Inorganica Chimica Acta, 165 (1989) 231–239

Vibrational Spectra and Normal Coordinate Analyses of Bis(ethene)tetracarbonyl Complexes of Molybdenum and Tungsten

GEORGE DAVIDSON* and CLAIRE L. DAVIES

Department of Chemistry, Nottingham University, University Park, Nottingham NG7 2RD (U.K.)

(Received July 12, 1989)

Abstract

IR and Raman spectra of $(C_2H_4)_2M(CO)_4$, where M = Mo or W, in liquid xenon and hexane solutions, have been assigned. The νCO and νM–CO assignments are consistent with D_{2d} symmetry, showing that the 'local symmetry' approximation is not valid for assigning the $M(CO)_4$ modes, and that the two ethene ligands maintain a staggered conformation in solution. Assignment of the $(C_2H_4)_2M$ modes shows that vibrational coupling between the two ethene ligands is negligible. The only mode showing definite splitting, compared with the numbers expected for a $(C_2H_4)M$ unit of C_{2v} symmetry, is the symmetric M–C_2 stretch.

Approximate normal coordinate analyses show that the (C_2H_4)–M interaction is very strong for Mo^0 and W^0, compared to other transition metal ethene complexes, and that the carbon–carbon bond is essentially single, i.e. the compounds can be regarded as metallacyclopropanes.

Introduction

Vibrational spectroscopy has been used extensively to probe the structure and bonding in transition metal ethene complexes, but detailed studies are restricted to such complexes containing only one ethene ligand, e.g. refs. 1–5.

It has recently been shown that the complexes *trans*-$(C_2H_4)_2M(CO)_4$, where M = Cr, Mo or W, can be prepared by the photolysis of $M(CO)_6$ in ethene-saturated pentane solutions, and that they are stable species [6]. These compounds provide an opportunity to extend the vibrational studies to *trans*-$(C_2H_4)_2M$, to study the vibrations of the metal carbonyl fragment, and to investigate the bonding by carrying out normal coordinate analyses.

Liquefied noble gases are extremely good solvents for infrared spectroscopy, as they are inert and have no competing spectrum [7–9]. It has also been possible to use liquid xenon as a solvent for Raman spectroscopy [10], and in the present work liquid xenon solution spectra are reported for $(C_2H_4)_2M(CO)_4$ (IR only for M = Mo; IR and Raman for M = W). These results, together with solid phase and hexane solution data, are used to obtain vibrational assignments. It was, unfortunately, not possible to carry out experiments on isotopically substituted samples and so some assignments may be approximate. All, however, are reasonable by analogy with data on other organo-transition metal carbonyl complexes [2, 5]. The assignments, with normal coordinate analyses, give valuable insights into the structure and bonding.

Experimental

The samples of $(C_2H_4)_2M(CO)_4$, where M = Mo or W, were kindly supplied by Professor F. W. Grevels (Max-Planck-Institut für Strahlenchemie, Müllheim, F.R.G.) and used without further purification.

Raman spectra were obtained using a Spex Ramalog spectrometer, with Spectra-Physics Kr^+ (excitation wavelength 647 nm, for solid samples and hexane solutions) or Ar^+ (excitation wavelength 514.5 nm, for liquid xenon solutions of the tungsten complex) as excitation sources. Solid samples and hexane solutions were held in conventional glass capillaries. Experimental techniques for obtaining the Raman spectra of liquid xenon solutions have been described elsewhere [10]. These solution spectra were run with the samples at a temperature of approximately 0 °C. All Raman spectra were run from 50–2000 cm^{-1} and from 2800–3200 cm^{-1}. Band positions, except for very weak or broad features are accurate to ±1 cm^{-1}, following calibration of the spectrometer with liquid indene. Depolarisation ratios were measured for hexane solutions of $(C_2H_4)_2W(CO)_4$, and calibrated with respect to known standards (CCl_4, CS_2 and C_6H_6).

Solid-phase IR spectra were obtained using a Perkin-Elmer 983 dispersive spectrometer, and liquid

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*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

xenon solution spectra using a Nicolet MX-3600 FT-IR spectrometer (these latter were kindly run, at a temperature of –70 °C by Miss S. A. Jackson). All IR spectra covered the range 350–3200 cm^{-1}.

Results

The IR and Raman spectra of $(C_2H_4)_2W(CO)_4$ are listed in Table 1, together with the assignments which will be discussed below. Analogous data for $(C_2H_4)_2Mo(CO)_4$, for which less complete Raman spectra were obtained, are in Table 2.

