Spectroscopic Studies on C_2 Hydrocarbon Fragments. Part 2.[1] Vibrational Group Frequencies and Carbon-13 Nuclear Magnetic Resonance Chemical Shifts of Cluster-bound C_2H_n (n = 1—4) Fragments †

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Vibrational and ^{13}C n.m.r. spectra have been recorded on $[Os_3(CO)_{11}(\eta^2\text{-}C_2H_4)]$, $[M_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CMe)]$ (M = Ru or Os), $[Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}HCCH)]$, $[Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}CCH)]$, $[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CHMe)]$, $[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CMe)]BF_4$, and $[Os_3(CO)_9(\mu\text{-}H)(\mu\text{-}SPr^n)L]$ (L = CO, C_2H_4, or C_2H_2). In conjunction with published data, ^{13}C n.m.r. shift ranges of C_1 and C_2 cluster-bound hydrocarbon fragments have been identified. Vibrational group frequencies of the C_2H_n (n = 1—4) moieties have also been proposed. On this basis, acetylene is suggested to rearrange to a μ_3-η^2-vinylidene on Ni(111) and Fe(110) surfaces.

We have shown that the vibrational frequencies of vinyl and vinylidene groups are dependent upon their co-ordination modes and established group frequencies for these moieties co-ordinated to triosmium clusters.[1] In this paper we extend this survey to a wider range of two-carbon fragments (C_2H_n, n = 1—4) to determine group frequencies for these systems which might be applied to unknown organometallic complexes and also to species on metal surfaces. Carbon-13 n.m.r. spectroscopy has been recently employed to study CO on rhodium dispersed on high surface area alumina.[2] The observed shifts could be correlated with those of discrete metal carbonyl complexes and so we are also establishing chemical shift ranges from cluster-co-ordinated C_2 fragments which may be of future use in the study of chemisorbed hydrocarbons. The high resolutions possible by combined cross polarisation and magic angle spinning[3] make this a probable area of study; the approach has been successfully applied to the structure of solid polypropylene.[4]

Experimental

The equipment used was as in ref. 1, with additional ^{13}C n.m.r. spectra recorded at 100.63 MHz on a Bruker WH-400. Compounds were characterised by mass, ^1H and ^{13}C n.m.r., and i.r. (carbonyl region) spectroscopy. Unless otherwise stated, data were in agreement with those published previously.

Preparations.—$[Os_3(CO)_{11}(\eta^2\text{-}C_2H_4)]$ (1). The complex $[Os_3(CO)_{11}(MeCN)]$ was prepared from $[Os_3(CO)_{12}]$ (0.12 g), MeCN and Me_3NO in CH_2Cl_2.[5] The solvent was removed under reduced pressure at room temperature, the residue dissolved in $ClCH_2CH_2Cl$ (*ca.* 9 cm^3) and treated with ethylene (20 atm) at room temperature for 16 h. The solvent was removed by passing a stream of ethylene through the solution to afford complex (1) (0.097 g, 81%).[5]

^{13}C-{^1H} N.m.r.: in CH_2Cl_2–CD_2Cl_2 at −20 °C (25.2 MHz), δ 22.4, 170.1, 171.0, 173.2, 173.5, 175.3, 182.8, 183.9, and 185.2; in $CDCl_3$ at −20 °C (100.63 MHz), δ 22.0, 169.3, 172.1, 172.9, 174.7, 175.1, 182.1, 183.0, and 184.3. I.r.: CsI and KBr, 3 085vw, 3 021vw, 1 485vw, 1 464vw, 1 439vw, 1 262w, 1 207w, 1 190m, 986w, 959w, 840vw, 710vw, 632s, 601s, 583s, 562s, 494s, 454s, 407s, and 394m cm^{-1}; in CCl_4, 3 072vw and 3 009vw cm^{-1}; in $CDCl_3$, 3 075vw, 3 010vw, 1 439vw, and 1 190w cm^{-1}.

$[Os_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CMe)]$ (2). Complex (2) was prepared by reacting $[Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}CCH_2)]$ (3) with H_2 in refluxing n-heptane for 24 h according to ref. 6 (yield 73%). N.m.r.: ^1H ($CDCl_3$), δ 4.45 (s), −18.68 (s); ^{13}C ($CDCl_3$), δ 45.3 (CH_3), 154.7 (C–CH_3), 166.9 (CO *trans* to CMe), and 167.8 (CO *trans* to H). I.r. (C_6H_{12}): 2 076vs, 2 069w, 2 017vs, and 2 004m cm^{-1}. Other i.r. spectra (excluding carbonyl bands): in CCl_4, 2 916w, 2 892w, 2 864vw, 2 836w, 2 711vw, 1 438w, 1 367vw, 1 144vw, 1 118vw, and 1 035s cm^{-1}; in CS_2, 2 911w, 2 889w, 2 866vw, 2 831w, 2 707vw, 1 366vw, 1 143vw, 1 116vw, 1 034s, 734m, and 697s cm^{-1}; KBr at 298 K, 2 915m, 2 889m, 2 860vw, 2 831m, 2 700w, 1 361w, 1 147w, 1 114w, 1 037s, 732m, 704s, 693s, and 605s cm^{-1}; KBr at 77 K, additional bands at 1 388w br and 1 365w cm^{-1}; CsI (600—200 cm^{-1}), 560s, 532vs br, 499vs, 478s, 468s, 432vs, 421vs, 404s, and 390m (sh) cm^{-1}; CsI at 77 K, additional bands at 1 392s and 1 366s cm^{-1}. Raman: CH_2Cl_2, 2 108w and 2 016w cm^{-1}; solid, 2 917w, 2 892w, 2 833w, 2 105s, 2 007vs, 1 988vs, 1 440vw, 1 364w, 527w, 500s, 487m, 469w, 420m, 391w, 208w, 178w, 118vs (sh), 109vs, 88vvs, 68m, and 44w cm^{-1}.

