

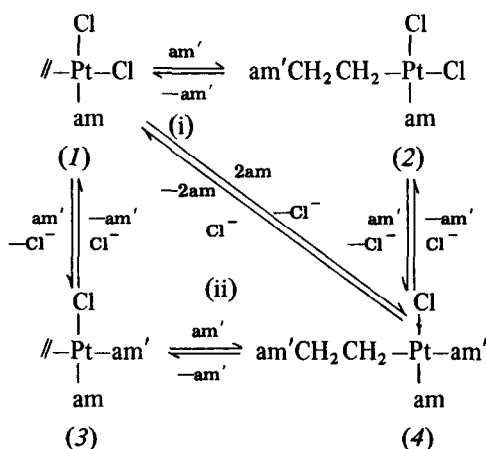
Neutral and Cationic η -Ethene and σ -(Ammonio)-ethanide Complexes of Platinum(II)

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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 $1/[am']$, but against its square. This clearly indicates a 1:2 stoichiometry in the reac-

tion between (1) and Mepy pointing to equilibrium (ii) and the formation of (4). $K_{ii}(298) = 672$ mol⁻² dm⁶, $\Delta H_{ii}^\circ = -32 \pm 2$ kJ mol⁻¹, $\Delta S_{ii}^\circ = -54 \pm 4$ 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 ¹H NMR. At 0 °C K_{ii} is ca. 2220 mol⁻² dm⁶, 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 ¹H NMR data for (1) and (4).

Studies on the *trans*-compounds [PtCl₂(η -ethene)-py], [PtCl₂(CH₂CH₂py)py] and [PtCl₂(CH₂CH₂am)-py] (am = ^tBu or morpholine), show that the H_{py}^α resonances of pyridine move to higher and lower δ values on going from the (η -C₂H₄)Pt-py to the (σ -CH₂CH₂)Pt-py and to the py-CH₂CH₂Pt systems respectively. Thus the peaks at δ 9.27 and δ 8.36 in (4) can be assigned to H^α in *trans*-CH₂CH₂P-Mepy and Mepy-CH₂CH₂Pt respectively. (As [9] in *trans*-[PtCl₂(CH₂CH₂py)py] and may be for the same reason [9], neither has platinum satellites.) Thus the resonance in (4) at δ 8.7, which has satellites, must be due to the H^α protons in *cis*-CH₂CH₂Pt-Mepy. 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 H^α at δ 8.45 and a CH₃ singlet at δ 2.48, suggesting the presence of a further Mepy containing compound, the value of δ 8.45 is compatible with H^α in the Mepy-CH₂CH₂Pt group in (2), but not, however, with *trans*-(η -C₂H₄)Pt-Mepy in (3), since H^α proton resonances in amines tend to move to higher δ values on coordination to platinum and since H^α in Mepy absorbs at δ 8.55. It is then necessary to assume that the H^α peak for the *cis*-CH₂CH₂Pt-Mepy 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 δ 8.65-8.70. 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 CH₂CH₂ 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*-[PtCl₂(CH₂-CH₂am)am'] systems when the two amines are different and interchange, so that four compounds coexist [4]. Peak areas indicate that $K_1(273) =$ ca. 50 mol⁻¹ dm³.

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

	CH_2	CH_3	$\text{H}^{\alpha,\alpha'}$	$\text{H}^{\beta,\beta'}$	CH_2N	PtCH_2
<i>cis</i> -[PtCl ₂ (Mepy)(η -C ₂ H 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	—	—
<i>cis</i> -[PtCl ₂ (CH ₂ CH ₂ -Mepy)- (Mepy)] ⁺ Cl ⁻	—	3.02 2.32 2.64	9.27 8.7 8.36 J(H-H) 6 Hz	7.8 7.32 7.15 J(H-H) 6 Hz	4.85(t) J(H-H) 8 Hz	2.12(t) J(Pt-H) 88 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 C₂H₄ peak and satellites of (1) broaden on cooling, presumably owing to loss of freedom of rotation of the ethene ligand. The C₂H₄ 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 $\delta 4.55$ and $\delta 5.5$. Unfortunately, the NCH₂CH₂ protons in (2) and (4) absorb at $\delta 4.85$ as a 1:2:1 triplet (without satellites, in contrast to many other systems [4]). However there are no irregularities in the spectrum between $\delta 4.55$ and $\delta 5.5$ [in particular at $\delta 4.79$ where the new cationic π -complex, [Pt(η -C₂H₄)Cl(Me₄en)]-[ClO₄], absorbs [10]] which could be ascribed to a main peak and satellites η -C₂H₄ protons in (3). Moreover the C₂H₄ 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, $K = [(3)]/[2)] \geq 50$. The existence [10] of [Pt(η -C₂H₄)-Cl(Me₄en)] [ClO₄] 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 $\delta 4.12$. This would be due to a five coordinate species [11].

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