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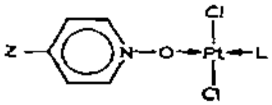
PYRIDINE *N*-OXIDE COMPLEXES OF PLATINUM(II):



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CONTENTS

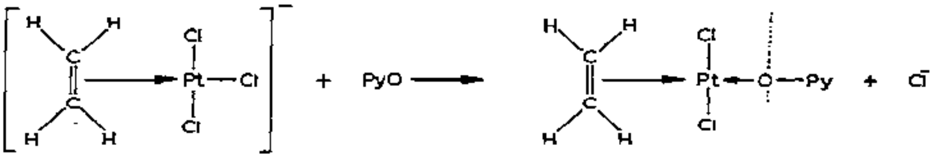
A. INTRODUCTION

Catalytic chemistry has undergone a revolution in the past decade partly because soluble complexes of transition metals have been found to be catalysts of unusual activity and selectivity. In particular, the isolation and characterization of platinum, palladium, and rhodium complexes and their demonstrated catalytic activity have given new impetus to the view that many of the important heterogeneous reactions of petrochemical interest, catalyzed by these supported metals, depend on the formation and reaction of complexes as intermediates.

Platinum(II) complexes are particularly amenable to study because they are readily prepared and are stable crystalline compounds. The bonding of the ligands to the metal is of intrinsic interest because catalytic properties must be intimately linked with such a coordination process. During the past ten years our laboratory has been concerned with the nature of the bonding between the ligand and the metal. If several olefins are competing for a site on platinum, which olefin will win, by how much, and why? Can the multiple bond character of an unsaturated ligand (and hence its reactivity) coordinated to platinum be influenced by the other ligands simultaneously coordinated and how can this effect be measured and controlled? Can olefin coordination influence the bonding strength of the protons on the olefinic carbons? What effect does solvent have on labilizing coordinated ligands? These are some of the questions we have tried to answer by the study of platinum complexes; their importance to catalytic activity is obvious.

In this review we will confine our discussions to the complexes in which pyridine *N*-oxide is one of the ligands, as shown in structure **1** below the title. The work that will be discussed in greatest detail is work that has been done in our laboratories during the period 1961–67.

The *N*-oxide investigations grew out of a study in which 4-vinylpyridine was used as a ligand with Pt^{II} in an effort to learn whether the coordination site on the ligand would be at the nitrogen or at the vinyl group. The preliminary work indicated nitrogen coordination and in order to force vinyl coordination various methods of tying up the nitrogen lone pair electrons were investigated. In order to determine the coordinating ability of the *N*-oxide group, pyridine *N*-oxide (PyO) was stirred with K_2PtCl_4 in aqueous solution for several days without apparent reaction*, but when $[Cl_3PtC_2H_4]K$, Zeise's Salt, was stirred with the N-oxide, the complex containing N-oxide[1] formed almost immediately:



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It is of course well known that C_2H_4 is a much better *trans* directing group than chloride; hence the relative ease of displacement.

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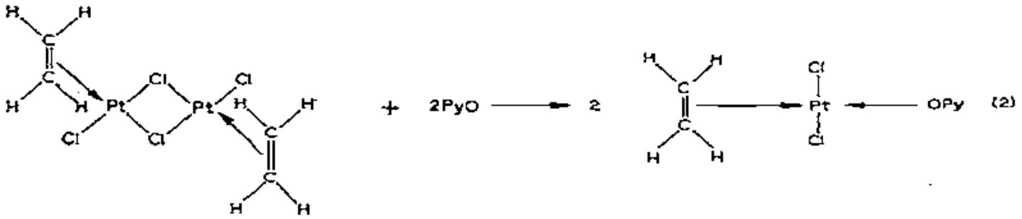
* Two groups of workers[2a,b] simultaneously reported the preparation of hexakis (pyridine *N*-oxide) complexes of Cr^{3+}, Mn^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Hg^{2+} by adding a warm methanolic solution of pyridine *N*-oxide to a methanolic solution of the appropriate hydrated metal perchlorate. The ultraviolet spectra reported were determined in acetonitrile.

B. PREPARATION AND PROPERTIES OF THE PYRIDINE N-OXIDE COMPLEXES (1)

(i) Olefinic complexes

Treatment of an aqueous solution of $[Cl_3PtC_2H_4]K$ (*e.g.* 1 mmole in 25 ml water) with excess PyO and cooling after a few minutes, precipitates the complex, **1** (L, C_2H_4). The complex may be recrystallized from chloroform or methylene chloride, or it may be thrown out of chloroform solution by dilution with pentane or hexane. An alternate and sometimes more convenient preparation consists of splitting the dimeric complex with PyO:



Reaction (2) is carried out in organic solvents because all the species are neutral.

The replacement of ethylene by other olefins is readily achieved by adding the ethylene complexes, **1**, (*e.g.* 1 mmole) to an excess of the appropriate olefin in a $CHCl_3$ solution (20 ml) in accordance with the well-known procedure[10]. Frequently, ethylene is immediately evolved. The solution is warmed and then ethyl ether or pentane is added to precipitate the new complex. Occasionally it is necessary to evaporate some of the chloroform before the ether or pentane addition.

In the case of low-boiling olefins (*e.g. cis* and *trans*-2-butene), excess olefin itself may be used as the solvent. The complexes may be recrystallized (or reprecipitated) from chloroform–ether or chloroform–pentane; the series we have prepared are shown in Table 1.

TABLE 1

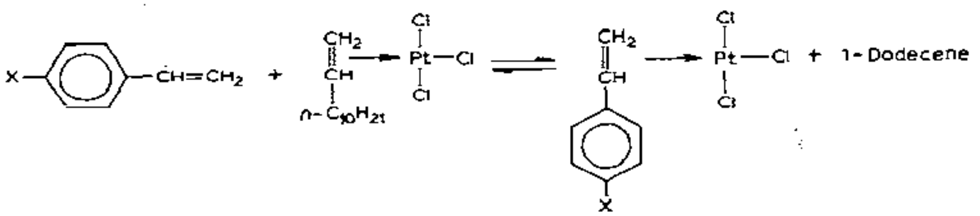
PYRIDINE N-OXIDE COMPLEXES (1) AND THEIR DECOMPOSITION TEMPERATURES[a]

$Z \diagdown L$	C_2H_4	C_3H_6	*1-Dodecene*	*cis-2-*C_4H_8	*CO*
H	146[1]	127[5]	122[6]	130[7]	151[8]
NO_2	170[2]	159[5]	154[6]		190[8]
Cl	171[3]		158[6]	156[7]	
OCH_2Ph	169[3]	128[5]			135[9]
CH_3	152[4]	126[5]	153[4]	122[7]	155[8]
OCH_3	155[4]	140[5]	124[6]		149[8]
CO_2CH_3	150[4]	148[5]	93[6]	126[7]	
CN				143[7]	170[9]

[a] Practically all these complexes decompose rather than melt. Decomposition temperatures usually depend on rate of heating and decomposition occurs over a range. These temperatures are those at which appreciable decomposition commences. The superscripts in the table are literature references. These comments apply to the data of the other tables as well.

(ii) Styrene complexes

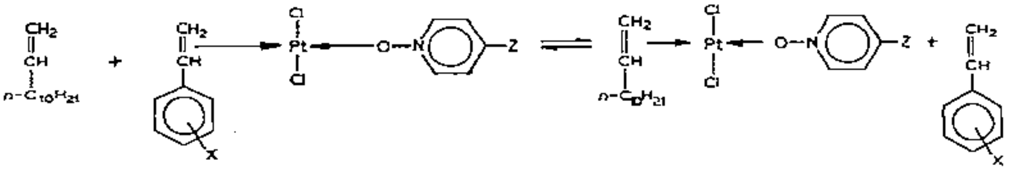
One of our early studies[11] on the stabilities of various styrene complexes concerned the effect of para substitution in styrene on the equilibrium:



(3)

This equilibrium was found to favor the dodecene complex, perhaps not unexpectedly, because the π and π^* systems are localized on the 2pπ carbons of the aliphatic olefin. However, in styrene both the highest occupied and the lowest unoccupied orbitals are delocalized over the entire carbon skeleton with the result that the overlap integrals in the appropriate metal-ligand molecular orbitals are about 30 percent lower for the styrene complex than for the dodecene complex[11].

The analogous equilibria have been investigated in which the chloride trans to the styrene has been replaced by a pyridine *N*-oxide[6]:



(4)

The compounds prepared in this series are listed in Table 2.

TABLE 2

PYRIDINE *N*-OXIDE COMPLEXES (1 L = $CH_2=CH—C_6H_4—X$) AND THEIR DECOMPSOTION TEMPERATURES[a]

X \ Z	*H*	*OCH₃*	*CH₃*	*Cl*	*NO₂*	*CO₂CH₃*	*OCH₂Ph*
4-OCH_3	118	134	152	142	137	154	
3-OCH_3	134	133	130	134	140	158	
4-CH_3	90	140	142	142	133	145	
3-CH_3	119	135	132	146	140	158	
H	139[a]	150	148	162[a]	168[a]	150	147[a]
4-Cl	131	153	172	183	164	170	
3-Cl	133	156	133	155	148	148	
4-NO_2	138	147	161	159	160	156	
3-NO_2	137	155	177	150	156	162	

[a] All these were reported in ref. 6 unless otherwise noted.

