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Bonding Properties of *trans*-$PtCl_2(C_2H_4)L$. (L = Cl^-, nitrogen- or oxygen-bonded ligands)

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Vibrational (infrared and Raman) and nuclear magnetic resonance (^1H and ^{13}C) spectra of the complexes tr-$PtCl_2(C_2H_4)L$ are discussed in terms of the trans influence of L on the ethylene group. The $\nu(C=C)$ and $\nu_s(Pt–C_2)$ frequencies, the ^{13}C chemical shift and the coupling constant $^1J(^{195}Pt–^{13}C)$ of ethylene all show a small dependence on L. A lowering of the C–C bond order in ethylene as indicated by a decrease of $\nu(C=C)$ is linearly connected with a higher upfield shift of the ^{13}C carbon resonance of this ligand. The ^{35}Cl NQR spectra of these complexes do not show any cis effect of the ligands L.

Introduction

Recently we investigated the complexes *tr*-$PtCl_2(C_2H_4)$(4R-pyridine) with R varying from electron releasing (NH_2) to electron withdrawing (CN)[1,2,3].

The vibrational spectra of these complexes showed hardly any influence of R on the ethylene vibrations. Only ν(Pt–N) appeared to depend on R.

The ^{13}C NMR spectra showed a linear dependence, albeit small, of the chemical shift of the coordinated ethylene on the Hammett σ_p parameter of the 4R-pyridine group[3].

In order to study larger effects on the ethylene group the 4R-pyridine ligand has been replaced by a series of other ligands, which coordinate to the platinum by a nitrogen or oxygen donor atom.

We have also compared the spectroscopic results for these complexes with those for Zeise's salt ($KPtCl_3(C_2H_4)\cdot H_2O$)[4]. Some of these complexes have been studied before by Fritz and Sellmann[5,6], by infrared and ^1H NMR spectroscopy.

Experimental

Most of the compounds were prepared from Zeise's salt ($KPtCl_3(C_2H_4)\cdot H_2O$), by mixing one equivalent Zeise's salt with one equivalent ligand in an ethanolic solution. The compounds were recrystallised from CH_2Cl_2 or acetone. The complexes with L = urea or dimethylformamide (DMF) were prepared from Zeise's dimer ($(PtCl_2(C_2H_4))_2$ in a CH_2Cl_2 solution.

The latter two complexes are less stable than the other ones. The analytical data are listed in Table I.

Infrared spectra were recorded on Beckman IR 11 and IR 12 spectrophotometers. IR spectra were taken for the solid compounds between 100 and 4000 cm^{-1}.

Raman spectra were obtained with a Coderg PH 1 spectrophotometer with dc detection. The 6471 Å line of a CRL 52 Kr^+ laser was used as the exciting line.

Raman spectra of *tr*-$PtCl_2(C_2H_4)$(DMF) and *tr*-$PtCl_2(C_2H_4)(CH_3CN)$ had to be measured with the spinning cell as described by Kiefer[7], because of decomposition by the laser beam.

Raman spectra were run from solids and CH_2Cl_2 solutions (dp measurements) between 100 and 2000 cm^{-1}.

^1H NMR spectra were obtained in deuterated acetone with a Varian HA-100 NMR spectrometer.

^{13}C NMR spectra were recorded in deuterated acetone at 20 MHz on a Varian CFT-20 spectrometer with full proton decoupling.

TABLE I. Analyses for *tr*-$PtCl_2(C_2H_4)L$.

L	%C		%H	
	calc.	exp.	calc.	exp.
$4CH_3$-Py-NO	23.82	23.94	2.73	2.76
DMF	16.35	16.19	3.00	3.05
Urea	10.17	10.34	2.26	2.10
$NH(Me)_2$	14.16	13.37	3.24	3.41
Cl^-	6.21	6.45	1.55	1.42
CH_3CN	14.33	14.68	2.09	2.10
NH_3	7.72	7.69	2.36	2.39
Collidine	28.92	29.03	3.61	3.65
Pyridine	22.52	22.32	2.43	2.36
Aniline	24.93	25.18	2.85	2.90
4CN-pyridine	24.12	24.39	2.02	1.95

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TABLE II. Infrared and Raman Frequencies of the Complexes *trans*-$PtCl_2(C_2H_4)(L)$[a].

