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Synthesis and Characterization of some Olefin/Phosphine–tert-Amine *N*-Oxide Platinum(II) Complexes

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Abstract

Eighteen olefin (or tert-phosphine)–tert-amine *N*-oxide platinum(II) complexes of the general formula *trans*-[PtL(tert-amine *N*-oxide)Cl_2] have been prepared, where L is ethylene, styrene, or triethylphosphine. The tert-amine *N*-oxides used in the complexation were of the *N*-aryl saturated heterocyclic type substituted at the *ortho*- or *para*-position with an electron withdrawal group, *i.e.* NO_2, CN, $COCH_3$, COC_6H_5, and $COOC_2H_5$. The complexes were characterized by elemental analysis, IR, and ^{1}H NMR spectroscopy.

Linear relationships were obtained between the stretching frequencies of the N–O bonds of the platinum complexes and Hammet constants, *viz.* σ and $\bar{\sigma}$, which indicate the presence of inductive and field effects for the *para*-substitution.

Introduction

It was found that tert-amine *N*-oxide can coordinate to some transition metals, e.g. Mn, Co, Zn and Cd, to give complexes containing (transition metal–tert-amine *N*-oxide) species, *viz.* transition metal–oxygen bonds [1–4]. This bond was found to be a pure σ bond [5], and appeared at *ca.* 323 cm^{-1} in IR spectroscopy.

Platinum metal was also involved in the coordination with amine *N*-oxide ligands. However, it was first noted by Garcia and Orchin [6] that pyridine *N*-oxide can react with either Zeise's salt (K[Pt(C_2H_4)Cl_3]) or the platinum bridged complex, di-μ-chlorodichlorodiethylenediplatinum ([Pt(C_2H_4)Cl_2]$_2$), to give a new type of platinum complex that contains both ligands, the ethylene and the pyridine *N*-oxide, in *trans*-relationship to one another. Some other work on platinum metal with substituted pyridine *N*-oxide ligands was reviewed by Orchin and Schmidt [7].

In this work, we examined the reactions between some *N*-aryl tert-amine *N*-oxides (those containing saturated heterocyclic rings substituted at the *ortho*- or *para*-position) and the platinum complex, di-μ-chlorodichlorodiolefin (or ditert-phosphine) diplatinum. The products were characterized by their elemental analyses and IR and NMR spectroscopy.

Experimental

General

^{1}H NMR spectra were recorded on a Varian FT80A, operating at a nominal frequency of 80 MHz, using the deuterium signal of the solvent as a field lock signal.

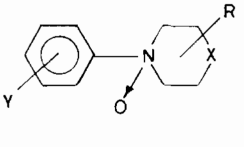
IR spectra were recorded on an SP2000 spectrophotometer at a range between 200 and 4000 cm^{-1} using Nujol mull.

Analyses of the complexes were carried out on a CHN Analyser, type 1106 (Carlo Erba).

Preparation of Compounds

Tert-amine N-oxides

The tert-amines and their corresponding N-oxides (below)** were prepared and characterized at our laboratories [8a, b].



The platinum starting materials

[PtLCl_2]$_2$ (where L is ethylene, styrene, and triethylphosphine) were prepared as described in the literature, refs. 9, 6c and 10 respectively.

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**For R, X and Y see Table I.

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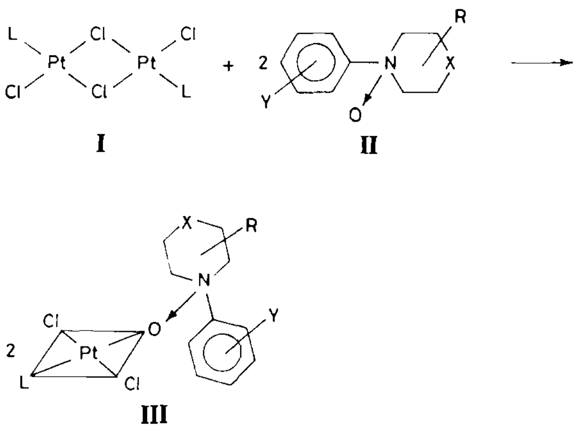
Preparation of tert-amine N-oxide platinum(II) complexes

