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Bonding Properties of *trans*-$PtCl_2$(olefin)(L). Part II**. Spectroscopic Properties

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A series of complexes, trans-*$PtCl_2$(olefin)(L) (L = a nitrogen or oxygen bonded ligand or Cl^-, and olefin-*cis*-2-butene or a monosubstituted olefin), has been studied by infrared, Raman, UV and ^{13}C NMR spectroscopy.*

The trans-*influence of L on the olefinic group is in the order of O < Cl^- < N. This is reflected in a decrease of $\nu(Pt–C_2)$, in the summed percentage lowering of the coupled $\nu(C=C)$, $\delta(CH)$ and $\delta(CH_2)$ vibrations and in the increasing downfield δ $^{13}C_{mean}$ shifts of the olefinic carbon atoms.*

The shift in δ $^{13}C_{mean}$ after complexation is a measure of the variation of charge distribution between platinum and the olefin with respect to the ethylene compound.

The lowest energy band in the electronic absorption spectra shifts to lower energy on going from collidine to 4CN-pyridine and on the introduction of an electron withdrawing substituent in the olefin ligand.

$^1J(^{195}Pt–^{13}C)$, which is an indication of σ-bond strength between platinum and the olefinic carbon atoms, decreases in the order of O < Cl^- < N.

Introduction

The spectroscopic (vibrational, electronic and ^{13}C NMR) properties of the complexes *trans*-$PtCl_2(C_2H_4)$(L) with L = nitrogen or oxygen bonded ligand or Cl^- have been studied by us in some detail [1–3] in order to obtain information about the *trans* influence of L on the platinum–ethylene bond.

The *trans* influence of L was found to increase in the order O < Cl^- < N from various spectroscopic results such as a decrease in $\bar{\nu}(Pt–C_2)$ frequency and an increasing downfield shift of the carbon-13 shift of the ethylene carbon atoms. This same trend is also observed by Iwayanagy and Y. Saito [4].

Further confirmation was needed, however, and the work has been extended, therefore, to a whole series of complexes *trans*-$PtCl_2$(olefin)(L), in which both the ligand L and the olefin are varied. L is $4CH_3$-pyridine N-oxide, Cl^-, CH_3CN or a substituted pyridine ligand, while the olefins are styrene (ST), *cis*-2-butene (BU), propylene (PR), vinyl acetate (VA), ethylene (ET) and methyl acrylate (MA). Various compounds of this series have been prepared for the first time such as the complexes of methyl acrylate.

Experimental

Preparation

Most of the complexes *trans*-$PtCl_2$(olefin)(substituted-pyridine) were prepared by methods described in ref. 5. In the case of *trans*-$PtCl_2$(olefin)(CH_3CN) and *trans*-$PtCl_2$(olefin)($4CH_3$-pyridine N-oxide), the BU, PR and ET complexes were prepared by mixing one equivalent of Zeise's salt analogue with one equivalent of CH_3CN or $4CH_3$-pyridine N-oxide in acetone solution. The compounds were recrystallized from a CH_2Cl_2–hexane mixture.

The ST, VA and MA complexes were synthesized from the corresponding *trans*-$PtCl_2(C_2H_4)$(L) complexes [3]. Acetonitrile often gives both *cis* and *trans* isomers.

The analytical data are listed in Table I.

The MA complexes did not give good analytical data. Free methyl acrylate or the recrystallization solvent was generally observed in the infrared and NMR spectra of these complexes.

The compound *trans*-$PtCl_2$(VA)(CH_3CN) could also not easily be purified. The complex formed was almost insoluble. Mostly *cis* compound has been formed, presumably.

Although attempts were made to prepare the complexes with vinylchloride and acrolein ligands, no pure compounds could be isolated.

Spectroscopic Measurements

Infrared spectra were recorded on Beckman IR-12 and IR-4250 spectrophotometers for the solid compounds and, in the case of the pyridine complexes, also in CH_2Cl_2 solution.

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**For part I see ref. 5.

TABLE I. Analytical Data for *trans*-$PtCl_2(X)(L)$.

