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The vibrational spectra and structure of tris(ethylene)metals

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Abstract

The IR and Raman spectra of $[Pt(C_2H_4)_3]$, $[Pt(C_2D_4)_3]$ and IR spectra of $[Ni(C_2H_4)_3]$ 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 $[Ni(C_2H_4)_3]$ 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° C throughout transfer to the cells and for the measurements. A Specae liquid nitrogen-cooled cryostat was used. Raman measurements were performed with a Coderg T800 triple monochromator with photoncounter 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° C by use of a Coderg Cryocirc cryostat. The preparations of the compounds have been described previously [5-8].

Table 1

Vibrational spectra and assignments for tris(ethylene)metal complexes

IR IR IR IR IR IR solution room temp. soluticlis room room temp. solution	$[\operatorname{Ni}(\operatorname{C_2H_4})_3]$	$[Pd(C_2H_4)_3]$	$[Pt(C_2H_4)_3]$		Raman	Proposed
Solution - 50° C Solution room temp. colution room temp. -40^{+} C 3070.6S 3072m 3060s 3072.8 3031.6s = 2999.0m ² 3015sh 3027.1m 3048.5w, dp 3028.5w, dp 3020.1sh r_{13}, e' 2999.0m ² 30006s ? 2112.5w $3024.6m, e'$ 2999.0m ² 30006s ? r_{13}, e' 2999.0m ² 30000s ² 3000.6s ? r_{13}, e' 2112.5vw 2031.5vw $2r_{33}, a'_1 + a'_2 + e'$ $r_{4} + r_{16}, a''_2, r_{16} + r_{23}, e'$ 2118.vw 2031.5vw 2 $r_{33}, a'_1 + a'_2 + e'$ $r_{24} + r_{16}, a''_2, r_{16} + r_{23}, e'$ 1218.vw 1849.2w $r_{5} + r_{20}, e'$ $r_{21} + c'$ 1350.4 1500.5 1500w 1617.1w, p r_{21}, e' C S stretching 1520s 1500w 1424.2m 1445.2 " $r_{21} + c'$ $r_{22} + c'$ 1423.9w 1417.5h 1420w 1424.2m 1445.2 " r_{21}, e' C H ₂ scissor 1362.3m 1365.1w 1361.0w 137.7s, p $r_{3}, a'_{1} + a'_{2} + e$	IR	IR	IR	IR	solution	assignments
-2.0 C Iow temp. room temp. room temp. 3070.6s 3072m 3060s 3072.0s r_{14}, a_2^{\prime} CH stretching 30301.6s 3015sh 3027.1m 3048.5w, dp $r_{29}, e^{\prime\prime}$ 2999.0m ⁶ 3000.sh 3002.1sh 3004.5.yr $r_{15}, a_2^{\prime\prime}$ CH stretching 2999.0m ⁶ 3000.sh 3002.1sh 3004.5.yr $r_{16}, a_2^{\prime\prime}$ CH stretching 2995.0m ⁶ 3000m ⁴ 3000.lsh 3004.5.yr $r_{16}, a_2^{\prime\prime}$ if $a_2^{\prime} + a_2^{\prime}$ 2112.5vw 2031.5vw 2 $r_{33}, a_1^{\prime} + a_2^{\prime} + a_2^{\prime}$ 2112.5vw $r_{4} + r_{16}, a_2^{\prime\prime}$; $r_{16} + r_{23}, e^{\prime}$ 2118.vw 1928.6w 2 $r_{33}, a_1^{\prime} + a_2^{\prime} + a_2^{\prime}$ 1913.1vw 1830.2m 1849.2w 1617.1w, p r_{20}, e^{\prime} 120 1559.4vvw 1525s 1507m 1503.1m 1500.7w, dp r_{20}, e^{\prime} 1423.9w 1417.sh 1422m 1443.4 9w ^a r_{21}, e^{\prime} CH ₂ scissor 1424.4vw 1345.1w 1365.1w 1361.0w 1337.sp r_{3}, a_1^{\prime} CH ₂ scissor 1349.3vs 1316w 1365.1w 1361.0w	solution	solid	solid	solution	-40°C	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-30 C	low temp.	room temp.	room temp.		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3070.6s	3072m	3060s	3072.0s		v_{14}, a_2'' CH stretching
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					3067.5w, dp	v ₂₈ , e''
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					3048.5w, dp	v ₂₉ , e''
2999.0m e^{0} 3002.1sh3004.3s, p r_{13}, a'_{1} 2995.0m e^{0} 3000m e^{0} 3000.6s? r_{13}, e' 2095.0m e^{0} 2000.6s? $2r_{23}, a'_{1} + a'_{2} + e'$ 2157.4w2031.5vw $2r_{33}, a'_{1} + a'_{2} + e'$ 2118.vvw1928.6w $2r_{33}, a'_{1} + a'_{2} + e'$ 1965.7w1928.6w $2r_{33}, a'_{1} + a'_{2} + e'$ 1830.2m1849.2w $s_{7} + v_{20}, e'$ 1830.2m1551w, b1500.7m1559.4vvw1551w, b1520.51507m1503.1m1505.4vvw1525s1500w1424.2m1445.2 a' 1435.6vs a' 1427s1435.6vs a' 1427s1435.6vs a' 1427s1444.4vw1445.2 a' 1444.4vw1445.2 a' 1444.4vw1385vw1365.1w1361.0w1364.3m1320vw1365.1w1361.0w1365.1w1361.0w1335vw1315w, b1228.vvw1225vx1269.vvw1225vx1269.vvw1225vx1269.vvw1225vx1269.vvw1225vx1269.vvm1225vx127.sh127.sh127.sh127.sv133.w1315w, b1242.9vx1225vx1262.vs1225vx121.1vx121.6sh1242.9vx1225vx124.9vx146.6w123.8v106.5sh124.9vx1085w, b125.9vx1094vx<	3031.6s a		3015sh	3027.1m	3024.6m, dp	ν_{18}, e'
