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Bonding Properties of *Trans*-$PtCl_2XY$ and *Trans*-$PtBr_2XY$ ($X = C_2H_4$, CO; Y = 4R-Py). III. ^1H and ^{13}C NMR Spectra.

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The ^{13}C NMR chemical shifts of tr-$PtCl_2X(Py)$ ($X = C_2H_4$, CO) and of a series of 4-substituted pyridine derivatives were studied. Because of a linear correlation between the ^{13}C chemical shifts of the 4-substituted pyridine ligands and both the corresponding benzenes and the tr-$PtCl_2(C_2H_4)$(4R–Py) complexes similar shielding mechanisms are suggested for these three classes of compounds. The ^{13}C shifts of the C-2 atom of the 4R-pyridine ligand in the complexes can be correlated with a CT transition from the platinum to the 4R-pyridine ligand. A relationship has been found between the ^{13}C chemical shifts of coordinated C_2H_4 and the Hammett σ_p parameter of the 4R-pyridine group and an explanation is given for the observed high upfield shift of the C_2H_4 group in the complex. The ^{13}C NMR spectra of the carbonyl compounds show the carbonyl resonance only with ^{13}C-enriched CO. It is shifted about 30 ppm upfield with respect to free CO. This has been ascribed to anisotropy in the paramagnetic susceptibility of the platinum.

Introduction

The effect of variation of R on the properties of the above complexes has been studied by IR, Raman[1], UV[2] and ^1H NMR[3,4] spectroscopy. The vibrational spectra[1] showed that ν(C=C) of the ethylene and the Pt–ethylene vibrations are not dependent on the nature of R, but that only ν(Pt–N) varies with R. The UV spectra[2] possess a charge transfer absorption band which depends on the nature of R. The ^1H spectra[3,4] showed a small influence of R on the ethylene resonances.

In order to study the effect of substitution at the 4-position in the pyridine ring, we have recorded ^{13}C NMR spectra which exhibit considerably greater sensitivity to changes in bonding than do ^1H NMR spectra.

In this report we attempt to explain the ^{13}C NMR spectra of these complexes.

Experimental

The compounds tr-$PtCl_2(C_2H_4)$(4R-Py) were prepared by standard methods[4]. The tr-$PtCl_2$(CO)(4R-Py) complexes were synthesized from their corresponding ethylene analogues[5]. See ref. 1 for analytical data.

^1H NMR spectra were obtained in $CDCl_3$ solution on a Varian HA 100 NMR spectrometer.

^{13}C NMR spectra for the ligands and the ethylene complexes were recorded in CH_2Cl_2 at 25.2 MHz on a Varian XL-100 Fourier Transform spectrometer with proton decoupling. A micro insert tube with D_2O was used as an external field–frequency lock.

^{13}C NMR spectra of the carbonyl complexes were measured in $CDCl_3$ at 20 MHz on a Varian CFT-20 spectrometer. In three compounds we used enriched ^{13}CO in order to observe the carbonyl signal.

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

$$\delta_{TMS} = \delta_{CH_2Cl_2} - 54.0 \text{ ppm}; \delta_{TMS} = \delta_{CDCl_3} - 77.2 \text{ ppm}.$$

All shifts were found to be reproducible to within ±.2 ppm. The solubility of the complexes was small. Thus, for most compounds 25.000 pulses (AT = .8 sec and PD = .8 sec) were necessary to give reasonable spectra.

The spectra of some tr-$PtCl_2$(CO)(4R-Py) complexes were recorded at –10° C, because the compounds decomposed during pulsing at normal probe temperature.

Results and Discussion

In Tables I and II, thc ^1H and ^{13}C NMR results for the tr-$PtCl_2X$(4R-Py) ($X = C_2H_4$, CO) complexes are compiled. In Table III the ^{13}C NMR shifts of the 4R-pyridines are compared with the shifts of the analogous benzene derivatives. Our data and assignments for compounds which have been previously reported are in agreement with the literature[4,6]. A proton decoupled ^{13}C spectrum is shown in Figure 1.

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TABLE I. ^1H NMR Chemical Shifts for *tr*-$PtCl_2(X)(4R\text{-}Py)$ with X = C_2H_4, CO. Only the values for protons in the pyridine ring and ethylene are given.[a]

R	NH_2	CH_3	CH_2CH_3	CH_2OH	H	Cl	Br	COOH	$CO_2C_2H_5$	$COCH_3$	CN
X = C_2H_4											
H_2	8.47	8.75	8.77	8.81	8.95	8.89	8.82	9.18	9.10	9.13	9.20
H_3	6.56	7.31	7.32	7.46	7.57	7.51	7.71	8.12	8.06	7.93	7.78
$H_{C_2H_4}$	4.79	4.86	4.85	4.87	4.92	4.89	4.93	4.99	4.95	4.94	4.97
X = CO											
H_2		8.57			8.77	8.74	8.63				9.06
H_3		7.32			7.57	7.55	7.71				7.78

[a] NMR spectra were recorded in $CDCl_3$ relative to an internal TMS standard.