L	% C calc.	exp.	% H calc.	exp.	% C calc.	exp.	%H calc.	exp.	% C calc.	exp.	% H calc.	exp.
	X = ST				X = BU				X = VA			
$4CH_3$-Py-NO	35.07[c]	34.50	3.13	3.19	27.84	27.49	3.48	3.36	26.03[c]	25.56	2.82	2.88
Cl^-[a]	21.60[c]	21.65	1.80	1.90	12.12[c]	12.00	2.02	1.99	11.25	11.20	1.41	1.50
CH_3CN	29.20	29.20	2.68	3.06	19.83	19.75	3.03	3.00	18.32	19.47	2.29	2.96
collidine	39.10	39.30	3.87	4.01	32.51	32.52	4.30	4.30	30.44	30.52	3.59	3.53
$4CH_3$-pyridine	36.29	36.11	3.24	3.30	28.92	28.83	3.61	3.55	26.97	27.05	2.92	2.89
pyridine	34.74[c]	34.63	2.90	2.85	26.93[c]	26.90	3.24	3.20	25.05[c]	25.05	2.55	2.45
4CN-pyridine	35.44	35.08	2.53	2.50	28.17	28.13	2.82	2.81	26.32	26.27	2.19	2.29
	X = PR				X = ET				X = MA			
$4CH_3$-Py-NO	25.90[c]	26.18	3.12	3.14	23.82[c]	23.94	2.73	2.76	26.03	28.25	2.82	3.01
Cl^-[a]	9.41[c]	9.66	1.57	1.87	6.21[c]	6.45	1.55	1.42	11.25[b]	–	1.41	–
CH_3CN	17.19	16.79	2.58	2.50	14.33[c]	14.68	2.09	2.10	18.32	18.77	2.29	2.46
collidine	30.77	30.89	3.96	3.93	28.92[c]	29.03	3.61	3.65	30.44	30.12	3.59	3.24
$4CH_3$-pyridine	26.93	27.12	3.24	3.25	24.81[c]	24.80	2.86	2.92	26.97	29.20	2.92	3.19
pyridine	24.81[c]	25.13	2.70	2.84	22.52[c]	22.32	2.43	2.36	25.05[c]	26.44	2.55	2.74
4CN-pyridine	26.21	26.44	2.43	2.43	24.12[c]	24.39	2.02	1.95	–	–	–	–

[a] The data are for dehydrated complexes except for $KPtCl_3(C_2H_4)\cdot H_2O$. [b] No analysis was possible because the compound was very hygroscopic. [c] These compounds have already been reported [1, 3, 6, 7, 10, 30].

Raman spectra were obtained for the solid compounds and CH_2Cl_2 solutions (dp measurements) 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. The analogues of Zeise's salt generally gave bad Raman spectra.

Electronic absorption spectra were obtained with a Cary-14 spectrophotometer. Extinction coefficients were determined in CH_2Cl_2 except for the analogues of Zeise's salt. Their spectra were run in H_2O.

^{13}C NMR spectra were measured in $CDCl_3$ on a Varian CFT-20 (20 MHz) apparatus with full proton decoupling. Proton NMR spectra were only recorded to investigate the purity of the compound and the mode of coordination (upfield shifts for the olefinic protons and platinum coupling by coordination via the double bond).

Results and Discussion

Before discussing the various spectroscopic results some remarks will be made.

The infrared results of the acetonitrile complexes show the presence of both *cis* and *trans* isomers. The Pt–Cl frequencies at about 330 and 358 cm^{-1} are ascribed to the *cis* complex and the band at 345 cm^{-1} to the *trans* compound. The same frequencies have been observed by Spaulding *et al.* [6, 7] for the compound $PtCl_2(C_2H_4)(CH_3CN)$. Apparently acetonitrile and olefin ligands labilize each other if they are in a *trans* position with respect to each other, so that both *cis* and *trans* complexes are found in solution.

The presence of the *cis* configuration was also shown by the platinum coupling with the methyl group of acetonitrile at room temperature [6, 7].

VA and MA ligands both coordinate via the double bond as shown by the large upfield shifts and Pt–carbon couplings of the olefinic carbon atoms in the ^{13}C NMR spectra.

The MA complexes could not be easily prepared and often free methyl acrylate or recrystallization solvent was observed in the spectra. The purest compound is *trans*-$PtCl_2$(MA)(collidine), which is the first known Pt(II) complex with an electron withdrawing substituent on the olefin. Free MA possesses both *cis* and *trans* configurations. In most MA complexes a doubling of peaks in the NMR for the methyl group signal of MA and for the ligand carbon atoms was observed [5]. In *trans*-$PtCl_2$(MA)(collidine), however, MA is only present in one configuration (Fig. 1). The methyl groups in the *ortho* position of the pyridine ring presumably stabilize the compound, a result also found by Mansuy [8, 9] for the complexes *trans*-$PtCl_2(C_2H_4)$(methyl substituted pyridine).