(iii) Carbonyl complexes of **1**

The facile displacement of ethylene from complexes **1** (L, C_2H_4) by carbon monoxide[8] made available the carbonyl complexes **1** (L, CO) listed in Table 1. The ethylene complexes (1 mmole) are dissolved in carefully dried $CHCl_3$ or CH_2Cl_2 (25 ml) and carbon monoxide bubbled through (or passed over) the solution until the color changes from its initial yellow color (5–10 min). At the first sign of a color change, the carbon monoxide treatment should be interrupted. Pentane is added and the solution is concentrated by evaporation under reduced pressure. The procedure of evaporation and pentane addition is repeated until the product separates in a crystalline form.

(iv) Alkyne and vinyl complexes of **1**

Alkyne complexes of **1** may be prepared by the simple procedure of replacing ethylene in the PyO complex. Another procedure[12] is to prepare the Zeise's salt analog and treat the aqueous solution with the appropriate N-oxide:

$$[C_2H_4PtCl_3]^- + \text{Alkyne} \rightarrow [\text{AlkynePtCl}_3]^- \xrightarrow{\text{PyO}} \text{AlkynePt(PyO)Cl}_2 \qquad (5)$$

Only alkynes, RC≡CR, with bulky R groups lead to stable complexes;[13a,b] the ones which have been prepared are shown in Table 3.

TABLE 3

ALKYNE AND VINYL ESTER COMPLEXES OF **1**

$L \diagdown Z$	*H*	CH_3	*Cl*	*CN*	OCH_3	$OCH_2C_6H_5$	
$(CH_3)_3C{-}C{\equiv}C{-}CH_3$	93	75	87				204[a]
$(CH_3)_2C(OH)C{\equiv}C(OH)C(CH_3)_2$	114	108	88	115	104	115	
n-$C_3H_7CO_2CH{=}CH_2$		114					
$C_6H_5CO_2CH{=}CH_2$		135					
$C_2H_5CO_2CH{=}CH_2$		110					

[a] This compound is the acetylenic analog of Zeise's Salt in which the *N*-oxide has been replaced by Cl.

Complexes **1** where L are vinyl esters were prepared[12] by displacing the ethylene in the complex **1** by the appropriate vinyl esters. The complexes **1** (L, vinyl ester) prepared are listed in Table 3.

C. THE STRUCTURE OF THE PYRIDINE *N*-OXIDE COMPLEXES, 1

Very recently, the crystal structure of the complex (**1**) (Z, OCH_3; L, CO) has been determined in this laboratory[14]; the structure is shown in Fig. 1 and the bond distances and angles are listed in Table 4.

TABLE 4

BOND DISTANCES AND ANGLES IN $Pt(CH_3OC_5H_4NO)(CO)Cl_2$ (WITH ESTIMATED STANDARD DEVIATIONS OF LAST DIGIT)

	Bond distances		
Bond	*Distance Å*	*Bond*	*Distance Å*
Pt–Cl_1	2.25 (3)	N–C_6	1.37 (3)
Pt–Cl_2	2.26 (3)	C_2–C_3	1.32 (4)
Pt–O_2	1.99 (2)	C_3–C_4	1.45 (3)
Pt–C_1	1.74 (4)	C_4–C_5	1.35 (3)
C_1–O_1	1.16 (4)	C_5–C_6	1.39 (4)
O_2–N	1.35 (3)	C_4–O_3	1.33 (3)
N–C_2	1.33 (3)	O_3–C	1.46 (4)

	Bond Angles		
Atoms	*Angles, Degrees*	*Atoms*	*Angles, Degrees*
Cl_1–Pt–Cl_2	178.1 (3)	N–C_2–C_3	122 (2)
C_1–Pt–O_2	176 (1)	C_2–C_3–C_4	116 (2)
Pt–C_1–O_1	178 (3)	C_3–C_4–C_5	119 (2)
		C_4–C_5–C_6	123 (2)
Cl_1–Pt–O_2	85.3 (6)	C_5–C_6–N	113 (2)
Cl_2–Pt–O_2	93.5 (5)	C_6–N–C_2	126 (2)
Cl_1–Pt–C_1	91 (1)		
Cl_2–Pt–C_1	90 (1)	C_4–O_3–C_7	119 (2)
		C_3–C_4–O_3	124 (2)
Pt–O_2–N	120 (1)	C_5–C_4–O_3	116 (2)
O_2–N–C_2	121 (2)		
O_2–N–C_6	113 (2)		

Although the bond angles of a compound in its crystalline state are probably not the angles of the compound in solution, there is nevertheless much merit in analyzing the molecule in terms of its structure in the solid state, since the geometry in at least one conformation with respect to the bond angles is thus known.

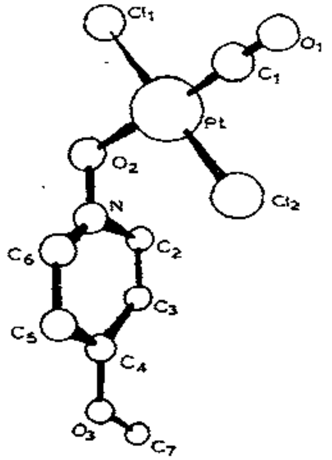


Fig. 1. The crystal structure of 1,3-dichloro-2-carbonyl-4-(4-methoxypyridine 1-oxide)platinum(II).

The position of the pyridine *N*-oxide ring is of special interest. The Pt–O–N angle is exactly 120°. The plane of the PyO ring is almost at right angles (87.5°) to the plane defined by the platinum atom and the four atoms bonded to it. Rotation around the N-O bond of about 90° in either direction would thus make the two planes co-planar and maximum steric interactions between Cl_2 (Fig. 1) and the H atoms on C_2 and C_6 would occur. Hence, with respect to rotation around N–O, the orientation shown in Fig. 1 minimizes repulsions.

The orientation with respect to rotation around the O–Pt bond is somewhat more difficult to understand. Let us analyze this particular orientation in terms of orbital overlap. For purposes of discussion let us use the coordinate system of Fig. 2 with the platinum square plane (including the Pt-O-N atoms) in the *xz* plane and the PyO in a plane parallel to the *yz* plane.

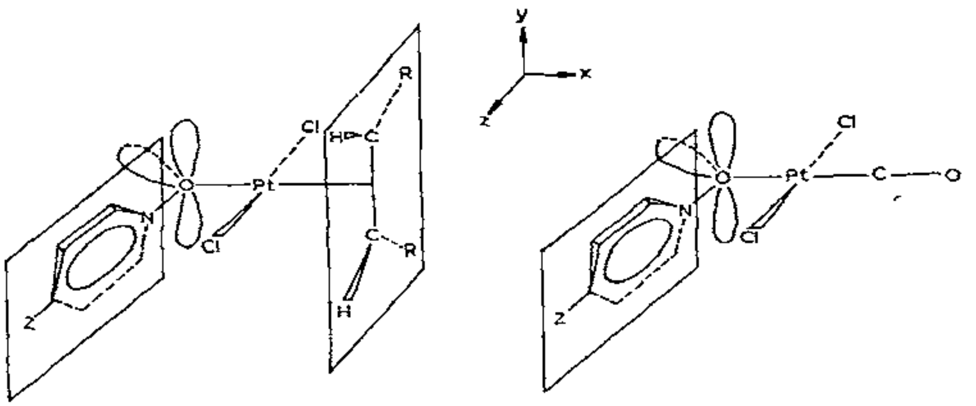


Fig. 2. Olefin and carbonyl complexes, 1 (L = olefin, CO).

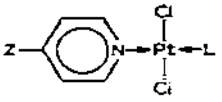
The oxygen atoms uses sp^2 orbitals for its bonding to platinum and nitrogen and thus there is a lone pair in the oxygen sp^2 orbital in the *xz* plane. There is probably little if any delocalization of this lone pair into the pyridine π system because of the somewhat unfavorable geometry, the high *s* character of the sp^2 orbital, and the low energy of the oxygen orbitals. However, the other lone pair on the oxygen atom is in an p_y orbital and in the orientation shown in Fig. 2 this orbital is parallel with and hence in the optimum geometry to overlap with the empty $6p_y$ orbital (or a dp hybrid) of platinum. Any other orientation achieved by rotation around the O-Pt bond would be less favorable. However, the overlap of O_{2p_y} and Pt_{6p_y} is probably very poor energetically. In addition, the plus charge on the nitrogen would further reduce transfer of electronic charge out of the oxygen atom. All factors considered, it is likely that the particular orientation is favored for crystal packing reasons.

The d^8 electronic configuration of the Pt^{II} atom leads to the dsp^2 square planar arrangement as expected. The filled d_{xy} and d_{xz} on platinum are of the proper symmetry to overlap the degenerate and empty π^* orbitals on C≡O. The extent of this interaction between filled d orbitals on Pt (or other transition metals) and empty π^* orbitals on CO (or on other unsaturated ligands such as olefins, or even phosphines, etc.) has been the subject of considerable discussion. To the extent that the π^* orbitals on C≡O become populated, the bonding contributions arising from population of the bonding C≡O π orbitals should be cancelled. Such cancellation should result in decreased C≡O bond order and force constant and increased C≡O bond length in the complex as compared to free carbon monoxide. Furthermore, the greater the interaction between the d and π^* orbitals, the shorter the Pt-C bond distance, if no other effects are present. The actual bond distances, and the value of the C≡O stretching frequency, should provide essential data for evaluating the extent of the backbonding. At this point, let us only consider the x-ray data.