L =	4CH$_3$-Py-NO		DMF[b]			Urea			NH(Me)2			Cl$^-$			CH$_3$CN		
IR	R		IR	R		IR	R		IR	R		IR	R		IR	R	
			98w														
130s			129s			119s			121s						126s		
152vw						160sh			151m			157sh			163s	150s	
178m			170s			176sh			186sh			180s	182m		191sh		
						185s											
									192s								
219m			205sh												200s	200m	
229sh			218s			215m			214m	213w	(212)		217vs				
257w															243m		
296m						299m	297sh	(305)	302s	300sh		307s	306m	(302)			
$\underline{323\text{sh}}$																	
	334sh	(336P)															
343vs	342s		341vs		(340)	335s	340s	(338P)	338vs	335vs	(334P)	342vs	332sh		345vs	337sh	
						365sh	406m	(408P)		340vs	(339P)		338vs			344vs	(342P)
	410vw	(404P)															
425m	442s	(428P)	397m		(406)	401m			402m	402s	(407P)	401m	402s	(402)	396m	394s	(394P)
$\underline{436\text{m}}$																	
$\underline{466\text{m}}$																	
503s	511m	(510)	484m	1240	(1238)	490w	488w	(490)	490m	491m		490m	492m		482m	479m	
$\underline{1224\text{m}}$	$\underline{1224\text{sh}}$	($\underline{1224\text{P}}$)				1233w	1238s	(1235P)	1230w	1236sh		1255vw	1255s	(1246)	1253w	1250s	(1250P)
	1232	(1232P)				1242w			1244w	1240m	(1238P)				1263sh		
		(1508)						(1517)		1523vw			1524w		1522w	1522w	
													1528w				

[a] The solution data are in parenthesis. The underlined bands are probably ligand bands. vs = very strong, s = strong, m = medium, w = weak, vw = very weak, p = polarized.
[b] This complex did not give good spectra.

^{13}C chemical shifts were measured relative to the internal solvent resonance and are given in ppm downfield from TMS using the following conversion:

$$\delta_{TMS} = \delta_{CD_3COCD_3} - 29.9 \text{ ppm}$$

CD_3COCD_3 was used as solvent because the solubility of most complexes in CH_2Cl_2 and $CDCl_3$ was small Some compounds show an exchange of ethylene with the solvent, so lower temperatures (–20° C) were necessary in order to observe platinum coupling with the ethylene group.

NQR spectra were obtained with a Wilks NQR 1A spectrometer. Most compounds had to be recrystallised several times, before NQR signals could be observed.

Results

In Table II the IR and Raman data are collected for the region of the skeletal vibrations of the complexes and for $\nu(C=C)$ and $\delta(CH)$. A typical Raman spectrum is shown in Figure 1. The assignments of the metal ligand vibrations and of $\nu(C=C)$ and $\delta(CH)$ are given in Table III. This assignment is based on a comparison with the spectra of the free ligands on the one hand and with the spectra of $KPtCl_3(C_2H_4) \cdot H_2O$[4] and *trans*-$PtCl_2(C_2H_4)$(4R-pyridine)[1] on the other.

Some uncertainty exists about the type of bonding between platinum and the urea, acetonitrile and DMF ligands because these ligands possess more than one coordination site.

In the complex *tr*-$PtCl_2(\text{urea})_2$[8] the urea ligand has been considered to be bound via the nitrogen atom because of the presence of a carbonyl vibration at 1725 cm^{-1} and four different N–H stretching vibrations between 3000 and 3400 cm^{-1}. In our urea complex the carbonyl vibration is observed at 1664 cm^{-1} together with four NH stretching vibrations: two more intense at 3465 and 3369 cm^{-1} and two weaker bands at 3270 and 3210 cm^{-1}. In accordance with previous results for complexes of urea[8], the shift of $\nu(C=O)$ to lower frequency (in free urea $\nu(C=O)$ is located at 1679 cm^{-1}) suggests a coordination via an oxygen atom.

For coordinated acetonitrile a shift to higher frequency for $\nu(C\equiv N)$ has been found on coordination via the nitrogen lone pair[9,10]. The same coordination of acetonitrile is assumed in *tr*-$PtCl_2(C_2H_4)(CH_3CN)$ in which compound $\nu(C\equiv N)$ is shifted 82 cm^{-1} to higher frequency. Furthermore, the ^{13}C NMR spectrum shows a shift for the cyano carbon atom which is much smaller than the shift for this atom would be when acetonitrile is coordinated via the triple bond.