Vibrational Results

In Table II the platinum–nitrogen stretching vibrations are compiled for the complexes *trans*-$PtCl_2$ (olefin)(substituted pyridine). These bands, which are only observed in the infrared, are assigned in the same way as for the ethylene complexes [1]. ν(Pt–N) shows a minimum for R = H in each olefin series. The

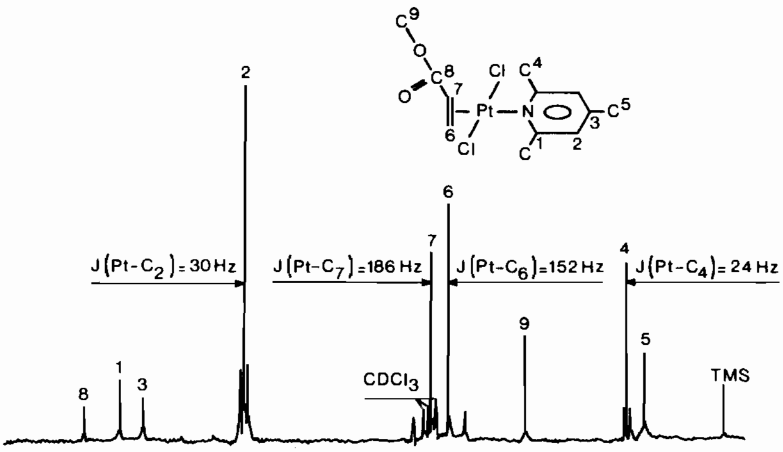

Figure 1. ^{1}H-decoupled carbon-13 spectrum of *trans*-$PtCl_2$(MA)(collidine) in $CDCl_3$ solution (20.000 scans; PW = 15 μsec; PD = 0.2 sec).

TABLE II. Platinum–Nitrogen Stretching Vibrations (cm^{-1})^a.

L olefin	collidine	4CH_3-pyridine	pyridine	4CN-pyridine
ST	324	286	232^b	243
BU	325	298	243^b	247
VA	327	284	233^b	242
PR	325	294	247^b	255
ET	329^b	290^b	240^b	254^b
MA	327	–	–	–

^{a}IR-data from CH_2Cl_2 solutions. ^{b}From references 1 and 5.

strong σ-bond between Pt and collidine or 4CH_3-pyridine and the strong π-bond of Pt with 4CN-pyridine are responsible for this effect.

On the other hand, variation of the olefin has an irregular influence on ν(Pt–N). The same result was found for the platinum–ethylene vibrations when the substituent of the pyridine ring was varied [1].

Table III presents the vibrational data for the other platinum–ligand bonds and for the most important frequencies of the coordinated olefins. Only the data for the *trans*-$PtCl_2$(olefin)(collidine) complexes are given, because all other pyridine complexes show about the same frequencies for these bands.

The results for $\bar{\nu}$(Pt–Cl) show that variation of the olefin or ligand L has hardly any *cis*-influence on the Pt–Cl bond, which is also not expected [10, 11]. Furthermore, coupling between the platinum–chloride vibrations and other skeletal modes must be small.

On the other hand, the Pt–olefin stretching vibrations are dependent on both the *trans* ligand L and the olefin itself. An increase of basicity of L on going from O→Cl^-→N bonded ligand gives a lowering of $\bar{\nu}$(Pt–C_2). The order of *trans*-influence is, therefore, O<Cl^-<N, a result which is obtained for each olefinic compound, in agreement with previous results [3, 4, 12, 13]. Larger $\bar{\nu}$(Pt–C_2) frequencies are found in the complexes of VA and MA. In part I of this series [4] this effect has been ascribed to stronger σ and π bonding properties of VA and the much stronger π bond between Pt and MA. This trend is observed for all compounds discussed here.

Finally, the ν(C=C), $\delta(CH_2)_{scis}$ and $\delta(CH)_{bend}$ will be considered. In the free olefins coupling exists [14] between these modes, which are all Raman active and polarized. Coordination of the olefin will change this coupling. Because this coupling strongly varies with the olefin no relationship can be deduced for complexes with different olefins. Only results for complexes with different L and the same olefin may be compared.

