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The vibrational spectra and structure of tris(ethylene)metals

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Abstract

The IR and Raman spectra of $[\text{Pt}(\text{C}_2\text{H}_4)_3]$, $[\text{Pt}(\text{C}_2\text{D}_4)_3]$ and IR spectra of $[\text{Ni}(\text{C}_2\text{H}_4)_3]$ are reported and assignments proposed. Comparisons are made with previously reported IR spectroscopic features of Pd, Co and Cu analogues. The results of a CNDO/2 geometry optimization calculation for $[\text{Ni}(\text{C}_2\text{H}_4)_3]$ are summarized, and reveal closely similar structural parameters for the ethylene ligand to those established for the Pt complex. Some comparisons are made between vibrational frequencies of the complexes and those of ethylene chemisorbed on single crystal metal surfaces.

Introduction

The nature of the bonding between a metal and an olefin is one of the most fundamental and significant problems in organometallic and coordination chemistry. Transition metal-ethylene complexes are therefore of theoretical interest as well as of practical importance. These complexes provide a primary model for the analysis of bonding in π -complexes and for other theoretical studies in this area of

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organometallic chemistry. Although the first example, $K[Pt(C_2H_4)Cl_3]H_2O$, was discovered by Zeise [1] in 1825, it was not until 1953 that its infrared spectrum was recorded [2]. There have been several subsequent studies of its infrared and Raman spectra (see [3] and references therein), leading to commonly accepted assignments [4].

The first reported binary heavy metal-ethylene complex was $[Ni(C_2H_4)_3]$, made by Wilke et al. [5] in 1973. Since then the platinum analogue [6–8], the palladium analogue [6,7], and $[Pt(C_2H_4)_2(C_2F_4)]$ [6] have been synthesized. Their IR spectra were recorded, and the presence of complexed ethylene inferred from the lowering of the frequency of the CC stretching band compared with that for free ethylene [5–8].

Cryochemical reactions of metal atoms with ethylene and with ethylene/argon mixtures gave the binary metal-ethylene complexes $[Ni(C_2H_4)_3]$ [9–11,15], $[Cu(C_2H_4)_3]$ [12,14], $[Pd(C_2H_4)_3]$ [13] and $[Co(C_2H_4)_3]$ [10]; their infrared spectra show bands regarded as characteristic of tris(ethylene)metal systems. The IR spectra of $[Ni(C_2F_4)_3]$, produced by a mixed cocondensation reaction [16], have also been reported. Skeletal modes of $[M(C_2H_4)_3]$ (where $M = Ni^0$ or Pt^0) have been assigned and skeletal force constants calculated in our recent publication [17]. To date, however, no complete vibrational spectroscopic studies have been performed for any of the tris(ethylene)metal compounds, and we describe here for the first time complete IR studies of $[Pt(C_2H_4)_3]$, $[Pt(C_2D_4)_3]$ and $[Ni(C_2H_4)_3]$, together with Raman studies of the platinum complex.

Coordination of ethylene to a metal leads to considerable changes in its structure compared with that in the free molecule. Simple MO considerations [18] indicates that tris(ethylene)nickel should adopt a D_{3h} configuration; such a structure has been established by X-ray and neutron-diffraction experiments for $[Pt(C_2H_4)_3]$ [19]. Because of its thermal instability direct studies have not been possible for the nickel complex, and the only way to get the structural information is to calculate its equilibrium geometry by quantum chemical methods appropriate for transition metal complexes and we present the results of a CNDO/2 calculation for the equilibrium geometry of $[Ni(C_2H_4)_3]$.

Experimental

Mid- and far-infrared spectra of $[M(C_2H_4)_3]$ ($M = Ni$ and Pt) were recorded with a Nicolet 7199A FTIR system, and some additional mid-IR data were obtained with a Digilab FTS 20C spectrometer. The complexes were studied as solutions in petroleum ether saturated with ethylene. For the nickel complex the solution was maintained at or below $-50^\circ C$ throughout transfer to the cells and for the measurements. A Specac liquid nitrogen-cooled cryostat was used. Raman measurements were performed with a Coderg T800 triple monochromator with photon-counter detection. The spectra were digitalized and solvent subtraction routines were performed by use of the Nicolet 7199A software system. The spectra were excited with 514.5 nm (250 mW at the sample) irradiation from a Coherent Radiation Laboratories Model 52 Argon ion Laser; throughout the measurements the petroleum ether solution was maintained at $-30^\circ C$ by use of a Coderg Cryocirc cryostat. The preparations of the compounds have been described previously [5–8].