The Pt-O bond length of 1.99 ± .02 Å agrees very well with the distance of 2.05 Å expected from the sum of the appropriate covalent radii[14]. Accordingly, there appears to be little if any double bond character between these atoms even though their p orbitals might be in a favorable orientation for small overlap, as pointed out above. The C≡O bond length of 1.16 ± .04 Å is not significantly different from the value of 1.13 Å observed for free carbon monoxide. This fact would argue for little, if any, backbonding from the Pt to the C≡O. However, the Pt-C bond distance of 1.74 ± 0.04 Å is considerably smaller than the 2.00 Å calculated as the sum of the Pt^{II} atomic radius (1.31 Å) and the sp carbon radius (0.689 Å). A similarly short Pt-C bond distance of 1.78 A has been found [15] in the square planar cation, *trans*-$[PtCl(CO)][P(C_2H_5)_3]_2]^+$. It may very well be that the normal Pt-C bond in the carbonyl is a very strong sigma bond resulting from excellent overlap of the very basic lone pair in the carbon of CO and a dsp^2 orbital of the platinum and no contribution from backbonding is required. The backbonding problem will be discussed further in connection with the infrared data.

D. DIPOLE MOMENTS OF THE PYRIDINE-*N*-OXIDE COMPLEXES (1)

Since the x-ray data of **1** (L = CO, Z = OCH_3) showed the *trans* structure and all the carbonyl complexes were prepared similarly, it can be assumed that all these complexes have the same configuration. Dipole moment measurements on the pyridine complexes, **2**, analogous to **1**, showed that the moments for the carbonyl complexes, **2** (L = CO) are higher than those of the corresponding olefin



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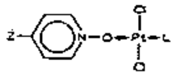
complexes of **2** (L = olefins)[9,16]. In the olefin complexes of **1** (L = C_2H_4) the dipole moments were again found to be lower than those of the corresponding carbonyl complexes. The dipole moment data for these complexes are shown in Table 5.

TABLE 5

DIPOLE MOMENT DATA FOR *N*-OXIDE COMPLEXES[a]



L	*Z*	$_TP^b$	$_EP^{b,c}$	$_OP$	*Complex.* μ *(D)*	*Free PyO* μ *(D)*[d]
C_2H_4	H	976	75	890	6.6	4.24
C_2H_4	CH_3	1145	79	1054	7.2	4.74
C_2H_4	OCH_3	850	86	751	6.1	5.08
C_2H_4	NO_2	150	81	57	1.7	0.69
CO	H	1298	69	1219	7.7	4.24
CO	CH_3	1566	73	1482	8.5	4.74
CO	OCH_3	1639	75	1553	8.7	5.08

[a] The dipole moment measurements were made by the procedure described by J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1959) 705 using a W.T.W. Dipolmeter, Type DMO1 in dry benzene at 25°. [b] $-\Delta\nu/\omega$ was assumed to be 0.65 for every complex. [c] $_AP$ is assumed to be 15 percent of $_EP$ and these latter values are calculated from the approximations given by A. Vogel, *J. Chem. Soc.*, (1948) 1842. [d] Values for the free PyO's: Z=H, E. P. Linton, *J. Am. Chem. Soc.*, *62* (1940) 1945; Z=CH_3, OCH_3, NO_2, A. R. Katritzky, E. W. Randall and L. E. Sutton, *J. Chem. Soc.* (1957) 1769.

E. THE INFRARED SPECTRA OF THE OLEFIN COMPLEXES, (**1**, L = OLEFIN)

(i) Introduction

Infrared spectra of the olefin complexes, **1**, have been studied in order to secure information with respect to four major problems: (a) the C=C stretching frequencies and hence the extent of double bond character in the complexed olefin; (b) the N-O stretching frequency in the free and complexed PyO; (c) the metal–oxygen stretching frequency as a function of substitution in the PyO ring and as a function of the nature of L; and (d) the metal–olefin stretching frequency.

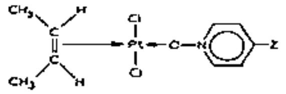
(ii) The olefin stretching frequency

It is of course well known that the olefin stretching frequency customarily found at about 1620 cm^{-1} is shifted appreciably to lower frequency ($\sim$1500 cm^{-1}) when the olefin is complexed to a transition metal. In the free olefin, the π bonding orbital is concentrated between the double bonded carbon atoms. On complexing, this orbital becomes shared by the metal atom and now the molecular orbital encompasses three atoms, thus obviously diluting the electron density between the doubly-bonded carbon atoms. The bond order is now considerably less than two, resulting in a smaller force constant and a C=C stretching frequency at lower frequency. Any back-donation from filled metal d orbitals into the antibonding orbitals of the olefin further reduces the bond order and augments the decrease in stretching frequency.

The C=C stretching frequency is generally a low-intensity band for highly symmetrical olefins and when an aromatic system such as the PyO moiety is also present, it is difficult to identify the band associated with the olefinic C=C. It was originally reported[4] that the $\nu_{C=C}$ of complexes 1 (L, C_2H_4) decreased linearly as the electron-releasing character of Z increased. These data, however, are now suspect because the ethylene stretching frequencies may have been confused with aromatic C=C stretching modes. When L is *cis*-2-butene it is comparatively easy to identify the C=C frequency. Accordingly, the *cis*-2-butene series of complexes 1 were prepared and the $\nu_{C=C}$ measured[7]. The results, reproduced in Table 6, show that the stretching frequency is essentially independent of the nature of the Z group on the PyO.

TABLE 6

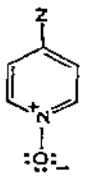
INFRARED SPECTRA OF



Z	$\nu_{C=C}$ (cm^{-1}) Mull	$\nu_{C=C}$ (cm^{-1}) KBr Pellet
H	1503	1502
Cl	1506	1503
CO_2CH_3	1503	1504
CH_3	1506	1502
CN	1504	1502

(iii) *The N-O stretching frequency*

There is no question but that in PyO the lone pair of electrons in a p-orbital on oxygen is delocalized over the ring:



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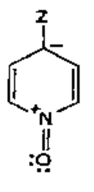
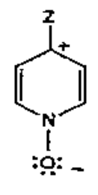


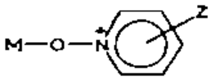
(b)



(c)

Electron-withdrawing substituents enhance the electron distribution represented by (b) with consequent shortening of the N-O bond, reduction in the dipole moment, and decreased basicity as compared to the unsubstituted PyO. When Z is electron-releasing, the enhancement of the electronic distribution represented by (c) results in the opposite effects. Protonation or metalation of PyO occurs exclusively with the oxygen atom 2pπ lone pair so that electronic distributions in the resulting species corresponding to the double bond N=O in (b) are no longer possible and hence complexation results in a lower N-O bond order and hence a lower ν_{N-O} in the complex as compared to the free ligand.

There is a considerable literature dealing with ν_{N-O} in complexes of the type



as a function of the position and nature of Z and as a function of M. The reader is referred to two recent excellent reviews that cover this problem in great detail[17,18].

All literature data are in agreement in showing that complexing PyO with a metal (or proton) lowers ν_{N-O}. The greater the electron-withdrawing effect of Z (positive σ or σ^+ values) the greater the lowering should be, since complexation involves transfer of electronic charge out of the N^+-O^- and into the metal, and the positive σ substituents place the highest concentration of electronic charge between N and O in the free ligand[17,20,21]

In the complexes **1** (L, C_2H_4) the opposite effect has been reported[4], but there is now considerable doubt about the validity of this conclusion. In the earlier correlation[4] the band at 1258 cm^{-1} was assigned to ν_{N-O} of the free 4-NO_2PyO whereas it now appears that the band observed and reported at 1271 cm^{-1} is the more appropriate one to use for the purpose. If the higher band is used for the free ligand, then the change in this band to 1250 cm^{-1} on complexation represents the largest shift in the series. Exact assignments of bands are very difficult because the bands selected may not be pure vibrational modes but may be coupled with other vibrational and rotational modes.

There is some question as to exactly which property of Z best correlates with ν_{N-O}. Some investigators have used σ^+ and others σ and still others[19,20] mixed values of σ, σ^- and σ^+. Das and Kitching[17] using σ^+ constants because complexation at oxygen, as shown above, enhances the development of positive charge at position-4. Ragsdale[18] prefers a substituent constant defined as

$$\rho\sigma_{PyO} = \Delta pK_{BH+}$$

where $\Delta pK_{BH+} = pK_{BHO+} - pK_{BHZ+}$, the pK's being experimental values of the conjugate acids of the unsubstituted and substituted PyO's. A value of 2.09 was chosen for ρ in order to get values of σ_{PyO} most in agreement with the reported values of σ^+, σ, σ^- and σ_R.

Excellent correlation of the ν_{N-O} and ν_{O-M} of 4-Z-pyridine *N*-oxides with the σ^+ values of Z have been obtained with nickel[20] and with the octahedral $TiF_4(PyO)_2$ complexes[21].

(iv) The Pt-O stretching frequency

There seems to be little question that the Pt-O bond is essentially a sigma bond with very little if any backbonding. This suggestion[22], made before the X-ray data were available, is reinforced by the normal Pt-O bond length recently determined. The stretching frequency ν_{Pt-O} in complexes **1** (L, C_2H_4) has been shown to occur in the far infrared as a weak shoulder at 323 cm^{-1}. The position of the band was constant and essentially independent of the substituent on PyO.