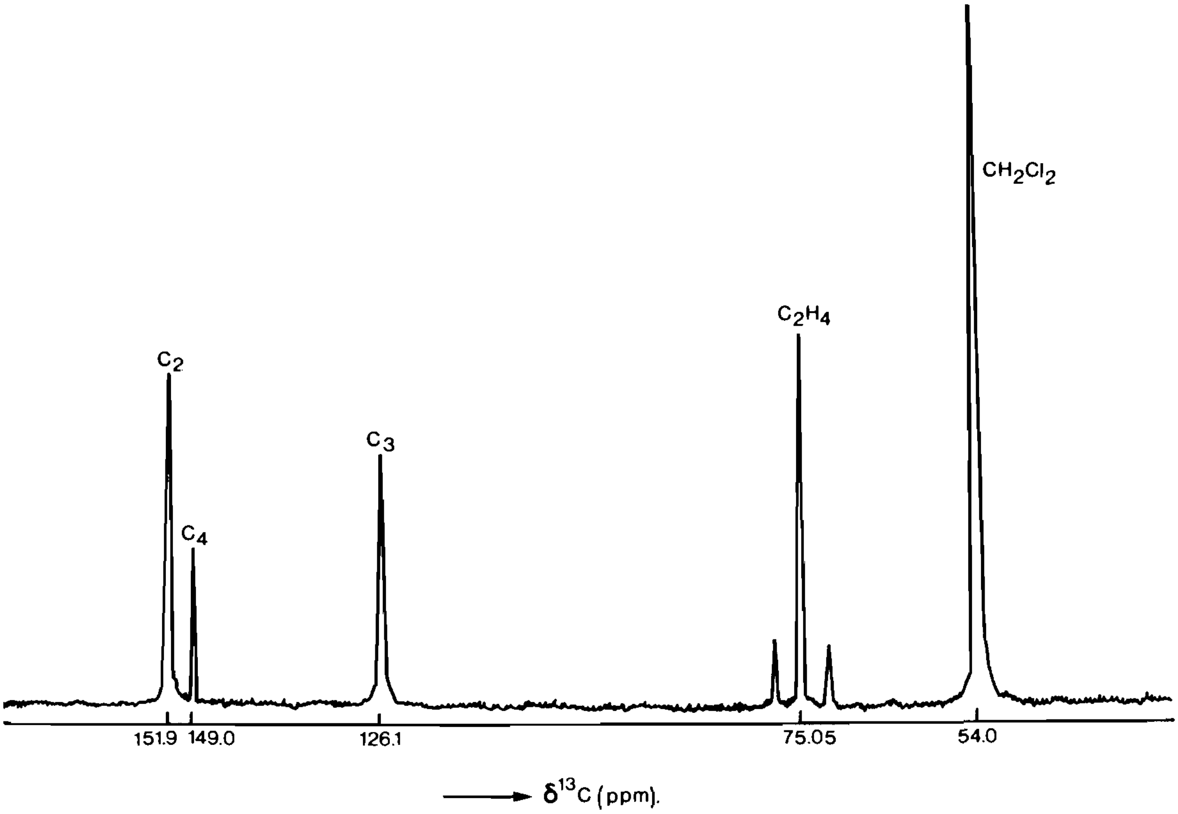

Figure 1. The ^1H-decoupled Fourier transform pulsed ^{13}C spectrum of *tr*-$PtCl_2(C_2H_4)(4Cl\text{-}Py)$ in CH_2Cl_2 solution (32.000 scans,. 8 sec pulse delay).

The ^{13}C NMR results of Tables II and III are plotted against each other in Figures 2 and 3 for positions 3 and 4 respectively in the pyridine ring.

It is clear from Table III that variation of R from electron releasing (NH_2) to electron withdrawing (CN) at the 4-position of the pyridine ring mainly influences the ^{13}C shift of C-4 (about 30 ppm). The chemical shift for C-2 is almost totally insensitive to this variation.

Figures 2 and 3 show good linear correlations between the δ ^{13}C shifts of the 4R-pyridines and their benzene analogues. The parameters derived from a linear regression analysis of these data are summarized in the following equations:

$$\delta\,^{13}C\,(C\text{-}4_{benz}) = +.95\,\delta\,^{13}C(C\text{-}4_{Py}) - .72\ (\text{st.dev. } 1.92)$$

$$\delta\,^{13}C\,(C\text{-}3_{benz}) = +.97\,\delta\,^{13}C(C\text{-}3_{Py}) + 9.74\ (\text{st.dev. } 1.28)$$

TABLE II. ^{13}C NMR Chemical Shifts for *tr*-$PtCl_2(X)(4R\text{-}Py)$ for X = C_2H_4, CO.[a]

R	NH_2	CH_3	CH_2CH_3	CH_2OH	H	Cl	Br	COOH	$CO_2C_2H_5$	$COCH_3$	CN
X = C_2H_4											
C-2	150.7	150.4	150.6	150.8	151.3	151.9	151.6	152.3	152.1	152.5	152.5
C-3	109.7	126.3	125.1	122.4	125.7	126.1	129.2	125.3	124.9	123.3	127.7
C-4	(156)[b]	153.2	158.7	155.7	140.4	149.0	138.0	140.5	141.2	145.3	124.5
C_2H_4	73.8	74.9	75.0	75.2	75.3	75.05	75.15	75.8	75.6	75.7	75.9
X = CO											
C-2		149.9			150.9[c]	151.5	151.2				152.3[c]
C-3		126.6			125.9	126.5	129.6				128.0
C-4		153.7			140.9	149.9	139.1				125.0
σ_p	–.660	–.170	–.151	+.10	.000	+.227	+.232	+.450	+.450	+.502	+.660

[a] The chemical shift of free ethylene is 122.8 ppm (ref 25 p. 70). σ_p is the Hammett σ_p parameter[23]. NMR spectra of the C_2H_4 complexes were recorded in CH_2Cl_2; the CO complexes were recorded in dry $CDCl_3$. They are reported relative to TMS, using $\delta_{TMS} = \delta_{CH_2Cl_2} - 54.0$ ppm and $\delta_{TMS} = \delta_{CDCl_3} - 77.2$ ppm. [b] Chemical shift not reliable. [c] Spectra of the CO compounds at –10° C.