According to Powell [19, 20], the summed percentage lowering of ν(C=C) and $\delta(CH)_{scis}$ is a measure for the decrease of double bond character of the olefin upon coordination. In the case of a monosubstituted olefin, however, not two but three vibrations (ν(C=C), $\delta(CH_2)_{scis}$ and $\delta(CH)_{bend}$) couple, so that the summed percentage lowering of these three frequencies have to be considered. The frequencies for the free olefins are the polarized Raman data from refs. 15–18. In the complexes these bands could be easily assigned because of the rather good Raman spectra obtained for these compounds. Most of these bands are medium to strong, except for the ethylene and *cis*-2-butene complexes. For the ethylene compounds the 1250 cm^{-1} band is much stronger than the 1520 cm^{-1} band while for the *cis*-2-butene complexes the 1520 cm^{-1} band is the stronger (Fig. 2).

Band II of the mono-substituted olefins shifts only about 1% upon coordination, but the frequency shifts of band I and III are larger (Table III).

For all complexes *trans*-$PtCl_2$(olefin)(L) the frequencies of band I and III increase in the order L = oxygen bonded ligand <Cl^- <nitrogen-bonded ligand. The summed percentage lowering of bands I, II and III, also decreases in this order. A higher frequency for the Pt–olefin vibration (O>Cl^->N) is also clearly connected with a lowering of the double bond character of the C–C bond [3, 4].

If we assume, according to Powell [19, 20], that the band with the largest ν(C=C) contribution will show the largest frequency shift, this has then to be band I at about 1520 cm^{-1} in all except the ethylene complexes. The discussion in the literature [19–23] on the correct assignment of the ν(C=C) stretching vibration can now be regarded in the following way. In the ethylene complexes the intense, polarized Raman band at 1250 cm^{-1} will be mainly ν(C=C), while for the substituted olefin complexes the 1520 cm^{-1} band will be largely the C=C stretching vibration, in accordance with the conclusions of Powell *et al.* [19].

For complexes with L = substituted pyridine ligand the variations in $\bar{\nu}$(Pt–C_2) and in the summed percentage lowering are only small (Table IV), also in agreement with our earlier observations [3].

Electronic Absorption Spectra

In a previous paper [1], attention has been paid to the absorption spectra of the complexes *trans*-$PtCl_2(C_2H_4)$(4R-pyridine), which all possess a band at about 32 kK at the low energy side of the $\pi\rightarrow\pi^*$ transition of the pyridine ligand. The position of this band appeared to be strongly dependent upon the substituent R on the pyridine ring. Because of this,

TABLE III. Mean Frequencies[a] of the Pt–Cl and Pt–C_2 Stretching Vibrations and the Frequencies of the Coupled ν(C=C) (I), $\delta(CH_2)_{scis}$ (II) and $\delta(CH)_{bend}$ (III) Vibrations[b] (values in cm^{-1}).

Assignment L[d]		$\bar{\nu}$(Pt–Cl)	$\bar{\nu}$(Pt–C_2)	I (%)[c]		II (%)[c]	III (%)[c]
ST	free [11]			1632		1414	1305
	1	340	452	1517	(7.05)	1398 (1.13)	1249 (4.29)
	2	336	441	1515	(7.17)	1398 (1.13)	1260 (3.45)
	3[e]	359	427	1514	(7.28)	1407 (0.50)	1264 (3.14)
	4	339	424	1526	(6.50)	1403 (0.78)	1267 (2.91)
BU	free [12]			1660			1255
	1	338	456	1507	(9.22)		1226 (2.31)
	2	338	449	1508	(9.16)		1250 (0.40)
	3	343	440	1513 (1505)	(8.86)		–
	4	336	435	1527	(8.01)		1252 (0.24)
VA	free [13]			1647		1386	1295
	1	340	481	1500	(8.93)	1373 (0.94)	1249 (3.55)
	2	337	465	1510	(8.32)	1377 (0.65)	1247 (3.71)
	3	352	456	1503 (1518)	(8.74)	1375 (0.79)	1256 (3.01)
	4	342	453	1517	(7.89)	1377 (0.65)	1262 (2.55)
PR	free [12]			1648		1415	1297
	1	339	458	1504	(8.74)	1392 (1.63)	1252 (3.47)
	2	335	447	1505	(8.68)	1398 (1.20)	1254 (3.32)
	3[e]	357	434	1517	(7.95)	1403 (0.85)	1255 (3.24)
	4	340	431	1519	(7.83)	1400 (1.06)	1261 (2.78)
ET	free [14]			1623		1342	
	1	339	469	1508	(7.09)	1232 (8.20)	
	2	339	446	1524	(6.10)	1246 (7.71)	
	3	343	438	1524	(6.10)	1251 (6.78)	
	4	345	435	1522	(6.22)	1256 (6.41)	
MA	free [13]			1633		1402	1283
	1	342	466	1505	(7.84)	1385 (1.21)	1235 (3.74)
	2	344	459	1500	(8.15)	1379 (1.64)	1235 (3.74)
	3	336	445	1504	(7.90)	1390 (0.86)	1250 (2.57)
	4	343	449	1520 (1506)	(6.92)	1389 (0.93)	1248 (2.73)