The Raman spectrum for $(C_2H_4)_2W(CO)_4$ in the low wavenumber range (to 500 cm^{-1}) is shown in Fig. 1, for the solid phase (a) and the liquid xenon solution (b). The signal-to-noise ratio is much smaller in the latter case, but most of the spectroscopic features are still clearly visible. Note that the very strong bands at 135 and 141 cm^{-1} in the solid-phase spectrum have disappeared in the solution spectrum, and thus they can be assigned as lattice modes.

Vibrational Assignment

In order to carry out the assignment, it is first necessary to consider the molecular geometry and conformation. X-ray diffraction studies on $(C_2H_4)_2Cr(CO)_4$ [11] have shown that the two ethene ligands are *trans*, and that they are staggered with respect to each other, but eclipsed with respect to the carbonyl ligands (s–e conformation, Fig. 2). These results are consistent with *ab initio* LCAO-MO-SCF calculations on $(C_2H_4)_2MoL_4$, where L = CO or PH_3 [12], which suggest the following orders of energy for the four most symmetrical conformers:

(L = CO) s–e < s–s < e–e < e–s

(L = PH_3) s–e < e–e < s–s < e–s

A mutually staggered conformation for the C_2H_4 ligands will give a molecular symmetry of D_{2d}, and this will be used in the assignment of $M(CO)_4$ modes (for $(C_2H_4)_2M$ modes, see below). The possibility of an eclipsed conformation in the solution phase must also be considered, however, and the feasibility of an assignment under D_{2h} symmetry must be tested, as must the 'local symmetry' of D_{4h}.

In considering the $(C_2H_4)_2M$ modes, the first question to be answered is whether there is significant vibrational coupling between the two ethene ligands? If the two ligands remain in the staggered conformation it is likely that such coupling will be small, and the vibrational assignment will be possible in terms of the C_{2v}, C_2H_4M model, which has been well established for mono-ethene transition metal complexes [1–5].

As will have been seen from Tables 1 and 2, the observed vibrational data are much more complete for $(C_2H_4)_2W(CO)_4$ than for the molybdenum analogue. Consequently, the discussion on vibrational assignments will relate to the tungsten complex, except where specific reference is made to $(C_2H_4)_2Mo(CO)_4$.

M(CO)$_4$ Modes

The possible symmetries under which these could be assigned are D_{2d}, D_{2h} or D_{4h} (see above – the last is the 'local symmetry' approximation). The numbers, symmetry types and spectroscopic activities for the $M(CO)_4$ modes under all three symmetries are listed in Table 3.

The clearest differentiation between these geometries will be possible for the CO stretches. For D_{4h} symmetry there should be one IR band and two non-coincident Raman features (one polarised, one depolarised); for D_{2h} symmetry there would be two IR bands and two (non-coincident) Raman features, both polarised. The point group D_{2d}, by contrast, has no centre of symmetry, the mutual exclusion rule does not apply, and here there would be two IR bands, coincident with depolarised Raman features, with an additional (polarised) Raman band having no IR counterpart.

Although it was not possible to obtain Raman polarisation data for the liquid xenon solution of $(C_2H_4)_2W(CO)_4$, it is immediately clear that there are IR/Raman coincidences, showing that the D_{2d} (staggered ethenes) conformation found for crystals of $(C_2H_4)_2Cr(CO)_4$ persists for the tungsten analogue in solution. Comparison of IR (liquid xenon) and Raman (hexane) solution spectra for $(C_2H_4)_2Mo(CO)_4$ shows that the same conclusion can be drawn here also.

The very strong IR bands at 1995 and 1964 cm^{-1} are clearly the B_2 and E modes, with their relative intensities suggesting that this is the correct order. The Raman data confirm this, with the stronger 1998 cm^{-1} band as the B_2 mode, and the weaker 1967 cm^{-1} band as the E mode (note that the B_2 and E modes correlate with D_{4h} modes of symmetries B_{1g} and E_u, which are IR and Raman inactive, respectively). This leaves the moderately strong Raman band at 2068 cm^{-1} as the A_1 mode; note that although formally inactive under D_{2d} symmetry there is a very weak IR band at 2060 cm^{-1}, presumably rendered very slightly active by the weak interactions still present in the liquid xenon solution.

The carbonyl stretching assignments thus show that the effective molecular symmetry for $(C_2H_4)_2M(CO)_4$, where M = Mo or W, in solution is D_{2d} (staggered ethenes), and that the 'local symmetry' approximation is not valid.