$[Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}HCCH)]$ (4). Complex (4) was prepared by passing acetylene through a refluxing solution of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CHCH_2)]$ (5) (0.08 g) in hexane (40 cm^3) as described by Deeming *et al.*[7] The major (orange-yellow) band obtained on a 20 × 20 cm silica t.l.c. plate (hexane as solvent) contained a mixture of (4) and (5). Development on 40 × 20 cm plates yielded (5), which was recrystallised from hexane (0.024 g, 30%). ^{13}C N.m.r. ($CDCl_3$): δ 123.4 (CH), 179 (br), and 175.2 (br). I.r. [excluding ν(CO)]: CsI, 2 991w, 2 942m, 1 297m, 1 228w, 1 203w, 1 032m, 975w, 847ms, 665ms, 570vs, 542s, 521vs, 504s, 483vs, 467.5s, 458s, 417m, 400m, 358m, 284m, 250w, 229w, and 204w cm^{-1}; CS_2, 848vw and 666vw cm^{-1}.

$[Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}CCH)]$ (6). Hydrogen was passed through a refluxing solution of (4) (0.06 g) in n-heptane (35 cm^3) for 45 min,[7] after which time all complex (4) was consumed. Recrystallisation from hexane afforded (6) (0.02 g, 35%). ^{13}C N.m.r. (100.63 MHz), $CDCl_3$: δ 41.6 (CH), 134.4 (C≡CH), 162.0 (d, $^1J_{HC}$ 12.1 Hz), 168.1, and 172.1. I.r. [excluding ν(CO)], CsI: 3 156m, 1 533m, 1 402vw br, 1 345vw, 1 259w, 858m, 762w, 690s, 584s, 552s, 529s, 497m, 448s, 420 (sh), and 347m cm^{-1}. At 77 K, the bands at 1 402 and 1 345 cm^{-1} sharpen and increase in intensity and the doublet at *ca.* 858 cm^{-1} also sharpens.

$[Ru_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CMe)]$ (7).[8] A solution of $[Ru_4(CO)_{12}H_4]$ (0.048 g) in cyclohexane (30 cm^3) was treated with ethylene (15 atm) and heated to 70 °C for 1 h. Purification was by t.l.c. (hexane on SiO_2), vacuum sublimation and recrystallisation from hexane. Yield 0.006 g (12%). N.m.r.: ^1H ($CDCl_3$),

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† *Non-S.I. unit employed:* 1 atm = 101 325 Pa.

δ 4.15 (s), −17.47 (s); ^{13}C ($CDCl_3$), δ 47.9 (CH_3), 189.9 (CO *trans* to C), 190.6 (CO *trans* to H), and 219.3 (*C*–CH_3). I.r.: C_6H_{12}, 2 079s, 2 074w (sh), 2 034s, 2 021w (sh), and 2 015m cm^{-1}; N_2 matrix at *ca.* 10 K, 2 926w, 2 893w, 2 861vw, 2 852vw, 2 835w, 2 108vw, 2 083vs, 2 077w, 2 062vw, 2 037s, 2 033w (sh), 2 018m, 1 996w, 1 980w, 1 363w, 1 129m, 1 028s, 730w, 691s, 610w, 595s, 550s, 527vs, 507w, 482m, 463w, 432w, 405m, and 392m br cm^{-1}; in CCl_4 [excluding ν(CO) bands], 2 915m, 2 886m, 2 856w, 2 830m, 1 432w, 1 361w, 1 120m, and 1 026s cm^{-1}; KBr [excluding ν(CO) bands], 2 916m, 2 881m, 2 855vw, 2 828m, 1 356w, 1 125m, 1 028s, 725m, and 688s cm^{-1}.

[$Ru_2(CO)_3(\eta^5$-$C_5H_5)_2(\mu$-CHMe)] (8).[9] I.r. [excluding ν(CO) bands], CsI: 3 127m (sh), 3 120m, 3 109 (sh), 2 098 (sh), 2 947m, 2 903m, 2 868 (sh), 2 835m, 2 686w, 1 445mw, 1 428m, 1 412m, 1 353m, 1 264m, 1 108w, 1 055m, 1 015vs, 996m, 968m, 906m, 837s, 818s, 716vw, 612vs, 593vs, 571m, 562m, 542mw, 517vs, 490m, 420w, 379vw, 339w, and 317w cm^{-1}. Raman: 3 130m, 3 099w, 2 900w, 2 832w, 1 940w, 1 913vw, 1 767w, 1 426w, 1 332w, 1 109m, 1 060w, 1 019vw, 522w, 488w, 459w, 382w, 344w, 314m, 267vw, 224ms, 149m, 129s, and 110s cm^{-1}. ^{13}C N.m.r. ($CDCl_3$): δ 200.09 (CO), 142.95 (*C*HMe), 91.95 and 91.06 (C_5H_5, *trans*), 90.34 (C_5H_5, *cis*), 89.32 (C_5H_5, *cis*, *anti*), 44.43 and 43.29 (CH*C*H_3).

[$Ru_2(CO)_3(\eta^5$-$C_5H_5)_2(\mu$-CMe)]BF_4 (9).[10] Complex (9) was prepared from the reaction of [$Ru_2(CO)_3(\eta^5$-$C_5H_5)_2(\mu$-$CCH_2)$] (10) with HBF_4.[10] This complex was found to react with CsI in discs, though reliable spectra could be produced if the disc was scanned immediately after pressing. I.r. [excluding ν(CO) bands]: CsI, 3 119m, 2 880vw, 1 430m, 1 412ms, 1 352w, 1 326mw, 1 287w, 1 196ms, 1 150—1 000vs br, 846vs, 829 (sh), 651vs, 604w, 563mw, 549mw, 508vs, 485ms, and 461 cm^{-1}; $Cl_2CC(Cl)C(Cl)CCl_2$, 3 115m, 2 874w, 1 432mw, 1 413m, 1 350w, 1 327mw, 1 284w, 1 197m, 1 100—1 030vs br, 848s, 650vs, 603s, 561vw, 547m, 507s, and 460s cm^{-1}.