[a] $\bar{\nu}$(Pt–C_2) and $\bar{\nu}$(Pt–Cl) are the mean frequencies on the symmetric and antisymmetric vibrations. [b] Bands are indicated as I, II and III according to Powell [15]. [c] Percentage lowering of band I, II and III after coordination in brackets. [d] 1 = $4CH_3$-PyN-oxide; 2 = Cl^-; 3 = CH_3CN; 4 = collidine. [c] Complex in *cis* configuration.

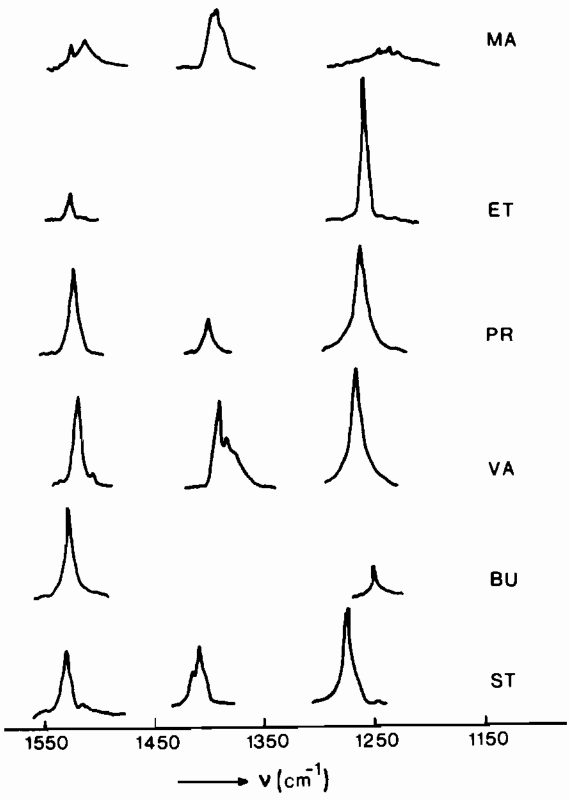

Figure 2. Raman spectra of bands I, II and III of the olefins in solid *trans*-PtCl$_2$(olefin)(collidine).

and in agreement with the results for the corresponding complexes *trans*-PtCl$_2$(4R-Py)$_2$ [27], Ru(NH$_3$)$_5$(4R-Py)$^{2+}$ [24] and W(CO)$_5$(4R-Py) [25, 26], this band has tentatively been assigned by us to a Pt to pyridine charge-transfer transition. Conclusive evidence for this assignment could, however, not be obtained but might be provided by the results for the whole series of complexes *trans*-PtCl$_2$(olefin)(substituted pyridine) which are presented in Table V.

These data show the same strong dependence on the substituent R for all olefin complexes, as found for the ethylene compounds. On the other hand, when the pyridine ligand in the complex is replaced by Cl$^-$ or 4CH$_3$-pyridine N-oxide, a band is found in about the same frequency region which becomes nearly as intense for the 4CH$_3$-pyridine N-oxide complexes as for the substituted pyridine compounds. Thus, an assignment of this band to a ligand field transition is preferred, although the dependence on R is of the same order of magnitude as for the corresponding complexes *trans*-PtCl$_2$(4R-Py)$_2$ [27].

It is, however, surprising that a variation of R so strongly affects both the ligand field splitting of the complex and the Pt–pyridine bond without any further influence on the other platinum–ligand bonds [1] (Table IV).

According to Table V variation of the substituent on the olefin from electron-releasing (BU) to electron-withdrawing (MA) influences the transition energy in much the same way as a corresponding

TABLE IV. $\bar{\nu}$(Pt–C$_2$)^a Frequencies and Summed Percentage Lowerings^b for the Complexes *Trans*-PtCl$_2$(olefin)(L).