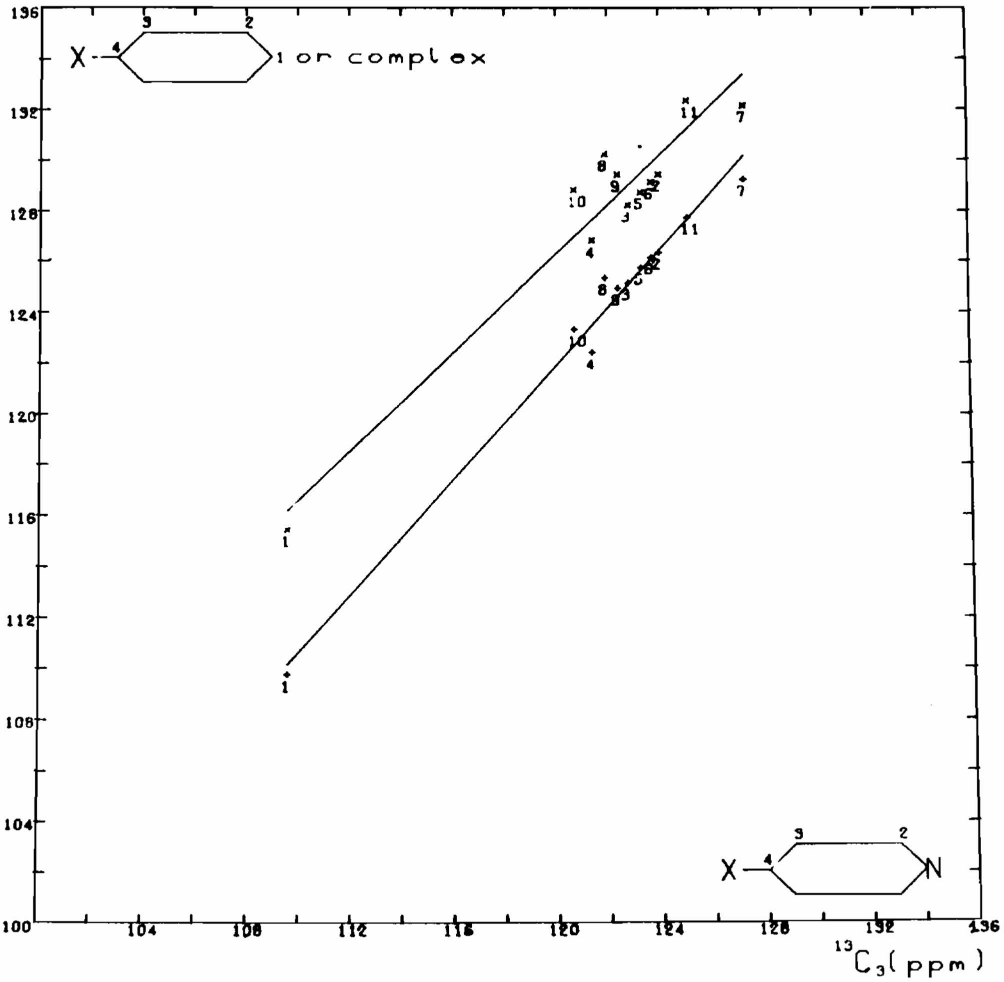

Figure 2. Plots of δ ^{13}C for 4R-Py *versus* δ ^{13}C for the analogous benzenes (denoted by x) or *versus* δ ^{13}C for *tr*-$PtCl_2(C_2H_4)(4R\text{-}Py)$ (denoted by +) for position 3 in the pyridine ring. The numbering scheme is given in Table III.

TABLE III. ^{13}C NMR Chemical Shifts for the 4R-Pyridines and Analogous Benzene Derivatives.[a]

R	4R-Pyridines			R-C_6H_5[c]		
	C-2	C-3	C-4	C-2	C-3	C-4
1. NH_2	150.2	109.6	153.0	129.6	115.4	146.7
2. CH_3	149.1	124.0	146.1	128.6	129.4	137.6
3. CH_2CH_3	149.4	122.8	152.1	128.7[d]	128.2	144.4
4. CH_2OH	149.0	121.4	152.2	128.2[e]	126.8	140.8
5. H	149.5	123.3	135.3	128.7	128.7	128.7
6. Cl	150.6	123.7	143.3	130.0	129.1	134.9
7. Br	151.1	127.3	132.7	130.4	132.1	123.2
8. COOH[b]	149.6	121.9	137.3	128.7	130.2	130.8
9. $CO_2C_2H_5$	150.4	122.4	137.3	128.2[d]	129.4	130.3
10. $COCH_3$	150.3	120.7	142.1	128.7	128.8	137.8
11. CN	150.4	125.1	119.9	129.3	132.3	113.3

[a] NMR spectra of 4R-Py were recorded in CH_2Cl_2 and are relative to TMS, using $\delta_{TMS} = \delta_{CH_2Cl_2} - 54.0$ ppm.
[b] in DMSO solution. [c] Values from G. L. Nelson, G. C. Levy and J. D. Cargioli, *J. Am. Chem. Soc.*, *94*, 3089 (1972).
[d] A. N. Nesmeyanov, N. V. Petrovskii, L. A. Fedorov, V. I. Robas and E. I. Fedin, *J. Struct. Chem.*, *14*, 12 (1973).
[e] L. F. Johnson and W. C. Jankowski, "^{13}C -NMR Spectra", Wiley.

