Inorganica Chimica Acta Letters, 45 (1980) L31–L32
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

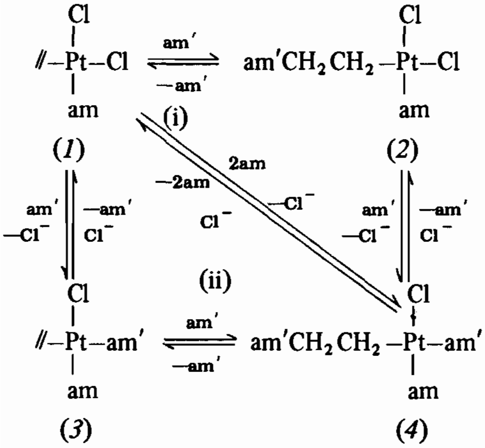
Neutral and Cationic η-Ethene and σ-(Ammonio)ethanide Complexes of Platinum(II)

MICHAEL GREEN* and JAMIL K. K. SARHAN

Department of Chemistry, University of York, Heslington, York YO1 5DD, U.K.

Received March 4, 1980

When a *cis*-amine(ethene)platinum(II) complex such as (*1*), is attacked by further amine, am′, in principle three products could be formed: a σ-(2-ammonio)ethanide complex [1–4], (*2*); a cationic ethene ion [5], (*3*); and a cationic σ-(2-ammonio ethanide) compound, (*4*).



While (*1*, am = pyridine, py) is insoluble in chloroform, a suspension of it on treatment with pyridine goes into solution. Al-Najjar and Green [6] have ascribed this to the formation of (*2*, am = am′ = py), Natile [7] to the production of (*4*, am = am′ = py). The evidence below indicates that (*2*) and (*4*) are both formed and that (*3*) is probably not.

Unlike its parent compound, (*1*, am = 4-methylpyridine, Mepy) is soluble in chloroform. (Hereafter am and am′ if not specified will be Mepy.) Using a solution of this compound at an approximate concentration of 2.6×10^{-4} mol dm^{-3}, we have followed the change in absorbance, ΔA, in the ultra-violet spectrum at 300 nm on addition of aliquots of Mepy in quantities corresponding to between 20 and 150 equivalents of added amine. Straight line Hildebrand–Benesi [8] graphs were obtained by plotting $1/\Delta A$ not against $1/[\mathrm{am}']$, but against its square. This clearly indicates a 1:2 stoichiometry in the reaction between (*1*) and Mepy pointing to equilibrium (ii) and the formation of (*4*). $K_{ii}(298) = 672$ mol^{-2} dm^{6}, $\Delta H^{\ominus}_{ii} = -32 \pm 2$ kJ mol^{-1}, $\Delta S^{\ominus}_{ii} = -54 \pm 4$ J K^{-1} mol^{-1}. The last value is compatible with the process in which the numbers of molecules falls by one.

Unfortunately there is not sufficient change in the UV spectrum for study of this system with less than 20 equivalent of Mepy; however the system can be studied by ^{1}H NMR. At 0 °C K_{ii} is *ca.* 2220 mol^{-2} dm^{6}, so that the concentration of free Mepy is negligible at and below this temperature provided that less than two equivalents are used. Table I summarizes ^{1}H NMR data for (*1*) and (*4*).

Studies on the *trans*-compounds [PtCl$_2$(η-ethene)-py], [PtCl$_2$(CH$_2$CH$_2$py)py] and [PtCl$_2$(CH$_2$CH$_2$am)-py] (am = ^{t}Bu or morpholine), show that the $\underline{H}^{\alpha}_{py}$ resonances of pyridine move to higher and lower δ values on going from the (η-C$_2$H$_4$)Pt–$\underline{py}$ to the (σ-CH$_2$CH$_2$)Pt–$\underline{py}$ and to the $\underline{py}$–CH$_2$CH$_2$Pt systems respectively. Thus the peaks at δ9.27 and δ8.36 in (*4*) can be assigned to $\underline{H}^{\alpha}$ in *trans*-CH$_2$CH$_2$P–Me$\underline{py}$ and Me$\underline{py}$–CH$_2$CH$_2$Pt respectively. (As [9] in *trans*-[PtCl$_2$(CH$_2$CH$_2\underline{py}$)$\underline{py}$] and may be for the same reason [9], neither has platinum satellites.) Thus the resonance in (*4*) at δ8.7, which has satellites, must be due to the $\underline{H}^{\alpha}$ protons in *cis*-CH$_2$CH$_2$Pt–Me$\underline{py}$. The closeness of this value to the corresponding one in (*1*) illustrates the insignificance of *cis* compared with *trans* effects in platinum(II) complexes.