Finally one has to consider the coordination of DMF in *trans*-$PtCl_2(C_2H_4)$(DMF). The IR spectrum of this compound shows a lowering of $\nu(C=O)$ of 19 cm^{-1} with respect to free DMF just as for the corresponding urea complex. Therefore, a coordination of DMF via oxygen is assumed in agreement with the results of Conti *et al.*[11] for *trans*-$PtCl_2$(1-pentene)(DMF). Fur-

NH_3			Collidine			Pyridine			Aniline			4CN-pyridine		
IR	R		IR	R		IR	R		IR	R		IR	R	
						131sh						132sh		
						135s			123s			137s		
			143m											
166m	155s		161s			176m	153m		159sh	150s		167vs		
185s									166s			195m		
	207w		204s	200s	(204)	201s	207s	(204)	206s			201s		
225m				215sh					216sh			205s	206vs	(205)
													221vw	
						238vs	237w					254m		
			329s	328sh										
	330sh								330sh	333s	(337P)		331sh	
332sh	336vs	(338P)	353vs	336sh	(338P)	343vs	332sh	(340P)	338s	338sh	(347P)		337vs	(340P)
338vs	348m			340vs			339vs		346s	351s		352vs	351m	
378s	381m	(386P)	376s	392vs	(386P)	377w	377s	(387P)	382m	388m	(385P)	381m	381s	(385P)
	392m						393w							
						446w	418vw		433m	438m	(430P)	397w	398w	
475s	475sh	(490)	489m	486s	(482)	470w	472m	(483)	474w	478w		475w	475m	(482)
	483vs													
1255sh,s	1252m	(1255P)	1253m	1254s	(1256P)	1260n	1261s	(1256P)	1253sh	1260s	(1257P)	1260vw	1260s	(1256P)
1267vs	1258s								1261m					
1521vw	1522m		1519w	1523w	(1522P)	1524vw	1528w	(1524P)	1522w	1526w	(1525P)		1522m	(1523P)

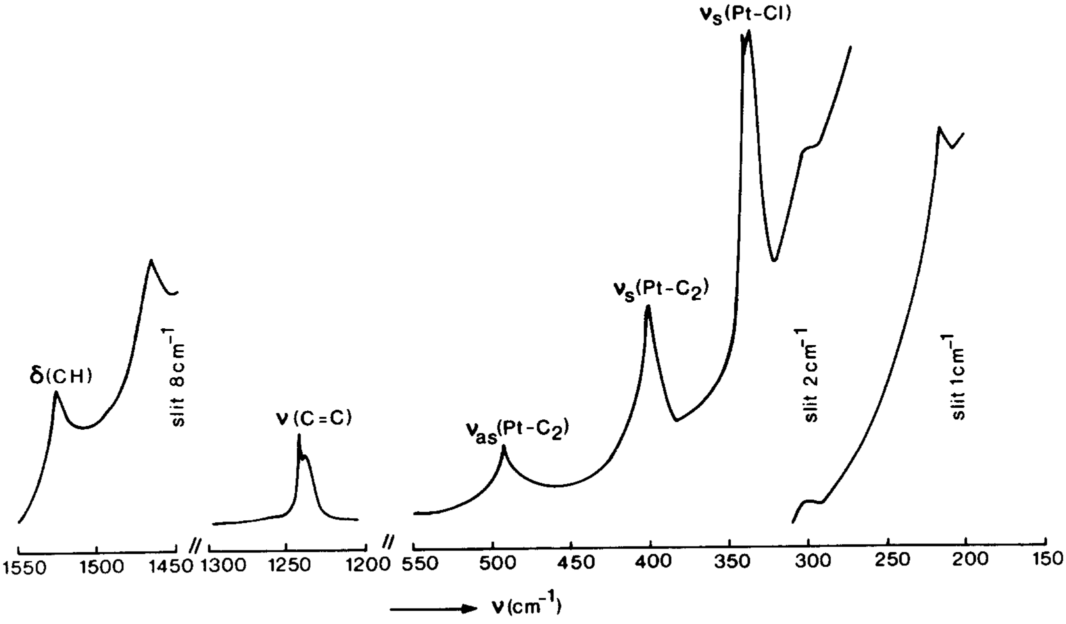

Figure 1. Raman spectrum of *tr*-PtCl$_2$(C$_2$H$_4$)(NHMe$_2$) for the solid compound.

thermore, coordination via nitrogen might experience much steric hindrance due to the two DMF methyl groups.