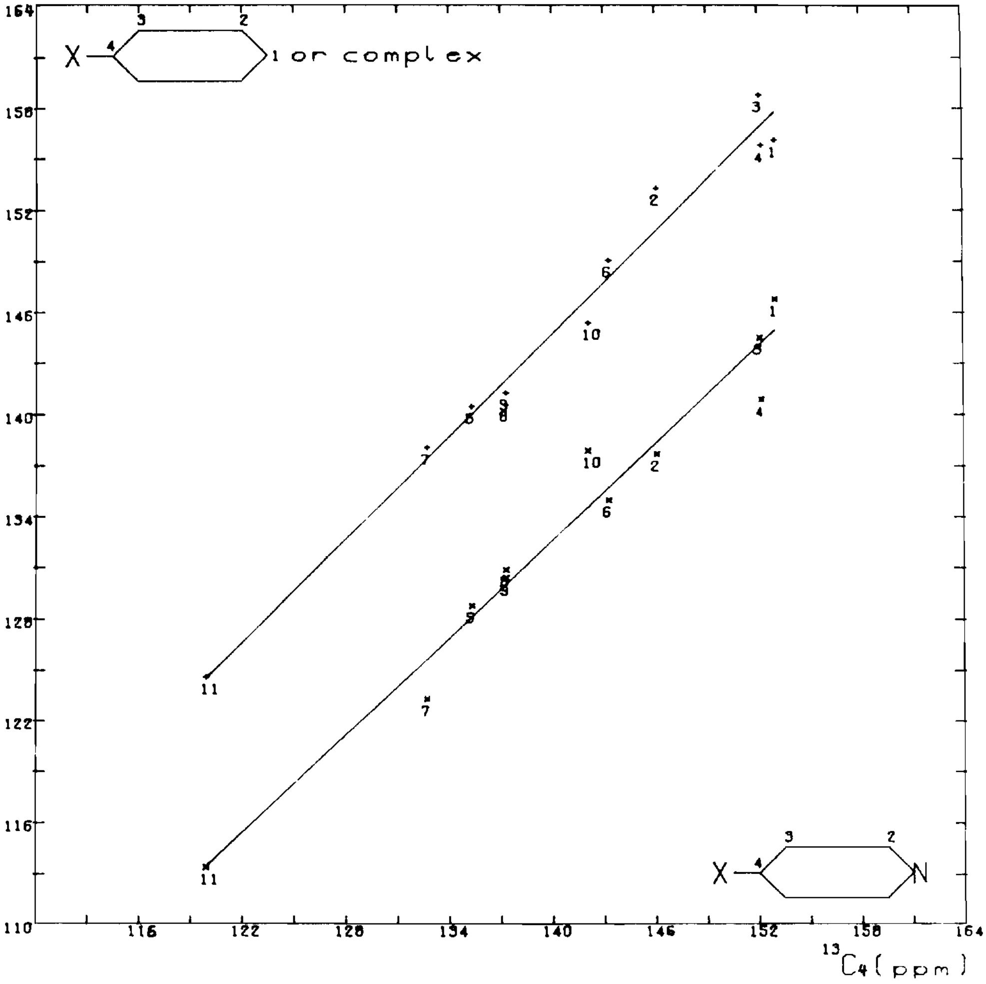

Figure 3. Analogous to Figure 2, for position 4 in the pyridine ring.

The same relationships exist between the 4R-pyridines and the corresponding complexes (Figures 2 and 3), which are summarized in the following equations:

$$\delta\ ^{13}C\ (C\text{-}4_{compl}) = +1.00\ \delta\ ^{13}C\ (C\text{-}4_{Py}) - 4.16 \quad \text{(st.dev. 1.50)}$$

$$\delta\ ^{13}C\ (C\text{-}3_{compl}) = +1.13\ \delta\ ^{13}C\ (C\text{-}3_{Py}) - 13.97 \quad \text{(st.dev. .69)}$$

The slope of about one in the plot implies that the effect of the substituent on the pyridine ring is about the same as for the benzene analogue, and that there is no significant change in the transmission of the substituent effects upon complexation[7].

The effect of complexation is the downfield shift of the pyridine ring and the upfield shift of the ethylene group (about 47 ppm, Tables II and III) for the ethylene complexes. This has also been concluded from the ^{1}H NMR spectra[3,4]. In the following sections we first discuss the *tr*-PtCl$_2$(C$_2$H$_4$)(Py) complex, and subsequently the effect of R and the effects of substituting Cl by Br and C$_2$H$_4$ by CO on the ^{13}C shifts.

A. ^{13}C Chemical Shifts for tr-PtCl$_2$(C$_2$H$_4$)(pyridine)

According to Saika and Slichter[8] the shielding constant σ may be considered to be the sum of three terms: local diamagnetic (σ_d), local paramagnetic (σ_p) contributions and contributions due to electron circulation in remote orbitals (σ'), which latter can be divided into a diamagnetic part (σ_d') and a paramagnetic part (σ_p'):

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

It should be borne in mind that this separation into quite distinct terms is largely artificial and has meaning only in the context of calculations such as used here. The only physically real term, which is a constant using a gauge invariant set of atomic orbitals[9], is the total screening constant σ.

Although ^{13}C chemical shifts in organic molecules are primarily determined by changes in σ_p[10], σ' might be of importance here because of the large number of platinum electrons (σ_d') and of the anisotropy in the magnetic susceptibility of the incompletely filled *d* orbitals of platinum (σ_p'). However in the following we shall see that the contribution of σ_p' is very small.

Buckingham and Stephens[11] have explained the anomalously high field proton shifts in square *trans*-PtH(X)(PEt$_3$)$_2$ complexes by the anisotropy in the magnetic susceptibility of the platinum atom. They predicted downfield shifts for protons lying above or below the square plane.

The anisotropy in the paramagnetic contribution is caused by the different orientations of the complex in the applied magnetic field, H$_o$, which give rise to differing susceptibilities χ_i along the molecular axis[12] (Figure 4).

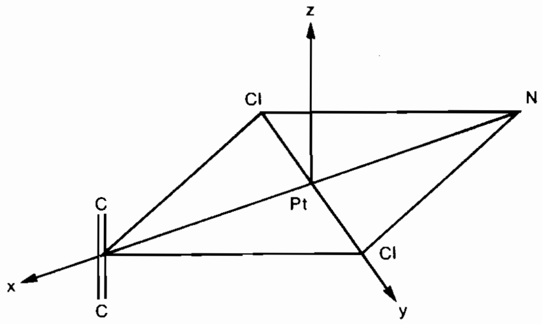

Figure 4. The molecular axes of *tr*-PtCl$_2$(C$_2$H$_4$)(4R-Py). The xy-plane is the platinum square plane.

The mean contribution to the shielding constant σ is obtained by averaging over the three orientations of H$_o$ along the molecular axes.

$$\sigma_p' = 1/3\ (R^{-3})\Sigma_i\chi_i(1-3\cos{}^2\Theta_i) \qquad (2)$$

where R is the Pt–C or Pt–H distance and Θ_i is the angle between the Pt–C or Pt–H line and the i-th direction, when H$_o$ is in the i-th direction[13]. In the following a rough calculation is made of the contribution of σ_p' to the proton and carbon shifts in *tr*-PtCl$_2$(C$_2$H$_4$)(pyridine) with distances taken from two crystal structures[15] (Figure 5).

However, we did not succeed in determining the C–H distances, but used the C–H distances for free C$_2$H$_4$ (1.06 Å) and for free pyridine (1.08 Å), which we consider justified because the C–N and C–C distances of the pyridine rings in the complexes are almost the same as for the free ligands.

