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Preparation and Reactions of Olefin–Pyridine N-Oxide Platinum(II) Complexes

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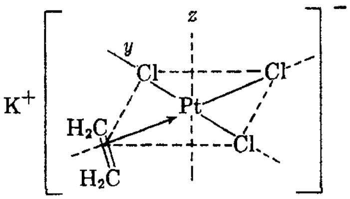
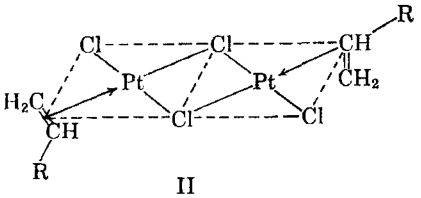
A new series of Pt(II) olefin–pyridine N-oxide complexes of the formula $Pt(Un)(4\text{-}ZC_5H_4NO)Cl_2$ have been prepared where Un is ethylene or styrene and Z is H, NO_2, Cl, or $OCH_2C_6H_5$. It is possible to replace one olefin by another or one N-oxide by another in these complexes under very mild conditions. Under similar conditions a complex containing both 1,5-hexadiene and an N-oxide could not be prepared.

Introduction

When a solution of potassium ethylenetrichloroplatinate(II), commonly called Zeise's salt (formula I), is treated with pyridine N-oxide, a chloride ion is replaced, probably the one *trans* to ethylene, and the non-ionic complex III (Z = H) is formed in excellent yield. The same product is produced when 1,3-bis-(ethylene)-2,4-dichloro-μ-dichlorodiplatinum(II) (II, R = H) is similarly treated.[1] Even though excess pyridine N-oxide is added, only one mole becomes incorporated, in contrast to the reaction of these olefin complexes with pyridine. With pyridine all the ligands are replaced by this relatively strong base with the ultimate formation of tetrapyridineplatinous chloride, $Pt(C_5H_5N)_4Cl_2$. It is the purpose of the present paper to present results which extend the series of olefin–N-oxide complexes and to report on some of the reactions of these compounds.



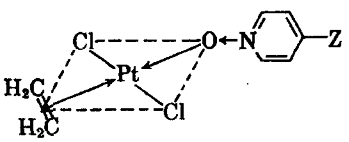
I



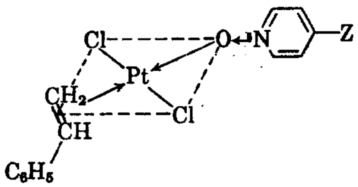
II

Preparation

4-Substituted (chloro, nitro, benzyloxy) pyridine N-oxides react smoothly with both I and II (R = H) to give III (Z = Cl, NO_2, $OCH_2C_6H_5$, respectively). The new compounds are characterized in Table I. The displacement occurs least rapidly with the 4-nitropyridine N-oxide, presumably because it is the weakest nucleophile in the series.



III



IV

Although it was not possible to displace ethylene from III by a second mole of pyridine N-oxide, it is possible to replace ethylene by other olefins, whereby a new series of complexes is obtained. Thus treatment of III (Z = H) with styrene gives (pyridine) N-oxide-styrenedichloroplatinum(II) (IV, Z = H). The same compound can be prepared by treating the styrene non-ionic dimer II (R = C_6H_5) with pyridine N-oxide or by treating the ethylene dimer II (R = H) with a benzene solution containing both styrene and pyridine N-oxide.

The new series of compounds IV (Z = OCH_3, NO_2, $OCH_2C_6H_5$) can be prepared not only by treating the appropriate III with styrene, or by allowing II (R = C_6H_5) to react with the appropriate N-oxide, but it also is possible to exchange one pyridine N-oxide in IV by another. This last method is of more theoretical than practical importance.

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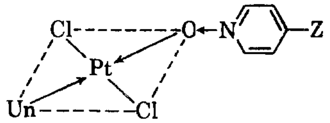
(1) L. Garcia and M. Orchin, *J. Chem. Soc.*, 2254 (1961).