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2999.0m ^b			3002.1sh	3004.3s, p	ν_1, a_1'
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2995.0m ^b	3000m ^c		3000.6s	?	v_{19}, e'
2157.4vw 2031.5vw $\nu_4 + \nu_{16}, a_2'', \nu_{16} + \nu_{23}, e'$ 2118.vvw 1928.6w $2\nu_{33}, a_1' + a_2' + e'$ 1913.1vw 1884.2w $\nu_5 + \nu_{20}, e'$ 1830.2m 1551w, b 1617.1w, p ν_2, a_1' CC stretching 1559.4vvw 1525s 1507m 1503.1m 1500.7w, dp ν_{20}, e' 1425.6vs 1427s 1430w 1445.2 a 1434.9w a' ν_{21}, e' CH ₂ scissor 1423.9w 1417sh 1422m 1434.9w a' ν_{21}, e' CH ₂ scissor 1425.6vs 1365.1w 1365.1w 1361.0w 1361.0w 1315w, b 1277sh 1218.vv ν_{22}, e' CH ₂ scissor 1375.4s 1270w, b 1225.6vs, p ν_4, a_1' CH ₂ scissor 128.0000 1315w, b 1277sh 1218.1vs 1225.6vs, p ν_4, a_1' CH ₂ wag 121.1w ν_{23}, e'' CH ₂ cock 114.10000 131.10000 131.10000 131.10000 131.10000 131.10000 131.10000 132.10000 122.10000 122.10000 122.10000 122.10000 122.10000 122.10000 122.10000 122.10000 122.100000 122.10000 122.100000				2112.5vw		$2\nu_{32}, a_1' + a_2' + e'$
2118vvw 1928.6w $2r_{33}, a_1' + a_2' + e'$ 1965.7w 1913.1vw $r_{s3}, a_1' + a_2' + e'$ 1830.2m 1849.2w $r_{s2} + r_{20}, e'$ 1859.4vvw 1551.w 1507m 1559.4vvw 1520s 1507m 1500.7w 1500.7w, dp r_{20}, e' 1422.1w 1445.2 " 1423.9w 1417sh 1422m 1445.4 " 1445.2 " 1423.9w 1417sh 1422m 1445.4 " 1434.9w" r_{21}, e' CH ₂ scissor 1362.3m 1365.1w 1361.0w 1335vw 1310w 1315w, b 1361.0w 1335vw 1310w 1315w, b 1250vvw, b 1263.2vvw 1262vs 1220vv, b 1225.6vs, p r_4, a_1' CH ₂ wag 1242.9vvs 1262vs 1225vv 1216sh r_{23}, r_{24}, e' CH ₂ wag 1242.9vvs 1262vs 1225vvs 1218.7vs 1216sh r_{23}, r_{24}, e' CH ₂ wag 1242.9vvs 1262vs 1225vvs 1218.7vs 1216sh r_{23}, e'' CH ₂ cock 1123.2vv	2157.4vw			2031.5vw		$v_4 + v_{16}, a_2''; v_{16} + v_{23}, e'$
1965.7w $2v_{33}$, $a'_1 + a'_2 + e'$ 1913.1vw 1928.6w $2v_{33}$, $a'_1 + a'_2 + e'$ 1913.1vw 1849.2w $v_5 + v_{20}$, e' 1830.2m 1849.2w $v_5 + v_{20}$, e' 1559.4vvw 1551 w, b 1617.1w, p v_2 , a'_1 CC stretching 1559.4vvw 1525 s 1507 m 1500.7w, dp v_{20} , e' 1422.1w 1445.2 " 1445.2 " 1422.9w 1422.9w 1423.6vs ^a 1427 s 1430 m 1424.2m 1434.9w ^a v_{21} , e' CH ₂ scissor 1423.9w 1417 sh 1422 m 1385 vvw $v_4 + v_{17}$, a''_2 1362.3m 1340.3vs 1316 w 1365.1w 1361.0w 1337.7s, p v_3 , a'_1 CH ₂ scissor 1328vvw 1316w 1310vw 1315w, b 1225.6vs, p v_4 , a'_1 CH ₂ scissor 1263.2vvw 1220vs 1225.6vs, p v_4 , a'_1 CH ₂ wag 121.33 w v_{23} , e'' CH ₂ rock 1233eh 1229w, m 1218w, m 1146.6w v_{30} , e'' CH ₂ rock 1233eh 1229w, m 121.1 w v_{23} , e''' CH ₂ rock	2118vvw					
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1965.7w					
$\begin{array}{c c c c c c c c c c c c c c c c c c c $				1928.6w		$2\nu_{33}, a_1' + a_2' + e'$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $				1913.1vw		
1830.2m 1849.2w 1559.4vvw 1551w, b 1511.9s 1525s 1520s 1500w 1411.10s 1525s 1520s 1500w 1445.2 a 1445.2 b 1441.4vw 1444.4vw 1385vvw 1362.3m 1349.3vs 1365.1w 1365.1w 1365.1w 1365.1w 1316w 1310w 1218w, m 1225.0vs, p 124.9vs 124.9vs 124.9vs 124.9vs				1884.2w		$v_5 + v_{20}, e'$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	1830.2m			1849.2w		
1559.4vvw1551w, b1511.9s1525s1507m1503.1m1500.7w, dp ν_{20} , e' 1492.1w1445.2 a1445.2 a1445.2 a1445.2 a1435.6vs a'1427s1430w1424.2m1434.9w a' ν_{21} , e' CH2 scissor1423.9w1417sh1422m1424.2m1434.9w a' ν_{21} , e' CH2 scissor1414.4vw1385vvw $\nu_4 + \nu_{17}$, a''_2 ν_{22} , e' CH2 scissor1362.3m1349.3vs1365.1w1361.0w13160.0w1349.3vs1319w1315w, b1250vvw, b1255.0vs, p ν_4 , a'_1 CH2 scissor1328vvw1319w1315w, b1250vvw, b1225.6vs, p ν_4 , a'_1 CH2 wag1242.9vvs1262vs1225vs1218.7vs1216sh ν_{21} , e' CH2 rock1233sh1229w, m1225.vv1216sh ν_{31} , e'' CH2 rock1121.1w1148sh1146.6w ν_{30} , e'' CH2 rock1121.1w ν_{31} , e'' CH2 twist1123.2vvs1094vs978s960sh ν_{32} , e'' CH2 twist1074sh1030vs1055sh1035w, b1074.6w ν_{32} , e'' CH2 twist1044w1030vs1055sh1035w, b1074.6w ν_{32} , e'' CH2 twist913s998m832m820.4w ν_{16} , a''_2 CH2 twist					1617.1w, p	ν_2, a_1' CC stretching