The lower wavenumber modes associated with the $M(CO)_4$ fragments may be extensively mixed,

TABLE 1. Infrared and Raman spectra of $(C_2H_4)_2W(CO)_4$ (cm^{-1})

IR		Raman			Assignment
Solid phase	Xenon solution	Solid phase	Hexane solution	Xenon solution	
		3080vw		3072vw	CH stretch (A_2)
3056vw	3067mw	3063vw		3064vw	CH stretch (B_2)
		3048vw		3040vw	?
	3015vw	3010w		3014w	?
3003vw	2998mw			3001w	CH stretch (A_1)
				2979w	2 × 1494
	2950br	2955vw			CH stretch (B_1)
		2945vw			
	2923br				1494 + 1427
2517vw					
	2462vw				
	2432mw				
2426vw	2420vw				
	2393mw				
2385vw	2383mw				
2083vw	2087w			2087vw	CO stretch (mono-ethene)
	2060w	2059mw	2065mw	2068m	CO stretch (A_1)
	1995s		1996mw	1998s	CO stretch (B_2)
	1991mw				^{13}CO stretch (B_2)
1981w	1983mw	1982m			CO stretch ($W(CO)_6$)
1940vs	1964vs			1967w	CO stretch (E)
	1953ms	1946vw			CO stretch (mono-ethene)
	1936ms*				^{13}CO stretch (E)
	1836w				
	1810w				
	1494vw				CH_2 scissors (A_1)
1427vw	1427vw	1433vw			CH_2 scissors (B_1)
1186ms	1181m	1185m	1176w		CC stretch (A_1)
	1164vw	1171vw			CH_2 twist (B_2)
1121w					
1103w	1101vw				
1042w	1046w		1036vw		CH_2 wag (B_1)
996w	1001w				?CH_2 rock (A_2)
962w	957w				
	938w	949mw	937vw	935w	CH_2 wag (A_1)
926mw	926mw	931w		923w	
895vw					
834vw	832vw				?CH_2 twist (A_2)
737vw	732vw				CH_2 rock (B_2)
	595w				W–C–O deformations
585ms	587s				
	577w				
560ms	566s				
		486w		482w	W–C_2 stretch (B_1)
459w		463w		449w	W–CO stretch (B_2)
		428s	425m,pol	425m	W–CO stretch (A_1)
415w	417w	417sh^{r}		414sh^{r}	W–CO stretch (E)
				388w	
353w	362s	358w	369vw	366w	W–C_2 str. (A_1, out-of-phase)
		339ms	334m,pol	335m	W–C_2 str. (A_1, in-phase)
		233w	233vw	238w	W–ethene rock (B_2) lattice modes
		141s			
		135s			
		112vs	120s,dp	118s	C–W–C def. (B_1)
			104s,dp		C–W–C def. (E)
			81vs,dp	82s	skeletal def.
		70s		76m	skeletal def.

The specific assignments for the W–C–O deformations are discussed in the text.

TABLE 2. Infrared and Raman spectra of $(C_2H_4)_2Mo(CO)_4$ (cm^{-1})

IR		Raman		Assignments
Solid phase	Xenon solution	Solid phase	Hexane solution	
3063vw	3075w			CH stretch (B_2)
	3005w			CH stretch (A_1)
	2963w			CH stretch (B_1)
	2369w			
2357vw	2361w			
		2098vw		
	2087vw	2078vw		CO stretch (mono-ethene)
	2057vw	2057m		CO stretch (A_1)
	1998s	1992s	1992w	CO stretch (B_1)
1989m	1989s			CO stretch ($Mo(CO)_6$)
	1975sh^r			CO stretch (?mono-ethene)
1939vs	1965vs	1964w	1957vw	CO stretch (E)
	1935s	1936vw		^{13}CO stretch (E)
1497w	1498w	1500vw		CH_2 scissors (A_1)
	1433vw			CH_2 scissors (B_1)
1209m	1205ms	1210w		CC stretch (A_1)
	1190w			CH_2 twist (B_2)
1035w	1046w			CH_2 wag (B_1)
1021w	1024w			?CH_2 rock (A_2)
978w	981w			
948w	943w	941w		CH_2 wag (A_1)
918w	918w			
832w	831w			?CH_2 twist (A_2)
708w				
703w	698w			CH_2 rock (B_2)
	618w			
596w	593s			Mo–C–O deformations
590mw				
564m	568s			
452w	456w		444w	Mo–CO stretch (B_1)
			417w	Mo–CO stretch (A_1)
393w	395w	405m	400w	Mo–CO stretch (E)
352m	359s		368w	Mo–C_2 str. A_1, out-of-phase)
		312mw	305w	Mo–C_2 str. (A_1, in-phase)
		220br		Mo–ethene rock (B_2)
		138s		lattice mode
			117m	C–Mo–C def. (B_1)
		109vs	103m	C–Mo–C def. (E)
		84vs		skeletal
		70sh^r		deformations

probably involving the $M(C_2H_4)$ fragment, and all descriptions of modes will be approximate. For the present, the convention that the M–C–O deformations are at a higher wavenumber than the M–CO stretches will be adhered to.