The Pt–H$_{eth}$, the Pt–H$_{Py}$ and the Pt–C$_{Py}$ distances have been calculated with the help of the known distances and angles. The resulting angles for Θ_x between the x-axis and the Pt–C$_{eth}$, Pt–H$_{eth}$, Pt–C$_{Py}$ and Pt–H$_{Py}$ lines are 18°, 37°, 23° and 44° respectively. The same for Θ_y: 90°, 70°, 90° and 90° respectively and for Θ_z: 72°, 60°, 67° and 46° respectively. Using these values in eq. 2, we obtain the following contributions to σ:

$$\begin{aligned} \sigma_{P_{C_{eth}}}' &= -.057\chi_x + .033\chi_y + .024\chi_z \\ \sigma_{P_{C_{Py}}}' &= -.019\chi_x + .012\chi_y + .007\chi_z \\ \sigma_{P_{H_{eth}}}' &= -.018\chi_x + .013\chi_y + .005\chi_z \\ \sigma_{P_{H_{Py}}}' &= -.007\chi_x + .012\chi_y - .005\chi_z \end{aligned} \qquad (3)$$

However, in *tr*-PtCl$_2$(C$_2$H$_4$)(pyridine) constrained rotation about the x-axis will be operative for the ethylene[14] and the pyridine ligands. Thus, the coefficients of χ_y and χ_z in eq. 2 will each vanish and the remaining contribution will deshield the atoms in question.

According to Ballhausen[16] the value of χ is small, because it is proportional to 1/ΔE, where ΔE represents the energies of ligand field transitions, which occur for this complex in the UV region. Thus, σ_p'

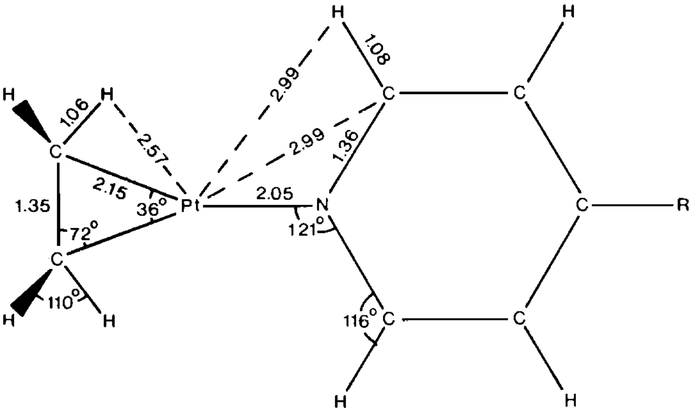

Figure 5. Distances and angles for that part of the *tr*-$PtCl_2(C_2H_4)$(4R-Py) complex which is important for calculation of the platinum paramagnetic contribution to the shielding constant.

causes only slight changes in shifts for all these atoms and the ^{13}C chemical shifts in these complexes will be mainly determined by σ_d' and σ_p. Flygare and Goodisman[17] have suggested a simple formula for estimating this contribution:

$$\sigma_d' = \frac{e^2}{3mc^2} \sum_\alpha \cdot \frac{Z_\alpha}{r_\alpha} \qquad (4)$$

where α runs over all nuclei except the ethylene carbon nucleus, Z_α is the atomic number of the αth nucleus and r_α is the distance from the carbon nucleus to the αth nucleus. Calculation of the value of σ_d', due to the platinum nucleus results in a large upfield shift of about 340 ppm. Thus, σ_d' is an important contribution to the total shielding constant σ in transition metal complexes. The observed upfield shift is 47.5 ppm, in agreement with the results for other metal–olefin complexes[18, 19].

Thus, the large σ_d' term must be partly opposed by the local paramagnetic term σ_p.

The formula for the local paramagnetic contribution[10] is:

$$\sigma_p = -\text{const.} \frac{\langle r^{-3} \rangle_{2p}}{\Delta E} (Q_{AA} + \sum_{A \neq B} Q_{AB}) \qquad (5)$$

Here ΔE is the average excitation energy, $\langle r^{-3} \rangle_{2p}$ is the mean inverse cube radius for a carbon $2p$ orbital, Q_{AA} is related to the electron density on carbon A and Q_{AB} is connected with the multiple bond character between A and B. Q_{AA} does not change much with excess charge densities[10]. It is a difficult task to describe the changes in the different terms in eq. 5, when ethylene is coordinated to the platinum, because the bond between platinum and ethylene is not a simple one, but consists of a σ- and a π-bond[1]. However, from the total shift of 47.5 ppm it follows that the paramagnetic effect is a downfield shift of about 290 ppm, which indicates that the contribution of the ring current, which is possible in the three-ring structure of the platinum and the ethylene carbon atoms, may be important here. The shielding in the pyridine ring will also be mainly determined by σ_p and σ_d'.

The contribution of σ_d' (eq. 4) in this case is about 240 ppm for the 2-position in the pyridine ring.

The pyridine ring shows a small downfield shift on complexation. Thus, the paramagnetic term σ_p will largely negate σ_d'. The decrease in the paramagnetic contribution of the nitrogen lone pair[20], when it is used in the σ-bond between platinum and pyridine will also contribute to the shielding of the C-2 in the pyridine ring.

B. The Effect of Variation of R in the Pyridine Ring

The ^1H and ^{13}C NMR spectra (Tables I and II) show a downfield shift on varying R from NH_2 to CN for the ethylene atoms and for the 2-position in the pyridine ring.

In section A we have seen that the shifts are mainly determined by σ_p and σ_d'. However, the σ_d' contribution will not change much in this series of complexes, so that the shift differences recorded on variation of R will be mainly due to changes in the σ_p term (eq. 5). Factors contributing to σ_p are ΔE, Q_{AB} and $\langle r^{-3} \rangle_{2p}$. All low energy transitions can contribute to the factor ΔE if they are rotationally allowed[21].