(1) [Pt(olefin)(tert-amine N-oxide)Cl$_2$]. The bridged platinum complex [Pt(μCl)Cl(olefin)]$_2$, olefin is ethylene or styrene, (0.2 mmol) was dissolved in distilled water (3 ml) and the solution was placed in a Schlenk tube. The solution was cooled in ice, and a pre-cooled solution of the tert-amine *N*-oxide (0.5 mmol) in distilled water (3 ml) was added under nitrogen; fast precipitation of a yellow product was observed. The mother liquor was decanted, and the solid was washed with small portions of cold water, cold ethanol and then with n-hexane and dried under vacuum for several hours.

(2) [Pt(PEt$_3$)(tert-amine N-oxide)Cl$_2$]. The bridged platinum complex, [Pt(μCl)Cl(PEt$_3$)]$_2$ (0.2 g, 0.26 mmol) was suspended in ethanol (10 ml) in a Schlenk tube and a solution of the tert-amine *N*-oxide (0.6 mmol) in ethanol (5 ml) was added under nitrogen. The mixture was stirred for *ca.* 10 min. until all the solid had gone into solution. The yellow solution thus formed was filtered through Celite. The clear solution was reduced in volume until *ca.* 5 ml and n-hexane was added to the point of turbidity. The mixture was allowed to stand in the refrigerator overnight. Yellow crystals formed, which were dried *in vacuo* for several hours.

Results and Discussion

Previous investigations of platinum complexes with tert-amine *N*-oxides concentrated on the aromatic type only, *viz.* the pyridine *N*-oxides [7]. We are therefore presenting here the synthesis and characterization of platinum complexes with tert-amine *N*-oxides containing saturated heterocyclic nuclei (Scheme 1).



Scheme 1. Reactions of platinum bridge complex with tert-amine *N*-oxide. L is $CH_2=CH_2$, $PhCH=CH_2$, and PEt$_3$ (for R, X and Y, see Table I).

The work began with the preparation of the platinum bridged complex (**I**), then cleavage of the bridge by the tert-amine *N*-oxide (**II**) to yield complex **III**. We prepared ten platinum complexes with L = ethylene, five complexes with L = styrene, and three complexes with L = triethylphosphine, which to our knowledge had not been previously attempted.

The complexes prepared were characterized by their elemental analysis and IR spectra (Table I), and NMR spectra (Table II). It was found that the platinum pyridine *N*-oxides analogue have the ***trans***-configuration [7]. Our findings were in agreement with those obtained previously and were confirmed by the stretching frequency of Pt–Cl bond, which appeared as a single band at more than 300 cm^{-1} (*vide infra*).

Infra Red Spectra

The complexes prepared in this work showed many signals in the IR spectrum which are as follows:

(a) The stretching frequency of the double bond, *i.e.* ν(C=C) for complex **III** ranges between 1600–1620 cm^{-1}, which is *ca.* 105–110 cm^{-1} more than that for the bridged complex **I**, and *ca.* 20–60 cm^{-1} less than that for the free ethylene [11].

(b) The stretching frequency of the Pt–O bond for complex **III** (Table I) ranges between 270–320 cm^{-1} and appears in the spectrum as a very weak band. This agrees with that observed for the pyridine *N*-oxide complex [12], which appeared at *ca.* 323 cm^{-1}.