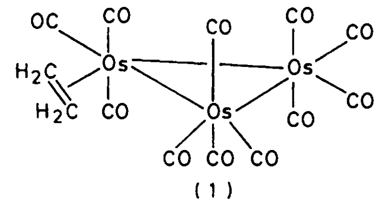
[$Os_3(CO)_{10}(\mu$-H)(μ-SPr^n)] (11).[11] I.r. [excluding ν(CO) bands], CsI: 3 642w, 2 974m, 2 935m, 2 876w, 1 462m, 1 454m, 1 430m, 1 379m, 1 332s, 1 292m, 1 260m, 1 219vs, 1 084vs, 1 040s, 1 022s, 861m, 803s br, 734m, 725w, 686vs, 620—530vs br, 490vs br, 460s, 436s, 428s, 408vs, 328m, and 295m br cm^{-1}. At 77 K, additional bands at 1 233vw and 1 210vw cm^{-1} and sharpening of the peak at 1 454 cm^{-1} occurred.

[$Os_3(CO)_9(\mu$-H)(μ-SPr^n)(η^2-C_2H_4)] (12). I.r. [excluding ν(CO) bands], CsI: 2 969m, 2 933m, 2 872w, 2 856w, 1 486m, 1 463s, 1 457s, 1 448m, 1 427m, 1 379m, 1 331w, 1 287w br, 1 260vw, 1 227m, 1 205m, 1 194m, 1 088m, 1 044w, 1 020vw (sh), 997w, 956w (sh), 948w, 892w, 837vw, 832vw, 800vw br, 770w, 740m, 668vs, 622vs, 600—560vs, 535vs, 491vs, 479vs, 467 (sh), 452m, 434m, 397s, 355m, and 340m cm^{-1}.

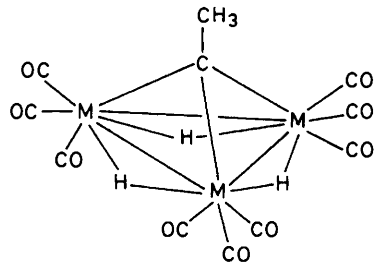
[$Os_3(CO)_9(\mu$-H)(μ-SPr^n)(η^2-C_2H_2)] (13).[12] I.r. [excluding ν(CO) bands], CsI: 3 200—2 900br, 1 462s br, 1 433m, 1 381ms, 1 331w, 1 284s, 1 270 (sh), 1 233ms, 1 211vw, 1 150vw, 1 134vw, 1 088ms, 1 076w (sh), 1 049ms, 1 014ms, 898m, 861s, 791vw, 743vw, 690vs br, 600—450vs, and 420—350vs cm^{-1}. At 77 K, sharpening of band at 1 267 cm^{-1} and intensity increase at 1 211 cm^{-1} occurred. The i.r. spectrum of a $Cl_2CC(Cl)C(Cl)CCl_2$ mull includes bands at 2 960w, 2 927w, 2 870vw, and 2 853vw cm^{-1}.

Results

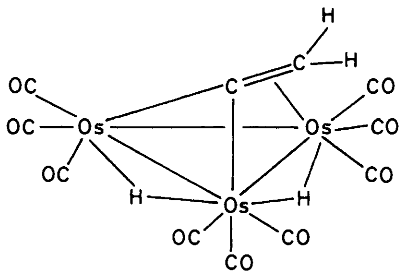
Ethylene Complexes.—At −20 °C, the ^{13}C n.m.r. spectrum of [$Os_3(CO)_{11}(\eta^2$-$C_2H_4)$] (1) contained eight carbonyl resonances of approximate relative intensity 1 : 1 : 1 : 1 : 1 : 1 : 2 : 2 : 2 (starting from the low-field signal), as expected for an equa-



(1)



(2) M = Os, (7) M = Ru



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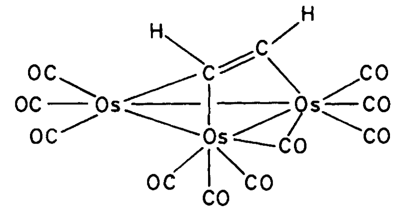

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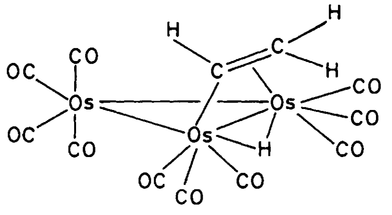

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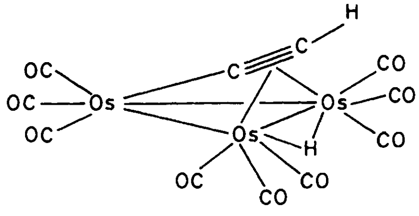

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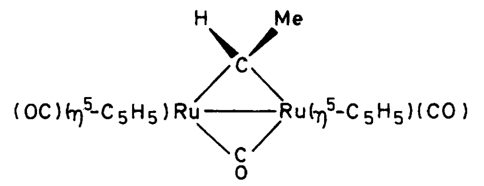
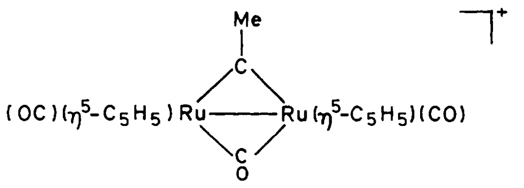
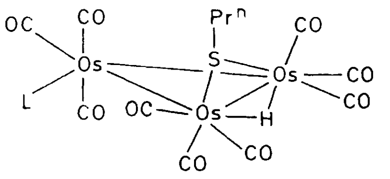


(8)



(9)



(11) L = CO, (12) L = η^2-C_2H_4, (13) L = η^2-C_2H_2

torial substituent. (An axial ethylene site would yield six carbonyl environments of population ratio 2 : 2 : 2 : 2 : 2 : 1.) A single ethylenic carbon resonance was observed at δ 22.4 (in dichloromethane) and, together with the single proton resonance that this complex exhibits at room temperature,[5] suggests olefin rotation. On the basis of the n.m.r. evidence, the C–C axis could be perpendicular to, or parallel with the Os_3 plane. However, comparison with [$Os_3(CO)_8$(μ-H)(μ-SMe)-(η^2-C_2H_4)] [13] and *cis*-[$Os_3(CO)_{11}${η^2-$CF_3C(H)CC(H)F_3$}],[14] the latter geometry is more probable, with rotation about the Os–C_2H_4 axis averaging the ends of the alkene. The rotation barrier is low as the proton singlet only broadens at −80 °C. Two separate broad resonances were observed 30 Hz apart at −112 °C in CD_2Cl_2–$CHFCl_2$ solution with a coalescence temperature of -102 ± 2 °C ($\Delta G^{\ddagger}_{171}$ = *ca.* 35 kJ mol^{-1}). Ethylene rotation is not coupled to any carbonyl motion. Indeed, carbonyl exchange was not evident at −20 °C, unlike the phosphine derivative [$Os_3(CO)_{11}(PEt_3)$].[15]

