Nucleophilic Attack on π-Etheneplatinum(II) Complexes: *cis*-Isomers

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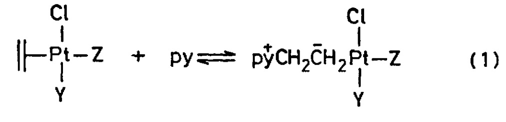
Summary ^{1}H-n.m.r. spectroscopy has been used to demonstrate that nucleophilic attack by pyridine on the C=C bond in *cis*-dichloro(π-ethene)(pyridine)platinum(II) readily leads to the formation of the σ-bonded complex, *cis*-dichloro(pyridine)(2-pyridinioethanide)platinum(II), which is much more stable than the corresponding *trans* isomer.

PYRIDINE (py) can attack *trans*-dichloro(π-ethene)(pyridine)platinum(II), (I_{tr}), reversibly to give a σ-bonded adduct,[1,2] (II_{tr}), as in equilibrium (1); between −40 and −15 °C (I_{tr}) and (II_{tr}) coexist in the presence of excess of pyridine, but the latter is not detectable at 25 °C. While degradative studies indicate that ammonia can attack *cis*-amine(π-ethene)dichloroplatinum(II) systems,[3] nothing is known of the position of equilibrium between the *cis*-isomers, (I_{cis}) and (II_{cis}) in equation (1).



(1)

(I_{tr}) Y = Cl, Z = py   (II_{tr}) Y = Cl, Z = py

(I_{cis}) Y = py, Z = Cl   (II_{cis}) Y = py, Z = Cl

The complex (I_{cis}) is not very soluble in $CHCl_3$. However we find that on treatment with excess of pyridine, a suspension of it in $CDCl_3$ at 25 °C dissolves rapidly, giving a solution whose ^{1}H-n.m.r. spectrum contains two 1:2:1 triplets of equal area at δ 5·0 and 2·25 both with ^{195}Pt satellites (Table). These features are typical of formation of a σ-adduct,[1,4] which we conclude in this case to be the *cis* compound, (II_{cis}). Incidentally the ^{195}Pt–^{1}H coupling constants are larger than in (II_{tr}) as often occurs in a *cis*-isomer compared with the corresponding *trans* one.[5] As there is no trace in the new solution of the absorption at δ 4·65 caused by the π-C_2H_4 protons of the starting π compound, (I_{cis}), and no sign of any suspended material, it is concluded that in this case reaction (1) goes to completion. The n.m.r. spectrum remains unchanged for several hours at 25 °C and is not altered by cooling to −60 °C. Thus nucleophilic attack by pyridine on the co-ordinated olefin takes place much more readily on the *cis* isomer (I_{cis}), than on the *trans*, (I_{tr}); it is interesting that a mild π-acceptor like pyridine when placed *cis* to the olefin stabilizes the σ-adduct in a similar manner as stronger π-acceptors such as phosphines and sulphoxides.[6]

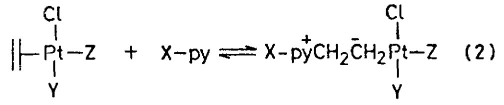
To investigate the relative stabilities of the σ-adducts, (II_{tr}) and (II_{cis}), a sample of the former was left in $CDCl_3$ for 12 h at −20 °C. After removal of the yellow and the white deposits of *trans*-$[PtCl_2(py)_2]$[1] and $[Pt(py)_4]Cl_2$,[7] respectively, which are rather insoluble in $CHCl_3$, the

TABLE
^{1}H-n.m.r. data in $CDCl_3$ (δ values).[a]

	π-C_2H_4		py$CH_2$$CH_2$Pt		py$CH_2$$CH_2$Pt	
X	(I_{cis}), (III_{cis})	(I_{tr}), (III_{cis})	(II_{cis}), (IV_{cis})	(II_{tr}), (IV_{tr})	(II_{cis}), (IV_{cis})	(II_{tr}), (IV_{tr})
H[b]	4·65(s)[c]	4·9(s)[d]	5·0(t)[e]	4·54(t)[f]	2·25(t)[g]	2·45(t)[h]
4-Me[i]	4·55(s)[j]	4·9(s)[k]	4·95(t)[e]	4·5(t)[f]	2·25(b)[l]	2·45(b)[l]
3,5-Me_2[i]	4·55(s)[j]	4·95(s)[k]	4·9(t)[e]	4·5(t)[f]	2·25(b)[l]	2·45(b)[l]

[a] s = singlet, t = triplet, b = broad; temperature for (I_{cis}) and (III_{cis}): 25 °C; others: −40 °C; data for (I_{tr}), (II_{cis}), (III_{tr}), and (IV_{cis}) at 25 °C are very similar to those here. [b] Complexes (I) and (II). [c] *J*(Pt–H) 68 Hz. [d] *J*(Pt–H) 61 Hz. [e] *J*(Pt–H) 40, *J*(H–H) 8 Hz. [f] *J*(Pt–H) 36, *J*(H–H) 7·5 Hz. [g] *J*(Pt–H) 90, *J*(H–H) 8 Hz. [h] *J*(Pt–H) 86, *J*(H–H) 7·5 Hz. [i] Complexes (III) and (IV). [j] *J*(Pt–H) 67 Hz. [k] *J*(Pt–H) 60 Hz. [l] *J*(Pt–H) and *J*(H–H) not detectable.

solution was found to have an n.m.r. spectrum identical with that attributed to (II_{cis}).



$$\|\!-\overset{Cl}{\underset{Y}{Pt}}-Z \;+\; X\text{-}py \rightleftharpoons X\text{-}\overset{+}{py}CH_2\overset{-}{C}H_2\overset{Cl}{\underset{Y}{Pt}}-Z \quad (2)$$

(III_{tr}) Y = Cl, Z = X-py (IV_{tr}) Y = Cl, Z = X-py

(III_{cis}) Y = X-py, Z = Cl (IV_{cis}) Y = X-py, Z = Cl

In the *trans* system based on substituted pyridines (reaction 2, III_{tr}, IV_{tr}, X = 4-Me or 3,5-Me_2) the $^+\sigma$-adducts cannot be detected at temperatures > -40 °C.[8] However, treatment in $CDCl_3$ of the *cis*-π-complexes, (III_{cis}), and of the *trans*-σ-adducts, (IV_{tr}), in comparable ways to those just described enables n.m.r. spectra to be obtained which appear to be those of *cis* σ-adducts, (IV_{cis}), (Table).

For many platinum(II) complexes containing two π-accepting ligands, the *cis*-isomer is more stable than the *trans*. It is interesting here to see that the strongly σ-donating $CH_2CH_2^-$ group and the π-accepting pyridine prefer to adopt a *cis* configuration.

(*Received*, 31*st August* 1977; *Com.* 916.)

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