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1559.4vvw		1551w, b			
1520s1500w1492.1w1427s1430w1424.2m1434.9w a^{-1} v_{21} . e^{-1} CH2 scissor1423.9w1417sh1422m1434.9w a^{-1} v_{21} . e^{-1} CH2 scissor1414.4vw1385vvw $v_{4} + v_{17}$. a_{2}^{-1} 1376.4s b^{-1} 1385vvw $v_{4} + v_{17}$. a_{2}^{-1} 1376.4s b^{-1} 1385vvw v_{22} . e^{-1} CH2 scissor1362.3m1385vvw1365.1w1361.0w1335vw1319w1315w, b1337.7s, p1328vvw1319w1315w, b1238vvw1270w, b1225.0vs, p1263.2vvw1220vv, b1225.vs1242.9vvs1262vs1225vs1242.9vvs1262vs1225vs1233sh1229w, m1218w, m1244.9v1146.6w v_{30} , e^{-1} CH2 rock1154.1w1146.6w v_{30} , e^{-1} CH2 rock1123.2vvs1094vs978s960sh937s924.7m1074.6w v_{32} , e^{-1} CH2 twist1074sh1030vs1055sh1035w, b1018vw1055sh1035w, b v_{33} , e^{-1} CH2 twist913s915.5w898m832m820.4w v_{16} , a_{2}^{-1} CH2 rock d^{-1}	1511.9s	1525s	1507m	1503.1m	1500.7w, dp	ν_{20}, e'
1492.1w1445.2 a1435.6vs a1427s1430w1424.2m1434.9w a ν_{21} , e' CH ₂ scissor1423.9w1417sh1422m1434.9w a ν_{21} , e' CH ₂ scissor1414.4vw1385vvw $\nu_4 + \nu_{17}$, a_2'' 1376.4s b1385vvw $\nu_{4} + \nu_{17}$, a_2'' 1362.3m ν_{22} , e' CH ₂ scissor1362.3m1365.1w1361.0w1355vw1365.1w1361.0w1328vvw1319w1316w1310vw1315w, b1277sh1270w, b1263.2vvw1225vvs1262.vv1225vs1242.9vvs1262vs1229.w, m1225vs1218w, m1146.6w1233sh1229w, m1218w, m1146.6w1154.1w1146.6w1148sh1146.6w1123.2vvs1094vs965w950.1m937s924.7m937s924.7m944.4w1030vs1018vw1055sh1035w, b968.1vw913s915.5w898m832m820.4w ν_{16} , a_2'' CH ₂ rock d		1520s	1500w			
1445.2 a 1435.6 vs a 1427s1430w1424.2m1434.9w a v_{21} , e' CH2 scissor1423.9w1417sh1422m1434.9w a v_{21} , e' CH2 scissor1414.4vw1385vvw $v_4 + v_{17}$, a_2'' 1376.4s b 1385vvw v_2 , e' CH2 scissor1376.4s b 1385vvw v_{22} , e' CH2 scissor1349.3vs1365.1w1361.0w1335vw1365.1w1361.0w1316w1310vw1315w, b1270w, b1225.6vs, p v_4 , a_1' CH2 scissor1262vs12270w, b1225.6vs, p v_4 , a_1' CH2 wag1242.9vvs1262vs1225vs1218.7vs1216sh1233sh1229w, m1229w, m v_{21} , v_{24} , e' 1144.1w1146.6w v_{30} , e'' CH2 rock1154.1w1146.6w v_{30} , e'' CH2 rock1123.2vvs1094vs978s960sh937s924.7m1074.6w v_{32} , e'' CH2 twist1074sh1030vs1055sh1035w, b1044w1030vs1055sh1035w, b913s915.5w898m832m820.4w	1492.1w					
1435.6vs a° 1427s1430w1424.2m1434.9w a° v_{21} , e^{\prime} CH2 scissor1423.9w1417sh1422m1385vvw $v_{4} + v_{17}$, a_2° 1376.4s b° 1385vvw $v_{4} + v_{17}$, a_2° 1376.4s b° 1385vvw v_{22} , e^{\prime} CH2 scissor1349.3vs1365.1w1361.0w1335vw1365.1w1361.0w1335vw1319w1315w, b1316w1310vw1315w, b1277sh1270w, b1262.vs1225.6vs, p v_4 , a_1^{\prime} CH2 scissor1242.9vvs1262vs1225vs1263.2vvw1225vs1218.7vs1242.9vvs1262vs1225vs1242.9vvs1262vs122sv1242.9vvs1262vs122svs1242.9vvs1262vs122svs1233sh1229w, m 1218w, m1146.6w 1211.w1144sh1146.6w 937s v_{30} , $e^{\prime\prime}$ CH2 rock1123.2vvs1094vs978s 960sh 950.1m937s924.7m1074.6w 937s1074sh1030vs 1018vw1055sh 1035w, b1044w 1018vw1055sh 1035w, b1035w, b913s913s832m 820.4w v_{16} , $a_2^{\prime\prime}$ CH2 rock d					1445.2 ª	
1423.9w 1417sh 1422m 1414.4vw 1385vvw $\nu_4 + \nu_{17}, a_2''$ 1376.4s $\nu_{22}, e' \text{ CH}_2 \text{ scissor}$ 1362.3m $\nu_{22}, e' \text{ CH}_2 \text{ scissor}$ 1349.3vs 1365.1w 1361.0w 1335vw 1365.1w 1361.0w 1335vw 1319w 1317.7s, p 1316w 1310vw 1315w, b 1277sh 1270w, b 1250vvw, b 1263.2vvw 1225.evs, p $\nu_4, a_1' \text{ CH}_2 \text{ wag}$ 1242.9vvs 1262vs 1225.vs 1218w, m 1146.6w $\nu_{30}, e'' \text{ CH}_2 \text{ rock}$ 1148sh 1146.6w $\nu_{30}, e'' \text{ CH}_2 \text{ rock}$ 1123.2vvs 1094vs 978s 960sh $\nu_{15}, a_2'' \text{ CH}_2 \text{ twist}$ 937s 924.7m 1074.6w $\nu_{32}, e'' \text{ CH}_2 \text{ twist}$ 1044w 1030vs <t< td=""><td>1435.6vs a</td><td>1427s</td><td>1430w</td><td>1424.2m</td><td>1434.9w ^a</td><td>v_{21}, e' CH₂ scissor</td></t<>	1435.6vs a	1427s	1430w	1 424 .2m	1434.9w ^a	v_{21} , e' CH ₂ scissor