Specific assignments can be made for the predominantly A_1 W–CO stretch (425 cm^{-1}) on the basis of Raman polarisation measurements. The Raman bands at 449 (weak) and 414 (weak, shoulder) cm^{-1} are tentatively assigned as B_2 and E W–CO stretches, respectively, by analogy with the related modes in $W(CO)_6$ [13]. In all cases some coupling with $W(C_2H_4)_2$ modes (see below) is likely, but cannot be quantified.

For the predominantly W–C–O deformations, the strong IR bands at 587 and 566 cm^{-1} can be assigned to the E mode (in-plane) and the B_2 mode (out-of-plane). Both are derived from the only allowed modes under D_{4h} symmetry, and would be expected to be the strongest features; the specific assignments are tentative, however, although comparison with related modes of $W(CO)_6$ [13] indicates that the suggested order may be correct. Two remaining features in this part of the IR spectrum, 595 and

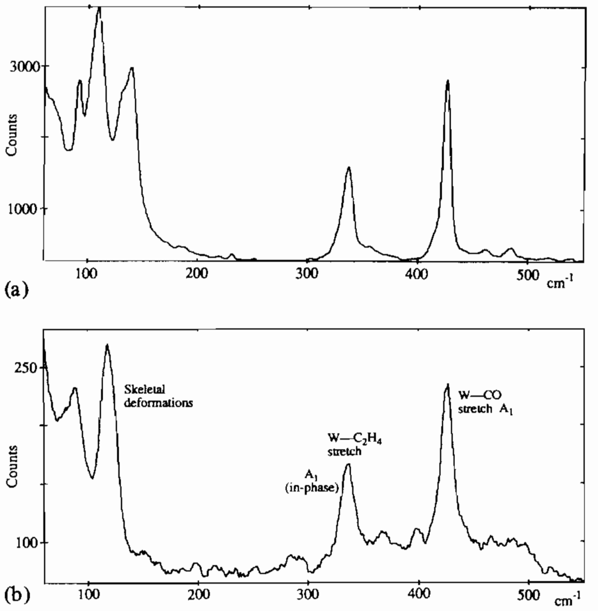

Fig. 1. Raman spectra of $(C_2H_4)_2W(CO)_4$: (a) solid, (b) liquid xenon solution.

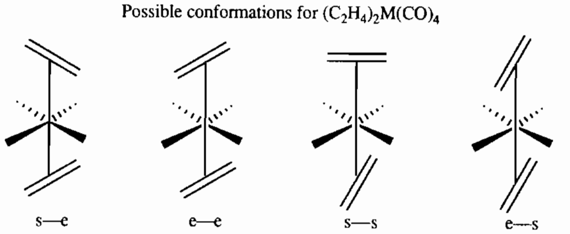

Fig. 2. Possible conformations for $(C_2H_4)_2M(C)_4$: s = staggered, e = eclipsed.

577 cm^{-1} are assigned, very tentatively, to the B_1 (in-plane) and E (out-of-plane) W–C–O deformations.

In the low wavenumber region, extensive mixing of modes is likely, and assignments are tentative. Two bands are seen in the Raman spectrum of $(C_2H_4)_2W(CO)_4$ in hexane (120, 104 cm^{-1}). These are both depolarised, and are likely to involve the B_1 and E OC–W–CO deformations, but no individual assignments can be made (there is only one strong, broad band, at 118 cm^{-1}, in liquid xenon solution).

For all modes below 600 cm^{-1}, the molybdenum complex gives similar wavenumbers, but the paucity of solution-phase data makes specific assignments even more difficult.

$(C_2H_4)_2M$ Modes

If there is any significant vibrational coupling between the two ethene ligands, the overall D_{2d} symmetry already established must be used, with in-phase and out-of-phase combinations of all C_2H_4 internal modes possible. Otherwise a simple C_2H_4M unit, of C_{2v} symmetry, will be adequate, and direct comparison with mono-ethene complexes possible.

Comparing the data in Tables 1 and 2 shows that in nearly all cases the numbers of features assignable to internal C_2H_4 modes are very similar to those for a mono-ethene complex, such as $(C_2H_4)Fe(CO)_4$ [1,2]. Thus it seems that interligand coupling between the two ethene ligands is (at most) very small, which is reasonable in view of their orientation at right angles to each other. The expected number and symmetries of modes for C_2H_4M (C_{2v}) and for $(C_2H_4)_2M$ (D_{2d}) are given in Table 4. Because the latter predicts more bands (especially in the Raman) than are observed experimentally, the former will be used as a first approximation for the assignment.