There has been considerable discussion[17] about the expected effect of Z on ν_{M-O} in complexes of PyO; one might expect that the effect of Z should be similar but opposite to the effect on ν_{N-O} and one such example[21] has been reported. The effect of Z on acid strength of substituted $PyOH^+$ is quite pronounced; the conjugate acid of 4-nitropyridine *N*-oxide has a pK_a of -1.7 while that of the 4-dimethylamino compound is 3.9. One would think that if the metallation, being a sigma bonded process, were similar to the protonation, it would be similarly responsive to changes in Z. It may very well be that in the complexes **1**, where the Pt-O bond is almost exclusively a sigma bond, most of the effect of Z is felt at the N-O bond and little at the Pt-O bond. The fact that ν_{Pt-O} is a weak band doesn't help matters. This aspect of the PyO complexes needs further investigation.

(v) The olefin-platinum stretching frequency

Recently[23,24] infrared and normal coordinate analyses of Zeise's Salt, $K[Cl_3Pt(C_2H_4)]H_2O$, and Zeise's dimer, $[Cl_2Pt(C_2H_4)]_2$, were reported. The platinum-olefin stretching frequency was assigned at 407 and 408 cm^{-1} in the salt and dimer respectively.

However, in another investigation[25] the band at 403 and a second band at 491 cm^{-1} were assigned to the antisymmetric and symmetric ring deformations respectively in Zeise's Salt. These deformations of the platinum–carbon–carbon ring were considered equivalent to the Pt-C stretching modes. The failure to properly assign the band at 490 cm^{-1} in the earlier work was attributed to the overlapping of this band with the broad vibrational band of water which is centered at about 500 cm^{-1} in the spectrum of the ethylene complex. The bands at 482, 410 and 365 cm^{-1} were assigned[25] to the infrared active platinum–olefin stretching modes of the dimer.

In the ethylene pyridine *N*-oxide complexes[22], there is a band in the spectra of all the complexes at approximately 412 cm^{-1}, which may tentatively be assigned to the platinum–olefin stretching frequency and which appears to vary only slightly as a function of Z in the pyridine *N*-oxide.

For the corresponding *cis*-2-butene series, the platinum–olefin frequency remains approximately constant at 405 cm^{-1}; this is virtually the same frequency as for the *cis*-2-butene analogue of Zeise's Salt[24,25].

F. THE INFRARED SPECTRA OF THE CARBONYL COMPLEXES, 1 (L, CO)

The carbonyl stretching frequencies of complexes, 1 (L, CO) are particularly susceptible to experimental investigation because ordinarily only one intense, easily identifiable band is present in the infrared spectrum. The positions of this band in some carbonyl complexes are shown in Table 7. The data[26] show that $\nu_{C\equiv O}$ is largely independent of Z in the 4-position of PyO in these complexes. This also appears to be the case when the ligand is aniline instead of PyO. With both ligands, there is essentially no backbonding from the platinum atom. With pyridine (Py) as a ligand, there does appear to be a small but definite trend toward higher $\nu_{C\equiv O}$ with increasing electron-withdrawing character of Z[9]. There is of course much better backbonding possibilities with Py than with either PyO or aniline; with larger σ, the bonding with the Ptd_{xz} (assuming perpendicular orientation of the Py ring, Fig. 2) orbital is enhanced and the *trans* carbon monoxide becomes more like free carbon monoxide with its higher $\nu_{C\equiv O}$.

TABLE 7

CARBONYL STRETCHING FREQUENCIES (cm^{-1}) IN THE INFRARED SPECTRA OF COMPLEXES, L–Pt(Cl)$_2$CO

Z/L	*4-Z-PyO*					
	CHCl$_3$	*Acetone*	*4-Z-Py*[a]	*4-Z-Aniline*[a]	σ	σ^+
$OCH_2C_6H_5$	2118	2104, 2085	2128		–.42	
OCH_3	2116	2107, 2087	2129	2131	–.27	–.80
$C(CH_3)_3$			2131		–.19	
CH_3	2117	2108, 2088	2132	2132	–.17	–.32
C_2H_5			2132		–.15	
H	2122	2106, 2087	2133	2132	0	0
C_6H_5			2134		0.01	
CH_2OH			2134		.10	
Cl				2130	.23	.11
CO_2CH_3			2139		.31	
$COCH_3$			2135		.52	
CN	2127	2090	2140		.63	
NO_2	2124	2087	2147		.78	.79

[a] Determined in CHCl$_3$ solution.

The magnitudes of the stretching frequencies shown in Table 7 are of interest. Free carbon monoxide, which has essentially a zero dipole moment, is thought to possess essentially triple bond character and a bond order of approximately three. Its solution in CHCl$_3$ shows $\nu_{C\equiv O}$ of 2143 cm^{-1}, the center of the

TABLE 8

ν_{C-O} (cm^{-1}) IN SOME CARBONYL COMPOUNDS

Compound	ν_{C-O}, *cm*$^{-1}$
CO^+	2184[a]
H_3BCO	2165[b]
CO (solution)	2143[a]
$Ni(CO)_4$	2057[b]
CO (chemisorbed on Pt)	2050[c]
$CH_2{=}C{=}O$	1935
$F_2C{=}O$	1928
$[Co(CO)_4]^-$	1883[b]
$Cl_2C{=}O$	1835
$[Fe(CO)_4]^{--}$	1788[b]
H_2CO	1735
$(C_6H_5)_2CO$	1700
$4\text{-}NO_2Py\text{-}Pt(Cl_2)CO$	2147[d]
$[PtCOCl_2]_2$	2152[e]

[a] G. Herzberg, *Spectra of Diatomic Molecules*, D. Van Nostrand Co., Princeton, N.J. (1955) pp.522, 534. [b] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, J. Wiley and Sons (1963) p. 177. [c] J. F. Harrod, R. W. Roberts and E. F. Rissmann, *J. Phys. Chem.*, *71* (1967) 343. [d] A. R. Brause, M. Rycheck and M. Orchin, *J. Amer. Chem. Soc.*, *89* (1967) 6500 [e] R. J. Irving and E. A. Magnusson, *J. Chem. Soc.*, (1956) 1860.

doublet P (2120 cm^{-1}) and R (2175 cm^{-1}) branches, which characterize the gaseous molecule. The stretching frequencies of a variety of C≡O compounds are shown in Table 8.

These stretching frequencies in general make sense in terms of the known bonding characteristics of carbon monoxide. There are two lone pairs of electrons on CO, neither involved substantially in bonding the carbon to the oxygen atom. One pair is on oxygen in an orbital largely *s* in character, while the other lone pair is on the carbon atom and has a high degree of *p* character (Fig. 3a). It is the pair of electrons in this latter orbital which is responsible for coordination to metal atoms forming a strong *σ* bond with the metal—in the case of Pt by overlap with

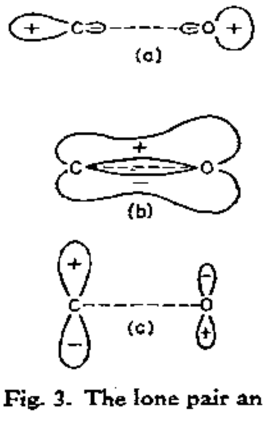


Fig. 3. The lone pair and *π* orbitals of carbon monoxide.

a dsp^2 empty orbital. The bonding between carbon and oxygen in carbon monoxide results from a σ bond mostly in the oxygen atom, and a set of π orbitals mostly on the oxygen atom. Fig. 3b shows one of the π orbitals; the other is at right angles, *i.e.*, in front and behind the plane of the paper. There is in addition a set of π^* orbitals, mostly on the carbon atom and Fig. 3c shows one set; the other set is at right angles, *i.e.*, in front and behind the plane of the paper. In the transition metal complexes, it is assumed that backbonding from a metal orbital results from overlap between the metal orbital, *e.g.*, d_{xz} and the empty π^* orbital of CO, which is conveniently mostly on the carbon, as shown in Fig. 3c. Electron occupation of the π^* orbitals reduces the contribution to the C≡O bond order made by electrons in bonding orbitals with a resulting decrease in the bond strength and a decrease in $\nu_{C\equiv O}$. Occupation of antibonding orbitals and electronegative effects can be systematically invoked to explain the data of Table 7. From these data one would conclude that in the complexes (**1**, L, CO) there is relatively little backbonding from the platinum, and the bonding between CO and the Pt results almost exclusively from sigma bonding between the two moieties*.

A study of the effect of solvent[26] on the spectra of the carbonyl complexes **1** uncovered some unusual behavior. Infrared spectra of acetone solutions of most of the complexes showed two carbonyl bands, the relative intensities of which changed with time. These results are shown in Table 7 under the acetone column. A typical example of the change which occurs with the $4\text{-}CH_3PyOPt(Cl)_2CO$ in acetone is shown in Fig. 4. The band at 2108 cm^{-1} observed initially diminishes