1414.4vw 1385vvw $\nu_4 + \nu_{17}, a_2''$ 1376.4s h $\nu_{22}, e' \text{ CH}_2 \text{ scissor}$ 1362.3m $\nu_{22}, e' \text{ CH}_2 \text{ scissor}$ 1339.vs 1365.1w 1361.0w 1335vw 1365.1w 1361.0w 1335vw 1319w 1317.5, p $\nu_{3}, a_1' \text{ CH}_2 \text{ scissor}$ 1328vvw 1310vw 1315w, b 1237.7s, p $\nu_{3}, a_1' \text{ CH}_2 \text{ scissor}$ 1242.9vvs 1262vs 12250vvw, b 1225.6vs, p $\nu_4, a_1' \text{ CH}_2 \text{ wag}$ 1242.9vvs 1262vs 1225vs 1218.7vs 1216sh 1233sh 1229w, m 1218.7vs 1216sh 1218w, m 1146.6w $\nu_{30}, e'' \text{ CH}_2 \text{ rock}$ 1154.1w 1146.6w $\nu_{30}, e'' \text{ CH}_2 \text{ rock}$ 1123.2vvs 1094vs 978s 960sh $\nu_{15}, a_2'' \text{ CH}_2 \text{ twist}$ 937s 924.7m 1074.6w $\nu_{32}, e''' \text{ CH}_2 \text{ twist}$ 1044w 1030vs 1055sh 1035w, b $\nu_{33}, e''' \text{ CH}_2 \text{ twist}$ 913s 913s 913. 920.4w $\nu_{16}, a_2'' \text{ CH}_2 \text{ twist}^d$	1423.9w	1417sh	1422m			
$1385vvw \qquad p_4 + p_{17}, a_2''$ $1376.4s^{b}$ $1362.3m$ $1362.3m$ $1349.3vs$ $1349.3vs$ $1335vvw$ $1335vv$ $1365.1w$ $1361.0w$ $1337.7s, p$ $p_3, a_1' CH_2 scissor$ $1328vvw$ $1319w$ $1316w$ $1310vw$ $1315w, b$ $1270w, b$ $1250vvw, b$ $1225.6vs, p$ $p_4, a_1' CH_2 wag$ $1242.9vvs$ $1262vs$ $1225vs$ $1218.7vs$ $1216sh$ p_{23}, p_{24}, e' $CH_2 wag$ $p_{1242.9vvs}$ $1228w, m$ $1218w, m$ $1146.6w$ $p_{30}, e'' CH_2 rock$ $1121.1w$ $p_{31}, e'' CH_2 rock$ $1123.2vvs$ $1094vs$ $978s$ $960sh$ $p_{15}, a_2'' CH_2 twist$ $968.1vw$ $p_{33}, e'' CH_2 twist$ $913s$ $915.5w$ $898m$ $832m$ $820.4w$ $p_{16}, a_2'' CH_2 rock d$	1414.4vw					
1376.4s b ν_{22} , $e' CH_2 scissor 1362.3m \nu_{22}, e' CH_2 scissor 1349.3vs 1361.0w 1335vw 1310vw 1316w 1310vw 1277sh 1270w, b 1263.2vvw 1220vv, b 1242.9vvs 1262vs 1229w, m 1225.6vs, p 1218w, m 1225.6vs, p 1218w, m 1225.6vs 1146.6w \nu_{23}, \nu_{24}, e' CH2 wag \rho 1154.1w 1146.6w \nu_{30}, e'' CH2 rock 1121.1w \nu_{31}, e'' CH2 rock 1085w, b 937s 924.7m 1074.6w \nu_{32}, e'' CH2 twist 1044w 1030vs 1055sh 1035w, b 913s 913s 924.7m 968.1vw \nu_{33}, e''' CH2 twist 913s 913s 924.7m 1074.6w \nu_{33}, e''' CH2 twist <$				1385vvw		$\nu_4 + \nu_{17}, a_2''$
1362.3m ν_{22} , $e' CH_2 scissor 1349.3vs 1365.1w 1361.0w 1335vw 1319w 1317.7s, p \nu_3, a'_1 CH_2 scissor 1328vvw 1319w 1315w, b 1337.7s, p \nu_3, a'_1 CH_2 scissor 1328vvw 1319w 1315w, b 1270w, b 1225.6vs, p \nu_4, a'_1 CH_2 wag 1242.9vvs 1262vs 1225vs 1218.7vs 1216sh \nu_{23}, \nu_{24}, e'_2 1233sh 1229w, m 1218w, m 1146.6w \nu_{30}, e'' CH_2 rock 1124.1w 1148sh 1146.6w \nu_{30}, e'' CH_2 rock 1123.2vvs 1094vs 978s 960sh \nu_{15}, a''_2 CH2 twist 1123.2vvs 1094vs 978s 960sh \nu_{15}, a''_2 CH2 twist 1074sh 1074.6w \nu_{32}, e'' CH2 twist 1044w 1030vs 1055sh 1035w, b \nu_{33}, e'' CH2 twist 913s 913s 913s 920.4w \nu_{16}, a''_2 CH2 rock d' $	1376.4s ^b					
1349.3vs1365.1w1361.0w1335vw1319w1328vvw1319w1316w1310vw1316w1310vw1316w1310vw1316w1310vw1316w1310vw1277sh1270w, b1262.vvw12250vvw, b1242.9vvs1262vs1229w, m1225vs1218w, m1218.7vs1218w, m1146.6w123sh1229w, m1218w, m1146.6w123.vvs1094vs965w950.1m937s924.7m1074.6w v_{32} , e'' CH ₂ twist1044w1030vs1018vw1055sh1018vw1055sh915.5w898m832m820.4w v_{16} , a''_2 CH ₂ tock d	1362.3m					v_{22} , e' CH ₂ scissor
1335vw1337.7s, p v_3 , $a_1' CH_2 scissor1328vvw1319w1316w1310vw1316w1310vw1316w1310vw1316w1310vw1277sh1270w, b1263.2vvw1250vvw, b1263.2vvw1250vvw, b1242.9vvs1262vs1242.9vvs1262vs1229w, m1218.7vs1218w, mv_{23}, v_{24}, e'1218w, m1146.6w1218w, m1146.6w123.2vvs1094vs978s960sh965w950.1m937s924.7m1074.6wv_{32}, e'' CH_2 twist1044w1030vs1018vw1055sh1031vs1055sh1035w, b1035w, b1018vw968.1vw913.5938m832m820.4wv_{16}, a_2'' CH_2 rock d'$	1349.3vs			1365.1w	1361.0w	