(c) The ν(N–O) for complex **III** appeared between 900–1000 cm^{-1} which is more or less similar to that obtained for the free ligand, *i.e.* tert-amine *N*-oxide (**II**) [8], *viz.*, very little difference. They were, however, less than that obtained for the pyridine *N*-oxide (1271 cm^{-1}) and its platinum complex (1250 cm^{-1}) [6d]. We have found that there is a good relationship between the stretching frequencies of the N–O bond in the platinum complex (**III**) at both the lower field and the higher field (Table I), and σ and $\bar{\sigma}$ Hammet constants (Fig. 1). In this Figure, we have taken the plot for the higher and lower values of ν(N–O) bonds for four complexes, sequenced in Table I as **IIIa, h, i** and **j**. The relationships obtained, with *r* values equal to 0.997, 0.870, and 0.950, (the fourth value of *r* obtained from the plot between σ Hammet constants and the higher values of ν(N–O) is too poor, so that it is not listed here), indicated that there are inductive and field effects caused by the substituent at the phenyl group, and these correlate linearly with the Hammet constants. This correlation indicates that these effects caused by the substituent reaches the N–O bond systematically.

(d) The ν(Pt–Cl) for complex **III** appeared between 330–345 cm^{-1} (Table I) as a single band,

TABLE I. The Properties of the Platinum Complexes (III) (Scheme 1)

Complex III	L	R	X	Y	Colour	Melting point (dec.) (°C)	Analyses, found (calc.)			IR data[b] (cm^{-1})			
							C (%)	H (%)	N (%)	ν(N–O)	ν(Pt–Cl)	ν(Pt–O)	ν(Pt–olefin)
a	$H_2C=CH_2$	H	CH_2	p-NO_2	yellow–orange	82–84	30.7 (30.2)	3.2 (3.5)	5.4 (5.4)	940w 975m	333	310	410
b		H	O	p-NO_2	yellow	70–72	27.3 (27.8)	3.5 (3.1)	5.7 (5.4)	910s 913m	335	305sh	440
c		H	CH_2	o-NO_2	yellow	111–113	30.7 (30.2)	3.6 (3.5)	6.0 (5.4)	913m 930s	330	310	420
d		H	O	o-NO_2	yellow	111–113	27.3 (27.8)	3.4 (3.1)	5.7 (5.4)	913sh 940m	340	305	420
e		2-CH_3	CH_2	p-NO_2	yellow	88–90	31.5 (31.7)	3.5 (3.8)	4.8 (5.3)	940m 950sh	330	310sh	410
f		3-CH_3	CH_2	p-NO_2	yellow–orange	92–94	31.2 (31.7)	3.9 (3.8)	4.8 (5.3)	950m 975m	335	310sh	410
g		4-CH_3	CH_2	p-NO_2	yellow–orange	92–93	31.4 (31.7)	3.8 (3.8)	4.8 (5.3)	945m 968m	330	310sh	445
h		H	CH_2	p-$COCH_3$	yellow–green	96–97	35.1 (35.1)	4.1 (4.1)	3.2 (2.7)	932m 968s	345	310	410
i		H	CH_2	p-$COOC_2H_5$	yellow	110–114	35.1 (35.4)	4.8 (4.2)	2.4 (2.6)	931m 960m	335	295	[a]
j		H	CH_2	p-CN	yellow	120–123	33.3 (33.7)	3.5 (3.6)	5.3 (5.6)	938m 980(broad)	340	310sh	405
k	$C_6H_5CH=CH_2$	H	CH_2	p-NO_2	yellow–brown	75–76	38.1 (38.5)	3.7 (3.7)	4.7 (4.7)	920w 940m	330	310sh	410
l		3-CH_3	CH_2	p-NO_2	yellow	102–106	39.1 (39.6)	4.0 (4.0)	4.9 (4.6)	958w 980(broad)	335	310	410
m		4-CH_3	CH_2	p-NO_2	yellow	90–92	39.2 (39.6)	4.2 (4.0)	4.4 (4.6)	920w 942w	335	315	[a]
n		H	CH_2	p-$COCH_3$	yellow	93–95	42.5 (42.8)	4.3 (4.2)	2.6 (2.4)	920w 945m	340w	315w	415
o		H	CH_2	p-CN	yellow	126–128	41.5 (41.8)	4.0 (3.8)	5.2 (4.9)	938m 980(broad)	335	310vw	445
p	$P(C_2H_5)_3$	H	CH_2	p-$COOC_2H_5$	yellow	92–94	37.6 (37.9)	5.2 (5.4)	2.0 (2.2)	940w 955m	335	350sh	440
q		H	CH_2	p-COC_6H_5	yellow	103–105	43.0 (43.3)	5.1 (5.1)	1.9 (2.1)	938m 948m	340	270	445
r		H	CH_2	p-CN	yellow	82–84	36.0 (36.7)	4.9 (4.9)	4.8 (4.8)	928w 948m	340	320sh	440

[a] Not resolved.