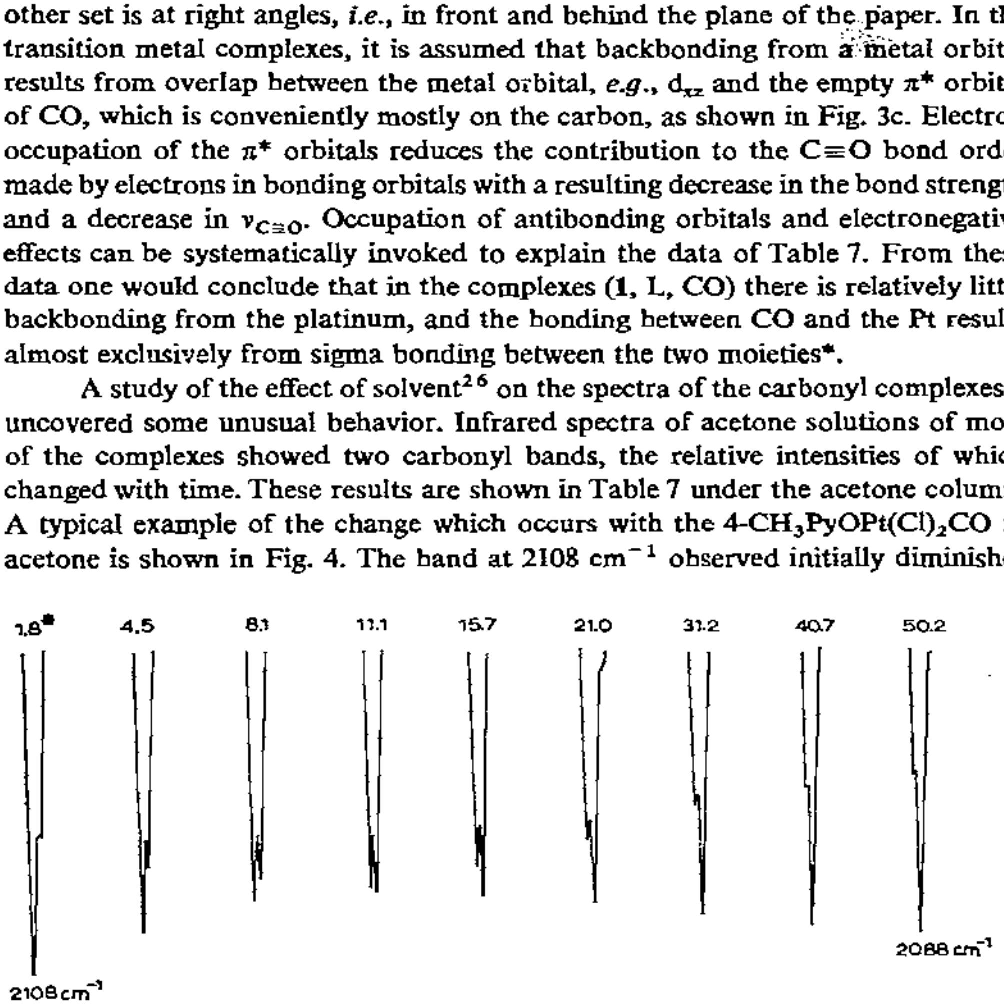


Fig. 4. The carbonyl bands of $(CH_3PyO)Pt(CO)Cl_2$ in acetone solution (concentrations: complex, 0.13 mmol/ml; H_2O, 0.16 mmol/ml). * minutes after preparation of solution.

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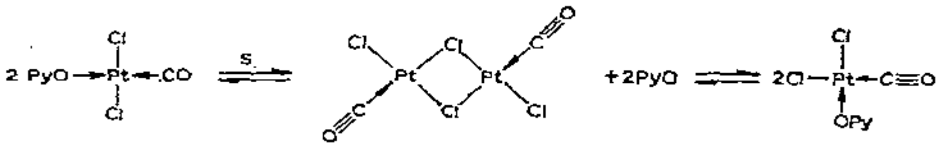
* Very recently, a study[27] of the intensities of the $\nu_{C\equiv O}$ in a variety of carbonyls and chemisorbed CO has appeared. In this article it is pointed out that CO chemisorbed on *e.g.* ZnO has $\nu_{C\equiv O}$ of 2210 cm^{-1}. It is suggested that a reversal of the normal dipole direction in C≡O occurs in adsorbed CO and that σ and π bonding contributions affect the bond dipole oppositely where π bonding becomes important. It remains to be determined how these arguments accommodate the spectra of complexes **1**.

on standing and a new band at 2088 cm^{-1} appears. The rate of change was found to be a function of: (a) the quantity of water present in the acetone and (b) the nature of Z. Using acetone distilled from P_2O_5, a solution of 50 mg/ml $C_6H_5CH_2$-PyPt$(Cl)_2$CO was prepared. The time required for the two bands to reach equal intensity was 28 min; a second solution with 0.25% (by vol) H_2O required 9.5 min; and a third solution with 0.50% (by vol) H_2O required 2.8 min. The rate of change for different Z substituents using the same supply of acetone was $-NO_2 \equiv CN \gg H > CH_3 > OCH_3 \cong OCH_2C_6H_5$. In these time experiments ($Z = OCH_3$) the chemical shift of the water was observed[26] to move downfield with time. The experiment was repeated with an olefin complex and a similar down field shift of the water protons was observed. Although further work is required to explain this phenomenon, it is clear that water is participating by coordination to the platinum.

The observed changes are difficult to explain with certainty at this time. There are a group of possible explanations. The complexes may in fact be partially dissociated in solution, or they may be highly solvated, thus loosening the ligand–metal bond. Finally, there may be a true *trans* → *cis* isomerization in solution or some combination of the above possibilities.

It is instructive to consider the possibility that the observed changes are due to a *trans* → *cis* isomerization. The *cis* isomer would be expected to possess the higher dipole moment and thus be more stable in the more polar acetone as compared to chloroform or benzene. A small amount of water may initiate the isomerization; it may also increase the dielectric constant of acetone and hence accelerate the isomerization. However, the change to lower frequency in the more polar solvent needs to be rationalized. It would be expected that a π-bonding ligand *trans* to CO would compete for the Pt d_{xy} (Fig. 2) orbital and that such competition would lead to a $\nu_{C\equiv O}$ higher than one to be expected in the absence of a *trans* π ligand. If PyO were a π-bonding ligand, its acetone-catalyzed isomerization from a *trans* to a *cis* position relative to CO would account for the lower $\nu_{C\equiv O}$. However, we have indicated above that PyO *trans* to CO is probably not a π-bonding ligand; if it were, perhaps even slightly, the change to lower $\nu_{C\equiv O}$ would be consistent with the *trans* → *cis* isomerization.

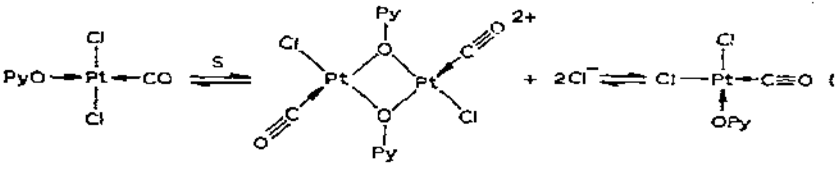
If a (reversible) isomerization does occur, what is its mechanism? The most probable[28,29] sequence for obtaining a *cis* isomer is:



(6)

In support of such a possibility, the infrared spectrum of the 4-NO_2PyO complex in acetone was carefully examined and bands due to free 4-NO_2PyO were observed. The dimer may thus exist in solution but when pentane is added, the equilibrium is rapidly shifted and only the relatively insoluble complex is isolated. However, the dimer in solution should be capable of detection. The spectrum of the dimer has been reported[30] to show a $\nu_{C\equiv O}$ of 2152 cm^{-1} in mull but this high frequency was not observed in the acetone.

Alternately, the PyO can act as a bridging ligand (7):



(7)

Copper complexes with bridging PyO's are known[31].

The fact that the complexes in which Z is most electron withdrawing undergo a very fast change in acetone is not unexpected. Electron-withdrawing substituents should facilitate solvent (nucleophilic) attack and should weaken the Pt-O bond. In fact with $Z=NO_2$ and CN, only one isomer, the one with the relatively low $\nu_{C\equiv O}$ could be observed in the acetone. It is assumed that the conversion is so fast in these cases that the other isomer with the (presumed) higher $\nu_{C\equiv O}$ could not be detected. Addition of hexane to the acetone solution of the 4-NO_2PyO complex precipitated an isomeric complex with a lower $\nu_{C\equiv O}$ (mull) and other small changes elsewhere in the infrared spectrum. Dipole moment measurements in benzene of the two isomers gave the same value and in benzene both isomers have the same $\nu_{C\equiv O}$. Clear-cut evidence that we are dealing with isomers is still lacking. Recent work indicates that when N-oxide complexes are dissolved in coordinating solvents partial replacement of the PyO occurs[20]. Part of the difficulty in interpretation of the solvent effects may be due to the fact that a variety of species are in solution. Attempts to isolate the isomer with the low $\nu_{C\equiv O}$ frequency in other 4-Z-PyO cases, *e.g.*, by precipitation out of an aged acetone solution, always resulted in the isolation of the original isomer with the higher $\nu_{C\equiv O}$ (mull). Solution in acetone produced the same cycle of initial high $\nu_{C\equiv O}$, gradually changing to the lower $\nu_{C\equiv O}$.

G. NMR SPECTRA OF THE PYRIDINE N-OXIDE COMPLEXES (1)

(i) Introduction

In analyzing the nmr spectra of the complexes (**1**) (L, C_2H_4), the data of interest are the chemical shifts of the olefin protons, the chemical shifts of the protons on the N-oxide moiety, the spin-spin coupling constant J between ^{195}Pt-^{1}H (ethylene), and the way in which these parameters vary as a function of Z. The Pt-H coupling occurs because the platinum 195 isotope with a nuclear spin of 1/2 is present to the extent of 33.7% in naturally-occurring Pt. The spins of this isotope of Pt and the protons of ethylene can couple and as a result the proton signal appears as a triplet at about 5 ppm with the two side peaks equal in total area to 1/2 that of the center peak; the center peak represents 2/3 of the protons which are not coupled because 2/3 of the Pt present consists of isotopes of Pt with zero spin. No coupling between the ^{195}Pt and the 2,6 protons of the *N*-oxide is observed; low temperature experiments were not performed.