TABLE I

PROPERTIES OF OLEFIN–PYRIDINE N-OXIDE PLATINUM(II) COMPLEXES



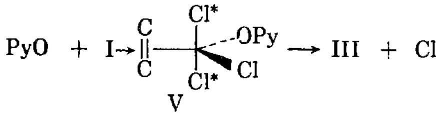
					Ultimate analysis					
					Calcd.			Found[b]		
Un	Z	M.p.[a]	Appearance	Formula	C	H	N	C	H	N
Ethylene	H	149°	Pale green needles	$C_7H_9NOPtCl_2$	21.6	2.3	3.6	22.0	2.4	3.6
	NO_2	170°	Yellow prisms	$C_7H_8N_2O_3PtCl_2$	19.4	1.9	...	20.0	2.0	...
	Cl	171°	Light green flakes	$C_7H_8NOPtCl_3$	19.8	1.9	...	19.7	2.0	...
	$OCH_2C_6H_5$	169°	Light yellow needles	$C_{14}H_{15}NO_2PtCl_2$	33.9	3.1	2.9	33.5	3.4	3.0
Styrene	H	139°	Light orange	$C_{13}H_{13}NOPtCl_2$	33.6	2.8	...	33.7	2.9	...
	NO_2	168°	Orange	$C_{13}H_{12}N_2O_3PtCl_2$	30.8	2.8	6.0	30.6	2.4	5.6
	Cl	162°	Red-orange	$C_{13}H_{12}NOPtCl_3$	31.3	2.4	...	31.4	2.6	...
	$OCH_2C_6H_5$	147°	Light orange	$C_{20}H_{19}NO_2PtCl_2$	42.0	3.3	...	42.2	3.3	...

[a] With decomposition. [b] Geller Microanalytical Laboratories, Bardonia, New York.

Discussion

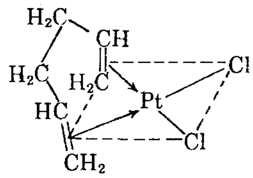
It is now generally accepted that Pt(II)–olefin complexes owe their stability in large part to the donor–acceptor role[2] of the olefin and the presence of empty and filled d-orbitals on the Pt(II). Earlier work in this Laboratory[3] on the relative stabilities of *p*-substituted styrene–Pt complexes presented chemical evidence consistent with such a "double bond" between the metal and the olefinic ligand.

It has been postulated[4] that a transition state involving fivefold coördination around the platinum, with approximate trigonal bipyramid geometry, is formed during the displacement. In this trigonal bipyramid transition state, it is assumed that the entering group, the leaving group, and the olefinic (*trans*-directing) ligands are all in the equatorial positions defining the trigonal plane; the other two ligands take up the apical positions of the bipyramid. Such a configuration requires that the partners in any pair of *cis* groups in the original square planar complex take up one equatorial and one apical position. The displacement of chloride by pyridine N-oxide in Zeise's salt, for example, may be written as follows, where Cl* represent chlorines *cis* to ethylene in the original and final square planar complexes



V

Under conditions (room temperature for 1 hr.) that result in *trans*-substitution in other olefin complexes, 1,5-hexadienedichloroplatinum(II) (VI) does not react with pyridine N-oxide.



VI

Possibly a transition state similar to that of V, involving one double bond in the equatorial and the second in an apical position, is unfavorable when the two double bonds are linked by a dimethylene group. However, the stronger base pyridine reacts almost instantaneously with VI to give the known[5] tetrapyridineplatinous chloride, $(C_5H_5N)_4PtCl_2$. It is of interest to note that 1,5-hexadiene will displace ethylene or styrene from I or II (R = H, C_6H_5) but does not react under similar conditions with III, in which an N-oxide instead of a chlorine is *trans* to the olefin. Accordingly, we have not been successful thus far in preparing a complex in which 1,5-hexadiene and an N-oxide both are

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[2] (a) M. J. Dewar, *Bull. soc. chim. France*, **18**, 71 (1951); (b) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

[3] J. Joy and M. Orchin, *J. Am. Chem. Soc.*, **81**, 305 (1959).

[4] *E.g.*, F. Basolo and R. G. Pearson in "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 177 ff.

[5] H. D. K. Drew, F. W. Pinckard, W. Wardlow, and E. G. Cox, *J. Chem. Soc.*, 1004 (1932).

coördinated to platinum. These reactions are being investigated further.

Experimental

Potassium Ethylenetrichloroplatinate(II) (I).—Fifteen g. of potassium chloroplatinite, K_2PtCl_4, was dissolved in 85 ml. of 4% aqueous HCl in a bottle which then was mounted on a standard Parr gas apparatus. The system was flushed with nitrogen gas and then charged with ethylene to a gage pressure of 50 p.s.i. The mixture was shaken while maintaining the ethylene pressure at 50 p.s.i. and after 36 hr. the red solution changed to yellow. The mixture was filtered to remove traces of insoluble material and the filtrate concentrated to 50 ml. and cooled. The yellow needles which precipitated were separated and dried. The complex started to decompose without melting at 160°.

1,3-Bis-(ethylene)-2,4-dichloro-μ-dichlorodiplatinum(II). (II, R = H).—This complex, prepared as described previously,[3] was recrystallized from hot benzene, forming fine orange crystals which decomposed without melting at about 170°.

1,3-Bis-(styrene)-2,4-dichloro-μ-dichlorodiplatinum(II).—One mmole of II (R = H) (0.5884 g.) was dissolved in 20 ml. of benzene. Two mmoles of styrene was added and the mixture warmed, whereupon all of the complex dissolved. After filtration of some insoluble material, the product crystallized from the filtrate as fine orange crystals. Recrystallization from benzene and washing with petroleum ether gave material melting with decomposition at 171°.

