Bonding Properties of *trans*-PtCl₂ (olefin)(pyridine).
Part I: Influence of Variation of the Olefin

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The bonding properties of a series of complexes trans-PtCl₂(olefin)(pyridine) *have been investigated. The spectroscopic data (IR, Raman and ¹³C NMR) of the complexes and the positions of the π- and π*-energy levels of the olefins with respect to the platinum (5d) levels are discussed. The π-energy levels of some olefins have been measured by photoelectron spectroscopy.*

Introduction

In the last ten years many platinum(II) compounds with unsaturated ligands have been investigated by us [12, 32] and other investigators [1–4]. Complexes with ethylene, propylene, styrene, *cis*-2-butene [5] and tetramethylethylene [6] have been exhaustively studied and are well understood. Up till now, little attention has been paid to Pt complexes possessing electron withdrawing substituents such as acrylonitrile or methyl acrylate, presumably because these molecules do not easily coordinate to platinum.

In this paper the preparations of Pt complexes with these electron withdrawing olefins are discussed and their spectroscopic and bonding properties compared with the results for the corresponding complexes with electron donating olefins. Apart from Raman, IR and ¹³C NMR use has been made of PES results for the coordinating olefins.

Experimental

Most of the complexes *tr*-PtCl₂(X)(pyridine), with X = substituted olefin, were prepared by standard methods [7]. For X = *cis*-2-butene (BU), propylene (PR) and styrene (ST) the corresponding ethylene (ET) compound (*tr*-PtCl₂(C₂H₄)(pyridine)) was dissolved in CH₂Cl₂ after which the olefin was added [8]. Normally, this reaction had to be repeated in order to obtain a complete replacement of the ethylene.

In the case of vinyl acetate (VA) the ethylene compound was dissolved in vinyl acetate and the solution then heated to 50 °C. The complexes formed were recrystallized from a mixture of CH₂Cl₂ and hexane.

For the preparation of *tr*-PtCl₂(methyl acrylate) (pyridine) the ethylene compound was dissolved in methyl acrylate (MA) and the solution stirred for about two days and then heated to 90 °C for a short time. This procedure had to be repeated. Recrystallization of the compound often resulted in an oil. Solution of the complex in CH₂Cl₂ and evaporation under vacuum for some days gave the best results. However, satisfactory analytical data could not be obtained (Table I).

TABLE I. Analytical Data for *tr*-PtCl₂(X)(pyridine).

X	%C		%H	
	Calc.	Exp.	Calc.	Exp.
ST = styrene	34.74	34.63	2.90	2.85
BU = *cis*-2-butene	26.93	26.90	3.24	3.20
VA = vinylacetate	25.05	25.05	2.55	2.45
PR = propylene	24.81	25.13	2.70	2.84
ET = ethylene	22.52	22.31	2.43	2.22
MA = methylacrylate	25.05	26.44	2.55	2.74
AN = acrylonitrile	24.12	24.50	2.01	2.28

Spectroscopic Measurements

IR spectra were recorded on Beckman IR-12 and IR-4250 spectrophotometers.

Raman spectra for the solids and CH₂Cl₂ solutions were obtained using a Coderg PH 1 Raman spectrophotometer with dc detection. The 6471 Å line of a CRL-52 Kr⁺ laser was used as the exciting line.

¹³C NMR spectra were measured on a Varian CFT-20 (20 MHz) apparatus with full proton decoupling.

Photoelectron spectra of the olefins were run on a Perkin Elmer PS-18 instrument, equipped with a 584 Å (21.21 eV) He discharge source. All samples being liquids or solids, a volatile sample inlet system

TABLE II. Assignment of Bands to the Vibrations Which are Most Sensitive to Metal—Ligand Interactions (in approximate description) and the ^{13}C NMR Parameters[a] for the Olefinic Group.

Assignment X	ν(Pt–N)[b] cm^{-1}	ν_s(Pt–C$_2$)[c] cm^{-1}	ν_{as}(Pt–C$_2$)[b] cm^{-1}	$\delta^{13}C(C_\alpha)$[d] ppm	$\delta^{13}C(C_\beta)$[d] ppm	^1J(Pt–C$_\alpha$) (Hz)	^1J(Pt–C$_\beta$) (Hz)
ST	232	380	476	98.2 (137.7)	62.1 (112.3)	136	167
BU	243	380	487	91.0 (123.3)	91.0 (123.3)	150	150
VA	233	394	517	111.6 (141.7)	52.9 (96.4)	171	166
PR	247	378	477	99.5 (133.1)	71.4 (115.0)	152	159
ET	240	387	470	75.3 (122.8)	75.3 (122.8)	165	165
MA[e]	–	393	500	73.1 (128.7)	71.6 (129.9)	183	150
AN				(107.7)	(137.8)		