Table 1 (continued)

[Ni(C ₂ H ₄) ₃] IR solution - 50 ° C	[Pd(C ₂ H ₄) ₃] IR solid low temp.	[Pt(C ₂ H ₄) ₃] IR solid room temp.		Raman solution - 40 ° C	Proposed assignments
896.3w	881m				
846.2m	828s	823m			
834.6vw	820w				
822.9vw	813m				
794.5w	760m	783w			
740vvw			733vvw		$\nu_5 + \nu_{26}, e'$
726m, w			708.6w		
	626m		693w		
	614w		649w, b		
				500w	$\nu_{17} + \nu_{26}, e''$
462sh			468.7w		
440sh			440sh	448.3vw	ν_{25}, e' ML tilt
				398.2vs, p	ν_5, a'_1 ML ₃ sym str.
			385sh		
			363sh		
374.6vs	305vs ^c		331.3vs	331.7m, dp	ν_{26}, e' ML ₃ asym str.
280vw			240vw, b		
255.3w			163w, sh		ν_{17}, a''_2 ML ₃ o.o.p. bend
227.3m			147.1vw	145.4m, dp	ν_{27}, e' ML ₃ i.p. bend
130.2w(?)					
108.8w(?)					

^a Coincidence with solvent's band. ^b Uncertain band after subtraction of solvent bands. ^c From the infrared spectra of metal-ethylene codeposition at 60 K. Spectra were recorded at 180–190 K [10]. All solution spectra were taken in 40/60 petroleum ether. ^d Two sets of frequencies expressing metal sensitivity.

For optimization of the geometry of [Ni(C₂H₄)₃], Clack's modified CNDO/2 method [20] and a modified version of Rinaldi's GEOME program [21], with the correction suggested by Mayer et al. [22], were used. Optimization of the geometry was based on Pulay's gradient technique [23,24] utilising the very efficient GDITS algorithm [25].

Vibrational assignment

We started from the premise that the assignments for Zeise's anion would provide a good basis for interpreting the spectra of [M(C₂H₄)₃] complexes; however, as outlined below, the similarities were much fewer than expected. The infrared and Raman spectra are listed in Tables 1 and 2.

The [M(C₂H₄)₃] molecules are of *D*_{3h} point group. The internal modes are:

$$\Gamma(\text{internal}) = 5a'_1 + 4a'_2 + 10e' + 4a''_1 + 4a''_2 + 7e''$$

The *a''*₂ and *e'* modes are IR active, *a''*₁, *e'* and *e''* Raman active, but *a''*₁ and *a''*₂ are inactive. Because of the large frequency separation between the internal vibrations of the ethylene ligands and those of the skeleton the two sets can be treated separately.

*C*₂H₄ vibrations. [Pt(C₂H₄)₃], four polarized Raman lines, 3004.3, 1617.1, 1337.7 and 1225.6 cm⁻¹, are assigned to *a''*₁ species. The assignments of ν_1 and ν_2 are

Table 2
Vibrational spectra and assignments proposed for [Pt(C₂D₄)₃]

Infrared		Raman	Proposed
mull	solution	(solution)	assignments
2313.2m, s	2337m, w 2315.5m	2314vw, b 2267vw 2250w	ν_1, a_1' ; ν_{14}, a_2'' CD stretching ν_{28}, e'' ν_{29}, e''
2214.4w	2215.9w	2214m	ν_{18}, e'
2179.2s	2181.1s	2184vw	ν_{19}, e'
1530vw, b	1530vw, b		
1415vw	1414vw		
1365vw			
1332.8vs	1333.7vs 1315sh	1336w	ν_{20}, e' CC stretching
		1301vw	ν_2, a_1' CC stretching
1230sh	1233vww		
1220.6vw	1220.8	1225vww 1166vww 1120w	ν_3, a_1' CD ₂ scissor
1078vw	1075vw	1075vww	
1060.0w	1061.1w		ν_{21}, e' CD ₂ scissor
982vw	978vw 955sh		ν_{22}, e' CD ₂ scissor ν_{24}, e' CD ₂ wag
945.9s	946.5s		ν_{23}, e' CD ₂ wag
885vw			
800w, b			
769.3vw	769.9vw		ν_{15}, a_2' CD ₂ twist
745vww	743sh	747vw	
719vw	720vw, b		
685vw, b			
	660.5vw		ν_{16}, a_2'' CD ₂ rock
589.1vw	589.1vw		
523vww			
	490vw 463vw 415vw	400vw	ν_{25}, e' ML tilt
	376vw 363vw	380m	ν_5, a_1' ML ₃ sym. stretch.
	323.4vw	326vww	ν_{26}, e' ML ₃ asym. stretch.
	147.7sh		ν_{17}, a_2'' ML ₃ o.o.p. bend
	136.8vs	136w	ν_{27}, e' ML ₃ i.p. bend