In the CH stretching region there may possibly be too many bands for a single C_{2v} ligand, but most are extremely weak. The following tentative assignments are suggested: there are reasonably strong IR bands at 3067, 2998 and 2950 cm^{-1}, and analogy with other C_2H_4M systems suggests that these are of B_2, A_1 and B_1 symmetry respectively. There are Raman bands corresponding to the first two. The A_2 mode can be assigned to the Raman band at 3072 cm^{-1} with no IR counterpart. A slight possibility that there is some coupling between C_2H_4 ligands exists,

TABLE 3. Symmetries of vibrational modes for $M(CO)_4$

	D_{4h}	D_{2d}	D_{2h}
M–C stretch C–O stretch	$A_{1g} + B_{1g} + E_u$	$A_1 + B_2 + E$	$2A_g + B_{2u} + B_{3u}$
C–M–C bend	$B_{2g} + E_u$	$B_1 + E$	$B_{1g} + B_{2u} + B_{3u}$
M–C–O bend			
(in-plane)	$A_{2g} + B_{2g} + E_u$	$A_2 + B_1 + E$	$2B_{1g} + B_{2u} + B_{3u}$
(out-of-plane)	$A_{2u} + B_{2u} + E_g$	$A_1 + B_2 + E$	$B_{2g} + B_{3g} + 2B_{1u}$

Spectroscopic activities

D_{4h} A_{1g} R(pol), A_{2g} inactive, B_{1g} R(dp), B_{2g} R(dp), E_g R(dp), A_{2u} IR, B_{2u} inactive, E_u IR
D_{2d} A_1 R(pol), A_2 inactive, B_1 R(dp), B_2 IR + R(dp), E IR + R(dp)
D_{2h} A_g R(pol), B_{1g} R(dp), B_{2g} R(dp), B_{3g} R(dp), B_{1u} IR, B_{2u} IR, B_{3u} IR

TABLE 4. Vibrational modes for the $(C_2H_4)_2M$ fragment of $(C_2H_4)_2M(CO)_4$

	$(C_2H_4)M$ (C_{2v})	$(C_2H_4)_2M$ (D_{2d})
CH stretches	$A_1 + A_2 + B_1 + B_2$	$A_1 + A_2 + B_1 + B_2 + 2E$
CC stretch	A_1	$A_1 + B_2$
CH_2 scissors	$A_1 + B_1$	$A_1 + B_2 + E$
CH_2 wag	$A_1 + B_1$	$A_1 + B_2 + E$
CH_2 twist	$A_2 + B_2$	$A_2 + B_1 + E$
CH_2 rock	$A_2 + B_2$	$A_2 + B_1 + E$
$M-C_2$ stretch	$A_1 + B_1$	$A_1 + B_2 + E$
M–ethene torsion	A_2	$A_2 + B_1$
M–ethene rock	B_2	E
M–alkene wag	B_1	E

The last three groups arise from the motion of the C_2H_4M group with respect to the rest of the molecule. For C_{2v} all modes are IR and Raman active except those of A_2 symmetry (IR inactive); A_1 modes will give polarised Raman lines. The selection rules for D_{2d} are as follows: A_1 R, pol.; A_2 inactive; B_1 R, depol.; B_2 IR + R, depol.; E IR + R, depol.

in that there are two very weak Raman bands (one with an IR counterpart) at wavenumbers which cannot correspond to overtone or combination bands (3040, 3014 cm^{-1}).

Bands formally assigned as the CH_2 scissors deformation modes have been found previously in the range 1540–1420 cm^{-1} for C_2H_4M systems [1–5]. For $(C_2H_4)_2W(CO)_4$ there are two IR bands, as expected for C_{2v} or D_{2d} symmetry, at 1494 and 1427 cm^{-1} in liquid xenon solution (the latter has a corresponding Raman band at 1433 cm^{-1} in the solid phase only). The weakness of the Raman spectrum in this region makes it impossible to differentiate between the C_{2v} and D_{2d} models, but by analogy with previous work the two IR bands are assigned as the A_1 and B_1 CH_2 deformations respectively, although the A_1 mode is at lower wavenumbers than usual, and it would normally have been expected to appear in the Raman spectrum.

