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Stabilization of σ Adducts Formed by Nucleophilic Attack on Ethene π Bonded to Platinum(II)

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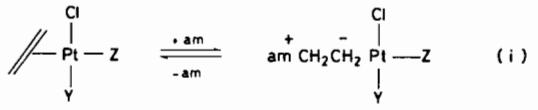
Particularly stable 2-ammonioethanide compounds are formed when amines attack the π bonded ethene in chloro(pyridine-2-carboxylato, isoquinoline-1-carboxylato or 8-quinolinato) η-etheneplatinum(II).

It is well known that amines (am) attack olefins coordinated to platinum bringing about a π → σ rearrangement [1–5] as in (i).



(1) (2) (i)

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However 2-ammonioethanide compounds, or σ-adducts, (2) are not particularly stable with relation to (1).

Thus in the systems in which Y = Cl, Z = am = aliphatic amine, K_i is rarely greater than 30 dm^3 mol^{-1} [5] and usually somewhat smaller (see below); $CHCl_3$ or $CDCl_3$ is the solvent and the temperature 298 K throughout. However we have observed that greater stabilization can be achieved by the introduction of a conjugated π-accepting system in the Y–Z position.

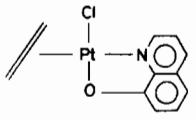
When a cold aqueous solution of $K[PtCl_3(C_2H_4)]$ is treated with pyridine-2-carboxylic acid, fine yellow crystals of (1, X = Y = Cl, Z = pyridine-2-carboxylic acid) appear. *Anal.* Found: C, 23.0; H, 2.3; N, 3.5; Cl, 16.8%. Calc.: C, 23.0; H, 2.15; N, 3.35; Cl, 17.0%. On treatment with alkali (*e.g.* $KHCO_3$ or amine) this compound readily losses HCl to give the bidentate complex (3a). *Anal.* Found: C, 25.4; H, 2.3; N 3.7%. Calc.: C, 25.2; H, 2.1; N, 3.7%. When isoquinoline-1-carboxylic acid or 8-hydroxyquinoline is used, pale yellow crystals of the bidentate compounds (3b) or (3c) are formed directly. (3b) *Anal.* Found: C, 33.3; H, 2.45; N, 3.2; Cl, 8.15%. Calc.: C, 33.35; H, 2.3; N, 3.2; Cl, 8.1%.

(3a) (3b)

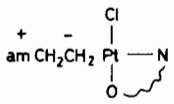
TABLE I. Values of K_i/dm^3 mol^{-1} in $CHCl_3$ at 298 K. Data in normal and italic type obtained by UV and NMR respectively (see text).

am	(3a)	(3b)	(3c)	(1, Y = Cl, Z = am)[a]
Pr^nNH_2	*>100*	*>100*		20
Pr^iNH_2	*ca. 100*	*ca. 100*		10
Bu^nNH_2		97		25
Bu^iNH_2		60		27
$PhCH_2NH_2$		*ca. 100*		*ca. 1*
Me_2NH	*>100*	410	*100*	*100*
Et_2NH	*>100*	220		12
Pr^n_2NH	*>100*	140		7
Pr^i_2NH	*10–30*	*10–30*		*ca. 0.2*
Bu^i_2NH	*10–30*	*10–30*		*ca. 0.2*
Et_3N	*ca. 10*	*ca. 10*		*<0.2*
py	*ca. 1*	*ca. 1*		*<0.1*

[a]All this column, except Me_2NH, from reference 5.



(3c)



(4a, b, or c)

Using these three new bidentate compounds (3), we have continued earlier studies [5] on the values of K_i by following either the changes in absorption in the UV spectrum or monitoring the disappearance of the η-C_2H_4Pt NMR spectrum on the addition of aliquots of am. (The first method is accurate but laborious, the second fast but approximate). Values of K_i for the bidentate systems are given in the Table I, being compared with corresponding values for (1, Y = Cl, Z = am). Throughout the equilibrium lies farther towards the σ-adduct for the former compounds than the latter, whether am is a simple unhindered aliphatic amine, a bulky one or pyridine.

The new bidentate σ-adducts (4) implied in the Table I can nearly all be obtained as solids by mixing stoichiometric quantities of amine (am) and (3) in $CHCl_3$ at 0 °C and evaporating if necessary. The exceptions are those from $^iPr_2NH$, $^iBu_2NH$, Et_3N where a slight excess of amine is needed, and pyridine where both excess amine and a temperature of −40 °C are required. The solids are intense yellow or orange, and are stable for several weeks under normal conditions with the exception of the pyridinio compounds which tend to decompose above 0 °C. They analyse satisfactorily, *e.g.* (3a, am = $^tBuNH_2$) Found: C, 31.6; H, 4.0; N, 6.05; Cl, 7.5%; Calc.: C, 31.75; H, 4.18; N, 6.15; Cl, 7.85%. (3b, am = $^iPrNH_2$) Found: C, 36.7; H, 3.75; N, 5.9%; Calc.: C, 36.8; H, 3.7; N, 5.8%. (3c, am = Me_2NH) Found: C, 35.0; H, 3.7; N, 6.3%; Calc.: C, 34.8; H, 3.8; N, 6.25%.

In $CHCl_3$ free amine reacts with the bidentate σ-adducts (4) displacing ethene. (This was a nuisance in the UV studies and necessitated observations being made rapidly). However the compounds are unusually stable with respect to the corresponding ethene complexes (3) as judged by the values of K_i, and this is the particular point of interest.

Similarly stability of the σ adduct is not exhibited by related systems in which cyclization cannot occur, *e.g.* (2 Y = Cl; Z = pyridine, pyridine-4-carboxylic acid, 2,6-dimethylpyridine, pyridine-2-oxime, 2-ethylpyridine, 2-benzylpyridine, 2-chloropyridine, 4-cyanopiridine, quinoline, 2-methylquinoline, isoquinoline). (Unfortunately if one starts with Z as above and am = strong amine, formation occurs of the σ-adduct with the strong amine in both the am and Z positions [5]. NMR studies using diethylamine as am indicate that $K_i < ca.\ 20$ $dm^3\ M^{-1}$ for the bidentate analogues of (3) containing the following ligands: acetylacetonate, aminobenzene-2-carboxylate, N-phenyl-aminobenzene-2-carboxylate, quinoline-2-carboxylate, pyrrolidine-2-carboxylate (*i.e.* deprotonated l-proline). This suggests that in order to stabilize the σ adducts it is necessary to have a heterocyclic amine group and a bidentate ligand.

We offer the following explanation for the stabilization, in the sense of equilibrium (i) lying well to the right. Ethene and pyridine derivatives are both π-acceptors. Platinum(II) complexes containg two π accepting ligands *trans* to each other are not particularly stable [6–9] anyway, but here there is another factor. An olefin ligand prefers to arrange itself with its C=C axis perpendicular to the PtClNO plane, so that the π-bond between the ethene and platinum atom is also regarded as being perpendicular to the plane. The coordination of the carboxylate group forces the pyridine to lie in the PrClNO plane, and hence one d-orbital has to donate π-electrons to both ligands. While frequently the instability in *trans* isomers is removed by isomerisation to a *cis* form, here the same result is achieved by $\pi \rightarrow \sigma$ rearrangement.

To test this idea, the quinoline-2-carboxylate analogue of (3) was prepared. While the ligand is a heterocyclic amine and bidentate, as required above, its skeleton cannot be completely coplanar with the PtClNO system, because of steric interaction between the Cl and the 8-H atom of the quinoline ring ($K_i < ca.\ 1$ for this system).

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