straightforward, but nothing corresponding to the lowest frequency band has commonly been observed for other ethylene complexes. Very few Raman solution measurements have been performed for systems with bound-ethylene, and assignments have been based mainly on IR studies involving C₂H₄ and C₂D₄ analogues. Hiraishi [3] observed only one polarized band for Zeise's anion in this region, at 1241 cm⁻¹, which he assigned to CC stretching strongly coupled with the CH₂ scissoring motion at 1522 cm⁻¹; for the wagging mode, the band at 945 cm⁻¹ was assigned. From this study of [Pt(C₂H₄)₃] we suggest assigning 1617.1 cm⁻¹ as CC stretching, 1337.1 cm⁻¹ as CH₂ scissoring, and 1225.6 cm⁻¹ as CH₂ wagging.

Previous work [9–15] on IR spectra of matrix-isolated $[M(C_2H_4)_3]$ had assigned a weak band at 1510 cm^{-1} to CC stretching and a very strong band at 1230 cm^{-1} to CH_2 scissoring, largely on the basis of Hiraishi's assignments [3], but our work suggests that these generally accepted conclusions for tris(ethylene)metal complexes should be modified. It also points to a need for the assignments for Zeise's anion to be reinvestigated.

For $[Pt(C_2H_4)_3]$, bands at 3073.0 and 820.4 cm^{-1} are only IR active and must consequently be associated with a_2'' modes, CH stretching, and CH_2 rocking, respectively. The dynamical dipole moment for a_2'' modes is perpendicular to the σ_h molecular plane which involves metal displacement. It means the CH_2 rocking and twisting modes must show metal sensitivity. There are two sets of frequencies for rocking modes with different extents of metal sensitivity. For Ni, Pd and Pt, respectively, the sequence 915.5 , 898 and 820.4 cm^{-1} has a strong metal dependence while the set 846 , 828 and 820.4 cm^{-1} relatively insensitive. There are very strong IR bands at 1123.2 and 1094 cm^{-1} for Ni and Pd derivatives. In accord with the mass sensitivity of the metal atom the corresponding band for $[Pt(C_2H_4)_3]$ is observed as a strong band in the solid state at 978 cm^{-1} . We suggest assignment of these bands to CH_2 twisting modes of a_2'' species.

Bands active in both IR and Raman spectra have been assigned to e' species. The Raman bands which have IR counterparts for $[Pt(C_2H_4)_3]$ were observed at 3024.6 , 1500.7 , 1434.9 , 1361 and 1216 cm^{-1} , and must consequently be associated with CH stretching, CC stretching, CH_2 scissoring (next two bands) and CH_2 wagging, respectively.

The two depolarized Raman bands at 3067.5 and 3048.5 cm^{-1} for $[Pt(C_2H_4)_3]$ do not have counterparts in the IR and must be the CH stretching modes of e'' species. The remaining weak Raman bands at 1146.6 , 1121.1 , 1074.6 and 968.1 cm^{-1} can be assigned to CH_2 rocking and twisting modes. The choice of the order of CH_2 twisting modes is based on the assumption that one of them must be close to the same mode of a_2'' species. Therefore the first two bands, at 1146.6 and 1121.1 cm^{-1} , are chosen for rocking and the lower two, at 1074.6 and 968.1 , for twisting modes.