In the UV spectra[2] the lowest absorption bands belong to charge transfer transitions from platinum to 4R-pyridine. These transitions from $Pt(5d_{xy})$ to pyridine π^* orbitals are rotationally allowed, since the pyridine ligands rotate in the complexes. They will therefore contribute to the σ_p of the pyridine atoms, mainly to σ_p for the 2-position in the ring. Variation of R from NH_2 to CN in the pyridine group causes a lowering of ΔE and this effect is reflected in a corresponding downfield shift of δ ^{13}C for C-2 in 4R-pyridine.

Further proof for the importance of the contribution of ΔE to σ_p comes from a comparison of the chemical shifts of C-2 in *tr*-$PtCl_2(C_2H_4)$(pyridine) and *tr*-$PtCl_2(C_2H_4)$(2,4,6-trimethylpyridine).

The 2,4,6-trimethylpyridine ligand cannot rotate in the latter complex because of steric hindrance[22] and is perpendicular to the square plane. The $5d_{xy} \rightarrow \pi^*$ transition is therefore rotationally forbidden in this configuration and we expect a smaller downfield shift for this complex with respect to the free ligand than the difference recorded for pyridine and its complex. In fact we find a downfield shift of 0.8 ppm for C-2 in *tr*-$PtCl_2(C_2H_4)$(2,4,6-trimethylpyridine) complex relative to the free ligand, compared with 1.8 ppm for the pyridine complex.

Variation of R has much less influence on the shifts of ethylene (Table IV).

Of course we do not expect that the factors which change σ_p of the pyridine atoms by variation of R will influence the shifts of ethylene as much. However, contrary to the results from the vibrational spectra, which do not show any change of the strength of the Pt–C_2H_4 bond on variation of R, the ^{13}C shifts of ethylene show a slight dependence on R.

In fact, a linear correlation is found between the ^{13}C shifts of ethylene and the Hammett σ_p[23] parameter of the pyridine ligand (Figure 6).

The change in σ_p, related to a change in Q_{AB} (eq. 5) may be estimated in the following way:

Powell[24] has stated that the summed percentage lowering of the coupled $\nu(C{=}C)$ and δ(C–H) frequencies gives a rough estimate of the decrease in double bond character of the olefin. In our series of complexes these frequencies are shifted from 1623 and 1343 cm^{-1} for all complexes to 1524 and 1256 cm^{-1} respectively[1]. This gives a constant lowering of 12.5%. Thus the bond order of the C=C bond and consequently the Q_{AB} term in σ_p hardly changes on variation of R. Therefore, the observed shift differences between the complexes can be mainly explained by variation in the ΔE and $\langle r^{-3} \rangle_{2p}$ terms.

TABLE IV. Influence of Variation of R on ^{13}C NMR Shifts of Ethylene and Pyridine (C-2) in *tr*-$PtCl_2(C_2H_4)$(4R-Py). Values are related to *tr*-$PtCl_2(C_2H_4)(Py)$[a].

R	NH_2	CH_3	CH_2CH_3	CH_2OH	H	Cl	Br	COOH	$CO_2C_2H_5$	$COCH_3$	CN
$\Delta\delta\,^1H_{C_2H_4}$	–.13	–.06	–.07	–.05	–	–.03	+.01	+.07	+.03	+.02	+.05
$\Delta\delta\,^1H_{Py}$	–.48	–.20	–.18	–.14	–	–.06	–.13	+.23	+.15	+.18	+.25
$\Delta\delta\,^{13}C_{C_2H_4}$	–1.5	–.4	–.3	–.1	–	–.25	–.15	+.5	+.3	+.4	+.6
$\Delta\delta\,^{13}C_{C\text{-}2}$	–.7	–.9	–.7	–.5	–	+.6	+.3	+1.0	+.8	+1.2	+1.2
ΔE^b	32.520	32.150	32.340	32.120	32.030	31.850	31.750	30.940	31.700	30.940	30.960

[a] Upfield shifts are indicated by –. Downfield shifts are indicated by +. [b] ΔE is the charge transfer energy in cm^{-1}.

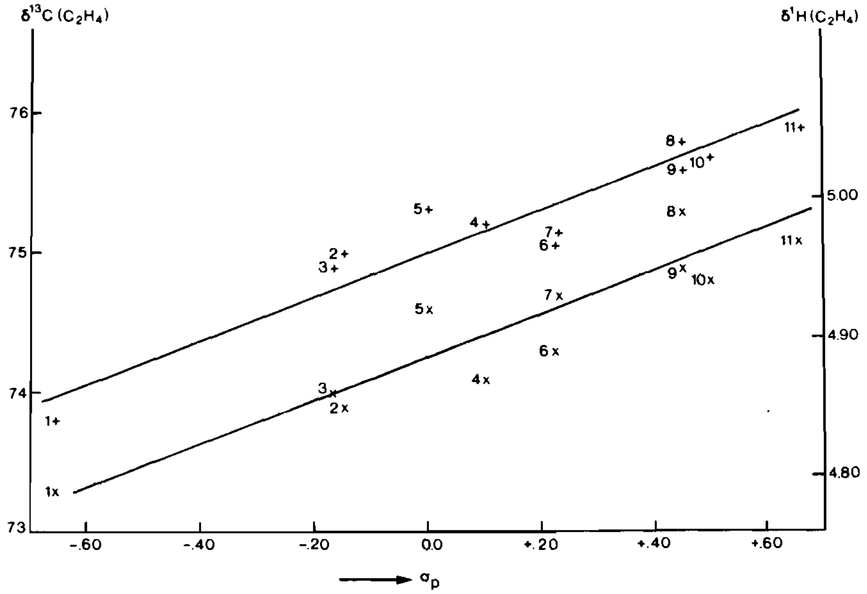

Figure 6. Plots of δ $^{13}C(C_2H_4)$ (denoted by +) and δ $^1H(C_2H_4)$ (denoted by x) *versus* Hammett σ_p parameter[23] (Table II). σ_p for R = CH_2OH is taken from ref. 5.

C. The Effect of Substituting Cl by Br

In order to study the *cis*-effect, we replaced Cl by Br. The vibrational spectra[1] showed hardly any influence of this change on the $\nu(C=C)$ and the $\nu(Pt–C_2)$ vibrations, but there is some effect in the NMR spectra (Table V).