The *trans* influence of the ligands L will mainly affect the ν(C=C) and the ν(Pt–C$_2$) frequencies and the NMR results of the ethylene group (Table III). The ν(C=C) frequency which is observed in the Raman spectra as a strong, polarized band at about 1240 cm^{-1} increases from O→Cl→N-bonded ligands in agreement with a corresponding decrease in electronegativity of these coordinated atoms. The platinum bond with ethylene should be weaker in this order. In

TABLE III. Assignment of Bands to the Vibrations that are Most Sensitive to Metal–Ligand Interactions (in approximate description) and the NMR Data of the Ethylene Group.

L Assignment (in cm^{-1})	4CH$_3$-Py-NO	DMF	Urea	NH(Me)$_2$	Cl$^-$	CH$_3$CN	NH$_3$	Collidine	Pyridine	Aniline	4CN-Py
ν(Pt–L)	296^a?		299^a?	302^a	307^a	243^a	475^a	329^a	238^a	433^a 346^a	254^a
ν_s(Pt–Cl)	336^p	340	338^p	334^p 339^p	338^p	342^p	338^p	338^p	340^p	337^p	340^p
ν_{as}(Pt–Cl)	343^p	341^a	335^a	338^a	342^a	345^a	338^a	353^a	343^a	338^a	352^a
ν_s(Pt–C$_2$)	428^p	406	408^p	407^p	402^p	394^p	386^p	386^p	387^p	385^p	385^p
ν_{as}(Pt–C$_2$)	503^a	484^a	490^a	490^a	490^a	482^a	475^a	489^a	470^a	474^a	475^a
ν(C=C)	1232^p	1238	1235^p	1238^p	1246^p	1250^p	1255^p	1256^p	1256^p	1257^p	1256^p
δ(CH)	1508		1517	1523^a	1524	1522	1522	1522^p	1524^p	1525^p	1523^p
δ^{13}C(C$_2$H$_4$)(ppm)	60.0	64.0	67.1	67.7	67.2	70.7	73.9	74.9	75.5	75.6	76.0
^{1}J(^{195}Pt–^{13}C)(Hz)	214	216	195	195	194	199	167	167	167	163	170
δ^1H(C$_2$H$_4$)(ppm)	4.14	4.38	4.26	4.31	4.26	4.60	4.51	4.75	4.84	4.53	4.90
^{2}J(^{195}Pt–^{1}H)(Hz)	68	71	64	65	64	70	60	62	61	62	63

^{a} These data are IR-values. p = polarised.

fact, a decrease of ν_s(Pt–C$_2$) in this order is observed (Table IV). Thus, the stronger the platinum–ligand L bond, the weaker the platinum–ethylene one and the higher the C–C bond order of ethylene.

The only anomaly is found for the complex *tr*-PtCl$_2$(C$_2$H$_4$)(NHMe$_2$). The ligand NHMe$_2$ is more basic than NH$_3$ due to its methyl groups. Thus, we expect a weaker Pt–C$_2$H$_4$ bond and a higher ν(C=C) frequency in comparison with the NH$_3$ complex. However, the opposite is found. This may be caused by the greater steric hindrance in the NHMe$_2$ complex due to the two methyl groups, giving a weaker Pt–N bond than for the corresponding ammonium complex.

The same argument has been used by Weil *et al.* to explain the ^{1}H NMR results in *tr*-PtCl$_2$(C$_2$H$_4$)(NH$_{3-n}$X$_n$) complexes[12].

A comparison of the Pt–L vibrations in the complexes is prevented by the different masses of the ligands. Furthermore, an assignment of these vibrations will be tentative because of possible interactions with other skeletal modes. However, coupling with ν(Pt–Cl) has to be weak because the ν(Pt–Cl) frequencies do not vary much in these complexes (see Table III). A tentative assignment is given based on earlier data for some complexes and by comparison of the spectra with each other and with the spectra of the free ligands (Table III).