For $[Pd(C_2H_4)_3]$ we have only solid state IR data, and so the assignment is rather complicated because of solid state band splittings of ν_{21} , ν_{23} , (ν_{24}), and ν_{16} vibrations. There are some weak bands in the 1000 – 1400 cm^{-1} range and some more intense bands in the 850 – 450 cm^{-1} range, which we have not spectrally assigned, particularly for Ni and Pd complexes. It is difficult to assign them to combination or overtones since they could contain frequency components of a_1'' and a_2' inactive or Raman active species on which we have no information.

The ethylene motions ν_{15} and ν_{16} show a fairly marked metal dependence and the intensity of the ν_{15} infrared band decreases markedly from Ni through Pd to Pt. From ν_{20} and ν_{23} bands there is not a consistent frequency trend, the Pd complex having the highest frequency in the series.

Relative to the data for free ethylene, the largest shifts on complexation are for the CH_2 wagging modes; these are greater than those for CC stretching and CH_2 scissoring and rocking motions, which are in turn greater than those for CH_2 twisting vibrations.

Skeletal modes. The form of the vibrations involving displacement of C and M atoms and the metal–ligand motions are shown in Fig. 1. The ν_3 and ν_{13} modes are inactive. The e'' torsional mode (ν_{34}) about the M–L bond should be Raman

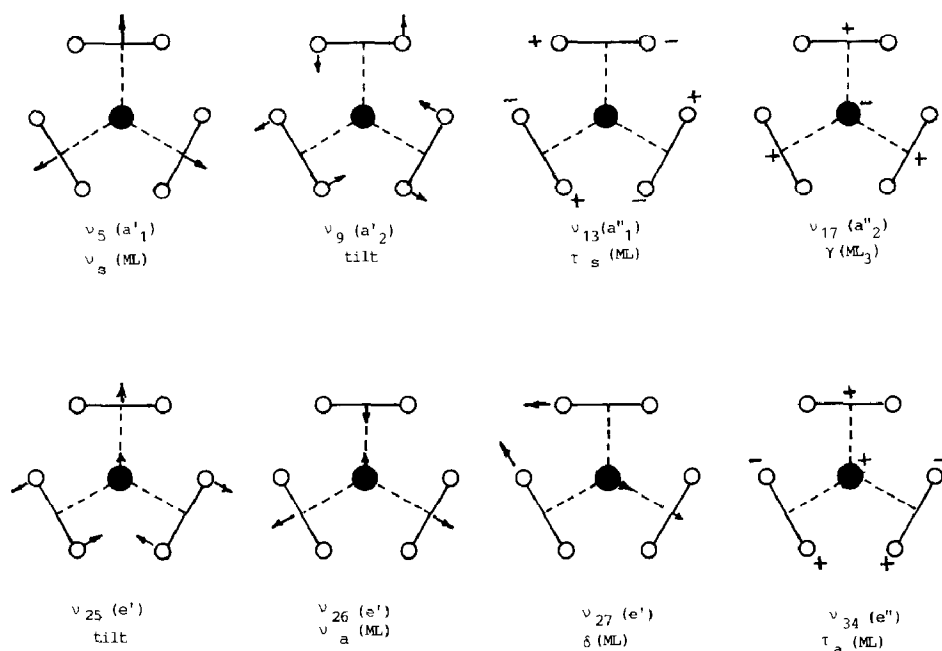


Fig. 1. Skeletal modes of tris(ethylene)metal complexes.

active, but would be expected to be at very low wave numbers, because the rotation of ethylene about the axis to the metal is essentially free, and is not observed. The low frequency parts of the spectra for $[\text{Pt}(\text{C}_2\text{H}_4)_3]$ are shown in Fig. 2. The polarized Raman line at 398 cm^{-1} is assigned to the symmetric ML_3 stretching mode and the neighbouring depolarized line at 332 cm^{-1} , which is also IR active, to the asymmetric mode, ν_{26} . The corresponding bands for the C_2D_4 sample are at 380 and 323 cm^{-1} , respectively. The only active ethylene-tilting mode (ν_{25}) is observed at 448 cm^{-1} , which is shifted to 415 cm^{-1} by deuteration. The shoulder in the IR spectrum at 163 cm^{-1} can reasonably be assigned to the ML_3 out-of-plane bending mode (ν_{17}). The corresponding IR and Raman features around 146 cm^{-1} can be attributed to the ML_3 in-plane deformation (ν_{27}). For the deuterated complex the 163 cm^{-1} band is shifted to 148 cm^{-1} and the 146 cm^{-1} band to 137 cm^{-1} (see Table 2). The modes ν_{17} , ν_{26} and ν_{27} should show a strong frequency dependence on the mass of the metal, and this is demonstrated by a comparison between $[\text{Ni}(\text{C}_2\text{H}_4)_3]$ and $[\text{Pt}(\text{C}_2\text{H}_4)_3]$.