(ii) The olefinic protons

The chemical shift of the protons of pure ethylene dissolved in $CDCl_3$ occurs at 5.41 ppm. Complexation of the ethylene to platinum results in an upfield shift of the proton signal. The extent of this shift is influenced by the ligand *trans* to the ethylene. When this ligand is a 4-substituted pyridine *N*-oxide, the nature of the substituent also influences the chemical shift, as can be seen from the data[32] in Table 9. The Pt atom shifts the magnetic dipole of the ethylenic π bond toward the metal with the expected upfield shift. The data show that when Z on PyO is NO_2, the chemical shift of the ethylene protons is closest to the free ethylene. This is the expected result, since the NO_2 is the strongest electronegative group and would tend to pull Pt electrons away from the ethylene, thus decreasing the shielding of the ethylene protons.

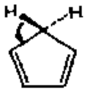
TABLE 9

NMR DATA OF ETHYLENIC PROTONS IN COMPLEX 1 (L, C_2H_4)

Z	*Chemical shift of ethylenic proton in* 1^a, δ	$J_{Pt^{195}-H^1}$ *cps*	*Solvent*
NO_2	4.656[b]	—[c]	$CDCl_3$
$COOCH_3$	4.438	71.0	$CHCl_3$
Cl	4.383		$CHCl_3$
H	4.383	68.8	$CDCl_3$
CH_3	4.323	69.0	$CDCl_3$
OCH_3	4.350	67.5	$CDCl_3$
$OCH_2C_6H_5$	4.296	67.1	$CDCl_3$
$[(C_2H_4)PtCl_3]^-K^+$	4.408	66.0	CH_3OH
	4.408	66.0	4% w/v HCl in CH_3OH
	4.678	65.2	D_2O

[a] The internal reference is tetramethylsilane or 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt. [b] We are indebted to Dr. T. Flaut for obtaining this spectrum at 100 mc using a Varian C-1024 Time Averaging Computer. [c] $J_{(Pt-H)}$ appears to be 71.7 cps after 23 scans; however, after 100 scans all peaks broaden and the satellite peaks are indefinite, while after 491 scans they are no longer present and the ethylene peak is broad. This may be a consequence of a time-averaged phenomenon initiated by a catalyst.

The coupling constants reported in Table 8 require comments: Internuclear coupling between near-neighbor atoms with nuclear spin occurs when the atoms are linked through orbitals with some *s* character. In a compound containing a CH_3-Pt bond, as in $[(CH_3)_3Pt]NO_3$, in which the carbon atom is bonded to Pt *via* an sp^3 orbital on carbon overlapping a dsp^2 orbital on Pt, the ^{195}Pt-^{1}H coupling constant[33] has the very high value of 77.3 cps. It will be noted from Table 9 that the coupling constants for ethylene protons in the ethylene-Pt complexes are all quite high and in the range 66–71 cps. Since the metal → ligand (Fig. 2) π bond made from Pt d_{xy} and $C_{2p\pi^*}$ orbitals has no *s* character, the ligand → metal bond is obviously responsible for the coupling. Three different kinds of atomic orbitals are involved; the carbon sp^2 orbitals bonding the H atoms, the $2p\pi$ orbitals of the carbon atoms which constitute the donor portion of the σ bond of the complex and a dsp^2 orbital of Pt. In order for the $C_{2p\pi}$ orbitals to obtain some *s* character, there must be some mixing of the σ and π bonds of ethylene analogous to that which occurs in cyclopropane or analogous to that which occurs in hyperconjugation, as for example in cyclopentadiene:



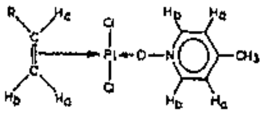
In the case of coordinated ethylene, there must be substantial *s* character in the C_2H_4 → Pt sigma bond because the coupling is large. The question remains as to why this coupling should be sensitive to Z in the *trans* PyO and why the coupling constant decreases as the electron-donating properties of Z increase.

It was indicated earlier in connection with the discussion of the infrared spectra that there appears to be little effect of Z on the π bonding metal → ligand interaction. One may, on this basis, neglect any rehybridization of the carbon orbitals as a result of differences in occupation of the π^* orbital of ethylene caused by changes in Z. On the other hand, as the electron-releasing effect of Z increases, one might expect increasing charge being brought into the metal atom with a resulting larger crystal-field repulsion between the donor ethylene and the acceptor metal. This repulsion could increase the equilibrium distance between the complexed olefin and Pt and lead to the observed decrease in coupling. Alternately, it has been suggested[34] that the strong electron-withdrawing Z groups reduce the *N*-oxide-Pt interaction and makes the metal a better acceptor of the C_2H_4 sigma bond. This is accomplished by the electron-withdrawing Z groups increasing the *s* character of the Pt orbital and thus increasing the coupling constant. Other investigators have also commented on this point[35].

Finally, if we do assume some Pt d_{xy}–$C_{p\pi^*}$ interaction increase with increasing electron-releasing character of Z, the ethylene carbon atom orbitals should show a shift toward ethane carbon orbitals, *i.e.*, a partial rehybridization from sp^2 to sp^3. The decrease in *s* orbital character in the carbon hydrogen bond would decrease the Pt-H coupling as observed. The effect of Z on the coupling is real; the interpretation is still uncertain.

TABLE 10

NMR DATA FOR 1,3-DICHLORO-2-OLEFIN-4-(4-METHYLPYRIDINE *N*-OXIDE)PLATINUM(II) COMPLEXES AND THEIR RESPECTIVE UNCOMPLEXED OLEFINS[a]



3

Compound	*Olefin Coupling Constants, Cps*						*Chemical Shifts in ppm*						
	$J_{H-H'}$			J_{Pt-H}			*Olefinic*			*R*	*N-oxide*		
	H_a–H_c	H_b–H_c	H_a–H_b	Pt–H_a	Pt–H_b	Pt–H_c	H_a	H_b	H_c		CH_3	H_a	H_b
R=H				69.0			4.32				2.51	7.41	8.44
$R=CH_3$[b,c]	7.8	13.7	—	77.0	67.2	*ca* 79.0	4.24	4.27	5.10	1.66	2.54	7.41	8.42
Free propene[d]	10.0	16.8	2.0				4.88	4.96	5.73	1.71			
$R=CH_3CH_2CH_2COO$[e]	4.75	10.4	1.25	77.1	67.3	80.0	4.02	4.34	7.04		2.51	7.43	8.44
Free vinyl butyrate[h]	6.3	14.0	−1.3				4.36	4.70	7.16				
$R=C_6H_5COO$[e]	4.5	10.5	—	77.0[f]	67.5[f]	—	4.18	4.58	7.53[g]		2.63	7.45[g]	8.47
Free vinyl benzoate	6.5	14.5	−1.6				4.81	5.22	7.78				

[a] The internal reference is $CHCl_3$; the external is tetramethylsilane. All spectra were taken in $CDCl_3$.

[b] $J_{(Pt-CH_3)} = 40.5$ cps, $J_{(Hc-CH_3)} = 6.5$ cps in the complexed molecule, and $J_{(Hc-CH_3)} = 6.9$ cps in free propene.

[c] We are indebted to Dr. Tom Flaut of Procter and Gamble Company for having obtained this spectrum at 100 mc.

[d] A. Bothner-By and C. Naar Colin, *J. Am. Chem. Soc.*, *83* (1961) 231.

[e] We are indebted to Dr. N. Bhacca of Varian Associates for these spectra at 60 and 100 mc.

[f] The coupling constants are an average of those obtained at 100 mc and those obtained at 100 mc with a Varian C-1024 time averaging computer.

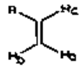
[g] Approximate value because the protons of the benzene ring, pyridine *N*-oxide and vinyl group give resonance signals in the same area.

[h] W. Brugel, T. Ankel and F. Kruckeberg, *Z. Electrochem.*, *64* (1960) 1121.

The nmr spectra of some mono-substituted ethylene complexes have been investigated[36] with results shown in Table 10. Consider first the three vinyl compounds, **3**, where R is CH_3, n-$C_3H_7CO_2$-, and $C_6H_5CO_2$-. With respect to all three ethylenic protons in each of these vinyl derivatives, the chemical shift of the complexed olefin moves upfield as compared to the free compound; the data of Table 11 more clearly focus these shifts. In the case of propene, the difference between all three protons, free and complexed, is about the same, whereas this is true only for protons H_a and H_b in the two examples where R now involves is a large carboxy group. In these cases, the difference between H_c free and complexed is rather small, but the chemical shift for H_c is large in both free and complexed compound. Analysis of the coupling constants ^{195}Pt-^{1}H for the complexes brings out an interesting observation. The coupling constants for H_a and H_c are very similar but that for H_b, the proton on the same side of the double bond as the R group, is much smaller. This suggests that the olefin plane is not perpendicular to the platinum square plane but is twisted around the axis joining the ethylenic

TABLE 11

OLEFINIC PROTON CHEMICAL SHIFT DIFFERENCE BETWEEN FREE AND COMPLEXED OLEFIN, 1a, 1b, 1c (ppm)



R	ΔH_a	ΔH_b	ΔH_c
CH_3	0.643	0.693	0.628
C_3H_7COO	.341	.360	.118
C_6H_5COO	.631	.635	*ca* .25

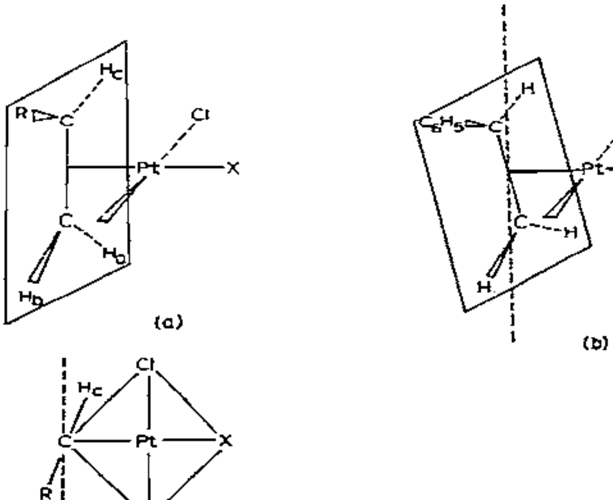


Fig. 5. Twist and bend of coordinated olefins; (a) Side and top view showing twist; (b) Side view showing styrene bend.

carbons, such that the two hydrogen atoms H_a and H_c on one side of the double bond are closer to the Pt atom than are the R and H_b groups as shown in Fig. 5(a).