1,5-Hexadienedichloroplatinum(II).—One mmole of II (R = H) was dissolved in 20 ml. of hot benzene. One mmole of 1,5-hexadiene was carefully added, whereupon the orange solution turned light yellow with rapid evolution of ethylene gas. The clear yellow solution was boiled gently to remove excess 1,5-hexadiene (b.p. 58°). On cooling to room temperature, a white crystalline product separated and was removed by filtration. Concentration of the filtrate under reduced pressure and cooling of the residue in an ice bath caused the separation of more white crystals. The two crops of crystals were combined, washed with petroleum ether, and dried, m.p. 172° (literature value 172°), yield 90%.

Anal. Calcd. for $C_6H_{10}PtCl_2$: C, 20.7; H, 2.9. Found: C, 21.2; H, 3.0.

This complex has been prepared previously[6] by a different synthetic method and the properties are in agreement. For further structure confirmation, the infrared spectrum of a powdered sample suspended in Nujol was determined with a Baird instrument equipped with sodium chloride optics. The C–H out-of-plane deformation of the free diene is reported[7] to occur at 995 and 915 cm.$^{-1}$ and the C=C stretching frequency at 1641 cm.$^{-1}$. In the complex, these peaks were observed at 940 and 865 cm.$^{-1}$ for C–H and 1516 cm.$^{-1}$ for C=C. No band remained at 1641 cm.$^{-1}$, indicating that both double bonds were involved in the complex. The lowering of the C=C stretching frequency by 125 cm.$^{-1}$ is the expected result of the bond-weakening effect of complex formation.[8] The monomeric nature of this complex was established previously.[7] The identical product was isolated from a reaction between the diene and styreneplatinous chloride (II, R = C_6H_5) in benzene solution. However, the reaction was much slower and the yield lower.

Pyridine N-Oxide.—This compound was prepared by the peroxide oxidation of pyridine and was isolated in the form of a hygroscopic white solid, b.p. 138–140° (15 mm.) in 89% yield.

4-Nitropyridine N-Oxide.—Ten g. of pyridine N-oxide was dissolved in a mixture of 20 ml. of concentrated sulfuric acid and 12 g. of nitric acid (specific gravity 1.49) and the solution heated for 3.5 hr. at 125–130°. The mixture was poured into ice and, with stirring, neutralized with portions of sodium carbonate. Just when crystals of sodium sulfate began to precipitate, the neutralization was interrupted and the precipitated crystals were collected, washed with ice water, and dried. The filtrate was extracted with chloroform and the extracts concentrated, whereupon more crystals precipitated. The two crops of crystals were combined and recrystallized from acetone. The yield of yellow needles of 4-nitropyridine N-oxide was 10 g. (68%), m.p. 159°.

Using 4-nitropyridine N-oxide as starting material, the other 4-substituted N-oxides were prepared according to the method of Ochai.[9] The chloro, hydroxy, and benzyloxy derivatives were prepared.

Olefin–Pyridine N-Oxide Platinous Chloride Complexes (III).—One mmole of Zeise's salt (I) was dissolved in 25 ml. of water and then treated with an excess of pyridine N-oxide. After a few minutes at room temperature the solution was chilled, whereupon yellow green needles of III (Z = H) separated. These were filtered and recrystallized from chloroform.

The identical compound (infrared spectrum, ultimate analysis, m.p., and general appearance) was isolated on treatment of an ethanol solution of II (R = H) with pyridine N-oxide. The twice-recrystallized yellow-green needles melted at 146° with decomposition.

A similar reaction of pyridine N-oxide with styreneplatinous chloride (II, R = C_6H_5) in ethanol gave orange crystals which, after recrystallization from chloroform, gave IV (Z = H), melting with decomposition at 139°.

No apparent reaction was observed on similarly treating an alcoholic solution of VI with pyridine N-oxide. Also no reaction occurred when an aqueous solution of K_2PtCl_4 was treated directly with pyridine N-oxide, although it has been reported that pyridine N-oxide complexes of other transition metals may be prepared directly from the metal perchlorates.[10]

Complexes of structures III and IV were prepared by the reaction of II (R = H, C_6H_5) with 4-nitro-, 4-hydroxy-, 4-chloro-, and 4-benzyloxypyridine N-oxides. All except the hydroxy compound formed isolable complexes, characterized in Table I.

Olefin Substitution in III.—One mmole of III (Z = H) (0.3893 g.) was dissolved in 25 ml. of hot benzene. To

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[6] K. Jensen, *Acta Chem. Scand.*, **7**, 866 (1953).