The CC stretching vibration is known to be strongly coupled to the CH_2 deformation mode (see normal coordinate analysis below) and the band normally so assigned occurs in the range 1280–1120 cm^{-1} in C_2H_4M complexes [1–5]. A medium-intensity IR band at 1181 cm^{-1} (liquid xenon), with a weak Raman band at 1176 cm^{-1} (hexane solution) is the only candidate for the CC stretch in $(C_2H_4)_2W(CO)_4$. In $(C_2H_4)_2Mo(CO)_4$ it is at a slightly higher wavenumber (1205 cm^{-1}). The presence of only one Raman band is good evidence for (at most) very slight interligand coupling involving internal C_2H_4 modes.

In all previous studies of ethene–transition metal complexes the assignment of the remaining CH_2 deformation modes has been tentative, and this is true for the $(C_2H_4)_2M(CO)_4$ compounds also. In the absence of Raman polarisation data analogy with related systems was used to give the following assignments for the tungsten complex, all for the C_{2v} model: CH_2 twist, 1164 cm^{-1} (B_2), ?832 cm^{-1} (A_2); CH_2 wag 1046 cm^{-1} (B_1), 937 cm^{-1} (A_1); CH_2 rock ?1001 cm^{-1} (A_2), 732 cm^{-1} (B_2). The A_2 assignments, in particular, are very tentative, as both are bands seen only in the IR, and such modes are inactive under C_{2v} symmetry.

Of the vibrations involving the whole C_2H_4M unit, the $M-C_2$ stretches are expected to give the strongest spectral features. For the tungsten complex there is a medium-intensity Raman band at 335 cm^{-1} in liquid xenon solution (the equivalent band in hexane solution is polarised), while there is a strong IR band at 362 cm^{-1} (liquid xenon solution – Raman counterpart at 366 cm^{-1}). For the liquid xenon solution, a further Raman band is seen at 482 cm^{-1}. Other C_2H_4M systems give the antisymmetric (B_1) $M-C_2$ stretch in the range 455–513 cm^{-1}, and so the 482 cm^{-1} band is assigned to this mode for $(C_2H_4)_2W(CO)_4$. The symmetric (A_1) $M-C_2$ stretch is normally found in the range 358–405 cm^{-1} in related systems. For the $(C_2H_4)_2W$ unit, there are clearly two bands corresponding to this mode. For vibrations involving the central metal atom, the two possible combinations of symmetric $M-C_2$ motions, i.e. in- and out-of-phase, are at significantly different wavenumbers. The polarised Raman band at 335 cm^{-1} thus corresponds to the in-phase combination (of A_1 symmetry under the overall symmetry of D_{2d}), while the out-of-phase combination (B_2 symmetry under D_{2d}) is at 362 cm^{-1} in the IR.

The remaining bands which have not so far been assigned are (all Raman only, for liquid xenon solution) 238, 82 and 76 cm^{-1} (the last two showing as a single, depolarised band in hexane solution). The first is in the region previously associated with M–(alkene) rocking vibrations [4, 14], and the last two with 'whole-molecule' skeletal deformations in organo-transition metal carbonyl complexes [e.g. 15], although they are likely to be heavily coupled with $M(CO)_4$ modes.

Normal Coordinate Analysis

In many carbonyl and organo-complexes of transition metals, there is extensive coupling of vibrational modes, and consequently it may be helpful to calculate vibrational force constants for such systems. Even though the resultant force fields (as in the present work) will only be approximate, they can give useful insights into bonding, especially when a series of related molecules can be studied, making the same approximations each time. For $(C_2H_4)_2M(CO)_4$, we have carried out such calculations for the $M(CO)_4$ and C_2H_4M fragments separately.

$M(CO)_4$

Because of difficulties in assigning specific modes, and the absence of isotopic data, it is expected that the results will be approximate, and only reveal broad trends. The definition of internal coordinates is as follows: M–C stretches, r_1–r_4; CO stretches t_1–t_4; OC–M–CO bends α_1–α_4; M–C–O bends (in-plane) β_1–β_4; and M–C–O bends (out-of-plane) γ_1–γ_4. When dealing with the $M(CO)_4$ fragment alone it is necessary to use the 'local symmetry' of D_{4h}, and the symmetry coordinates used are listed in Table 5, with the assignments summarised in Table 6.

The computational methods have been described earlier [16]. The calculated force constants are listed in Table 7, with comparative data for the hexacarbonyls, calculated for an '$M(CO)_4$' fragment of D_{4h} symmetry, with the same approximations as for the data on $(C_2H_4)_2M(CO)_4$, using published vibrational wavenumbers [13].