[a] ^{13}C chemical shifts are reported relative to TMS, using $\delta_{TMS} = \delta_{CDCl_3}$ –77.1 ppm. [b] Infrared data. [c] Polarized Raman data. [d] Free ligand chemical shifts in parentheses (ref. 15). [e] The complex gives very weak vibrational spectra in this region.

with a continuous gasflow of 0.2 torr was used. The spectra were calibrated with a mixture of Ar and Xe.

Results

The complexes of vinyl acetate and methyl acrylate can only be prepared at higher temperatures. Heating, however, must be performed very carefully because polymerization of the ligands and complexes may occur.

The ^{13}C NMR spectrum of the complex *tr*-PtCl$_2$-(MA)(pyridine) shows a doubling of the peaks for the methyl group of MA and the pyridine carbon atoms, so MA may be present in both its *cis* and *trans* configuration. VA and MA both coordinate *via* the C=C bond because the ν(C=O) vibrations shift somewhat to higher frequency (about 10 cm^{-1}). If bonding occurs *via* the C=O group a lowering in ν(C=O) frequency is expected [10, 11].

Preparation of the complex *tr*-PtCl$_2$(acrylonitrile) (pyridine) resulted in an insoluble product. The infrared spectrum indicates that acrylonitrile is coordinated to Pt *via* the nitrogen atom because ν(C≡N) (2260 cm^{-1}) is shifted to higher frequency with respect to free acrylonitrile [9, 12] (2230 cm^{-1}).

The influence of the substituent of the olefin on the spectroscopic properties of the complex *trans*-PtCl$_2$(olefin)(pyridine) will now be discussed. Table II presents the vibrational data for the skeletal vibrations (200–500 cm^{-1}) and the ^{13}C NMR results for the olefinic group in the complexes.

Although interactions with other skeletal modes have to be taken in consideration for the platinum—ligand vibrations, the Pt—Cl vibrations appear to be practically constant in this series.

Two platinum olefin vibrations are found at about 385 cm^{-1} (ν_s(Pt–C$_2$)) and 490 cm^{-1} (ν_{as}(Pt–C$_2$)) in agreement with earlier data [12]. The complexes of ST, BU and PR show nearly the same (Pt–C$_2$) frequencies as the ethylene complex. The complexes

of VA and MA, however, may absorb at higher frequencies indicating a stronger Pt—olefin bond.

The platinum—nitrogen vibrations, which are only observed in the infrared [12], are not sensitive to variation of the olefins.

The carbon-13 NMR shifts of the free and coordinated olefin are also given in Table II. The α-carbon atom is the atom with the substituent. The carbon-13 NMR spectra which are very useful for determining the type of bonding between metal and olefin show for all the complexes large upfield shifts (30–60 ppm) for the olefinic carbon atoms. This proves that all the olefins coordinate *via* the double bond in these complexes.

This also holds for the *tr*-PtCl$_2$(MA)(pyridine) compound, which is the first complex reported with an electron withdrawing substituent on the olefin. The β-carbon atom always shows a greater upfield shift than the α-carbon atom.

Both carbon atoms show platinum coupling. Some authors correlate the ^1H NMR parameters with the platinum—olefin distance [13]. Lazzaroni *et al.* [14] showed that ^2J(Pt–H$_\alpha$) increases regularly with the size of the substituent R on the olefin and that the mean value of the three platinum—proton coupling constants decreases when R becomes larger. Our carbon-13 NMR spectra, however, do not show these trends, factors other than the bulk of the substituent apparently being of more importance.

In order to explain the influence of variation of the olefin on the platinum—olefin bond, we determined the position of the π- and π^*-energy levels of the free olefins.

Photoelectron spectra [16–19] and $\pi \rightarrow \pi^*$ electronic transitions [21–25] are known for most olefins. For AN, MA and VA photoelectron spectra have been measured in our laboratory (Fig. 1).