The limited stability of complex (1) rendered it difficult to purify stringently from carbonaceous impurities which gave rise to ν(CH) absorptions at *ca.* 2 950 cm^{-1}; a similar difficulty was encountered with [$Os_3(CO)_9$(μ-H)(μ-SPr^n)(η^2-C_2H_4)] (12). Nevertheless, i.r. bands attributable to the ethylene moiety could be identified for both complexes (1) and (12). For the latter complex this involved comparison with [$Os_3(CO)_{10}$-(μ-H)(μ-SPr^n)] (11). Possible assignments for the C_2H_4 moiety vibrations for (1) and (12) are given in Table 1, and compared with published assignments for [$Fe(CO)_4(C_2H_4)$] [16] and Zeise's salt.[17] There is a discrepancy between the allocations of ρ_τ and ρ_r modes for these two mononuclear complexes, and the current choice is in line with a partial normal co-ordinate analysis on [$PtCl_3(C_2H_4)$]$^-$.[18]

Ethylidene Complex, (8).—On comparison between the i.r. spectra of [$Ru_2(CO)_4(\eta^5$-$C_5H_5)_2$] (14) and [$Ru_2(CO)_3(\eta^5$-$C_5H_5)_2$(μ-CHMe)] (8), seven absorptions were attributable to the ethylidene moiety: 2 947m, 2 903m, 2 868 (sh), 2 835m, 1 445mw, 1 264m, and 968m cm^{-1}. Three ν(CH) modes have been observed for $MeCHCl_2$,[19] and assigned as 3 015 [ν(CH)], 3 001 [$\nu(CH_3)_{asym}$], and 2 946 cm^{-1} [$\nu(CH_3)_{sym}$]. It is evident that these bands in (8) are markedly lower in frequency. A similar lowering has been reported from CH_2I_2 (3 048 and 2 968 cm^{-1}) to [$Os_3(CO)_{10}$(μ-H)$_2$(μ-CH_2)] (2 984 and 2 935 cm^{-1}),[20] [$Os_3(CO)_{10}$(μ-CO)(μ-CH_2)] (2 990 and 2 949 cm^{-1}),[20] and [$Rh_2(CO)_2(\eta^5$-$C_5H_5)_2$(μ-CH_2)] (2 961 and 2 901 cm^{-1}).[21] Terminal neopentylidene ligands have been found to exhibit very low ν(CH) frequencies near 2 500 cm^{-1},[22] so the 2 835 cm^{-1} absorption of (8), which is lower in frequency than any other C–H stretching vibration in this study, has been assigned to the alkylidene ν(CH); this vibration was also observed in the Raman spectrum (at 2 832 cm^{-1}). Making reference to the assignments reported for $MeCHCl_2$,[19] the following assignments have been made for complex (8): 2 947 [$\nu(CH_3)_{asym}$], 2 903 [$\nu(CH_3)_{sym}$], 2 868 [overtone of band at 1 445 cm^{-1}], 2 835 [ν(CH)], 1 445 [$\delta(CH_3)_{asym}$], 1 264 [δ(CH), ν(CC)], and 968 cm^{-1} [$\rho_r(CH_3)$]. The $\delta(CH_3)_{sym}$ mode is probably masked by the other chromophores in the molecule.

Table 1. Vibrational assignments (cm^{-1}) for the C_2H_4 fragments in (1), (12), [$Fe(CO)_4(C_2H_4)$],[16] and Zeise's salt [17]

Assignment (C_{2v} symmetry labels)		[$Fe(CO)_4$(C_2H_4)]	K[$PtCl_3$-(C_2H_4)]	(1)	(12)
	a_2		3 094	3 085	
ν(CH)	b_2	3 080 [a]	3 079		
	b_1	2 955	2 998	3 021	2 856
	a_1	2 920	3 013		
ν(CC)	a_1	1 195	1 243	1 190	1 194
δ(CH_2)	a_1	1 510	1 515	1 485	1 486
	b_1	1 467, 1 476	1 426	1 439	1 448
$\rho_r(CH_2)$	a_2	1 076, 1 080	841	840	837
	b_2	720	720	710	770
$\rho_\tau(CH_2)$	a_2	804	1 222 [b]	1 207 or 1 262	1 227
$\rho_w(CH_2)$	a_1	938	975	959	948
	b_1	1 030	1 010	986	997

[a] Gas phase spectra. [b] Calculated value.[18]

Table 2. Ethylidyne group vibration frequencies (cm^{-1}) in [$M_3(CO)_9$-(CMe)] (M = Co, RuH, or OsH) in KBr

[$Co_3(CO)_9$-(CMe)] [a]	[$Os_3(CO)_9H_3$-(CMe)]	[$Ru_3(CO)_9H_3$-(CMe)]	Assignment
2 930	2 915	2 916	$\nu(CH_3)_{asym}$
2 888	2 889	2 881	$\nu(CH_3)_{sym}$
1 420	1 438 [b]	1 432 [b]	$\delta(CH_3)_{asym}$
1 356	1 361	1 356	$\delta(CH_3)_{sym}$
1 163	1 147	1 125	ν(CC)
1 004	1 037	1 028	ρ(CH_3)

[a] Ref. 24. [b] In CCl_4 solution.