C_2D_4 vibrations. Experimental frequencies for $[\text{Pt}(\text{C}_2\text{D}_4)_3]$ are presented in Table 2. Because of the slight decomposition of the $[\text{Pt}(\text{C}_2\text{D}_4)_3]$ sample under laser exposure it was not possible to measure depolarization ratios for the Raman bands. Assignments of C_2D_4 ligand vibrations are based mainly on isotopic shifts of C_2H_4 bands predicted by normal coordinate calculations.

The two Raman active only CD stretching modes can be assigned to e'' species ν_{28} and ν_{29} . The sequence of other CD stretching modes is assumed to be identical to that of C_2H_4 vibrations (see Table 1).

The solely Raman active mode at 1301 cm^{-1} should be the in-phase symmetric CC stretching mode (ν_2). No Raman bands were detected between 1370 and 2000

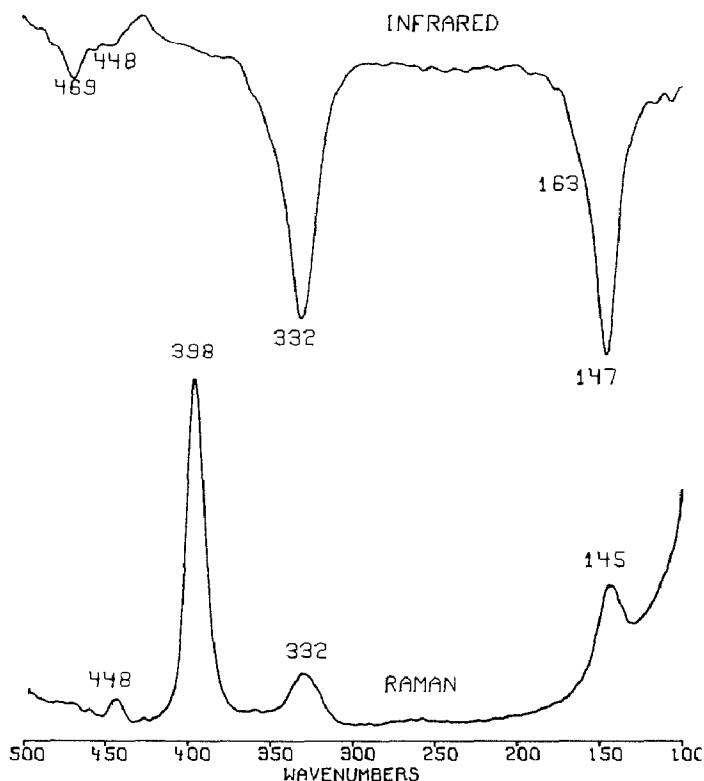


Fig. 2. Far-infrared (upper) and low frequency Raman (lower) spectra of $[\text{Pt}(\text{C}_2\text{H}_4)_3]$ in petroleum ether.

cm^{-1} . We conclude that the ν_2 mode is lower than ν_{20} in the deuterated complex, despite being the higher frequency CC stretching mode in $[\text{Pt}(\text{C}_2\text{H}_4)_3]$.

The CD_2 deformation modes were observed in the range $1120\text{--}660\text{ cm}^{-1}$. Unfortunately in the Raman spectrum on this region only a very few bands were detected, making assignment difficult. In this region the e'' type CD_2 rocking (ν_{30} , ν_{31}) and twisting (ν_{32}) modes are not observed, nor was the ν_4 (a_1') wagging mode.

The force constant calculations for these molecules are in progress, and the results may in due course modify the above assignments slightly.

Relationship with other work on binary metal-ethylene systems

All available assignments for $[\text{M}(\text{C}_2\text{H}_4)_3]$ ($\text{M} = \text{Ni}, \text{Pd}$ or Pt) and $[\text{Pt}(\text{C}_2\text{D}_4)_3]$ are summarized in Table 3.