In the complexes *tr*-PtCl$_2$(C$_2$H$_4$)(pyridine) and *tr*-PtCl$_2$(C$_2$H$_4$)(4CN-pyridine) ν(Pt–N) appeared to be located at 238 and 254 cm^{-1} respectively[1]. The much higher frequency of this vibration in the corresponding *tr*-PtCl$_2$(C$_2$H$_4$)(collidine) complex (ν(Pt–N) = 326 cm^{-1}) is in accordance with the trend discussed in ref. 1.

Fritz and Sellmann have already assigned the Pt–N frequencies in *tr*-PtCl$_2$(C$_2$H$_4$)(NH$_3$) and *tr*-PtCl$_2$(C$_2$H$_4$)(NHMe$_2$)[5].

However, we do not agree with the assignment of a band at 499 cm^{-1} to ν(Pt–N) in the Pt–NHMe$_2$ complex because this band is present in all C$_2$H$_4$ complexes and assigned to ν_{as}(Pt–C$_2$)[1]. A rough calculation of ν(Pt–N) based on the reduced masses of NH$_3$ and NHMe$_2$ predicts ν(Pt–N) at about 305 cm^{-1}. Our IR spectrum shows a strong band at about 302 cm^{-1} which appears as a shoulder in the Raman spectrum and which is not observed in *tr*-PtCl$_2$(C$_2$H$_4$)(NH$_3$) and *tr*-PtCl$_2$(C$_2$H$_4$)(aniline). This band has been assigned to ν(Pt–N). This assignment also underlines the suggestion (see before) that in the complex *tr*-PtCl$_2$(C$_2$H$_4$)(NHMe$_2$) steric hindrance is more important than the basicity of the NHMe$_2$ group in the Pt–N bond. In the spectra of *tr*-PtCl$_2$(C$_2$H$_4$)(CH$_3$CN) an extra band is observed at 243 cm^{-1} which is assigned to ν(Pt–N). In *tr*-PtCl$_2$(C$_2$H$_4$)(aniline) strong infrared bands are observed at 433 and 346 cm^{-1}, both polarized in Raman, which are not found in the free ligand spectra. One of these may be the ν(Pt–N) vibration in agreement with refs. 13 and 14.

TABLE IV. Correlations between Different Sets of Ethylene Data. The ^{35}Cl NQR Frequency and $\bar{\nu}$(Pt–Cl).

Ligand	$\delta^{13}C(C_2H_4)$ (ppm)	ν(C=C) (cm^{-1})	ν_s(Pt–C$_2$) (cm^{-1})	$^1J(^{195}Pt-^{13}C)_{C_2H_4}$ (Hz)	ν^{35}Cl (MHz)	ϱ_x	$\bar{\nu}$(Pt–Cl) (cm^{-1})
4CH$_3$-Py-NO	60.0	1232	428	214	20.596 21.290	.619	340
DMF	64.0	1238	406	216			340
Urea	67.1	1235	408	195			337
NH(Me)$_2$	67.7	1238	407	195	20.810	.621	339
Cl$^-$	67.2	1246	402	194	20.474	.627	340
CH$_3$CN	70.7	1250	394	199	21.332	.611	344
NH$_3$	73.9	1255	386	167			338
Collidine	74.9	1256	386	167	20.518 20.886	.622	345
Pyridine	75.5	1256	387	167	20.718 21.446	.616	342
Aniline	75.6	1257	385	163			338
4CN-pyridine	76.0	1256	385	170	20.387	.628	346

The assignment of the Pt–L vibration is more difficult for the complexes in which a ligand is bonded to platinum via an oxygen donor atom.

Frequencies of the metal oxygen vibrations in complexes of the 4R-pyridine N-oxides are given in refs. 15 and 16 with values between 300 and 340 cm^{-1}. We disagree with the assignment of Orchin and Schmidt[15] for ν(Pt–O) in *tr*-$PtCl_2(C_2H_4)$(4CH$_3$-pyridine-N-oxide) at 323 cm^{-1}, since the free ligand also shows a band at about 325 cm^{-1}. In the 4CH$_3$-pyridine N-oxide and urea complexes infrared bands are visible at about 300 cm^{-1}, but the origin of these bands is uncertain.