Ethylidyne Complexes.—The ^{13}C n.m.r. spectrum of [$Os_3(CO)_9$(μ-H)$_3$(μ_3-CMe)] (2) indicates a rigid carbonyl frame, as reported for the ruthenium analogue (7).[8] Whilst the ethylidyne methyl carbons exhibit very similar chemical shifts [δ 45.3 and 47.9 for (2) and (7) respectively], the quaternary carbons resonate 65 p.p.m. apart [δ 219.3 in (7) and δ 154.7 in (2)].

In cyclohexane solution, complex (2) exhibits four of the five expected ν(CO) bands in its i.r. spectrum ($2a_1 + 3e$) at 2 076, 2 069, 2 017, and 2 004 cm^{-1}. The Raman spectrum of a solid sample contains three ν(CO) features. One of these, at 2 105 cm^{-1}, can clearly be assigned to the first a_1 mode. The second, at 2 007 cm^{-1}, is nearly coincident with the i.r. band at 2 004 cm^{-1}, and the third Raman band, at 1 988 cm^{-1}, forms a sixth ν(CO) frequency. This is absent in solution and therefore probably arises from the formally forbidden a_2 mode, which is also the lowest frequency carbonyl stretch in [$Co_3(CO)_9$(μ_3-CH)].[23]

A detailed analysis of the vibrations of [$Co_3(CO)_9$(μ_3-CMe)] (15) has been reported.[24] We have made measurements in accord with those of Sheppard and co-workers,[24] and, in addition, we have recorded the i.r. spectrum of (15) in a nitrogen matrix at *ca.* 10 K. The ethylidyne frequencies were very similar to the solid-state values, and thus eliminate any doubts about the published assignments because of putative solid-state splittings. The ethylidyne vibrational frequencies of (2) and (7) are presented in Table 2, assignments being made by comparison with the cobalt derivative (15). As with the cobalt complex, the C–H stretching region is complicated by overtone bands. The two allowed overtones of the δ(CH_3) *e* mode are observed at 2 860 and 2 831 cm^{-1} for (2) and 2 855 and 2 828 cm^{-1} for (7), and the osmium complex also exhibited an overtone of the $\delta(CH_3)$ a_1 mode at 2 700 cm^{-1}. An attempt was made to confirm Sheppard's assignment of the $\nu(CC)$ and $\rho(CH_3)$ modes,[24] which were interchanged from the original suggestion,[25] by Raman polarisation measurements. However, neither band was observable in the Raman spectrum. It is evident, however, that the i.r. frequencies of this μ_3-co-ordination type are only slightly dependent upon the nature of the metal.

The Raman spectrum of complex (2) also exhibits six features between 40 and 190 cm^{-1}. On comparison with the reported $\nu(M-M)$ modes for $[Os_3(CO)_{12}]$ (158 and 117 cm^{-1}),[26] $[Os_3(CO)_{10}(\mu\text{-}OMe)_2]$ (172, 136, and 119 cm^{-1}),[27] $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CHCH_2)]$ (5) (168, 126, and 116 cm^{-1}),[28] and $[Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}CCH_2)]$ (3) (175, 150, and 115 cm^{-1}),[28] the most plausible $\nu(M-M)$ assignment for (2) is 178 (a_1) and 118 cm^{-1} (e) The lower frequency bands are probably deformations of the $Os(CO)_3$ moieties.

The i.r. spectrum of the ruthenium derivative (7) contains bands at 725 and 688 cm^{-1}, considered to be $\delta(MH)$ motions. The solid-state spectra of (2), however, exhibit three bands in this region (732, 704, and 693 cm^{-1}). However, in CS_2 solution, the two lower frequency bands are replaced by a single absorption at 697 cm^{-1}, pointing to solid-state splitting of the lower band in alkali halide discs. The solution Raman spectrum shows a single strong band at 702 cm^{-1}, which would suggest an assignment of 732 [$\delta(MH)$ e] and 702 cm^{-1} [$\delta(MH)$ a_1]. A site symmetry splitting, however, would indicate the opposite symmetry assignment, so perhaps the solid-state splitting is a correlation effect. Two additional bands at 1 388 and 1 365 cm^{-1} were clearly resolved when the KBr disc was cooled to 77 K. It has been shown that $\nu(Os-H)$ modes are often resolved at low temperatures,[29] suggesting these two features are due to modes of this type.

An alternative ethylidyne co-ordination mode is provided by $[Ru_2(CO)_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CMe)]BF_4$ (9).[10] Complex (9) discoloured a CsI disc, but spectra similar to those obtained in Nujol and $Cl_2CC(Cl)C(Cl)CCl_2$ mulls could be obtained if recorded expeditiously. However much of the spectrum is obscured by the remainder of the cation and the BF_4^- counter ion. Only four bands could be identified as associated with the ethylidyne moiety at 2 880, 1 326, 1 287, and 1 196 cm^{-1}. Only one of the $\nu(CH_3)$ modes, presumably the symmetric stretch, is observable and there are three peaks within the window between the $\nu(BF)$ absorption and cyclopentadienyl ring vibrations; four absorptions are anticipated between *ca.* 1 000 and *ca.* 1 450 cm^{-1}, *viz.* $\delta(CH_3)_{sym}$, $\delta(CH_3)_{asym}$, $\nu(CC)$, and $\rho(CH_3)$. The C–C bond length for (9) (1.462 Å) [9] is less than that of $[Ru_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CMe)]$ (7) (1.511 Å),[30] so the value of $\nu(CC)$ in the dinuclear complex would be anticipated to be higher than that of (7), *i.e.* at 1 196 or 1 287 cm^{-1}. It is probable that the CMe moiety in (9) is more electron deficient than that in (7). The effect of changing to increasingly electronegative halogens in CH_3CX_3 derivatives is (allowing for coupling with CF_3 vibrations) to increase the frequencies of all modes.[31] A tentative assignment is therefore 1 326 [$\delta(CH_3)_{sym}$], 1 287 [$\nu(CC)$], and 1 196 cm^{-1} [$\rho(CH_3)$].

Ethyne Complexes.—The room temperature ^{13}C n.m.r. spectrum of $[Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}HCCH)]$ (4) demonstrates that the carbonyl groups are exchanging and also located the acetylenic carbon at δ 123.4. Our i.r. data agree very closely with those reported by Sheppard and co-workers [32] after the completion of this work. We have no information which causes us to alter the published assignments.