1328vvw1319w1316w1310vw1315w, b1277sh1270w, b1263.2vvw1250vvw, b1263.2vvw1250vvw, b1242.9vvs1262vs1229w, m1218.7vs1218w, m r_{23}, r_{24}, e' 1218w, m1146.6w123sh1229w, m1218w, m1146.6w1148sh1146.6w1123.2vvs1094vs978s960sh965w950.1m937s924.7m1074sh1030vs1018vw1055sh1030vs1055sh1018vw1035w, b913s913s915.5w898m832m820.4w $r_{16}, a_2'' CH_2 rock d'$	1335vw				1337.7s, p	ν_3 , a_1' CH ₂ scissor
1316w1310vw1315w, b1277sh1270w, b1263.2vvw1250vvw, b1242.9vvs1262vs1242.9vvs1262vs1225.evs, p r_4 , a_1' CH ₂ wag1233sh1229w, m1218w, m r_{23} , r_{24} , e' 1218w, m r_{23} , r_{24} , e' 1218w, m1146.6w123.2vvs1094vs978s960sh965w950.1m937s924.7m1074sh1074.6w1044w1030vs1018vw1055sh1018vw968.1vw913s832m898m832m820.4w r_{16} , a_2'' CH ₂ rock d	1328vvw	1319w				
1277sh1270w, b1263.2vvw1250vvw, b1263.2vvw1225vs1242.9vvs1262vs1225.evs, p p_4 , a_1' CH ₂ wag1233sh1229w, m 1218w, m1218w, m1218.7vs1218w, m r_{23} , r_{24} , e' CH ₂ wag1154.1w1146.6w 1121.1w1148sh1146.6w 1121.1w1123.2vvs1094vs978s 965w 950.1m 937s960sh 950.1m 937s1074sh 1018vw1055sh1030vs 1018vw1055sh1030vs 1018vw1055sh1035w, b 913s968.1vw913s 915.5w898m832m820.4w r_{16} , a_2'' CH ₂ rock d	1316w	1310vw	1315w, b			
1263.2vvw1250vvw, b1242.9vvs1262vs1225vs1218.7vs1216sh1233sh1229w, m1218.7vs1216sh1218w, m1218w, m ν_{23}, ν_{24}, e' $CH_2 wag1154.1w1146.6w\nu_{30}, e'' CH2 rock1121.1w\nu_{31}, e'' CH2 rock1148sh1146.6w\nu_{30}, e'' CH2 rock1121.1w1123.2vvs1094vs978s960sh\nu_{15}, a''_2 CH2 twist1074sh937s924.7m1074.6w\nu_{32}, e'' CH2 twist1074sh1030vs1055sh1035w, b1044w1030vs1055sh1035w, b913s913s820.4w\nu_{16}, a''_2 CH2 rock d$	1277sh		1270w, b			
1242.9vvs 1262vs 1225vs 1218.7vs 1216sh = 1218.7vs 1216sh = 1218w, m = 1218	1263.2vvw			1 250vvw , b		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					1225.6vs, p	$v_4, a'_1 \operatorname{CH}_2 \operatorname{wag}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1242.9vvs	1262vs	1225vs	1218.7vs	1216sh	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	1233sh	1229w, m				ν_{23}, ν_{24}, e'
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1218w, m				CH ₂ wag)
1148sh 1146.6w v_{30} , e'' CH ₂ rock 1121.1w v_{31} , e'' CH ₂ rock 1123.2vvs 1094vs 978s 960sh v_{15} , a''_2 CH ₂ twist 1123.2vvs 1094vs 978s 960sh v_{15} , a''_2 CH ₂ twist 1123.2vvs 1094vs 978s 960sh v_{15} , a''_2 CH ₂ twist 1123.2vvs 1094vs 978s 960sh v_{15} , a''_2 CH ₂ twist 1074sh 1074.6w v_{32} , e'' CH ₂ twist 1044w 1030vs 1055sh 1035w, b 1018vw 968.1vw v_{33} , e'' CH ₂ twist 913s 913s 915.5w 898m 832m 820.4w v_{16} , a''_2 CH ₂ rock d	1154.1w					
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1148sh				1146.6w	$v_{30}, e'' \operatorname{CH}_2 \operatorname{rock}$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					1121.1w	$\nu_{31}, e'' CH_2 rock$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				1085w, b		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1123.2vvs	1094vs	978s	960sh		$v_{15}, a_2'' \operatorname{CH}_2$ twist
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			965w	950.1m		
1074sh 1074.6w v_{32} , e'' CH ₂ twist 1044w 1030vs 1055sh 1035w, b 1018vw 968.1vw v_{33} , e'' CH ₂ twist 913s 915.5w 898m 832m 820.4w v_{16} , a''_2 CH ₂ rock d			937s	924.7m		
1044w 1030vs 1055sh 1035w, b 1018vw 968.1vw ν_{33} , e ^{''} CH ₂ twist 913s 915.5w 898m 832m 820.4w ν_{16} , a ^{''} ₂ CH ₂ rock ^d	1074sh				1074.6w	v_{32} , e'' CH ₂ twist
1018vw 968.1vw v ₃₃ , e ^{''} CH ₂ twist 913s 915.5w 898m 832m 820.4w v ₁₆ , a ^{''} ₂ CH ₂ rock ^d	1044w	1030vs	1055sh	1035w, b		
968.1vw ν_{33} , $e'' \operatorname{CH}_2$ twist 913s 915.5w 898m 832m 820.4w ν_{16} , $a''_2 \operatorname{CH}_2$ rock d		1018vw				
913s 915.5w 898m 832m 820.4w r_{16} , a_2'' CH ₂ rock ^d					968.1vw	v_{33} , e'' CH ₂ twist
915.5w 898m 832m 820.4w $\nu_{16}, a_2'' \operatorname{CH}_2 \operatorname{rock}^d$		913s				<i>и и</i>
	915.5w	898m	832m	820.4w		v_{16} , a_2'' CH ₂ rock ^a