Olefin	ST		BU		VA		PR		ET		MA	
L	ν	%	ν	%	ν	%	ν	%	ν	%	ν	%
4CH$_3$-PyN-oxide	452	12.5	456	11.5	481	13.4	458	13.8	469	15.3	466	12.8
Cl$^-$	441	11.7	449	9.6	465	12.7	447	13.2	446	13.8	459	13.5
CH$_3$CN	427	10.9	440	8.9	456	12.5	434	12.0	438	12.9	445	11.3
collidine	424	10.2	435	8.2	453	11.1	431	11.7	435	12.6	449	10.6
4CH$_3$-pyridine	427	10.7	433	7.9	453	11.1	434	11.6	432	12.5	450	11.5
pyridine	428	10.0	432	8.3	455	11.2	427	12.1	429	12.5	446	11.0
4CN-pyridine	426	10.0	432	8.7	453	11.3	428	12.0	430	12.6	–	–

^{a}$\bar{\nu}$(Pt–C$_2$) is the mean of ν_s(Pt–C$_2$) and ν_{as}(Pt–C$_2$) [4]. ^{b}The summed percentage lowering of band I, II and III (see Table III).

TABLE V. Transition Energies (in kK) of the Lowest Electronic Transitions in PtCl$_2$(olefin)(L). The values of ϵ_{max} in CH$_2$CL$_2$ are given in brackets.

Olefin L	BU	PR	VA	ET	ST	MA
collidine	34.1 (840)	34.0 (830)	33.6 (720)	33.4 (870)	31.6 (1780)	31.1 (710)
4CH$_3$-pyridine	33.6 (1030)	33.2 (960)	33.0 (1010)	32.2 (1060)	31.1 (1630)	
pyridine	33.1 (1030)	32.8 (940)	32.6 (1060)	32.0 (920)	31.0 (2000)	
4CN-pyridine	30.7 (1080)	30.4 (790)	30.3 (1320)	31.0 (1470)	29.2 (1900)	
4CH$_3$-PyNO	30.0 (600)	30.2 (700)	29.7 (1500)	30.3 (800)	30.3 (1100)	
Cl$^-$	29.9 (140)	30.2 (150)	29.4	30.3 (300)	–	

TABLE VI. ^{13}C Chemical Shifts[a] (in ppm) for the Olefinic Carbon Atoms. The values of $^1J(Pt–C)$ are given in brackets (in Hz).

Olefin L	ST $\delta\ ^{13}C(C_\alpha)$	$\delta\ ^{13}C(C_\beta)$	BU $\delta\ ^{13}C$	VA $\delta\ ^{13}C(C_\alpha)$	$\delta\ ^{13}C(C_\beta)$	PR $\delta\ ^{13}C(C_\alpha)$	$\delta\ ^{13}C(C_\beta)$	ET $\delta\ ^{13}C$	MA $\delta\ ^{13}C(C_\alpha)$	$\delta\ ^{13}C(C_\beta)$
4CH$_3$-Py-NO	82.3	50.5	77.1 (204)	96.9[c]	41.7	83.4 (202)	59.1 (213)	61.1 (215)	61.3[c]	58.2
Cl$^-$ [b]	85.6[c] (172)	57.4 (196)	81.3[c] (184)	100.4 (216)	50.4 (191)	86.9 (188)	66.4 (190)	67.3 (194)	67.9[c] (212)	62.8 (182)
CH$_3$CN	93.6[d]	62.6	90.6[c] (189)	–	–	94.6[c]	71.6	74.9[c] (198)	75.9[c]	72.4
collidine	97.8 (140)	62.3 (166)	89.9 (153)	110.0 (174)	53.7 (166)	98.2 (156)	71.6 (160)	75.0 (166)	76.5 (187)	71.8 (152)
4CH$_3$-pyridine	97.7 (138)	62.1 (165)	90.6 (150)	111.1 (171)	52.9 (165)	98.9 (151)	71.2 (159)	74.9 (165)	72.7 (185)	71.0
pyridine	98.2 (136)	62.1 (167)	91.0 (150)	111.6 (171)	52.9 (166)	99.5 (152)	71.4 (159)	75.3 (165)	73.1 (183)	71.6 (150)
4CN-pyridine	100.1 (138)	62.1 (174)	92.2 (154)	112.4[c] (172)	52.9 (169)	101.1 (154)	71.6 (165)	75.9 (170)	–	–
free olefin[e]	137.7	112.3	123.3	141.7	96.4	133.1	115.0	122.8	128.7	129.9

[a] ^{13}C chemical shifts are reported relative to TMS, using $\delta_{TMS} = \delta_{CDCl_3} - 77.1$ ppm. [b] Spectra of the salts are obtained in CD_3COCD_3, using $\delta_{TMS} = \delta_{(CD_3)_2CO} - 29.9$ ppm. [c] Spectral data at low temperature (–20 °C or –50 °C). [d] Complex in *cis* configuration. [e] Free ligand chemical shifts from ref. 25.