Comparison between the i.r. spectra of $[Os_3(CO)_9(\mu\text{-}H)(\mu\text{-}SPr^n)(\eta^2\text{-}C_2H_2)]$ (13) and compound (11) revealed three bands ascribable to the ethyne ligand. Together with their likely assignments, these were at 1 134 [$\delta(CH)_{asym}$], 1 076 [$\delta(CH)_{sym}$], and 898 cm^{-1} [$\rho_T(CH)$]. Both of these complexes show sharpening of two bands when the alkali halide discs were cooled to 77 K. These are assigned as the metal hydride stretching vibrations and were observed at 1 233 and 1 210 cm^{-1} for (11) and 1 267 and 1 211 cm^{-1} for (13); generally, the asymmetric stretch has the higher frequency. More intense bands due to the hydride bending vibration were observed at 686 and 690 cm^{-1} for (11) and (13) respectively.

Ethynyl Complex.—Five carbonyl environments would be anticipated in the ^{13}C n.m.r. spectrum of $[Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}CCH)]$ (6). Only three were observed at 22 °C [δ 172.1, 168.1, and 162.0 (d, J_{HC} 12.1 Hz)], but it is evident from comparison with published data on $[Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}CCR)]$ [R = Bu^t (ref. 33) and $Si(OEt)_3$ (ref. 34)] that rotation of the unique $Os(CO)_3$ group occurs at a sufficient rate to cause coalescence at this temperature. Hence the three signals are due to the three pairs of carbonyl environments on the symmetry related osmium atoms, with that at δ 162.0 assigned to the carbonyls *trans* to the hydride bridge. Comparison of proton coupled and decoupled spectra indicated that the quaternary and methine carbenes of the ethynyl group resonated at δ 134.4 and 41.6 respectively.

Five i.r. absorptions were observed which may be associated with the ethynyl moiety. A single strong $\nu(CH)$ band was observed at 3 156 cm^{-1}. The $\nu(CC)$ frequency would be anticipated between the free acetylenic value of *ca.* 2 000 cm^{-1} and that of the $\mu_3\text{-}\eta^2\text{-}C{=}CH_2$ moiety in complex (3) (1 331 cm^{-1}). It therefore seems clear that the band at 1 533 cm^{-1} can be assigned to this mode. The three remaining bands are at 1 259m, 858s, and 762w cm^{-1}. A single bending vibration is observed at a lower frequency than these in σ-ethynyl species, *e.g.* 679 cm^{-1} for $HCCSiMe_3$.[35] There are ten remaining modes for the Os_3C_2H moiety [3 $\nu(Os-Os)$, 3 $\nu(Os-C)$, 2 $\delta(CCH)$, and 2 Os_3C_2 deformations] but only two C–C–H bending vibrations (in- and out-of- the CCH plane) would be expected in this region of the spectrum. Two options are possible. Firstly, in general accord with the frequencies of similar modes assigned for complex (4),[32] the in- and out-of-plane $\delta(CCH)$ bands could be at 858 and 762 cm^{-1} respectively, with the band at 1 259 cm^{-1} due to a combination band (involving the absorption at 762 cm^{-1} and one of several bands near 500 cm^{-1}). Alternatively, these in- and out-of-plane deformations may be involved with the absorptions at 1 259 and 858 cm^{-1} respectively; a partial normal co-ordinate analysis on $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CHCH_2)]$ (5) indicated these modes were important components in vibrations at 1 266 and 786 cm^{-1}.[1] The latter interpretation is more likely on intensity grounds, and the weak band at 762 cm^{-1} can be assigned as a combination band from the fundamentals at 347 and 420 cm^{-1}; these are in the region expected for $\nu(Os-C)$ vibrations of hydrocarbon ligands.[22] Bands due to $\nu(Os-H)_{asym}$, $\nu(Os-H)_{sym}$, and $\delta(OsOsH)$ were observed at 1 402, 1 345, and 690 cm^{-1} respectively.

Discussion

In conjunction with much published data, the ^{13}C n.m.r. shifts of the hydrocarbon ligands measured in this study allow the compilation of chemical shift ranges for C_2 species in different bonding modes (Figure 1). It is evident that both the shift and the shift ranges increase from primary through to quaternary carbon atoms. Indeed, the latter have been observed between δ *ca.* 100 and *ca.* 470 p.p.m. It is interesting that the alkylidyne carbons in face-bridging carbon atoms are spread over a range of 150 p.p.m. for a comparatively closely related series of complexes $[Co_3(CO)_9(\mu_3\text{-}CMe)]$ and

