Different Behaviour of *cis*- and *trans*-Amine-dichloro-(π-ethene)platinum(II) Complexes in Their Reaction with the Free Amine

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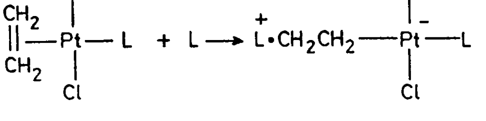
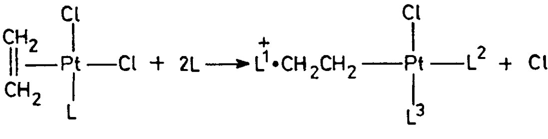
Summary The complexes *cis*-[Pt(π-C_2H_4)Cl_2(L)] (L = 3,5-dimethylpyridine or $H_2NCHMePh$) react in solution with two molecules of free L, undergoing substitution of the chlorine *trans* to ethene and nucleophilic attack on the π-bonded olefin to form *cis*-[Pt{σ-C_2H_4(L)}Cl(L)$_2$]Cl species.

A RECENT communication[1] dealt with the nucleophilic attack of excess of pyridine on *cis*-dichloro-(π-ethene)-(pyridine)platinum(II) which gave the σ-adduct *cis*-dichloro(pyridine)(2-pyridinioethanide)platinum(II) and pointed out that: (i) the attack takes place much more readily on the *cis*- rather than on the *trans*-isomer; (ii) the *cis*-pyridine stabilizes the σ-adduct in a similar manner as much stronger π-acceptors as phosphines and sulphoxides; and (iii) the strongly σ-donating ethanide group and the π-acceptor pyridine prefer the *cis*- to the *trans*-configuration. This prompted us to publish our evidence for a different formulation of these complexes.

In previous work[2] we investigated the reaction of a series of *trans*-[Pt(π-C_2H_4)Cl_2(py)] complexes with stoicheiometric amounts of free base (equation 1). Performing the same reaction on the *cis*-isomer we observed that complete dissolution of the starting material (which is sparingly soluble either in methanol or in chloroform) occurred after 2 mol of free base had been added per mol of platinum complex indicating that the soluble species contained two extra molecules of amine (equation 2). Using either a higher (4 : 1) or a lower (1 : 1) amine : platinum ratio (in the latter case not all the *cis*-complex dissolved) the same complexed species was formed in solution. We have now investigated the complexes (I)—(IV) (Table).



$$\underset{CH_2}{\overset{CH_2}{\|}}\text{—}\underset{Cl}{\overset{Cl}{Pt}}\text{—}L + L \longrightarrow \overset{+}{L}\cdot CH_2CH_2\text{——}\underset{Cl}{\overset{Cl}{\overset{-}{Pt}}}\text{——}L \quad (1)$$



$$\underset{CH_2}{\overset{CH_2}{\|}}\text{—}\underset{L}{\overset{Cl}{Pt}}\text{—}Cl + 2L \longrightarrow \overset{+}{L^1}\cdot CH_2CH_2\text{——}\underset{L^3}{\overset{Cl}{Pt}}\text{——}L^2 + Cl^- \quad (2)$$

Complex (I) showed in its n.m.r. spectrum three sets of pyridine signals; two of these had methyl resonances very similar to those observed in *trans*-[Pt{σ-C_2H_4(3,5-Me_2py)}-Cl_2(3,5-Me_2py)], the third set, having chemical shifts intermediate between the other two, was assigned to the pyridine *cis* to the σ-bonded ethene. The absorptions of the σ-ethene protons were analogous to those reported;[1] under our conditions too there was no trace of the absorption at δ 4·45 of the π-C_2H_4 protons of the starting complex indicating that the reaction goes to completion also in the absence of excess of pyridine.

Similar behaviour was shown by the already reported *cis*-[Pt(π-C_2H_4)Cl_2($H_2NCHMePh$)] complex.[3] The assignment of the σ-ethene proton resonances in this case was difficult as the NH_2 and N–CH resonances overlapped.

Reaction of the *cis* π-ethene complex containing L^1 with free L^2 gave the mixed complex having L^1 in its original *cis* position with respect to the σ-ethene; no isomerization was detected before decomposition occurred, indicating that the three different amine molecules of the σ-adduct do not exchange their sites.

Compounds (I)—(IV) (see Table) could be isolated easily in the solid state using the same procedure described earlier for the preparation of the σ-adducts starting from the *trans* complexes. The products, which in the present case are very soluble in methanol, could be precipitated in > 70% yield as white solids by adding diethyl ether; in all cases they gave satisfactory elemental analyses.

The substitution of the chlorine *trans* to ethene could, in principle, either precede or follow the nucleophilic attack by the amine on the π-olefin; in the first case (which is the more probable) a cationic π-ethene complex, very sensitive to attack by a nucleophile, would be formed.

TABLE. Proton chemical shifts[a] (δ), downfield from $SiMe_4$, of L protons in *cis*-$[Pt\{\sigma\text{-}C_2H_4(L^1)\}ClL^2L^3]^+$. The numbering of ligands (L^1, L^2, and L^3) is as in equation (2).

	L^1			L^2			L^3		
Complex	Me	*o*-H	*p*-H	Me	*o*-H	*p*-H	Me	*o*-H	*p*-H
cis-$[Pt\{\sigma\text{-}C_2H_4(3,5\text{-}Me_2py)\}Cl(3,5\text{-}Me_2py)_2]^+$ (I)	2·57	9·04	7·97	2·27	8·20	7·4[b]	2·40	8·53	7·4[b]
cis-$[Pt\{\sigma\text{-}C_2H_4(3,5\text{-}Me_2py)\}Cl(3,5\text{-}Me_2py)(H_2NCHMePh)]^+$ (II)	2·53	9·10	7·88	2·21	8·04	7·4[b]	1·73	—	—
cis-$[Pt\{\sigma\text{-}C_2H_4(H_2NCHMePh)\}Cl(H_2NCHMePh)(3,5\text{-}Me_2py)]^+$ (III)	1·80	—	—	1·50	—	—	2·23	8·21	c
cis-$[Pt\{\sigma\text{-}C_2H_4(H_2NCHMePh)\}Cl(H_2NCHMePh)_2]^+$ (IV)	1·6[b]	—	—	1·45[b]	—	—	1·6[b]	—	—

[a] All spectra were recorded in $CDCl_3$ solution at 0 °C. [b] Because of overlap the values are inaccurate. [c] Obscured by phenyl resonances.

The complexes *cis*-$[Pt\{\sigma C_2H_4(L)\}Cl(L)_2]^+$ do not have a formal charge on the platinum atom whereas there is a formal negative charge on platinum in *trans*-$[Pt\{\sigma\text{-}C_2H_4(L)\}Cl_2(L)]$; this could well explain the different stability of the *cis* compared with the *trans*-σ-adducts.

Decomposition studies in solution have also shown that stability increases going from (I) to (IV); this resembles the trend observed in *trans*-$[Pt\{\sigma\text{-}C_2H_4(L)\}Cl_2(L)]$ complexes (where the stability parallels the increasing basicity and decreasing steric hindrance of the amine).[4]

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