The spectra show more or less well resolved ionization potentials in the 9–16 eV region. The assignment is based upon comparison with the known spectra of ethylene [19], propylene [18] and *cis*-
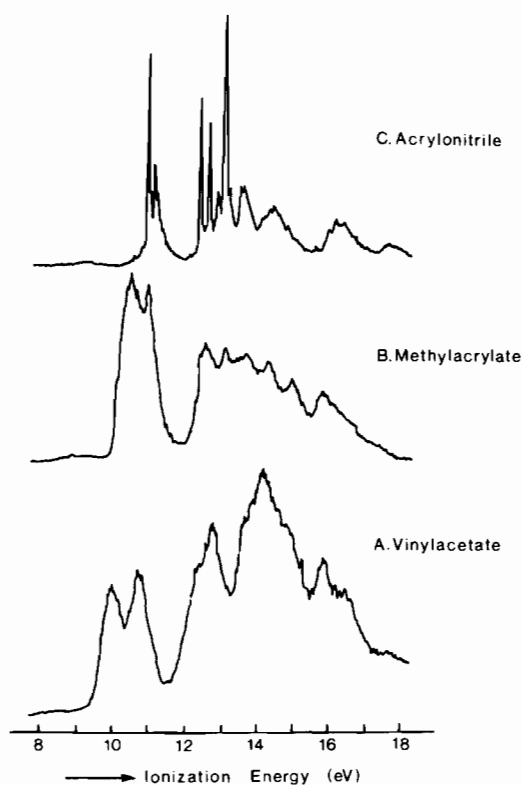
Figure 1. The photoelectron spectra of A: vinylacetate, B: methylacrylate and C: acrylonitrile.

2-butene [17] and upon vibration progression. The highest occupied orbitals in these molecules are the $\pi_{C=C}$ and, if present, the lone pair orbitals on the oxygen or nitrogen atom.

Acrylonitrile

The spectrum of this compound (Fig. 1) shows vibrational progression on the first ionization potential with spacing of 1290 cm^{-1} due to the C=C stretching vibration. The adiabatic IP is found at 10.81 eV, the vertical IP is observed at 10.95 eV. This value for the $\pi_{C=C}$ orbital fits very well with the corresponding IP's in the series of olefins. The second IP at 12.40 eV with spacing of 1920 cm^{-1} can be assigned to the bonding σ_{CN}. The third IP at 13.06 eV has hardly any fine structure and may originate from the lone pair on nitrogen [26]. The assignment of the bands at 13.7, 14.6, 16.2 and 17.7 eV, based upon MO calculations, will be published shortly [35].

Methyl Acrylate

From infrared and Raman studies [24, 27] and in agreement with the results of the MO calculations, we assumed the *trans* configuration to be the most stable one.

The 10–12 eV region shows two well resolved peaks belonging to the $\pi_{C=C}$ orbital and the lone pair orbital on oxygen. There is no well resolved vibration progression in these bands, presumably because the spectra had to be run fast since polymerization reactions diminished the number of molecules in the gas phase. The first band, however, shows somewhat more structure than the second one. Therefore, and in agreement with the MO calculations [35], the first peak is assigned to the $\pi_{C=C}$ orbital and the second to the lone pair on the oxygen atom. Further confirmation of this assignment is provided by the first ionization potential of methyl methacrylate (10.0 eV) which is lowered by 0.5 eV with respect to methyl acrylate. Approximately the same difference between the first IP's is found for ET and PR. The second peaks in methyl methacrylate and methyl acrylate differ hardly from each other.

Vinyl Acetate

The assignment of the photoelectron spectrum of VA is not so obvious. No vibrational structure is observed. The first two IP's originate from $\pi_{C=C}$ and the lone pair orbital on the oxygen atom. In comparison with molecules such as methoxyethylene studied by Bock *et al.* [28] and 4-methoxycylo-alkenes [29], we assigned the first band to $\pi_{C=C}$. Extended Hückel calculations also predict the same sequence [35].

Discussion

According to the Chatt–Dewar bonding model [30, 31] for these complexes, the strength of the platinum–olefin bond will depend on the contributions of both σ- and π-bonding. Introduction of an electron releasing group onto the olefin will strengthen the σ-bond and weaken the π-back bond with respect to ethylene, while a withdrawing substituent strengthens the π-back bond and weakens the σ-bond.

The total strength of the platinum–olefin bond will be determined by the energies, symmetries and overlaps of the orbitals involved. The symmetry properties of the orbitals will be the same for all complexes, but a change in overlap may occur.

In order to study the influence of both overlap and energy differences, a tentative energy level diagram for the orbitals involved in the platinum–olefin bond has been derived. The first ionization potentials and the $\pi \rightarrow \pi^*$ electronic transition energies of the olefins and the pyridine are known [15, 16] (Table III).