TABLE VII. Mean ^{13}C Shifts of the Olefinic Carbon Atoms and Δ_{mean}[a,b]. Mean values of $^1J(Pt–C)$ are given in brackets.

Olefin L	ST $\delta\ ^{13}C_{mean}$	Δ_{mean}	BU $\delta\ ^{13}C_{mean}$	Δ_{mean}	VA $\delta\ ^{13}C_{mean}$	Δ_{mean}	PR $\delta\ ^{13}C_{mean}$	Δ_{mean}	ET $\delta\ ^{13}C_{mean}$	Δ_{mean}	MA $\delta\ ^{13}C_{mean}$	Δ_{mean}
4CH$_3$-PyNO	66.4	57.6	77.1 (204)	46.2	69.3	49.7	71.3 (207)	52.7	61.1 (215)	61.7	59.8	69.5
Cl$^-$ [c]	71.5 (181)	52.5	81.3 (184)	42.0	75.4 (203)	43.6	76.7 (189)	47.3	67.3 (194)	55.5	65.4 (197)	63.9
CH$_3$CN	78.1[d]	45.9	90.6 (189)	32.7	–	–	83.1	40.9	74.9 (198)	47.9	74.2	55.1
collidine	80.1 (153)	43.9	89.9 (153)	33.4	81.9 (170)	37.1	84.9 (158)	39.1	75.0 (166)	47.8	74.2 (169)	55.1
4CH$_3$-pyridine	79.9 (151)	44.1	90.6 (150)	32.7	82.0 (168)	37.0	85.1 (155)	38.9	74.9 (165)	47.9	71.9	57.4
pyridine	80.2 (151)	43.8	91.0 (150)	32.3	82.3 (168)	36.7	85.5 (155)	38.5	75.3 (165)	47.5	72.4 (166)	56.9
4CN-pyridine	81.1 (156)	42.9	92.2 (154)	31.1	82.7 (170)	36.3	86.4 (159)	37.6	75.9 (170)	46.9	–	–
free olefin	124.0		123.3		119.0		124.0		122.8		129.3	

[a] $\Delta_{mean} = \delta\ ^{13}C_{mean}(C_\alpha + C_\beta)_{lig.} - \delta\ ^{13}C_{mean}(C_\alpha + C_\beta)_{compl.}$. [b] Data from $CDCl_3$ solution, using $\delta_{TMS} = \delta_{CDCl_3} - 77.1$ ppm. [c] Data from $(CD_3)_2CO$ solution, using $\delta_{TMS} = \delta_{(CD_3)_2CO} - 29.9$ ppm. [d] Complex in *cis* configuration.

variation of the substituent R on the pyridine ring. Such a regular shift is, however, not found for the complexes with L = Cl^- or 4CH_3-pyridine N-oxide.

^{13}*C NMR Results*

In Table VI the ^{13}C chemical shifts for the olefinic carbon atoms and the platinum–carbon coupling constants are given. The α-carbon atom represents the atom with the substituent. It was not possible even at low temperature (–25 °C to –50 °C), to obtain values for $^1J(^{195}Pt-^{13}C)$ for the complexes with 4CH_3-pyridine N-oxide or CH_3CN. Exchange between coordinated olefin and solvent is presumably the cause.

For all complexes, a regular increase in downfield shift for the olefinic carbon atoms is observed on going from $O \rightarrow Cl^- \rightarrow N$ bonded ligands, in agreement with the observed trend in *trans*-$PtCl_2(C_2H_4)$(pyridine) [3, 4]. As shown before (see Table IV) such an order of *trans*-influence is also found for the variation of $\bar{\nu}(Pt-C_2)$ and for the summed percentage lowering of $\nu(C{=}C)$, δ(CH) and $\delta(CH_2)$ frequencies. In fact, almost linear correlations are found between $\delta\ ^{13}C_{mean}$ of the olefins (Table VII) and these summed percentage lowerings, which are a measure of the decrease of olefin bond orders (Fig. 3).