Such twisting has also been suggested[37] in Zeise-type olefin complexes and has also been suggested[38] as an explanation for the larger Pt-H coupling in *cis*-2-butene as compared to coupling in *trans*-2-butene complexes, $C_4H_8Pt(C_5H_5N)Cl_2$.

These twisted olefins presumably still have the plane of the olefin perpendicular to the platinum square plane. The Pd dimeric complex, analogous to Fig. 5(b), has the double bond axis bent back 16° from the perpendicular in the crystalline form[39].

Although ^{195}Pt-^{1}H coupling increases with decreasing distance of the Pt-olefinic hydrogen atom, recent work[40] has shown that when a methyl group is attached to the pπ carbon atom, the coupling to the methyl protons $\mathrm{Pt}\text{Ⓒ}\mathrm{CH_3}$* decreases with decreasing distance between the Pt and the methyl protons. These results again emphasize the importance of distance factors in evaluating the coupling constants.

Before completing this short discussion of the nmr of olefinic protons, mention should be made of the effect of rotation of the olefin on the nmr spectrum. Cramer[41] has shown that ethylene rotates freely about its coordination axis in the compound bis(ethylene)π-cyclopentadienylrhodium(I), Fig. 6. Each ethylene has two sets of protons, the inner, H_i, and outer, H_o, protons. In $CHCl_3$ solution at room temperature there are two broad peaks at 2.77 and 1.12 ppm due to H_o and H_i respectively. However, at 57°, the two peaks converge to a single band at 1.93 ppm. This coalescence into one absorption signal, after eliminating other possibilities, was ascribed to free rotation around the coordination axis. On cooling the solution to −20°, the absorptions at 2.77 and 1.12 ppm were each split into two pairs of doublets.

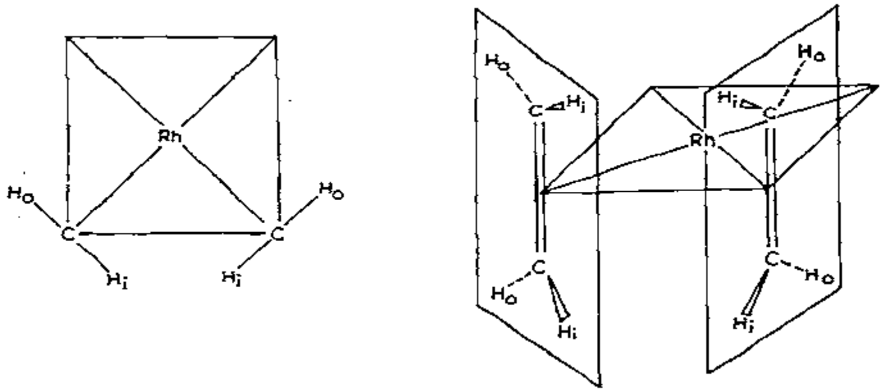


Fig. 6. The Bis(ethylene) complex of rhodium; (a) Top view; (b) Side view; (The π-cyclopentadienyl ring is omitted for clarity).

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* This notation presumes to illustrate a top view of the bonding, the circled atom eclipsing the bottom ethylenic carbon, and the Pt bond centered between the ethylenic carbons.

When rotation occurs around the coordination axis, the σ bond may be considered as remaining intact, but the π bond is alternately partially broken and re-made, as first the d_{xy} (Fig. 2) and then the d_{xz} metal orbital becomes involved. Rotation around the olefin axis would require breaking both the σ and π bond. The work on the platinum-methyl proton interaction reported above[40] showing the negative coupling of $\mathrm{Pt}{-}\textcircled{\scriptsize C}{-}\mathrm{CH_3}$ as a function of distance is another example of rotation around the coordination axis. With propene, two geometric isomers are possible, Fig. 7(a) and (b). (The olefin is viewed from above so that only the top carbon atom is shown.)

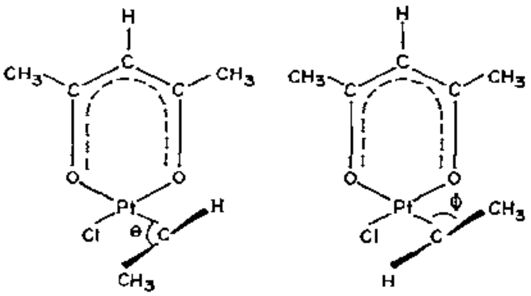


Fig. 7. Olefin twist acetylacetanato complex.

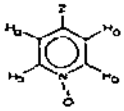
The relative amounts of isomers may be deduced by freezing out the olefin rotation which occurs rapidly enough to coalesce the proton resonance at room temperature. Relative peak heights indicate isomer ratios below the coalescence temperature and the averaged chemical shift above coalescence also permits estimation of the ratio of isomers. Isomer (b) with the least hindrance and hence the least twist ($\theta > \phi$) is assumed to be the most abundant isomer.

(iii) The NMR spectra of pyridine N-oxide protons

In Table 12 are shown the chemical shift data[32] for a variety of pyridine *N*-oxides, both free and complexed. A typical spectrum is shown in Fig. 8. The four protons on the 4-substituted pyridine *N*-oxide really constitute an AA'XX' system. For such a system under the conditions of ordinary resolution, each proton appears as a "pseudo" doublet (actually a quartet), A being split by B and B by A. The chemical shift for H_b, the proton on the carbon adjacent to the nitrogen atom, is always farther downfield than proton H_a because of the deshielding effect of the positive nitrogen atom. On the other hand, the change in chemical shift as a function of Z is much greater for H_a than for H_b, the expected result, since H_a is much closer to Z. As Z changes from the electron-withdrawing NO_2 to the

TABLE 12

NMR OF PYRIDINE *N*-OXIDES, FREE AND COMPLEXED



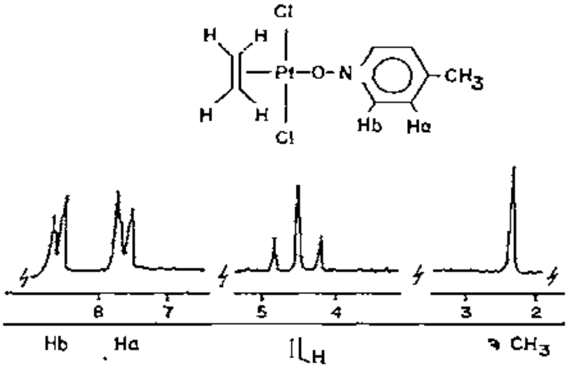
		Chemical Shift[a] in δ				Separation between H_a and H_b in ppm			
		10% w/w Solution		$CHCl_3$ or $CDCl_3$				$CHCl_3$ or $CDCl_3$	
Z		D_2O	D_2O/HCl	Uncomp.	Comp.	D_2O	D_2O/HCl	Uncomp.	Comp.
NO_2	H_a	8.326^{b}	8.715	8.102^{b}	8.30^{e}	0.20	0.308	0.236	0.305
	H_b	8.526^{b}	9.023	8.338^{b}	8.605^{e}				
$COOCH_3$	H_a	8.050	8.520	7.912	8.250	0.375	0.505	0.350	0.516
	H_b	8.425	9.025	8.266	8.766				
	CH_3	4.015	4.078	3.963	4.050				
Cl	H_a	7.70	8.168	7.315	7.50^{d}	0.638	0.712	0.875	0.975
	H_b	8.338	8.88	8.190	8.475				
H	H_a	7.692^{c}	8.065^{c}	7.383^{c}	7.695^{c}		0.85 (H_a–H_b)		0.940 (H_a–H_b)
	H_b	8.383	8.915	8.298	8.635	0.692	0.446 (H_a–H_c)	0.915	0.240 (H_a–H_c)
	H_c	7.691^{c}	8.512^{c}	7.383^{c}	7.918^{c}		0.403 (H_b–H_c)		0.70 (H_b–H_c)
CH_3	H_a	7.408	7.896	7.178	7.413	0.756	0.816	0.983	1.03
	H_b	8.165	8.713	8.162	8.443				
	CH_3	2.445	2.696	2.36	2.515				
OCH_3	H_a	7.13	7.48	6.865	7.050	1.076	1.20	1.318	1.392
	H_b	8.206	8.681	8.183	8.442				
	CH_3	3.95	4.13	3.883	4.016				
$OCH_2Ø$	H_a	7.05	7.433			1.153	1.236		
	H_b	8.203	8.67						
	CH_2	5.116	5.353		5.20				
	Ø	7.383	7.47		7.390				

[a] Tetramethylsilane is the internal reference in $CHCl_3$ and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt in D_2O. [b] The spectrum is composed of a quartet and the chemical shift for H_a and H_b are estimated as the mid-points of each side. [c] In the neutral molecule, H_a and H_c appear together as a quartet, whereas in the charged species H_c moves downfield from H_a and the chemical shifts for each are estimated. [d] The spectrum is partially obscured by solvent peaks. [e] We are indebted to Dr. T. Flaut at Procter and Gamble Company for having obtained this spectrum at 100 mc using a Varian C-1024 Time Averaging Computer.

electron-releasing OCH_3, H_a and H_b both move upfield but the effect on H_a is considerably greater than the effect on H_b.