When the stoichiometry of (*1*) to Mepy is about 1:1, there are more peaks than those due to just (*1*) and (*4*), in particular an extra doublet due to $\underline{H}^{\alpha}$ at δ8.45 and a C$\underline{H}_3$ singlet at δ2.48, suggesting the presence of a further Mepy containing compound, the value of δ8.45 is compatible with $\underline{H}^{\alpha}$ in the Me$\underline{py}$–CH$_2$CH$_2$Pt group in (*2*), but not, however, with *trans*-(η-C$_2$H$_4$)Pt–Me$\underline{py}$ in (*3*), since $\underline{H}^{\alpha}$ proton resonances in amines tend to move to higher δ values on coordination to platinum and since $\underline{H}^{\alpha}$ in Mepy absorbs at δ8.55. It is then necessary to assume that the $\underline{H}^{\alpha}$ peak for the *cis*-CH$_2$CH$_2$Pt–Me$\underline{py}$ in (*2*) coincides with the corresponding resonances in (*1*) and (*4*), which is reasonable as the last two are almost in the same place any way at δ8.65–8.70. Further the doublet with this δ value and particularly its satellites lose and then regain some of their resolution between the stoichiometries of 1:0 and 1:2. In addition the C$\underline{H}_2$C$\underline{H}_2$ resonances are not resolved well until a 1:2 composition is reached which suggests that at a 1:1 stoichiometry for example more than one σ-ethanide species may be present. Similar loss of resolution is observed in *trans*-[PtCl$_2$(CH$_2$-CH$_2$am)am′] systems when the two amines are different and interchange, so that four compounds coexist [4]. Peak areas indicate that $K_i(273) =$ *ca.* 50 mol^{-1} dm^{3}.

---

*Author to whom correspondence should be addressed.

TABLE 1. δ- and J-values in $CDCl_3$ at 0 °C.

	$C\underline{H}_2$	$C\underline{H}_3$	$\underline{H}^{\alpha,\alpha'}$	$\underline{H}^{\beta,\beta'}$	$C\underline{H}_2N$	$PtC\underline{H}_2$
cis-$[PtCl_2(Mepy)(\eta\text{-}C_2H_4)]$	4.55(s) J(Pt–H) 64.5 Hz	2.45	8.65(d) J(Pt–H) 36.6 Hz J(H–H) 6 Hz	7.35(d) J(H–H) 6 Hz	–	–
cis-$[PtCl_2(CH_2CH_2\text{-}\overset{+}{M}epy)(Mepy)]^+Cl^-$	–	3.02	9.27	7.8	4.85(t)	2.12(t)
		2.32	8.7 J(Pt–H) 40 Hz	7.32	J(H–H) 8 Hz	J(Pt–H) 88 Hz
		2.64	8.36 J(H–H) 6 Hz	7.15 J(H–H) 6 Hz		J(H–H) 8 Hz

The question of whether (*3*) is also formed is more difficult to answer. Though sharp at 25 °C, the $C_2\underline{H}_4$ peak and satellites of (*1*) broaden on cooling, presumably owing to loss of freedom of rotation of the ethene ligand. The $C_2\underline{H}_4$ protons in the weakly bonded ligand of (*3*) would be expected to absorb between those in the more robust complex (*4*) and those in free ethene, that is between δ4.55 and δ5.5. Unfortunately, the $NC\underline{H}_2CH_2$ protons in (*2*) and (*4*) absorb at δ4.85 as a 1:2:1 triplet (without satellites, in contrast to many other systems [4]). However there are no irregularities in the spectrum between δ4.55 and δ5.5 {in particular at δ4.79 where the new cationic π-complex, $[Pt(\eta\text{-}C_2H_4)Cl(Me_4en)][ClO_4]$, absorbs [10]} which could be ascribed to a main peak and satellites $\eta\text{-}C_2\underline{H}_4$ protons in (*3*). Moreover the $C_2\underline{H}_4$ resonance of (*1*) only decreases in intensity as Mepy is added; it does not move to higher δ-value. Formation of (*3*) to an extent of 10% or less might pass undetected by ^1H NMR, but with this proviso there is no evidence for this π-olefin cationic species. As ethene is *trans*-labilizing, the absence of formation of (*3*) from (*1*) must be thermodynamic. Of (*3*) and (*2*) the latter is clearly the more stable isomer, the data indicating that at 273 K, $K = [(3)]/[(2)] \geqslant 50$. The existence [10] of $[Pt(\eta\text{-}C_2H_4)Cl(Me_4en)][ClO_4]$ may depend on the reluctance of tertiary amines to attack coordinated ethene in neutral complexes [4].

Similar results are obtained using NMR at *ca.* –49 °C, except that when the number of equivalents of 4-methylpyridine exceeds *ca.* 3, an additional peak appears at δ4.12. This would be due to a five coordinate species [11].

References

1 P. D. Kaplan, P. Schmidt and M. Orchin, *J. Am. Chem. Soc., 90,* 4175 (1968).

2 A. De Renzi, G. Paiaro, A. Panunzi and U. Romano, *Chim. Indust. (Milan), 55,* 248 (1973); and ref. therein.

3 G. Natile, L. Maresca and L. Cattalini, *J. Chem. Soc. Dalton,* 651 (1977).

4 I. M. Al-Najjar and M. Green, *J. Chem. Soc. Dalton,* 1651 (1979).

5 *cf.* M. I. Gel'fman, N. M. Karpinskaya and U. U. Razumovskii, *Russ. J. Inorg. Chem., 15,* 1438 (1970); and D. G. Cooper and J. Powell, *Inorg. Chem., 15,* 1959 (1976).

6 I. M. Al-Najjar and M. Green, *J. Chem. Soc. Chem. Comm.,* 926 (1977).

7 G. Natile, *J. Chem. Soc. Chem. Comm.,* 654 (1978).

8 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc., 71,* 2703 (1949); see also reference 4.

9 M. Green, I. M. Al-Najjar and D. Hollings, *Transition Met. Chem., 4,* 308 (1979).

10 L. Maresca, G. Natile and G. Rizzardi, *Inorg. Chim. Acta, 38,* 53 (1980).

11 I. M. Al-Najjar and M. Green, *J. Chem. Soc. Chem. Comm.,* 212 (1977).