The decrease in the frequency of the M–L vibration for L = NH$_3$, aniline, pyridine N-oxide or pyridine is also observed in complexes of Cu, Zn and Co with these ligands[14, 17]. This underlines our assignment.

Discussion

In Table IV the complexes are arranged in order of increasing *trans* influence of L which is manifested by changes of the spectroscopic data for the platinum–ethylene bond.

Variation of L from 4CH$_3$-pyridine N-oxide to 4CN-pyridine gives a lowering of ν_s(Pt–C$_2$) from 428 to 385 cm^{-1}. This weakening of the Pt–ethylene bond is accompanied by a strengthening of the C=C bond of ethylene because ν(C=C) increases from 1232 to 1258 cm^{-1}. At the same time the ^{13}C chemical shift of the ethylene group varies with L in such a way that the weakening of the Pt–ethylene bond and the corresponding strengthening of the C=C bond are accompanied by a downfield shift of the ethylene carbon atoms. This relation between the ^{13}C chemical shift and the C=C bond order of ethylene will hereafter be discussed in some more detail. A typical example of a carbon-13 spectrum is hown in Figure 2.

Table IV also contains the results for the coupling constants $^1J(^{195}Pt-^{13}C)_{C_2H_4}$. These coupling constants are mainly determined by the Fermi contact mechanism which is strongly dependent on the metal *s* character of the bond[18, 19]. In olefin complexes this must occur through the σ-bond between ligand and metal in order to involve the metal *s* orbital[20]. Thus, the value of $^1J(^{195}Pt-^{13}C)_{C_2H_4}$ should be a measure for the σ-bond strength of the platinum ligand L bond (Table IV).

Now, according to the Chatt–Dewar–Duncanson model[21, 22] the Pt–ethylene bond consists of σ- and π-contributions which both can be affected by the *trans* influence of ligand L. Changes of both σ- and π-bond strengths are reflected in the ^{13}C chemical shift of ethylene, but the $^1J(^{195}Pt-^{13}C)_{C_2H_4}$ coupling constants will only be sensitive to variations of the σ-bond strengths. Therefore discrepancies between ^{13}C chemical shifts and $^1J(^{195}Pt-^{13}C)_{C_2H_4}$ coupling constants in the series are especially expected when the π-bonding between Pt and ethylene is strongly influenced by L. As seen from Table IV, this is the case for the complexes with L = DMF, CH$_3$CN and 4CN-pyridine which show relatively high coupling constants with respect to the ^{13}C chemical shifts and ν_s(Pt–C$_2$). Apparently, these ligands L posses a stronger *π-trans* influence than the other ligands. Furthermore, it should be noted that the ^{13}C spectra of the complexes with L = 4CH$_3$-pyridine N-oxide, DMF and acetonitrile only show ^{195}Pt–^{13}C–Pt–^{13}C coupling for the ethylene resonances at lower temperature (about –20° C) due to exchange between coordinated ethylene and acetone. At the same time, these labile complexes show the largest coupling constants in agreement with the results of Orchin and Schmidt[23].