Because photoelectron spectra of the platinum compounds could not be obtained because of their low volatility, the position of the highest occupied platinum orbital is determined from the platinum to pyridine charge transfer transitions in these complexes [32, 33].

TABLE III. Ionization Energies and $\pi\rightarrow\pi^*$ Electronic Transitions of the Olefins and of Pyridine.[a]

X	IP (vert) eV	Ref.	$\pi\rightarrow\pi^*$ eV	Ref.
ST	8.50	17	4.33	21
BU	9.36	16	7.10	22
VA	9.77	–	6.42	24
PR	9.88	18	7.20	23
ET	10.51	19	7.60	23
MA	10.52	–	6.39	24
AN	10.91	–	6.42	25
Pyridine	9.60	20	4.8	–

[a] If no reference is given the data are our own measurements.

For the complexes tr-PtCl$_2$(olefin)(pyridine), $d\rightarrow d$ transitions could not be observed because they are hidden under the CT band. The position of the lowest empty orbital, therefore, is estimated from the $d\rightarrow d$ transitions in the isostructural complex tr-PtCl$_2$-(C$_2$H$_4$)(NH$_3$) [32].

For the construction of this diagram (Fig. 2) it has been assumed that the positions of the π-levels of the olefins and of pyridine do not change much on coordination. This is, of course, an approximation but it will not influence the trends observed in the level scheme.
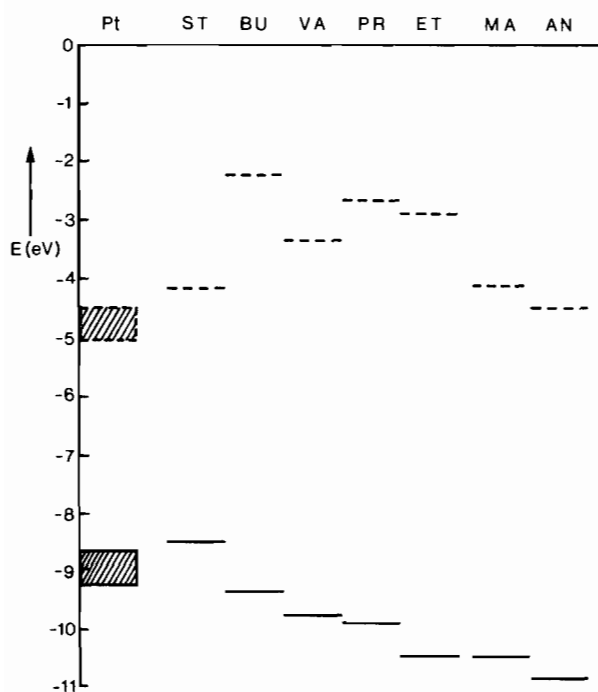

Figure 2. The approximate energy levels of platinum and olefin orbitals in $trans$-PtCl$_2$(olefin)(pyridine). —— filled platinum and olefin orbitals, – – – – unfilled platinum and olefin orbitals.

According to Fig. 2, the π-orbital of the olefin is lowered in energy on going from styrene to acrylonitrile, causing a decrease of the σ-bond strength. On the other hand, π-bonding will be stronger in the ST, VA and MA complexes than in the ethylene complex.

In order to correlate the results of this diagram with the variation of total bond strength of the Pt–olefin bond, we tried to measure the reaction enthalpies for the substitution of the olefins by CO. This was unsuccessful, however, and we therefore use the frequencies of the Pt–olefin vibrations as an indication of the bond strength (Table IV).

TABLE IV. Different Sets of Mean Values for the Olefinic Group.

X	$\bar{\nu}$ (Pt–C$_2$)[a] cm^{-1}	δ^{13}C$_{mean}$(C$_\alpha$ + C$_\beta$)$_{lig}$ ppm	δ^{13}C$_{mean}$(C$_\alpha$ + C$_\beta$)$_{compl.}$ ppm	Δ_{mean}[b] ppm
ST	428	124.0	80.1	43.9
BU	434	123.3	91.0	32.3
VA	456	119.0	82.2	36.8
PR	428	124.0	85.4	38.6
ET	429	122.8	75.3	47.5
MA	447	129.3	72.3	57.0
AN	–	122.7	–	–

[a] Mean value of symmetric and antisymmetric frequencies.
[b] $\Delta_{mean} = \delta^{13}C_{mean}$(C$_\alpha$ + C$_\beta$)$_{lig}$ $- \delta^{13}$C$_{mean}$(C$_\alpha$ + C$_\beta$)$_{compl}$.