Most significant in this table is the downfield proton shift and the upfield ^{13}C shift in ethylene, when Cl is replaced by Br.

In agreement with Stothers[25], we explain this effect by a sterically induced polarization of the C–H bond in ethylene by the Br atom.

A corresponding influence on the C–H bond at the 2-position in the pyridine ring would be expected. However, an irregular change in proton shifts is found and a downfield shift of about 1 ppm for the carbon-13 shift at this position while the shifts of the rest of the ring are almost invariant (Table V). Looking at the UV spectra of the Br complexes[2], we notice a shift of 500 cm^{-1} to lower frequency of the CT transition giving rise to a downfield shift contribution to σ. This effect should compete with the sterically induced polarization and may cause the observed downfield shift. On the other hand, the shifts in ethylene are practically unaffected by this change in CT energy and should only experience the effect of induced polarization by the Br atoms. The pyridine protons at the 2-position may be influenced by both effects and therefore show irregular changes in shift.

D. The Effect of Substituting C_2H_4 by CO

Table I and II also show the NMR data for the carbonyl complexes. Because of the long T_1 relaxation times of the metal bonded carbonyls, we did not succeed in obtaining their resonance signals in the normal way.

In three complexes (R = H, Cl and CN) we used enriched ^{13}CO, and found their signals at 151.4, 150.9 and 150.6 ppm respectively.

With respect to the ethylene complexes, the NMR shifts for the 2-position in the ring are moved somewhat upfield and those of the other part of the ring are shifted downfield. Considering the UV spectra, a large blue shift was observed for the charge transfer energy in the CO complex with respect to that in the C_2H_4 complex (Table VI). This blue shift is caused by the fact that the platinum $5d_{xy}$ orbital is used in the platinum–carbonyl π-bond. This shift of CT energy is reflected in the upfield ^{13}C shift obtained for the 2-position in the ring. The latter shift is small, but is opposed by a downfield shift of the whole ring in the CO complex with respect to that in the C_2H_4 complex (see shifts C-3 and C-4).

Because of an almost constant difference in CT energies between the various carbonyl and ethylene compounds, a constant upfield ^{13}C shift is expected, and accordingly is in fact found.

The ^{13}C NMR shift of the C-2 position of *tr*-$PtCl_2(CO)(4CN\text{-}Py)$ is small compared with that in the other complexes. Similarly anomalous behaviour is also

TABLE V. ^{13}C Chemical Shifts of Pyridine and Ethylene in *tr*-$Pt(Z)_2(C_2H_4)(4R\text{-}Py)$ with Z = Br, Cl.

	tr-$PtCl_2(C_2H_4)(4R\text{-}Py)$			*tr*-$PtBr_2(C_2H_4)(4R\text{-}Py)$		
	R = CH_3	H	Br	CH_3	H	Br
$C\text{-}2_{(H2)}$[a]	150.4	151.3	151.6	151.4	152.3	152.7
	(8.75)	(8.95)	(8.82)	(8.80)	(8.92)	(8.77)
C-3	126.3	125.7	129.2	126.4	125.7	129.3
C-4	153.2	140.4	138.0	152.6	139.9	137.5
$C_2H_{4(H)}$[a]	74.9	75.3	75.15	72.5	72.8	72.8
	(4.86)	(4.92)	(4.93)	(5.02)	(5.02)	(5.01)
ΔE^b	32.150	32.030	31.750	31.650	31.550	31.250

[a] These are proton shifts; see text for explanation; [b] ΔE is the charge transfer energy in cm^{-1}.

TABLE VI. Charge Transfer Energies (in cm^{-1}) and δ $^{13}C(C\text{-}2)$ for *tr*-$PtCl_2(X)(4R\text{-}Py)$ with X = CO or C_2H_4.

R	ΔE_a X = CO	ΔE_b X = C_2H_4	$\Delta E_a – \Delta E_b$	δ $^{13}C_a(C\text{-}2)$ X = CO	δ $^{13}C_b(C\text{-}2)$ X = C_2H_4	δ $^{13}C_a – \delta$ $^{13}C_b$
CH_3	35.090	32.150	2.940	149.9	150.4	–.5
H	34.970	32.030	2.940	150.9	151.3	–.4
Cl	34.840	31.850	2.990	151.5	151.9	–.4
Br	34.720	31.750	2.970	151.2	151.6	–.4
CN	32.360	30.960	1.400	152.3	152.5	–.2

found in the UV spectrum[2] (a much smaller CT energy) and in the vibrational spectrum[1] (higher value of ν(Pt–N) in the CO complex than in the C_2H_4 complex). It may be attributed to the strong π-acceptor property of the 4 CN-pyridine ligand, due to which the π-bond contribution to the total bond between Pt and CO is much lower than for the other CO complexes.

The carbonyl resonances observed for the enriched carbonyl complexes show a large upfield shift with regard to free CO (about 30 ppm).

Most carbonyl complexes show large downfield shifts of the carbonyl C atom ascribed to the strong π-bonding ability of CO in these complexes[26], or to changes in ΔE resulting from interaction of metal *d* orbitals with CO π^* orbitals[27,28]. However, our results are in agreement with the high upfield proton shifts in square *tr*-$PtX(H)(PEt_3)_2$ complexes[11], which have been explained in terms of the anisotropy in the magnetic susceptibility of the Pt atom for atoms lying in the square plane.

The trend in the shifts for CO arising from variation of R from H to CN is the result of the corresponding increase in π-bond ability of the 4R-pyridine ligand. The π-back bond to CO will then decrease resulting in a larger upfield shift[28]. This decrease in π-bond character has also been shown in the vibrational spectra[1], giving a higher ν(C≡O) frequency on varying R from CH_3 to CN.

E. The Platinum Coupling Constants

In Table VII some coupling constants for the *tr*-$PtCl_2X$ (4R-Py) (X = CO, C_2H_4) are compiled.

The whole series of ethylene complexes shows only small variations in these constants. The Pt–ethylene coupling is always present in the spectra at room temperature, hence there is no intermolecular ethylene exchange[4]. This coupling is mainly dominated by the Fermi Contact mechanism[29,30], which is strongly dependent on the metal *s* character of this bond[29,31].