[b] For IR data: m, medium; s, small; w, weak; sh, shoulder.

TABLE II. ^{1}H NMR Data for some of the Platinum Complexes listed in Table I

Complex **III**	δ^a olefinic protons (ppm)	$^2J(^1HC-Pt)$ (Hz)	δ^a Ph (ppm)	Others
b	4.5	65	8.9	δCH_2 (morpholine) = 4.6
e	4.5	65	9.1	$\delta CH_3 = 1.4^b$ ($J = 7$)
f	4.5	65	9.1	$\delta CH_3 = 1.2^b$ ($J = 8$)
g	4.5	65	9.1	$\delta CH_3 = 1.2^b$ ($J = 7$)
h	4.5	63	8.9	$\delta CH_3 = 2.9$
k	4.5^c	67	8.9	–
l	4.3^c	unresolved	8.9	$\delta CH_3 = 1.1^b$ ($J = 7$)
n	4.5^c	60	8.65	$\delta CH_3 = 2.85$

^{a}Downfield from internal TMS. ^{b}Signals observed as doublet. ^{c}Signal due to CH_2 protons.

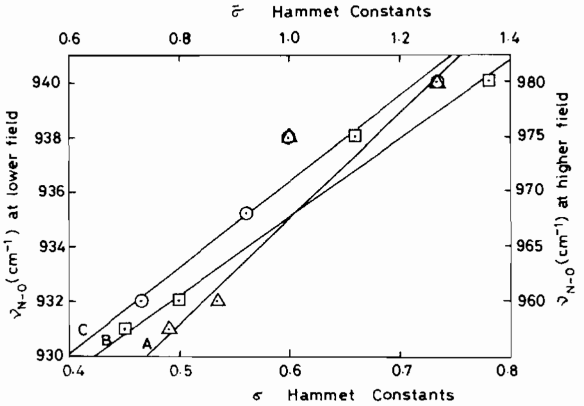


Fig. 1. Linear relationships between: (A) σ Hammet constants (0.78, 0.5, 0.45 and 0.66) [14] and ν(N–O) values at lower field (△); $\bar{\sigma}$ Hammet constants (1.27, 0.87, 0.68 and 1.0) [14] and ν(N–O) values at both (B) lower field (⊡) and (C) higher field (⊙) for the complexes **IIIa**, **h**, **i** and **j** respectively.

which is in agreement with the value obtained for *trans*-Cl–Pt–Cl complexes [12].

(e) The ν(Pt–P) for complex **III** where L = PEt_3 appeared as a single band ranging between 440–445 cm^{-1}, which is in agreement with that obtained for the complex *trans*-$[Pt(PR_3)_2Cl_2]$, *i.e.* 415–443 cm^{-1} [13].

Nuclear Magnetic Resonance Spectra

The NMR spectra were recorded by dissolving some of complex **III** in d_6-acetone at ambient temperature, using TMS as internal reference. We have concentrated here on the values of the chemical shifts (δ, ppm) and the $^1HC-^{195}Pt$ coupling constants (J, Hz) for the olefinic protons (Table II), which appeared in the spectrum as a simple 1:4:1 triplet.

The figures we have obtained are almost certainly similar to those obtained for the pyridine *N*-oxide complexes investigated previously [7]. It seems that the type of tert-amine *N*-oxide used in the coordination does not affect the ^{1}H NMR parameters very much, probably because of the effect of the substituents on the nitrogen atom is too far away to reach the olefinic protons.

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