TABLE 5. Symmetry coordinates for $M(CO)_4$ (D_{4h})

A_{1g}	$s_1 = r_1 + r_2 + r_3 + r_4$ $s_2 = t_1 + t_2 + t_3 + t_4$ $s_3 = \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4$ (redundancy)
A_{2g}	$s_4 = \gamma_1 + \gamma_2 + \gamma_3 + \gamma_4$
B_{1g}	$s_5 = r_1 - r_2 + r_3 - r_4$ $s_6 = t_1 - t_2 + t_3 - t_4$
B_{2g}	$s_7 = \alpha_1 - \alpha_2 + \alpha_3 + \alpha_4$ $s_8 = \gamma_1 - \gamma_2 + \gamma_3 + \gamma_4$
$(E_g)_a$	$s_9 = \beta_1 - \beta_3$
$(E_g)_b$	$s_{10} = \beta_2 - \beta_4$
A_{2u}	$s_{11} = \beta_1 + \beta_2 + \beta_3 + \beta_4$
B_{2u}	$s_{12} = \beta_1 - \beta_2 + \beta_3 - \beta_4$
$(E_u)_a$	$s_{13} = r_1 - r_3$ $s_{14} = t_1 - t_3$ $s_{15} = \alpha_1 - \alpha_2 - \alpha_3 + \alpha_4$ $s_{16} = -\gamma_2 + \gamma_4$
$(E_u)_b$	$s_{17} = r_2 - r_4$ $s_{18} = t_2 - t_4$ $s_{19} = \alpha_1 + \alpha_2 - \alpha_3 - \alpha_4$ $s_{20} = -\gamma_1 + \gamma_3$

TABLE 6. Summary of vibrational assignments for $M(CO)_4$ listed under D_{4h} symmetry (D_{2d} in brackets)

		M	
		Mo	W
A_{1g} (A_1)	νCO	2057	2068
	νMC	417	425
B_{1g} (B_2)	νCO	1992	1998
	νMC	444	449
B_{2g} (B_1)	δMCO i.p.	593	595
	δCMC	117	120
E_g (E)	δMCO o.o.p.	618	577
A_{2u} (B_2)	δMCO o.o.p.	593	566
E_u (E)	νCO	1957	1967
	δMCO i.p.	568	587
	νMC	405	417
	δCMC	109	104

TABLE 7. $M(CO)_4$ valence force constants (values derived from $M(CO)_6$ in brackets)

	M	
	Mo	W
Diagonal force constants		
CO stretch	15.14 (16.08)	15.19 (15.91)
MC stretch	2.57 (2.05)	2.85 (2.48)
CMC bend	0.65 (0.34)	0.62 (0.37)
MCO bend (in-plane)	1.05 (0.55)	0.93 (0.57)
MCO bend (o.o.p.)	0.81 (0.96)	0.87 (0.91)
Interaction force constants (stretch/stretch)		
MC/MC (*cis*)	−0.12 (0.03)	−0.11 (0.06)
MC/MC (*trans*)	0.78 (0.61)	0.62 (0.68)
MC/CO (*trans*)	−0.22 (−0.33)	−0.26 (−0.33)
CO/CO (*cis*)	0.31 (0.39)	0.33 (0.42)
(bend/bend)		
CMC/CMC (adj)	0.06 (0.06)	0.04 (0.06)
MCO/MCO (o.o.p., trans)	−0.07 (0.20)	−0.03 (0.20)
MCO/MCO (i.p., adj)	−0.03 (0.18)	0.01 (0.16)

Units: stretch or stretch/stretch interaction, mdyn A^{-1}; bend or bend/bend interaction, mdyn A rad^{-2}.

The CO stretching force constants for both bis(ethene) complexes are significantly lower than for the corresponding $M(CO)_6$, showing that back donation of electrons in the M–CO units is greater in the presence of two *trans* C_2H_4 ligands than for two *trans* COs. Hence the ethene ligands are better σ-donors and/or poorer π-acceptors than is CO. Comparison of the change on going from $Mo(CO)_6$ to $(C_2H_4)_2Mo(CO)_4$ with that on going from $W(CO)_6$ to $(C_2H_4)_2W(CO)_4$ suggests that the molybdenum discriminates more than does tungsten between the CO and C_2H_4

ligands, although this may not be significant at the level of approximation employed.

The M–CO stretching force constants follow the reverse trends from the CO stretches, as expected for the Dewar–Chatt–Duncanson model of carbonyl bonding.

Uncertainties in assignments make conclusions from the remaining force constants somewhat risky, but it appears that the M–C–O out-of-plane bending force constants for $(C_2H_4)_2M(CO)_4$ are higher than for $M(CO)_6$. This is consistent with increased steric effects in the former, where the C_2H_4 ligands are eclipsed with respect to the M–C–O axes.

C_2H_4M

As there appears to be very little vibrational coupling between the C_2H_4 ligands, the C_2H_4M unit is appropriate for a normal coordinate analysis. Direct comparison can then be made with results for a range of other C_2H_4M systems [5].