In Table 12 are also shown the effect on the chemical shift of H_a and H_b when the pyridine *N*-oxide is protonated and when it is complexed to the platinum. In all cases the protonation and the metalation cause downfield shifts of both H_a and H_b protons but now the effect on H_b is always greater than on H_a because the site of electronic change is closer to the H_b proton. The separation between H_a and H_b in free *N*-oxide is increased by complexation to either a proton or a metal and the extent of the increase is roughly the same for either type of complexation.

The H_b protons are separated from the Pt atom in the complex by four bonds and no coupling between $^{1}H_b$-^{195}Pt is observed at room temperature al-



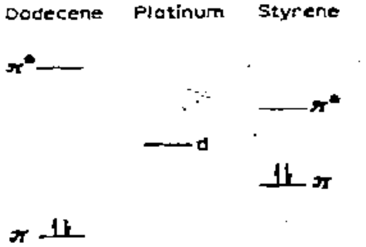


Fig. 8. NMR Spectrum of PyO complex 1 in $DCCl_3$ (L, C_2H_4; Z, CH_3).

Fig. 9. The qualitative orbital level diagram.

though four-bond coupling has been observed in other Pt systems[42,43]. When certain pyridines rather than pyridine *N*-oxides are complexed, the H_b protons do couple with platinum[38] and much useful information on the ligand lability of such complexes can be deduced from such coupling.

H. EXCHANGE REACTIONS OF THE PYRIDINE *N*-OXIDE COMPLEXES, (1)

(i) Olefin–olefin exchange

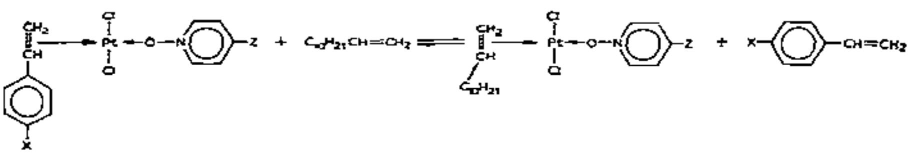
Olefin–olefin exchange in Zeise's Salt and its analogs was investigated several years ago[11] by means of the reaction (3). This reaction is particularly amenable to study because the equilibrium is obtained almost instantaneously and the analysis by ultraviolet spectrophotometry is readily achieved because styrene and its complex have very different spectra and 1-dodecene does not adsorb in the ultraviolet region of interest. This study showed that the equilibrium always favors the dodecene complex; the equilibrium ratio of the 1-dodecene complex to the unsubstituted styrene complex (X=H) was about 6:1 when stoichiometric quantities are employed. Furthermore, all meta and para substituents, X, either electron-releasing or electron-withdrawing stabilize the styrene complex relative to the unsubstituted styrene. The first observation may be rationalized on the basis that both the bonding pπ orbital and the corresponding antibonding orbital are localized on the ethylene linkage of the dodecene. Accordingly, the overlap integrals for both the sigma molecular orbital resulting from forward donation and the π-type orbital resulting from back-donation are larger than the overlap integrals of the molecular orbitals generated from the styrene in which all bonding and antibonding orbitals are delocalized over the entire molecular framework of the styrene. The fact that all substituents on the styrene moeity give rise to more stable complexes than does unsubstituted styrene is a little more difficult to rationalize. The most reasonable explanation appears to be that the unsaturated moiety is coordinated through both sigma and π type orbitals. The overlap of the pπ system with the Pt dsp^2 orbital to form the sigma orbital is enhanced by electron-releasing groups and the overlap of the pπ* system with the Pt d_{xy} orbital to form the π orbital is enhanced by electron-withdrawing substituents; hence both types of substituents enhance the styrene complexation.

The equilibrium studies represented by eq. (1) were extended[6] by replacing the *trans*-chloride with a series of pyridine *N*-oxides and then determining the equilibrium constant for the reaction (4).

The equilibrium constants determined from eq. (4) are shown in Table 13 for the 4-substituted styrenes. In this table, the larger the K_{eq} the greater the concentration of the dodecene complex at equilibrium; numbers smaller than unity indicate greater stability of the styrene complex and the smaller the number the greater the platinum preference for the styrene as compared to the dodecene.

TABLE 13

EQUILIBRIUM CONSTANTS FOR THE REACTION:



Z \ X	*CH_3O*	*CH_3*	*H*	*Cl*	*NO_2*
CH_3O	9.5 ± 2	7.1 ± 1	6.6 ± 1	3.2 ± 0.6	.045 ± 0.009
CH_3	0.30 ± 0.06	0.57 ± 0.01	.87 ± 0.2	0.099 ± 0.002	.0017 ± 0.0002
H	.26 ± 0.05	.016 ± 0.003	.052 ± 0.001	.071 ± 0.01	.00035 ± 0.0007
Cl	.18 ± 0.04	.51 ± 0.01	.10 ± 0.02	.11 ± 0.02	.010 ± 0.002
CO_2CH_3	.25 ± 0.05	.016 ± 0.003	.13 ± 0.03	.22 ± 0.04	.077 ± 0.01
NO_2	.0032 ± 0.0006	.078 ± 0.002	3.3 ± 0.7	0.52 ± 0.001	.0015 ± 0.0003
trans-Cl	19.4	26	37		21

The constants in Table 13 indicate that with the exception of most complexes with 4-methoxypyridine *N*-oxide, the styrene rather than dodecene prefers to be complexed to the metal. This is in sharp contrast to the Zeise's Salt series where chloride is the *trans* ligand and where the dodecene is the ligand of preference. In order to rationalize the two sets of data, it is necessary to discuss the relative energies of the orbitals involved. Not only do the geometry of the orbitals involved determine the extent of bonding, but the better the energy match of the orbitals involved in molecular bonding, the stronger the bonding. The qualitative orbital level diagram, Fig. 9, shows that the energy match of the platinum d orbitals is much better for the styrene highest occupied and lowest unoccupied orbitals than it is for the dodecene. It may be argued that when chloride is replaced by the much stronger base, PyO, the importance of backbonding to the olefin is enhanced and the better energy match between the lowest unoccupied π^* orbital on styrene and the highest filled on platinum results in better π bonding. However, were this the only effect, it might be expected that 4-methoxypyridine *N*-oxide would result in the most stable styrene complex, since it is the most basic of the PyO's and hence should call the backbonding effect into greater play. However, the data show that the methoxy group enhances the stability of the dodecene complex to a greater extent than other Z substituents.

In the orbital level diagram, the platinum d orbitals are shown as degenerate, which they certainly are not in the field of the ligands. The greater the electronic charge brought into the field of the metal by the ligands, the greater the d-orbital splitting. Thus with the 4-methoxypyridine *N*-oxide it may be that the ligand field splitting, which should be the largest in the series, is such that the overlap with the dodecene orbitals is much improved over that where less powerful electron-releasing groups are present on PyO. Obviously, the situation is quite complex and further measurements to more accurately determine the levels are in order. Furthermore, some of the analytical data need further scrutiny and dissociation of some complexes is possible. Bis olefin formation is also a complicating factor.

(ii) Pyridine N-oxide exchange

Not only can the olefin in complexes such as 1 be exchanged by other olefins in an equilibrium reaction such as that discussed above, but the PyO may be exchanged by another PyO in Pt-olefin and related complexes. Thus[26] when equimolar quantities of 4-methylpyridine *N*-oxide and the 4-nitro complex, $(4\text{-}NO_2\text{-}PyO)Pt(CO)Cl_2$, were mixed in methylene chloride solution and hexane added, the precipitated products were 4-nitropyridine *N*-oxide and the new complex, $(4\text{-}CH_3PyO)Pt(CO)Cl_2$. Although PyO exchange in a styrene complex has not been studied extensively, at least one system as been studied[3] in a preliminary manner. In $CHCl_3$, the equilibrium reaction:

$$(4\text{-}NO_2PyO)Pt(C_6H_5CH{=}CH_2)Cl_2 + PyO \rightleftharpoons (PyO)Pt(C_6H_5CH{=}CH_2)Cl + 4-NO_2PyO \qquad (8)$$

was studied from each direction independently. From the forward reaction, it was possible to isolate and identify the unsubstituted PyO complex and from the reverse reaction, free PyO was isolated and identified. The reaction appeared to proceed very slowly with some decomposition and was not thoroughly investigated.

Considerable caution must be exercised in drawing conclusions from any type of exchange reaction with Pt^{2+} complexes. Recent studies[38] have shown that the ligands can be quite labile even in the absence of any added free ligand. This has been found to be true of pyridine ligands *trans* to an unsaturated group since here the lability can be determined by nmr coupling of the pyridine protons to platinum. Naturally, the extent of this lability not only depends on the other ligands simultaneously coordinated to the metal, but it is also very sensitive to the solvent and to temperature. Since Pt^{2+} is readily oxidized to Pt^{4+}, another complication is introduced. However, with the powerful instrumental methods now available, there is reason to be hopeful that despite the complicated nature of the problem of exchange, progress will be rapid and extensive.

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