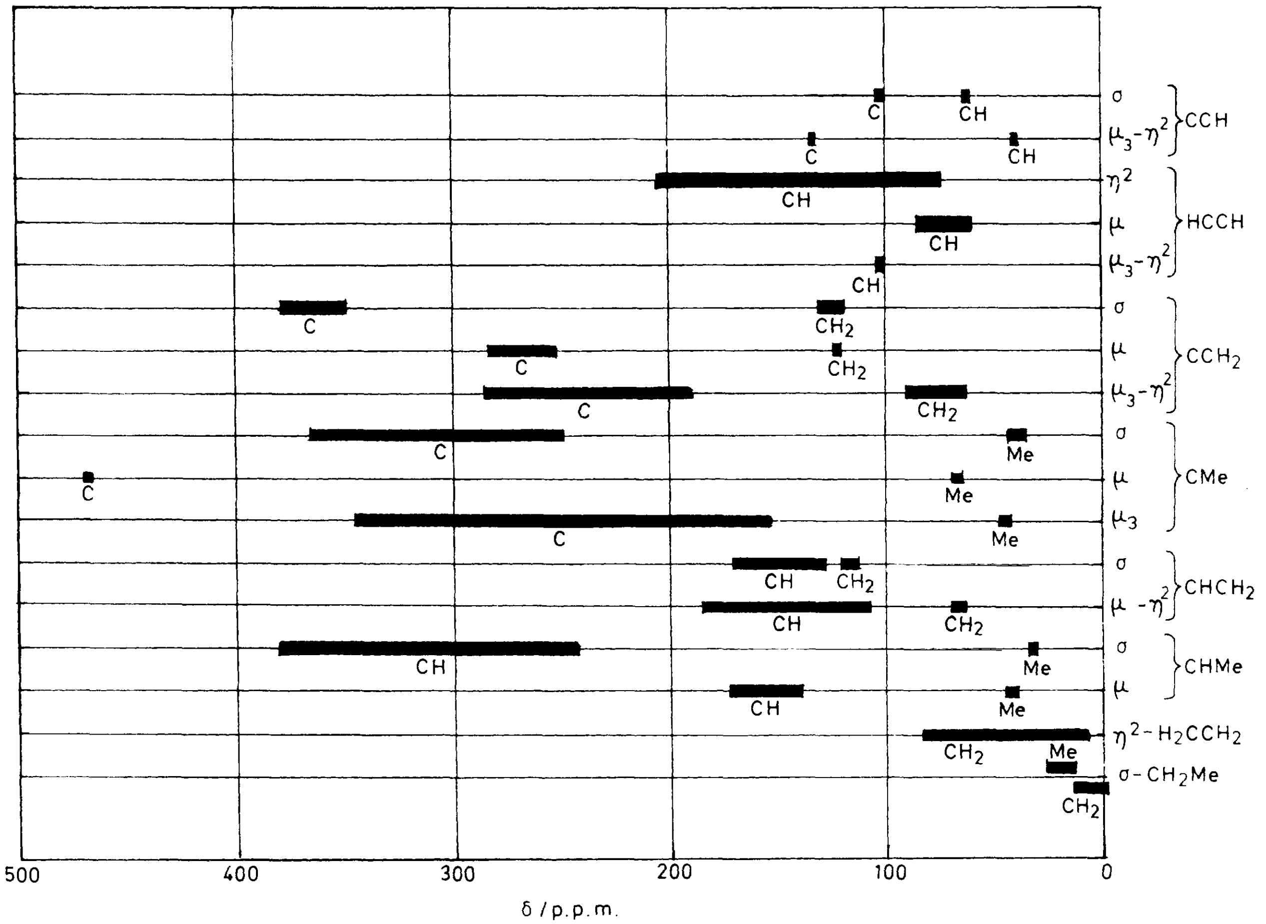


Figure 1. ^{13}C N.m.r. chemical shift regions for C_2 hydrocarbon ligands

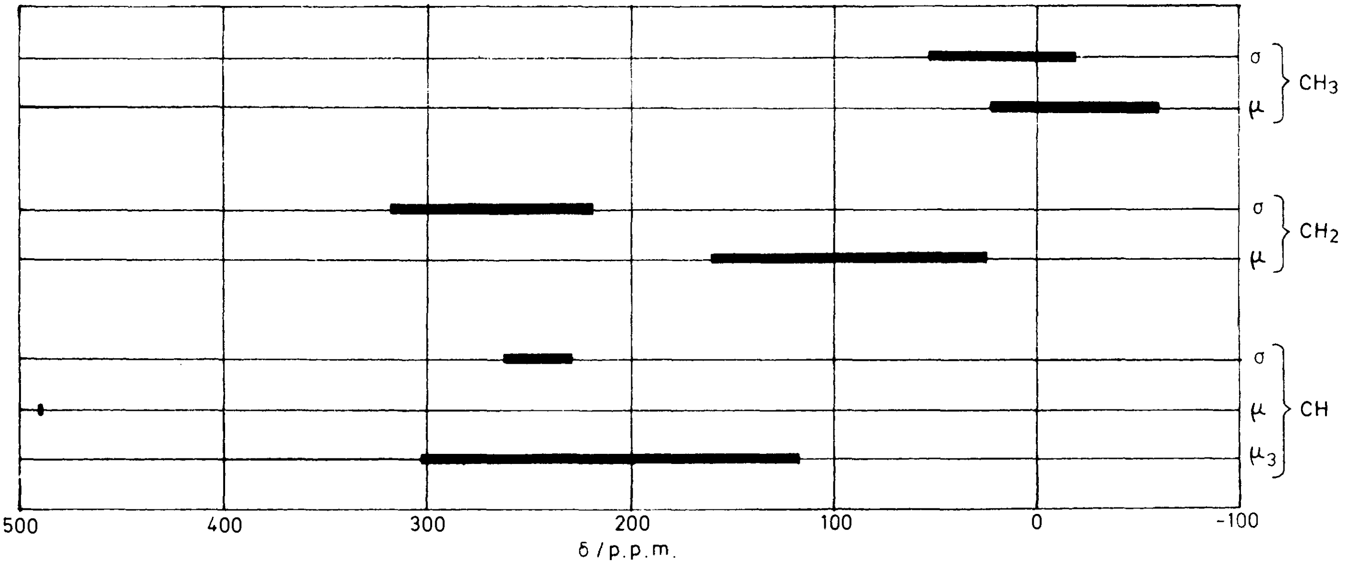


Figure 2. ^{13}C N.m.r. chemical shift regions for C_1 hydrocarbon ligands

$[M_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CMe)]$ (M = Ru or Os); the carbonyl shifts vary by only 30 p.p.m. for this same series. Nevertheless, when the shifts of *both* carbon atoms are considered, then ^{13}C n.m.r. data do not give strong evidence for a particular mode. For example, bridging (μ-η^2) and terminal (σ) vinyl ligands can be differentiated on the basis of methylene carbon shifts, and the quaternary carbon of the CMe group is extremely sensitive to its co-ordination mode. The shift of the methylene group in $[Co_3(CO)_9(CCH_2)]^+$ (δ 91.1)[36] suggests that it is co-ordinated in a μ_3-η^2-C=CH$_2$ group, as indicated