Table IV shows that $\bar{\nu}$(Pt–C$_2$) hardly varies for the complexes tr-PtCl$_2$(X)(pyridine) when X = ST, BU, PR and ET.

Apparently, the strengthening of the σ-bond on going from ET to PR and BU (Fig. 2) is compensated by the weakening of the π-bond. On the other hand, this explanation is not valid for the ST complex. This olefin shows an increase of π- and decrease of π^*-orbital energies with respect to ethylene without further strengthening of the Pt–olefin bond. This result is attributed to the relatively small overlap between Pt and ST orbitals because of the delocalization of both π- and π^*-orbitals of styrene.

$\bar{\nu}$(Pt–C$_2$) shows a higher value for the VA and MA complex in accordance with stronger σ- and π-bonding properties in tr-PtCl$_2$(VA)(pyridine) and the much stronger π-bonding in tr-PtCl$_2$(MA)(pyridine). The same trend in the $\bar{\nu}$(Pt–C$_2$) frequency is found for other tr-PtCl$_2$(olefin)(L) complexes [34].

More information about the electron densities in the σ- and π-bond can be obtained from the ^{13}C NMR chemical shifts of the olefins in the complexes. The substituent R on the olefin affects the double bond in two ways. R releases or withdraws charge from the C=C region (effect I) and R polarizes the electron density of this bond (effect II).
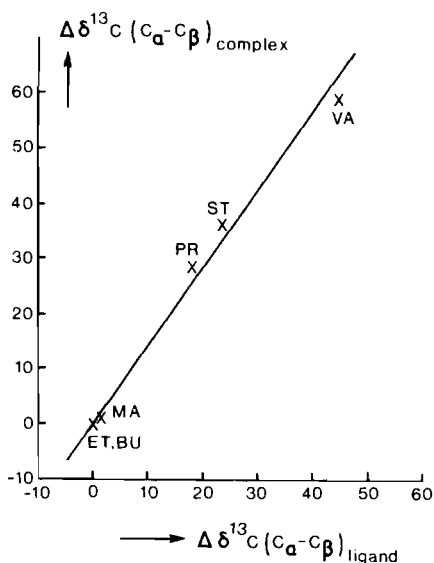
Figure 3. A plot of $\delta^{13}C(C_\alpha - C_\beta)_{complex}$ *versus* $\delta^{13}C(C_\alpha - C_\beta)_{ligand}$.

ization effects of R on the ethylenic and $\overset{C}{\underset{C}{\overset{\diagup}{|}}}$Pt groups are the same, although the polarizabilities of both groups differ.

Conclusions

Pt–C₂ frequencies indicate that VA and MA are more strongly bonded to platinum than the other olefins. The same result can be derived from the energy level diagram which shows that VA has a stronger σ- and π-bond than ethylene and MA is much more strongly π-bonded than ethylene.

The shift in $\delta^{13}C_{mean}(C_\alpha + C_\beta)$ after complexation can be explained as a shift of electron density to the σ- or from the π-orbital of platinum with respect to ethylene. This is consistent with the energy level diagram derived for these complexes.

Acknowledgments

Effect I causes a change in mean chemical shift of C_α and C_β relative to the mean shift of ethylene. The difference in shifts for C_α and C_β is caused by effect II. Table IV shows that the free olefins ST, BU, PR and AN have about the same mean shift as ethylene which means that no electron donation or withdrawal by R occurs with respect to ethylene. Vinyl acetate shows an upfield shift and the acetate group will therefore donate charge to the double bond. Methyl acrylate withdraws electron density from the C=C bond and shows a downfield shift with respect to ET. Effect II represents the polarization of the C=C bond by R, the order of increasing polarization being (Table II): VA > AN > ST > PR > MA > ET, BU.

Coordination of the olefins causes a smaller variation of the mean shift of C_α and $C_\beta(\Delta_{mean})$ with respect to the free ligands for ST, BU, PR and VA than for ethylene. Thus more charge has been withdrawn by platinum in the former complexes. This effect will be caused by the weaker σ-bond or stronger π-bond of ethylene or a combination of both effects. For the methyl acrylate complex Δ_{mean} is larger than for ethylene presumably because of the much stronger π-bond between Pt and this olefin. These variations of electron density in the σ- and π-bond between platinum and the olefin are in accordance with the position of the energy levels in the level scheme (Fig. 2).

In Fig. 3 the difference between the shifts of C_α and C_β for the free ligand is plotted against the difference in C_α and C_β shifts in the complexes. A linear relationship is found. This means that the polar-

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