(continued)

$[Ni(C_2H_4)_3]$	$[Pd(C_2H_4)_3]$	$[Pt(C_2H_4)_3]$		Raman	Proposed
IR solution -50°C	IR solid low temp.	IR solid room temp.	IR solution room temp.	solution – 40 ° C	assignments
896.3w	881m				
846.2m	828s	823m			
834.6vw	820w				
822.9vw	813m				
794.5w	760m	783w			
7 40 vvw			733vvw		$\nu_5 + \nu_{26}, e'$
726m, w			708.6w		
	626m		693w		
	614w		649w, b		
				500w	$\nu_{17} + \nu_{26}, e^{\prime\prime}$
462sh			468.7w		
440sh			440sh	448.3vw	v_{25}, e' ML tilt
				398.2vs, p	ν_5, a'_1 ML ₃ sym str.
			385sh	•	5 1 3 2
			363sh		
374.6vs	305vs ^c		331.3vs	331.7m, dp	ν_{26} , e' ML ₃ asym str.
280vw			240vw, b	•	20.
255.3w			163w, sh		$\nu_{17}, a_{2}^{"}$ ML ₃ o.o.p. bend
227.3m 130.2w(?) 108.8w(?)			147.1vw	145.4m, dp	ν_{27} , e' ML ₃ i.p. bend