The assignments of A_2 and B_2 modes in many C_2H_4M complexes are not very reliable, and so the calculation will be restricted to modes of A_1 and B_1 symmetry. The symmetry coordinates are those used by Komornicki *et al.* in their calculations on C_2H_4O [17]. Bond distances and angles were derived from X-ray data on $(C_2H_4)_2Cr(CO)_4$ [11].

The resultant GVFF force constants are listed in Table 8. In terms of the discussion on bonding in ethene complexes, the MC and CC stretching force constants are the most significant. The values for the former are greater than for other transition metal C_2H_4M systems for which data are available [5], showing that the metal–ligand interaction is strong, i.e. *c.* 2.8 mdyn A^{-1}, compared to 2.1 for $C_2H_4Fe^0$, 1.83 for $C_2H_4Pt^{II}$ and 1.60 mdyn A^{-1} for $C_2H_4Pt^0$. The correspondingly low value for the CC stretching force constant (*c.* 5.5 mdyn A^{-1}) is consistent with a formally single carbon–carbon bond (e.g. 5.05 mdyn A^{-1} for ethene oxide, C_2H_4O [5]), and the description of the C_2H_4Mo and C_2H_4W units as metallacyclopropanes.

TABLE 8. Valence force constants for C_2H_4M

	M	
	Mo	W
Diagonal force constants		
MC stretch	2.83	2.76
CC stretch	5.58	5.43
CH stretch	4.98	4.88
CH_2 scissors (δ)	1.06	1.05
CH_2 wag	0.70	0.77
Interaction force constants		
(stretch/stretch)		
MC/MC	−0.80[a]	−0.86
MC/CH (same C)	0	−0.70
CC/CH	−0.23	−0.23
(stretch/bend)		
MC/δ (same C)	−0.22	0.02
MC/wag (same C)	−0.81	−0.64
(bend/bend)		
δ/wag (same C)	−0.07	−0.08
δ/wag (diff. C)	0	−0.04
wag/wag	0	0.07

[a]Constrained to fixed value throughout. Units: stretch, stretch/stretch interaction, mdyn A^{-1}; stretch/bend interaction, mdyn rad^{-1}; bend, bend/bend interaction, mdyn A rad^{-2}.

TABLE 9. Potential energy distribution for the A_1 and B_1 vibrations of C_2H_4W

Observed wavenumber		Potential energy distribution
A_1	3001	CH str
	1494	40% wag + 40% CH_2 def + 20% CC str
	1176	55% CC str + 30% wag + 15% WC str
	987	55% CH_2 def + 35% CC str + 10% wag
	335	80% WC str + 20% wag
B_1	2950	CH str
	1427	50% CH_2 def + 50% wag
	1046	60% CH_2 def + 20% wag + 20% WC str
	482	55% WC str + 45% wag

The other diagonal force constants are consistent with earlier results, except that the CH_2 wag force constant appears to be smaller. The specific values for the interaction force constants may not be very significant, owing to the approximate nature of the calculations, but it is clear that there are strong interactions between the two M–C stretches and between the M–C stretch and the CH_2 wag, involving a common carbon atom.

The potential energy distribution for the vibrations of C_2H_4W is summarised in Table 9. This shows very clearly that, with the obvious exception of the CH stretches, there is very extensive mixing of modes, and that the simple descriptions given in the assignment bear little resemblence to the real atomic movements in each normal mode. The figures for the molybdenum complex are very similar.

Conclusions

We have obtained reasonably complete vibrational assignments for $(C_2H_4)_2M(CO)_4$ where M = Mo or W. For the tungsten complex, the data included Raman, as well as IR data from solutions in liquid xenon.

The $M(CO)_4$ modes are consistent with overall D_{2d} symmetry for both molecules, i.e. staggered ethene ligands. There is very little vibrational coupling between the C_2H_4 ligands, and assignments based on a C_{2v} C_2H_4M unit were proposed.

Approximate force constant calculations show that the C_2H_4 ligands are better σ-donors and/or poorer π-acceptors than CO, that the C_2H_4–M interaction is stronger than in other transition metal ethene complexes, and that the C_2H_4M unit can be regarded as a metallacyclopropane.

Acknowledgements

We are most grateful to Professor F. W. Grevels (Max-Planck-Institut für Strahlenchemie, Müllheim, F.R.G.) for kindly supplying samples of the complexes studied, and details of the crystal structure of $(C_2H_4)_2Cr(CO)_4$; to Miss S. A. Jackson for running the IR spectra of liquid xenon solutions; and to the S.E.R.C. for a Research Studentship (to C.L.D.).

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