[7] Infrared Spectral Data, API Research Project No. 44, Serial No. 1654 (1954).

[8] H. W. Kouwenhoven, J. Lewis, and R. S. Nyholm, *Proc. Chem. Soc.*, 220 (1961).

[9] E. Ochai, *J. Org. Chem.*, **18**, 534 (1953).

[10] R. L. Carlin, *J. Am. Chem. Soc.*, **83**, 3773 (1961).

the clear pale yellow solution, 0.5 ml. of styrene was added through a syringe. Minute bubbles of gas were evolved immediately and the solution turned orange. After filtration, the clear orange filtrate was concentrated *in vacuo* to one-third the original volume, whereupon orange crystals started to form. The mixture was diluted with an equal volume of petroleum ether, stirred briefly, and placed on an ice bath. The orange product IV (Z = H) was filtered, washed with petroleum ether, and recrystallized from chloroform.

Analogous ethylene displacements were performed on the various ethylene 4-substituted pyridine N-oxide platinum complexes. The properties of the products isolated corresponded to those of the complexes made directly by the interaction of styreneplatinous chloride with the appropriate pyridine N-oxide derivatives. The complexes are characterized in Table I.

N-Oxide Exchange Reactions.—The following equilibrium was studied independently from each direction

$$\text{IV}\ (\text{Z} = \text{NO}_2) + \text{C}_5\text{H}_5\text{NO} \leftrightarrows \text{IV}\ (\text{Z} = \text{H}) + 4\text{-NO}_2\text{C}_5\text{H}_4\text{NO}$$

An approximately 1.3×10^{-3} *M* chloroform solution of each complex was treated with an approximately 6.8×10^{-3} *M* solution of the N-oxide in chloroform. Concentration changes were measured spectrophotometrically but both forward and reverse reactions were slow and after 10 days equilibrium still had not been attained and the solutions were slowly depositing platinum. However, in the forward reaction, some complex IV (Z = H) was isolated, m.p. 139°; infrared spectrum identical with an authentic sample. In the reverse reaction, the mixture was worked up after 4 days at room temperature, whereupon some IV (Z = NO_2), m.p. 168°, was isolated; infrared spectrum identical with an authentic sample. From the same reaction mixture it also was possible to isolate some C_5H_5NO as its picrate, m.p. 176–177°, identical with an authentic sample.

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Contribution from the Inorganic Chemistry Research Laboratories,
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Mesityl Oxide Complexes of Palladium and Platinum

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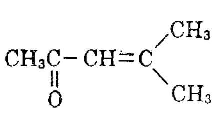
The long known complex of mesityl oxide and platinum(II) chloride has been shown to be a polymer of platinum(II) chloride units bridged by the olefin and ketone functions of mesityl oxide. The condensation product of mesityl oxide and palladium(II) chloride is a π-allyl complex, $[C_6H_9O{\cdot}PdCl]_2$.

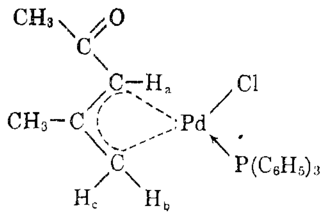
Among the oldest coördination compounds known is a crystalline complex of mesityl oxide (I) and platinum(II) chloride, $[C_6H_{10}O{\cdot}PtCl_2]$.[1] More recently, a different type of complex has been prepared from mesityl oxide and palladium(II) chloride.[2] The structure of these compounds has now been elucidated by proton magnetic resonance and infrared spectral studies.[3]

We have formulated the palladium complex as a π-allylic derivative (II). This yellow crystalline material is insoluble in non-polar organic solvents but dissolves readily in basic solvents which are known to cleave halogen bridges.

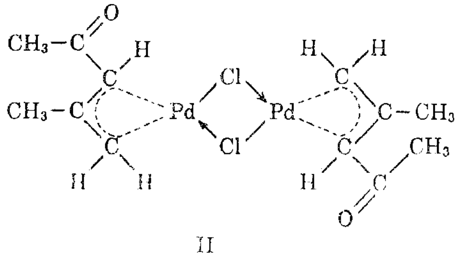


$CH_3C(=O)-CH=C(CH_3)_2$

I



III



II

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(1) H. Zeise, *J. prakt. Chem.*, **20**, 193 (1840); W. Prandtl and K. A. Hofmann, *Chem. Ber.*, **33**, 2981 (1900).

(2) I. I. Moiseev, E. A. Feodorovskaya, and Ya. K. Syrkin, *Zh. Neorg. Khim.*, **4**, 2641 (1959); *Russ. J. Inorg. Chem.* (English Transl.), **4**, 1218 (1959).

(3) Preliminary note, G. W. Parshall and G. Wilkinson, *Chem. Ind.* (London), 261 (1962).