The implications of our assignments for the full family of $[\text{M}(\text{C}_2\text{H}_4)_3]$ species are contained in Table 4. The most important difference from assignments proposed previously concerns the wagging mode. In ethylene the wagging mode induces a change in dipole moment perpendicular to the molecular plane, and in complexes this is along the M-L bond direction. The interaction with M-L bond stretching explains why this mode can be strongly shifted to higher wavenumbers and also allows the infrared intensity enhancement to be understood. Most of the earlier assignments [9,12] considered the bands just above 1200 cm^{-1} to be due to CH_2 scissoring.

Table 3

Fundamental frequencies (cm^{-1}) obtained for tris(ethylene)metal complexes

Species and approximate descriptions of modes			$[\text{Ni}(\text{C}_2\text{H}_4)_3]$	$[\text{Pd}(\text{C}_2\text{H}_4)_3]$	$[\text{Pt}(\text{C}_2\text{H}_4)_3]$	$[\text{Pt}(\text{C}_2\text{D}_4)_3]$
a_1'	ν_1	CH str			3004.1	2315.5
	ν_2	CC str			1617.1	1301.0
	ν_3	CH_2 sciss			1337.7	1120.0
	ν_4	CH_2 wag			1225.6	?
	ν_5	ML_3 sym str ^a			398.2	380.0
a_2''	ν_{14}	CH str	3070.6	3072	3072.0	2315.5
	ν_{15}	CH_2 twist	1123.2	1098	978	769.9
	ν_{16}	CH_2 rock	915.5	898	820.4	660.5
	ν_{17}	ML_3 o.o.p. bend	255.3	—	163	147.7
e'	ν_{18}	CH str	3031.6	3000	3024.6	2215.9
	ν_{19}	CH str	2995.0	—	(3000.6)	2181.1
	ν_{20}	CC str	1511.9	1522.5	1500.7	1333.7
	ν_{21}	CH_2 sciss	1435.6	1427	1424.2	1061.1
	ν_{22}	CH_2 sciss	1349.3	—	1361.0	978.0
	ν_{23}	CH_2 wag	1242.9	1262	1218.7	946.5
	ν_{24}	CH_2 wag	1233.0	1229	1218.7	955.0
	ν_{25}	ML tilt	440.4	—	448.3	415.0
	ν_{26}	ML_3 asym str	374.6	305	331.7	323.4
	ν_{27}	ML_3 i.p. bend	227.3	—	147.1	136.8
e''	ν_{28}	CH str			3067.5	2267.0
	ν_{29}	CH str			3048.5	2250.0
	ν_{30}	CH_2 rock			1146.6	?
	ν_{31}	CH_2 rock			1121.1	?
	ν_{32}	CH_2 twist			1074.6	?
	ν_{33}	CH_2 twist			968.1	
	ν_{34}	rotation around M-L			—	

^a The missing ν_6 – ν_9 and ν_{10} – ν_{13} fundamentals belong to inactive a_1' and a_2' species, respectively.

CNDO/2 geometry optimization

No structural analysis has been reported for tris(ethylene)nickel(0). In $[\text{Ni}(\text{C}_2\text{H}_4)_3]$ there are only 5 geometrically independent parameters (see Fig. 3) and it was expected that a full optimization of the geometry, complete with energy gradients with respect to nuclear coordinates, could be achieved in a small number of steps through the Hartree–Fock–SCF method. Unfortunately, the SCF procedure suffered from serious convergence problems. We have attempted to overcome these by incorporating level shifting and interpolation techniques. However, even these refinements did not lead to rapid SCF convergence. The required 2×10^{-1} a.u. threshold in the total Hartree–Fock energy could not be achieved in less than 40 steps.

The optimization of geometry was carried out by use of internal and local symmetry coordinates, and iteration continued until cycle to cycle changes in the coordinates used became less than 0.002 Å and 0.02° for bond lengths and bond angles (including dihedral angles), respectively.