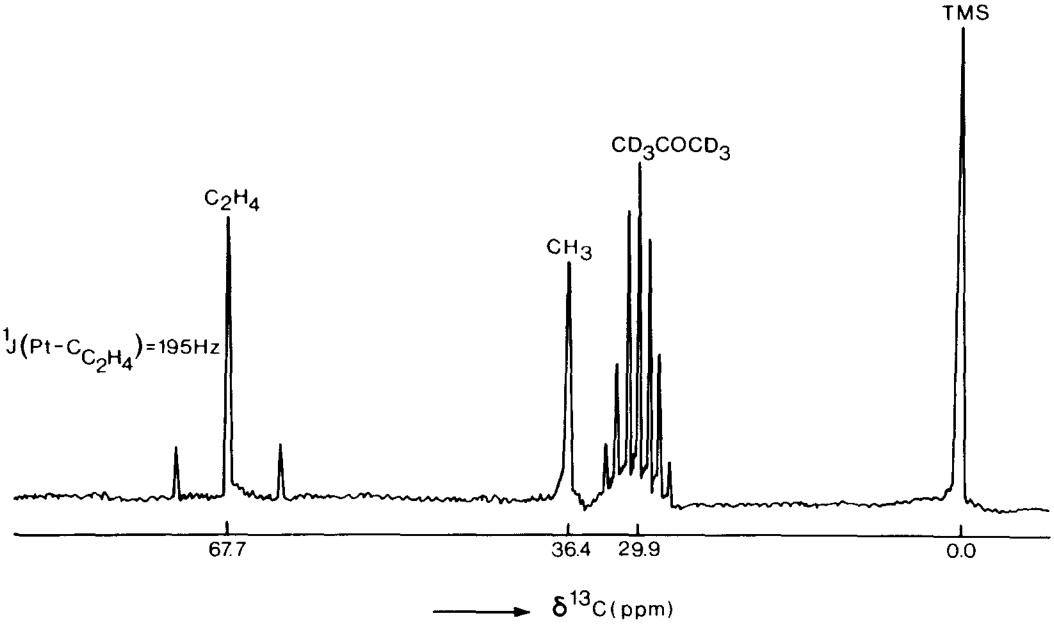

Figure 2. The ^1H-decoupled Fourier transform pulsed ^{13}C spectrum of *tr*-$PtCl_2(C_2H_4)(NHMe_2)$ in CD_3COCD_3 solution (13.000 scans, PW = 10 μsec, PD = 0 sec).

In our earlier publication[3], the causes of the high upfield shift of ethylene were studied.

The values of ^{13}C NMR shifts are determined by four terms[24]:

$$\sigma = \sigma_d + \sigma_p + \sigma_d' + \sigma_p' \qquad (1)$$

where σ_d represents the local diamagnetic contribution, σ_p the local paramagnetic term and σ' the contribution of neighbouring atoms, consisting of a diamagnetic (σ_d') and paramagnetic (σ_p') term.

We have demonstrated that σ_p' is not an important contribution to the ethylene shifts and that the upfield shift of ethylene on coordination will mainly be determined by variations in σ_p and σ_d' [25,26].

In this series of complexes the value of the σ_d' term will hardly change and the variations in shielding can mainly be ascribed to σ_p:

$$\sigma_p = -\text{const}\,\frac{\langle r^{-3}\rangle_{2p}}{\Delta E}\,(Q_{AA} + \sum_{A \neq B} Q_{AB}) \qquad (2)$$

The Q_{AB} term is connected with the multiple character of the bond between the atoms A and B. When ethylene is coordinated to platinum, electron density will be displaced from the C–C bonding orbital and into the C–C anti-bonding orbital by the platinum–ethylene σ and π bonds. The result is a decrease of bond order of ethylene which may be roughly estimated according to the method of Powell[27]. Powell correlated the summed percentage lowering of the coupled ν(C=C) and δ (CH) frequencies upon complex formation (band I and band II, see Table V) with the decrease in double bond character of the olefin.

In Table V these percentage lowerings and the ^{13}C shifts of ethylene are compiled. An almost linear correlation is observed in the plot of the summed percentage lowering *versus* the ^{13}C shifts of ethylene (Figure 3). This means that the ^{13}C shift is linearly dependent on the C=C bond order of ethylene according to equation 2.

Finally, we hoped to find a *cis* effect on the chloride atoms by recording the ^{35}Cl NQR spectra which, however, only gave very small, irregular shifts. Most complexes show two signals, which may be ascribed to crystal effects. Also the constancy of the ν(Pt–Cl) frequencies underlines the absence of a *cis*-effect (Table IV).

Conclusion

The following conclusions can be drawn about the *trans* influence of L in the complexes *trans*-$PtCl_2(C_2H_4)L$:

In agreement with the increase in basicity for the ligands L the order of *trans* influence is $O < Cl^- < N$. This is reflected in a decrease of the $\nu_s(Pt–C_2)$ frequencies and an increase of ν(C=C).

The ^{13}C shift of ethylene varies linearly with the bond character of ethylene and correlates well with the total strength of the Pt–ethylene bond.

TABLE V. Percentage Lowering of Band I and Band II[a] in Comparison with the NMR Results for Ethylene.