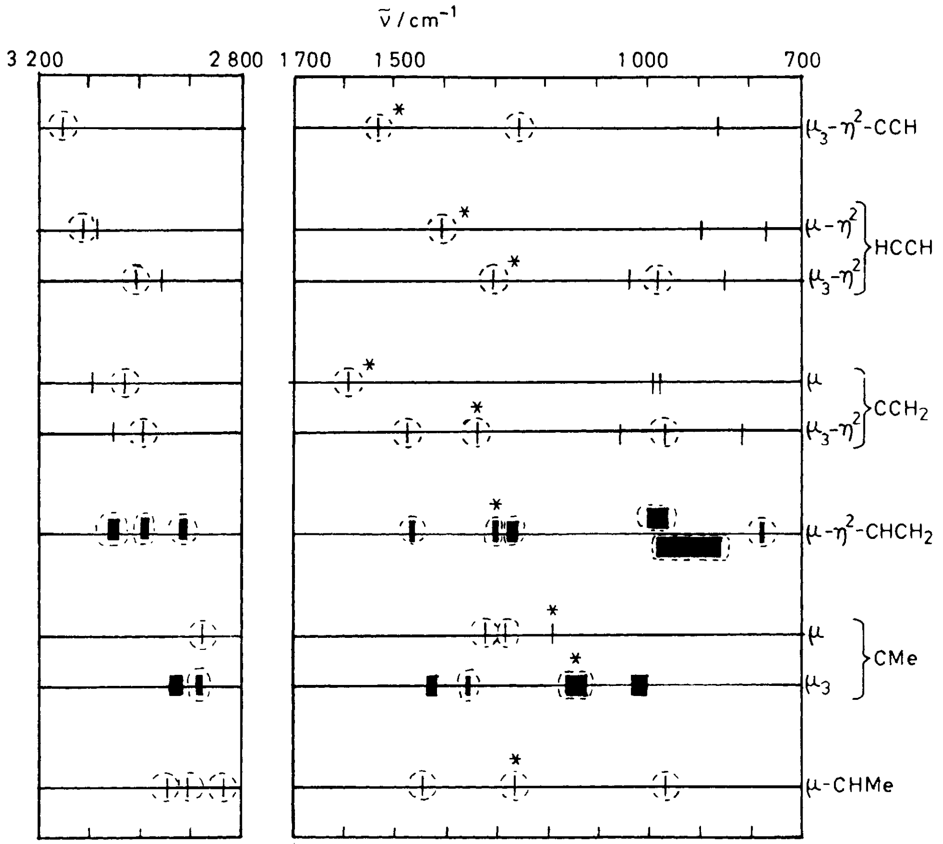


Figure 3. Vibrational frequencies of cluster bound C_2 hydrocarbon groups. Lines or bands within a dashed circle are likely to be dipole enhanced in electron energy loss spectra. Vibrations of high carbon-carbon stretching character are marked with an asterisk

Table 3. Comparison of the vibrational frequencies (cm^{-1}) of acetylene on Ni(111) and Fe(110) with those of $[Os_3(CO)_9H_2(CCH_2)]$

C_2H_2–Ni(111) [a]	C_2H_2–Fe(110) [b]	$[Os_3(CO)_9H_2(CCH_2)]$ [c]	Assignment
—	—	3 047	$\nu(CH_2)_{asym}$
2 920	2 940	2 986	$\nu(CH_2)_{sym}$
1 370	1 415	1 470	$\delta(CH_2)$
1 220	1 240	1 331	ν(CC)
1 080	1 150	1 051	$\rho_r(CH_2)$
860	870	963	$\rho_w(CH_2)$
690	700	811	$\rho_T(CH_2)$

[a] Ref. 45. [b] Ref. 46. [c] Ref. 1.

by extended Hückel molecular orbital calculations; [37] this has been confirmed by n.m.r. studies on the related $[Co_3(CO)_9(CCHPr^i)]^+$ ion.[38] So the regions defined in Figure 1 should aid structural assignments of new complexes of C_2 hydrocarbons, and, when ^{13}C n.m.r. data are obtained on adsorbed C_2 species, be useful in establishing chemisorption modes. A similar diagram was compiled for C_1 hydrocarbon ligands and is shown in Figure 2.

The conclusions drawn in Part 1 of this series,[1] namely that group frequencies could be transferred for the μ-η^2-CH=CH$_2$ moiety, and could be used to differentiate some co-ordination modes can be generalised rather more. Transferability has also now been demonstrated for η^2-C_2H_4 and μ_3-CCH_3 cluster bound species, and, albeit less clearly, μ- and μ_3-CCH_3 have been found to be differentiable. It is also clear from this and other work [32,39,40] that η^2-, μ-η^2-, and μ_3-η^2-HCCH co-ordination modes can be distinguished.

The vibrational frequencies of C_2 moieties co-ordinated to two or three metal atoms are shown in Figure 3. These frequencies are pertinent to species chemisorbed onto metal surfaces and therefore the bands likely to be dipole enhanced in electron energy loss spectra and the positions of the bands consisting largely of C–C stretching modes are indicated. As with the ^{13}C n.m.r. data, taking the frequencies of a particular moiety *in toto* provides good characterisation evidence. Care must be taken, however, in that not all the bands expected for all moieties in Figure 3 could actually be observed.

It is clear that the assignment of the stable species observed for C_2H_4 on Pt(111),[41] Rh(111),[42] and Pd(111) [43] surfaces using electron energy loss data from $[Co_3(CO)_9(\mu_3\text{-CMe})]$ [24] is on a firm footing since the vibrational frequencies of the μ_3-CMe groups are relatively insensitive to metal substitution. The bonding of acetylene to Pt(111) [41] and Pd(111) [44] in terms of a μ_3-η^2 mode has already been discussed.[32] The data on Rh(111)[42] are less clear, and could be assigned to either μ-η^2 or μ_3-η^2 modes. However the vibrational data obtained on the close-packed planes of nickel, Ni(111),[45] and iron, Fe(110),[46] differ significantly from those on Pd(111) and Pt(111). In both cases, there is a C–H bending vibration observed above the C–C stretching frequency near 1 400 cm^{-1}. This contrasts with the frequency order for the other two surfaces and also with compounds with η^2, μ-η^2, and μ_3-η^2 co-ordination modes. The data on these two surfaces match those of the μ_3-η^2-CCH_2 moiety more closely, as in $[Os_3(CO)_9(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-C=CH}_2)]$ [1] (Table 3), and may indicate rearrangement at low temperatures.

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