The results are given Fig. 3, and Table 5. They are consistent with the changes in geometry for ethylene expected to result from complexation. The characteristic

Table 4
Infrared frequencies (cm^{-1}) assigned to ethylene vibrations for $[\text{M}(\text{C}_2\text{H}_4)_3]$ complexes ^a

Assignments	C_2H_4 gas [26]	$[\text{Co}(\text{C}_2\text{H}_4)_3]$ matrix [9]	$[\text{Ni}(\text{C}_2\text{H}_4)_3]$ solution	$[\text{Pd}(\text{C}_2\text{H}_4)_3]$ solid	$[\text{Pt}(\text{C}_2\text{H}_4)_3]$ solution	$[\text{Cu}(\text{C}_2\text{H}_4)_3]$ matrix [12]
CH stretch a_2''	3104.9s	3055w	3070.6s	3072m	3072.0s	3054w
e'	3104.9s*		3031.6s		3027.1m	
e'	2988.7s	2980w	2999.0w/m	3000w/m	3000.6sh	
CC stretch e'	1630m(R)	1490m	1511.9s	1525s	1503.1m	1517w
CH ₂ sciss e'	1443.5s	1415m	(1435.6vs)	1427s	1424.2m	
e'	1342.2s(R)	1225w	1349.3s		1365.1vw	
CH ₂ wag e'	949.3m	1215w	1242.9vs	1262vs	1218.7vs	1252m
e'	939.6w(R)		1233m	1229m	950.1m	
CH ₂ twist a_2''	1023 (i.a.)		1123vs	1098vs	978s	
CH ₂ rock a_2''	826w	826w	915.5m	898m	820.4w	810w
				813s		

^a () strong overlapping with solvent band, * frequency used twice, (R) frequency from Raman spectrum, and (i.a.) inactive vibration.

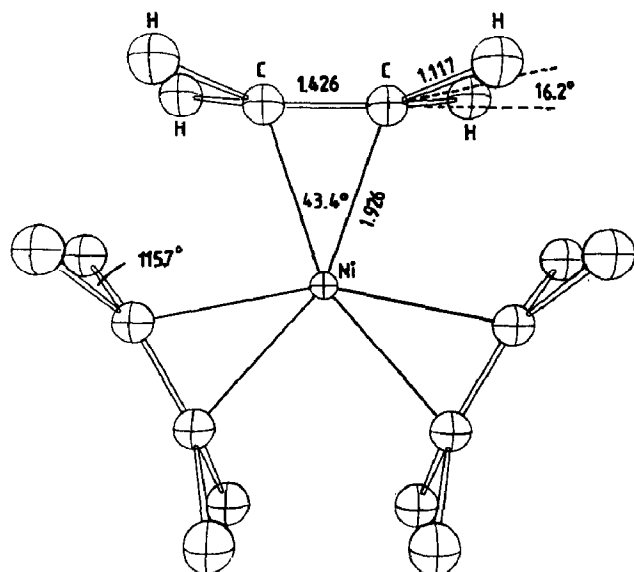


Fig. 3. Molecular geometry and molecular parameters of $[\text{Ni}(\text{C}_2\text{H}_4)_3]$ calculated by CNDO/2 method.

Table 5

Molecular parameters for $[\text{Ni}(\text{C}_2\text{H}_4)_3]$ calculated by the CNDO/2 method

Geometrical parameters		$[\text{Ni}(\text{C}_2\text{H}_4)_3]$	C_2H_4^a CNDO/2	C_2H_4^b exper.
$r(\text{C}=\text{C})$	(pm)	142.6	132.0	133.9
$r(\text{CH})$	(pm)	111.7	111.0	108.5
$r(\text{Ni}-\text{C})$	(pm)	192.6	-	-
$r(\text{Ni}\dots)$	(pm)	178.9	-	-
$\alpha(\text{HCH})$	($^\circ$)	115.7	113.4	117.83
ν (deviation from planarity)	($^\circ$)	16.2	0	0

^a Ref. 27. ^b Ref. 26.