Table 1 (continued)

^a Coincidence with solvent's band. ^b Uncertain band after substraction 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 $[Ni(C_2H_4)_3]$, 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 $[M(C_2H_4)_3]$ 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 $[M(C_2H_4)_3]$ 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_2H_4 vibrations. [Pt(C_2H_4)_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

Infrared	and a second	Raman	Proposed
mull	solution	(solution)	assignments
	2337m, w	·····	
2313.2m, s	2315.5m	2314vw, b	$v_1, a_1'; v_{14}, a_2''$ CD stretching
		2267vw	ν_{28}, e''
		2250w	ν_{29}, e''
2214.4w	2215.9w	2214m	ν_{18}, e'
2179.2s	2181.1s	2184vw	ν_{19}, e'
1530vw, b	1530vw, b		
1 41 5vw	1414vw		
1365vw			
1332.8vs	1333.7vs	1336w	v_{20} , e' CC stretching
	1315sh		20 0
		1301vw	ν_2, a'_1 CC stretching
1230sh	1233vvw		
1220.6vw	1220.8	1225vvw	
		1166vvw	
		1120w	$\nu_3, a_1' \text{CD}_2 \text{ scissor}$
1078vw	1075vw	1075vvw	5. 1 1
1060.0w	1061.1w		v_{21} , e' CD ₂ scissor
982vw	978vw		v_{22} , e' CD ₂ scissor
	955sh		ν_{24} , e' CD ₂ wag
945.9s	946.5s		v_{23} , e' CD ₂ wag
885vw			
800w, b			
769.3vw	769.9vw		v_{15} , a'_2 CD ₂ twist
745vvw	743sh	747vw	
719vw	720vw, b		
685vw, b			
	660.5vw		$v_{16}, a_2'' CD_2 rock$
589.1vw	589.1vw		
523vvw			
	490vw		
	463vw		
	415vw	400vw	v_{25} , e' ML tilt
	376vw	380m	ν_5 , a'_1 ML ₃ sym. stretch.
	363vw		
	323.4vw	326vvw	ν_{26} , e' ML ₃ asym. strech.
	147.7sh		ν_{17}, a_2'' ML ₃ o.o.p. bend
	136.8vs	136w	ν_{27} , e' ML ₃ i.p. bend
			217 J K

Vibrational spectra and assignments proposed for $[Pt(C_2D_4)_3]$

Table 2

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 C_2H_4 and C_2D_4 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(C_2H_4)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 CH₂ 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 CH₂ 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 CH₂ 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 CH₂ 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, CH₂ scissoring (next two bands) and CH₂ 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 CH₂ rocking and twisting modes. The choice of the order of CH₂ 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 $[Pt(C_2H_4)_3]$ are shown in Fig. 2. The polarized Raman line at 398 cm⁻¹ is assigned to the symmetric ML₃ 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 ML₃ out-of-plane bending mode (ν_{17}). The corresponding IR and Raman features around 146 cm⁻¹ can be attributed to the ML₃ 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 [Ni(C_2H_4)₃] and [Pt(C_2H_4)₃].

 C_2D_4 vibrations. Experimental frequencies for $[Pt(C_2D_4)_3]$ are presented in Table 2. Because of the slight decomposition of the $[Pt(C_2D_4)_3]$ 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 v_{28} and v_{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 $[Pt(C_2H_4)_3]$ 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 [Pt(C₂H₄)₃].

The CD₂ deformation modes were observed in the range 1120-660 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 CD₂ 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 $[M(C_2H_4)_3]$ (M = Ni, Pd or Pt) and $[Pt(C_2D_4)_3]$ are summarized in Table 3.

The implications of our assignments for the full family of $[M(C_2H_4)_3]$ 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 CH₂ scissoring.

Spec	ies and		$[Ni(C_2H_4)_3]$	$[Pd(C_2H_4)_3]$	$[Pt(C_2H_4)_3]$	$[Pt(C_2D_4)_3]$
appi	oximate	e de-				
scrip	otions of	modes	_			
a '1	v ₁	CH str			3004.1	2315.5
	v 2	CC str			1617.1	1301.0
	v ₃	CH ₂ sciss			1337.7	1120.0
	¥4	CH ₂ wag			1225.6	?
	v ₅	ML_3 sym str ^{<i>a</i>}			398.2	380.0
a_2''	V 14	CH str	3070.6	3072	3072.0	2315.5
	v 15	CH ₂ twist	1123.2	1098	978	769.9
	v ₁₆	CH ₂ rock	915.5	898	820.4	660.5
	¥17	ML ₃ o.o.p. bend	255.3	-	163	147.7
e'	v ₁₈	CH str	3031.6	3000	3024.6	2215.9
	P ₁₉	CH str	2995.0	-	(3000.6)	2181.1
	v ₂₀	CC str	1511.9	1522.5	1500.7	1333.7
	P21	CH ₂ sciss	1435.6	1427	1424.2	1061.1
	P ₂₂	CH ₂ sciss	1349.3	-	1361.0	978.0
	P ₂₃	CH ₂ wag	1242.9	1262	1218.7	946.5
	۳ ₂₄	CH ₂ wag	1233.0	1229	1218.7	955.0
	¥25	ML tilt	440.4		448.3	415.0
	V 26	ML ₃ asym str	374.6	305	331.7	323.4
	¥27	ML ₃ i.p. bend	227.3	~	147.1	136.8
e"	<i>v</i> ₂₈	CH str			3067.5	2267.0
	P 29	CH str			3048.5	2250.0
	v_{30}	CH ₂ rock			1146.6	?
	P ₃₁	CH ₂ rock			1121.1	?
	P ₃₂	CH ₂ twist			1074.6	?
	<i>v</i> ₃₃	CH ₂ twist			968.1	
	¥34	rotation around M	-L		-	