Braterman[32] has pointed out for Pt–olefin complexes that this mechanism should occur via the ligand–metal σ-bond in order to involve the metal *s* orbital. Thus, the order of increasing $^1J(Pt–^{13}C)$ should be the inverse of the order of the σ-bond strengths of the platinum–pyridine bonds. However, the variation is too small here to give a correct σ-bond strength order.

$^1J(^{13}C–H)$ of the ethylene is increased on coordination from 156 Hz to about 165 Hz, which supports a three–membered ring structure for the Pt–C_2H_4 bond, but not a change in hybridisation of the ethylene carbon atoms from sp^2 to sp^3. Coupling between platinum and the protons at the 2-position of the ring[4] are only found in the ethylene complexes at low temperature (about 35 Hz). On the other hand the carbonyl compounds show this coupling at room temperature (about 30 Hz). Further, the ^{13}C spectra show coupling between Pt and the pyridine ring in the carbonyl complexes, but not in the C_2H_4 compounds (Table VII.) We can conclude from this observation that the pyridine ligand is kinetically more labile in the ethylene than in the CO complexes.

On the other hand, the vibrational spectra show a lower value of ν(Pt–N) in the carbonyl complexes[1] than that in the ethylene species. Evidently the higher *trans*-influence (weakening of the *trans* bond in the ground state) causes the 4R-pyridine ligands to be thermodynamically less stable here than in the corresponding ethylene complexes.

The alternation in the value of the coupling constants between the platinum and the pyridine ring in the CO complexes, ($^3J(Pt–C\text{-}3) > {}^2J(Pt–C\text{-}2) > {}^4J(Pt–C\text{-}4)$) is in agreement with the results of *e.g.* $Pt(Py)_4^{2+}$[33]. At the moment we have no explanation for this effect.

Values of $^1J(C–H)$ for complexed 4R-Py are increased (about 6 Hz) with respect to the values for the free ligand, corresponding with observations for the complexes π-$(C_6H_5X)Cr(CO)_3$[7]. This has been explained by an increase in the effective nuclear charge via a withdrawal of electron density from the σ framework of the arene ring[34]. In the present complexes too this mechanism may be responsible for this increase in $^1J(C–H)$.

In the three ^{13}C-enriched CO complexes, we recorded $^1J(Pt–CO)$ constants of 1674, 1698 and 1729 Hz for R = H, Cl and CN respectively. The coupling constants, which can be correlated with the change in σ-bonding ability between the platinum and the CO[32], are found to increase when the σ-bond between Pt and pyridine weakens. It is not strange that such an effect could hardly be observed for the corresponding ethylene complexes, as the $^1J(Pt–C_2H_4)$ values are much smaller than the corresponding $^1J(Pt–CO)$ values.

Conclusion

From the ^{13}C NMR spectra of *tr*-$PtCl_2X$(4R-Py) (X = C_2H_4, CO) complexes the following conclusions can be drawn.

It has been shown that the largest contribution to the chemical shifts of both pyridine and ethylene in these complexes is given by the paramagnetic shielding constant σ_p and the diamagnetic contribution due to the platinum atom σ_d'. The values of σ_p appear to depend on low lying electronic CT transitions. This is mainly reflected in the chemical shift of C-2 of the 4R-pyridine ligand in the complex, since a direct relation is found between the chemical shift of C-2 and $(\Delta E)_{CT}$ for a series of 4R-pyridine–C_2H_4 and CO complexes. While the vibrational spectra do not show any influence of variation of R on the Pt–ethylene and Pt–CO bond, the ^{13}C shifts of both ethylene and CO depend on R.

TABLE VII. Coupling Constants (Hz) in *tr*-$PtCl_2(X)(4R\text{-}Py)$ for X = CO or C_2H_4 and for the free ligands (n = not observed).

	$^2J(Pt\text{–}H)_{C_2H_4}$	$^1J(Pt\text{–}C)_{C_2H_4}$	$^1J(C\text{–}H)_{C_2H_4}$	$^3J(Pt\text{–}H\text{-}2)$	$^2J(Pt\text{–}C\text{-}2)$	$^3J(Pt\text{–}C\text{-}3)$	$^4J(Pt\text{–}C\text{-}4)$	$^1J(C_2\text{–}H_2)$ Complex	$^1J(C_2\text{–}H_2)$ Ligand	$^1J(C_3\text{–}H_3)$ Complex	$^1J(C_3\text{–}H_3)$ Ligand
X = C_2H_4											
NH_2	61.0	164	164	n				182	175	165	160
CH_2CH_3	60.5	164	164	35.0[a]				182	175	165	160
CH_3	60.5	165	165	34.5[a]				177	174	172	160
CH_2OH	61.0	165	165	35.5[a]				191	176	167	163
H	61.0	165	164	36.0[a]				189	181	171	164
Cl	62.0	168	164	35.0[a]				188	181	175	169
Br	61.0	168	165	35.0[a]				193	180	175	168
COOH	64.0	165	168	35.0[a]				192	182	174	170
$CO_2C_2H_5$	61.0	165	167	35.0[a]				186	180	172	167
$COCH_3$	61.0	163	167	35.0[a]				185	178	170	164
CN	63.0	170	160	36.0[a]				185	183	175	170
X = CO[b]											
CH_3				30	12.6	32.5	7.8				
H				30	11.2	32.1	6.4				
Cl				~29		33.6					
Br				~28	14.0	34.0					
CN				31	11.8	33.0					
Free Ethylene			156[c]								

[a] The spectra have been run at low temperature to observe the coupling. [b] We have not taken non-decoupled spectra for these compounds. [c] ref. 25, p. 333.

A correlation is found between the ^{13}C shifts of the ethylene and the Hammett σ_p parameter of R.

Changes in the Pt–CO σ-bond on variation of R influence the ^{1}J(Pt–CO) coupling constant. However, no such effect could be detected for ^{1}J(Pt–C_2H_4) in the corresponding ethylene complexes because these coupling constants are much smaller.

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