Table 6

Molecular parameters for tris-(ethylene)metals

Geometrical parameters		$[\text{Ni}(\text{C}_2\text{H}_4)_3]^a$ (a)	$[\text{Pt}(\text{C}_2\text{H}_4)_3]^a$ (b)	$[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{F}_4)]^a$ (c)
$r(\text{C}=\text{C})$	(pm)	142.6	140.2	137.1 *
$r(\text{CH})$	(pm)	111.7	110.1 *	107.9 *
$r(\text{M}-\text{C})$	(pm)	192.6	217.6	222.9 *
$r(\text{M}\dots)$	(pm)	178.9	206.0	212.1 *
$\alpha(\text{HCH})$	($^\circ$)	115.7 *	111.5 *	116.7 *
$\beta(\text{HCH})$	($^\circ$)	120.7	122.6	120.3
ν (deviation from planarity)	($^\circ$)	16.2	15.2 *	16.0 *

^a (a) this work. (b) ref. 19. (c) data for C_2H_4 ligands from ref. 19. * Mean values of determined molecular parameters.

features are: (a) an increase in the C=C bond length due to back donation; 9b) a decrease in the HCH bond angle; (c) a bending of the CH₂ planes are away from the metal atom.

The lengthening of the C=C bonds is about 0.01 Å (see Table 6), similar to that found for [Pt(C₂H₄)₃] [19]. The Ni–C distances are 0.25 Å shorter than the Pt–C distances, but this is to be expected in view of the smaller atomic radius of nickel. The distortion of the C=CH₂ groups from trigonal planarity can be expressed by the angle between the C=C bond and the bisector between the bonds in the CH₂ plane. Our calculation for [Ni(C₂H₄)₃] gives 16.2° for this angle, which may be compared with the 15.7° observed experimentally for [Pt(C₂H₄)₃].

We conclude that the structures of the nickel and platinum tris(ethylene) complexes are very similar. It is not surprising, therefore, that there is a fair degree of similarity between the vibrational frequencies of the ethylene motions in the two cases (Table 3).

Comparison with chemisorbed ethylene

In recent years vibrational spectra of ethylene chemisorbed on single crystal metal surfaces have been studied extensively by high resolution electron energy loss spectroscopy (HREELS). In such spectra, according to "surface selection rules" only totally symmetric modes of a non-planar ethylene of C_{2v} symmetry should be dipole-active and observable [28] (although others may appear if the ethylene moiety is twisted or tilted). The dominant features should be symmetric CH stretching ν_1 , C–C stretching ν_2 , CH₂ scissoring ν_3 , CH₂ wagging ν_4 , and symmetrical metal–carbon stretching ν_5 . Interpretation of the spectra has mostly been concerned with two models, C₂H₄ π -bonded to a single metal centre or di- σ -bonded between two metals. Some examples are quoted in Table 7, together with the relevant modes (a_1' and e') of the [M(C₂H₄)₃] (M = Ni, Pd or Pt) complexes. The Pd(110) surface is representative of a π -bonded case [29]; its CH stretching (> 3000), C–C stretching (> 1500) and M–C stretching (< 400) wavenumbers show similarity to those of the binary complexes but its CH₂-scissoring and -wagging modes are substantially lower. For the cases involving di- σ -bonding, the pattern shows a number of important differences from the [M(C₂H₄)₃] complexes; in particular the CH

Table 7

Comparison of ethylene vibrations (cm⁻¹) in [M(C₂H₄)₃] complexes with dipole-active modes of ethylene bonded to metal single crystal surfaces

	CH str	CC str	CH ₂ scis	CH ₂ wag	MC ₂ str	Surface condition	Surface bonding	ref.
PdC (110)	3000	1546	1226	924	339	<1L, 110 K	π	[29]
Ni (111)	2950	1200	1430	1100	450	<1L, 150 K	di- σ	[30]
Ni (110)	2970		1435	1145	420	3L, 80 K	di- σ	[31]
Fe (110)	2960	1250	1410	1105	480	6L, 120 K	di- σ	[32]
Pt (111)	2940	1230	1420	990	470	2L, 140 K	di- σ	[33]
[Pt(C ₂ H ₄) ₃] a_1'	3004	1617	1338	1226	398			
[Pt(C ₂ H ₄) ₃] e'	3001	1501	1424	1219	332			^a
[Pd(C ₂ H ₄) ₃] e'	3000	1525	1427	1262	305			[13]
[Ni(C ₂ H ₄) ₃] e'	2995	1515	1436	1243	375			^a

^a This work.

stretching wavenumbers occur below 3000 cm^{-1} and are typical for sp^3 hybridised carbon, the low C–C stretching values (ca. 1240 cm^{-1}) are compatible with the loss of olefinic character and the MC stretching features ($> 400\text{ cm}^{-1}$) are in the region commonly associated with such modes in alkylmetals.

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