cm^{-1} in (1). A third band, largely ρ_w in nature, is more sensitive, covering a range of 874—989 cm^{-1} in the σ vinyl species, and dropping to 786 cm^{-1} in (1). A fourth band was predicted to occur at 544 cm^{-1} using this force field, in a region masked by $\nu(OsC)$ and $\delta(OsCO)$ vibrations; in $GeBr_3CH{=}CH_2$ this was observed at 525 cm^{-1}.

It is quite clear that π-co-ordination, making the difference between the μ_3-η^2 mode of the vinylidene $[Os_3(CO)_9(\mu\text{-}H)_2(C{=}CH_2)]$ (3) and the μ mode in $[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}C{=}CH_2)]$ (4) does have an effect on the vibrational frequencies, so these modes can be distinguished by vibrational spectroscopy. A slight lowering of the $\nu(CH)$ frequencies is observed between (4) and organic vinylidenes, $X_2C{=}CH_2$ (X = F, Br,[21] and CN [22]). For example, the antisymmetric and symmetric CH stretches are observed at 3 120 and 3 028 cm^{-1} in $Br_2C{=}CH_2$ and 3 094 and 3 032 cm^{-1} in (4). However π-co-ordination in (3) lowers these more markedly to 3 047 and 2 986 cm^{-1}. As in the vinyl complexes, π-bonding lowers the $\nu(C{=}C)$ from 1 590 cm^{-1} in $(NC)_2C{=}CH_2$ and (4) to 1 331 cm^{-1} in (3) and this is accompanied by an increase in the frequency of the vibration largely of $\delta(CH_2)$ character from $\sim$1 370 cm^{-1} in the organic analogues to 1 470 cm^{-1} in (3). Unfortunately no equivalent band was observed for (4) although it may be masked by the C_5H_5 ring vibration at $\sim$1 350 cm^{-1}. The π-co-ordinated vinylidene group in (3) is distorted from planar $X_2C{=}CH_2$ (C_{2v}) into a unit with no symmetry and distinguishing the deformation modes into ρ_r, ρ_w, and ρ_T categories is approximate. Nevertheless, the molecular motions of (3) can largely be separated in this way. As in the organic vinylidenes, the highest frequency for these vibrations was observed for the rocking mode. Its frequency varies from 1 306 cm^{-1} in $CH_2{=}CF_2$ to 1 067 cm^{-1} in $CH_2{=}CBr_2$, with (3) being slightly lower than this spreadat 1 051 cm^{-1}.

The ρ_w frequency of (3) (963 cm^{-1}) is within the large range observed for organic vinylidenes.[21-23] The complexed vinylidene also affords a vibration of torsional type at 811 cm^{-1}. A difference between the frequency order of the predominant mode contributing to the three vibrations between $\sim$800 and $\sim$1 050 cm^{-1} is apparent between (1) and (3). However, in view of the different geometries of the $Os_3(C_2H_n)$ moiety in these two complexes, this is not unexpected.

The most marked change on π-co-ordination of these hydrocarbon fragments is the lowering of the $\nu(C{=}C)$ frequency. This band weakening can only be estimated after a normal co-ordinate analysis because of the mixing with the $\delta(CH_2)$ mode in particular. The C=C stretching force constant was calculated to be 6.68 and 6.17 mdyn $Å^{-1}$ for (1) and (3) respectively (*cf.* 6.55 mdyn $Å^{-1}$ for Zeise's salt [20]) as compared with 7.19 and 7.55 mdyn $Å^{-1}$ for their respective organic fragments in vinyl chloride [18] and vinylidene bromide.[21]

The normal co-ordinate analysis on the Os_3H fragment of (1) also provided information about the bridging hydride in particular. At 0.7674 mdyn $Å^{-1}$, the Os–H force constant is less than half the values estimated for terminal M–H stretches in $[Re(CO)_5H]$ [24] and $[Os_3(CO)_{12}H_2]$ [25] (1.984 and 2.32 mdyn $Å^{-1}$ respectively). It is however comparable with the estimate of 1.08 mdyn $Å^{-1}$ for a series of μ-hydride complexes.[11] A high α_{OsOsH} force constant was required and both the absorption at 1 285 and that at 710 cm^{-1} are mixtures of the symmetric stretch and out-of-plane bend. So a simpler description as ν_{sym} (Os–H) and bending vibrations respectively is inaccurate. The value calculated for the osmium–osmium force constant (0.985 mdyn $Å^{-1}$) is lower than estimates reported for $[Os_3(CO)_{12}]$ [26] and $[Os_3(CO)_{12}H_2]$ [25] (1.6 and 1.54 or 1.34 mdyn $Å^{-1}$ respectively) on the basis of simple Os_3 cores. However these modes can mix strongly with δ(Os–Os–C) and δ(C–Os–C) motions and allowance for this markedly altered the value of R_{OsOs} obtained for $[Os_3(CO)_{12}]$ (to 0.91 mdyn $Å^{-1}$).[27] Hence the value of R_{OsOs} for (1) is only an estimate.

Conclusions

Group frequencies have been obtained for a μ-η^2-$CH{=}CH_2$ moiety which are transferable to a second complex. These are quite distinct from those of σ bonded vinyl groups. The μ and μ_3-η^2-co-ordination modes of a vinylidene group are differentiable by i.r. spectroscopy.

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