Ligand	Band I (cm^{-1})	Percentage Lowering	Band II (cm^{-1})	Percentage Lowering	Summed Percentage Lowering	$\delta^{13}C$ (C_2H_4)	$\delta^{1}H$ (C_2H_4)
Free Ethylene	1623		1343			122.8	5.41
$4CH_3$-Py-NO	1508	7.1	1232	8.3	15.4	60.0	4.14
DMF			1238	7.8		64.0	4.38
Urea	1517	6.5	1235	8.0	14.5	67.1	4.26
$NH(Me)_2$	1523	6.2	1238	7.8	14.0	67.7	4.31
Cl^-	1524	6.1	1246	7.2	13.3	67.2	4.26
CH_3CN	1522	6.2	1250	6.9	13.1	70.7	4.60
NH_3	1522	6.2	1255	6.6	12.8	73.9	4.51
Collidine	1522	6.2	1256	6.5	12.7	74.9	4.75
Pyridine	1524	6.1	1256	6.5	12.6	75.5	4.82
Aniline	1525	6.0	1257	6.4	12.4	75.6	4.53
4CN-pyridine	1523	6.2	1256	6.5	12.7	76.0	4.96

[a] Band I and band II are used in the same notation as Powell[27].

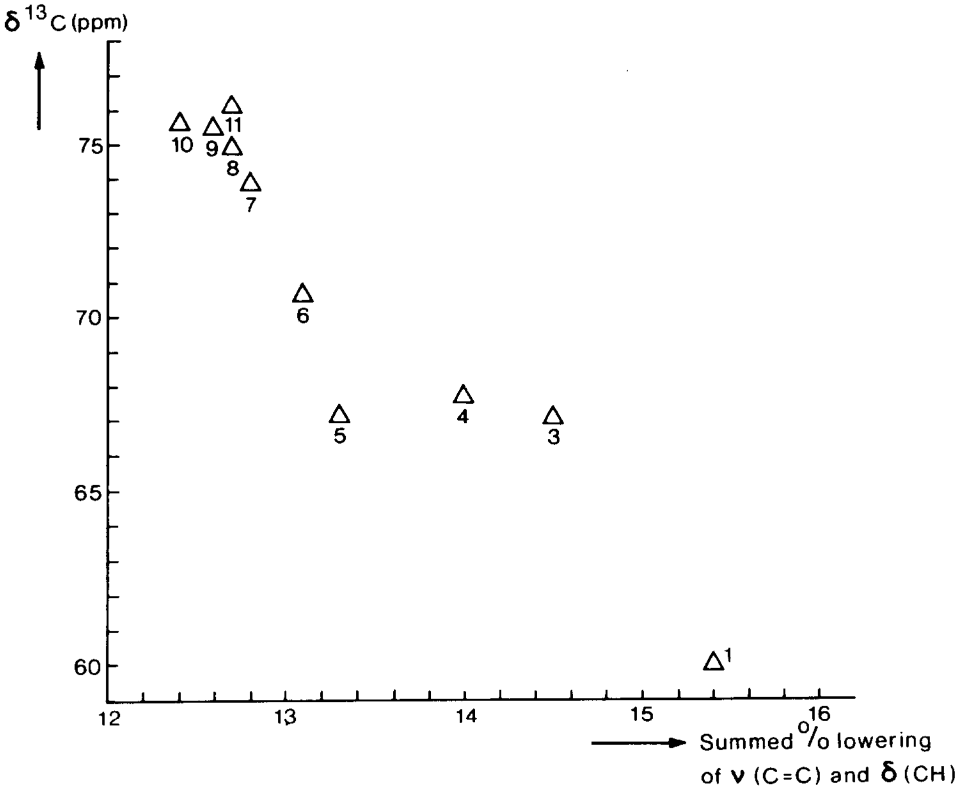

Figure 3. Plot of ^{13}C chemical shift of ethylene *versus* the summed percentage lowering of the $\nu(C{=}C)$ and $\delta(CH)$ frequencies, according to Powell[27]. For numbering scheme see Table I.

On the other hand, the $^1J(^{195}Pt-^{13}C)_{C_2H_4}$ coupling constant is only a measure for the strength of the σ-bond between platinum and ethylene.

The NQR measurements of ^{35}Cl and also the $\nu(Pt-Cl)$ frequencies do not show any *cis* effect.

In conclusion it can be said that all variations, agreements and differences between the various spectroscopic results can be explained in terms of the Chatt–Dewar–Duncanson[21,22] bonding scheme for these complexes.

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