Table 3

Fundamental frequencies (cm⁻¹) obtained for tris(ethylene)metal complexes

^a The missing $v_6 - v_9$ and $v_{10} - v_{13}$ 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 $[Ni(C_2H_4)_3]$ 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.n. 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

Assignment	S	C ₂ H ₄ gas [26]	[Co(C ₂ H ₄) ₃] matrix [9]	[Ni(C ₂ H ₄) ₃] solution	[Pd(C ₂ H ₄) ₃] solid	[Pt(C ₂ H ₄) ₃] solution	[Cu(C ₂ H ₄) ₃] matrix [12]	
CH stretch	a', o',	3104.9s 3104.9c*	3055w	3070.6s 3031.6s	3072m	3072.0s 3027.1m	3054w	
	u `e	2988.7s	2980w	2999.0wm	3000wm	3000.6sh		
CC stretch	`ə	1630m(R)	1490m	1511.9s	1525s	1503.1m	1517w	
CH ₂ seiss	`ə`ə	1443.5s 1342.2s(R)	1415m 1225w	(1435.6vs) 1349.3s	1427s	1424.2m 1365.1vw		
CH ₂ wag	`o`o	949.3m 939.6w(R)	1215w	1242.9vs 1233m	1262vs 1229m	1218.7vs 950.1m	1252m	
CH ₂ twist	a'' 2	1023 (i.a.)		1123vs	1098vs	978s		
CH ₂ rock	a ''	826w	826w	915.5m	898m 813s	820.4w	810w	
" () strong c	overlappin	ig with solvent band, *	frequency used twice, ((R) frequency from Rai	man spectrum, and (i.a.)) inactive vibration.		

Infrared frequencies (cm^{-1}) assigned to ethylene vibrations for $[M(C_2H_4)_3]$ complexes ^a

Table 4



Fig. 3. Molecular geometry and molecular parameters of $[Ni(C_2H_4)_3]$ calculated by CNDO/2 method.

Table 5

Molecular parameters for $[Ni(C_2H_4)_3]$ calculated by the CNDO/2 method

Geometrical parameters		$[Ni(C_2H_4)_3]$	C ₂ H ₄ ^{<i>a</i>} CNDO/2	C ₂ H ₄ ^b exper.	
r(C=C)	(pm)	142.6	132.0	133.9	
r(CH)	(pm)	111.7	111.0	108.5	
r(Ni-C)	(pm)	192.6		-	
r(Ni)	(pm)	178.9	-	-	
a(HCH)	(°)	115.7	113.4	117.83	
v(deviation from plana	(°) tity)	16.2	0	0	

^a Ref. 27. ^bRef. 26.

Table 6

Geometrical parameters		$\frac{[Ni(C_2H_4)_3]^{a}}{(a)}$	$\frac{[Pt(C_2H_4)_3]^{a}}{(b)}$	$\frac{[Pt(C_2H_4)_2(C_2F_4)]^{a}}{(c)}$
r(C=C)	(pm)	142.6	140.2	137.1 *
r(CH)	(pm)	111.7	110.1 *	107.9 *
r(M-C)	(pm)	192.6	217.6	222.9 *
r(M)	(pm)	178.9	206.0	212.1 *
a(HCH)	ີ (°)	115.7 *	111.5 *	116.7 *
B(HCH)	(°)	120.7	122.6	120.3
v(deviation	(°)	16.2	15.2 *	16.0 *
from plana	rity)			

^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 CH_2 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 $[Pt(C_2H_4)_3]$ [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 $[Ni(C_2H_4)_3]$ gives 16.2° for this angle, which may be compared with the 15.7° observed experimentally for $[Pt(C_2H_4)_3]$.

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 $C_{2\nu}$ 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 p_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, C_2H_4 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 $(a'_1 \text{ and } e')$ of the $[M(C_2H_4)_3]$ (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-o-bonding, the pattern shows a number of important differences from the $[M(C_2H_4)_3]$ complexes; in particular the CH

Table 7

Comparison of ethylene vibrations (cm^{-1}) in $[M(C_2H_4)_3]$ complexes with dipole-active modes of ethylene bonded to metal single crystal surfaces

	CH	CC	CH ₂	CH ₂	MC ₂	Surface	Surface	ref.
	str	str	scis	wag	str	condition	bonding	
PdC (110)	3000	1546	1226	924	339	<1L, 110 K	π	[29]
Ni (111)	2950	1200	1430	1100	450	<1L, 150 K	di-o	[30]
Ni (110)	2970		1435	1145	420	3L, 80 K	di-o	[31]
Fe (110)	2960	1250	1410	1105	480	6L, 120 K	di-o	[32]
Pt (111)	2940	1230	1420	990	470	2L, 140 K	di-o	[33]
$[Pt(C_2H_4)_3] a'_1$	3004	1617	1338	1226	398			
$[Pt(C_2H_4)_3] e'$	3001	1501	1424	1219	332			a
$[Pd(C_2H_4)_3] e'$	3000	1525	1427	1262	305			[13]
$[\operatorname{Ni}(\operatorname{C_2H_4})_3] e'$	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 cm⁻¹) are in the region commonly associated with such modes in alkylmetals.

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