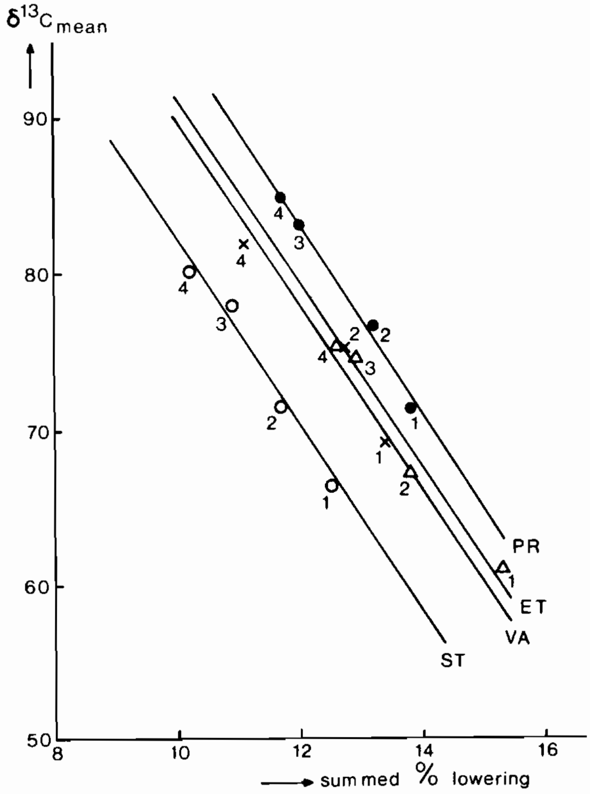

Figure 3. Plot of mean carbon-13 shift of C_α and C_β *versus* the summed percentage lowering of the $\nu(C{=}C)$, $\delta\ (CH_2)_{scis}$ and $\delta\ (CH)_{bend}$ frequencies. 1 = 4CH_3-pyridine N-oxide; 2 = Cl^-; 3 = CH_3CN; 4 = collidine.

In agreement with the results for the complexes *trans*-$PtCl_2(C_2H_4)$(substituted pyridine) [2], $\delta\ ^{13}C_{mean}$ appears to be linearly dependent on the Hammett σ_p parameter of the substituent in the pyridine ring for all complexes *trans*-$PtCL_2$(olefin) (substituted pyridine).

It has been shown for the complexes *trans*-$PtCl_2$ (olefin)(pyridine) [5] that the shift of $\delta\ ^{13}C_{mean}$ upon coordination (Δ_{mean}) is a measure of the withdrawal of charge from the olefin by platinum. The same trend is found here for all complexes *trans*-$PtCl_2$(olefin)(L), showing that platinum withdraws more charge from ST, BU, PR and VA than from ET, while it releases more charge to MA.

The coupling constants $^1J(Pt-C)$ (Table VI) are a measure of the strength of the platinum–olefin σ bond [28]. They are therefore largest for the 4CH_3-pyridine N-oxide compounds which all possess a strong Pt–olefin σ-bond. Furthermore, in the series *trans*-$PtCl_2$(olefin)(substituted pyridine) the value of $^1J_{mean}(^{195}Pt-^{13}C)$ regularly increases on going from the collidine to the corresponding 4CN-pyridine complexes.

The polarization effect of the substituent on the olefin manifests itself in the difference between the ^{13}C chemical shifts of C_α and C_β in the free olefin [5]. Upon coordination this difference ($\delta\ ^{13}C(C_\alpha - C_\beta)$) remains almost the same for the analogues of Zeise's salt, but for the other compounds *trans*-$PtCl_2$ (olefin)L a constant increase in $\delta\ ^{13}C(C_\alpha - C_\beta)$ is observed for each olefin in the order L = $Cl^- <$ CH_3CN < 4CH_3-pyridine N-oxide < collidine < 4CH_3-pyridine < pyridine < 4CN-pyridine for each olefin. This means that the $PtCl_2L$ moiety of the complexes polarizes all olefins in the same way.

Conclusions

The *trans* influence of L for the complexes *trans*-$PtCl_2$(olefin)(L), where L = nitrogen or oxygen bonded ligand or Cl^-, increases in the order $O < Cl^- < N$ [3, 4]. This is reflected in both a decrease of $\bar{\nu}(Pt-C_2)$ and the summed percentage lowering of $\nu(C{=}C)$, $\delta(CH_2)$ and δ(CH) frequencies [19, 20] (Table IV), and in the increasing downfield ^{13}C shift of the olefinic carbon atoms (Table VII).

In the complexes with the substituted olefins, $\nu(C{=}C)$ contributes mainly to the band at 1520 cm^{-1}, but in the complexes with ethylene mainly to the band at 1250 cm^{-1} [19, 20].

The shift of $\delta\ ^{13}C_{mean}$ upon coordination is a measure of the charge distribution between platinum and the olefin [5].

For each olefin series $^1J(Pt-C)$ decreases when the σ bond between Pt and the olefin is weakened.

The electronic absorption spectra possess a ligand field band which shifts to lower energy when the substituents of both the pyridine and olefin ligands become more electron withdrawing.

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