trans-Bonding Bidentate Macroligands in Platinum(II) Complexes

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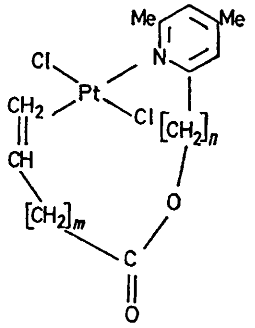
Summary Square-planar platinum(II) complexes containing *trans*-bonding bidentate macroligands, bound through pyridine and an olefin, are described; the large rings involving one platinum atom are 10, 11, 13 and 17-membered.

Results recently published by other workers concerning *trans*-bonding bidentate diphosphine ligands[1] prompt us to report data on the synthesis and stability of complexes (I) which we are investigating as a function of the *m* and *n* values. An aqueous solution of Zeise's salt and a dilute solution of the free ligand $CH_2{=}CH{-}[CH_2]_m{-}CO_2{-}[CH_2]_n{-}\{2\text{-}[4,6\text{-}Me_2C_5H_2N]\}$ (II) in chloroform (3×10^{-4}M) was stirred for several hours to give a mixture of mono, di and polynuclear complexes. Chromatography (Florisil) gave pure monomeric complexes (I). A high dilution is necessary to obtain the mononuclear complexes which are stable when crystalline or in dilute solution, but as an oil undergo slow polymerisation [ν(C=C–C=N) 1627 (bound pyridine), ν(C=C) 1512 (bound olefin), ν(Pt–Cl) (Ia) 338—357 sh, (Ib) 333 (asym), (Ic) 332—350, (Id) 337—347 cm^{-1}; M^+, (Ia) 499, (Ib) 513, (Ic) 541, (Id) 597].



(I)

a; *m* = 1, *n* = 3
b; *m* = 2, *n* = 3
c; *m* = 4, *n* = 3
d; *m* = 8, *n* = 3

When the reaction takes place at higher concentration ^1H n.m.r. shows fast co-ordination of the pyridine end of (II), leading to a new complex (III), and then a much slower displacement of the ethylene ligand by the olefinic end of (II). Treatment of a solution of (I) with an excess of ethylene leads only to complex (III). The *trans* configuration of complexes obtained by treating Zeise's salt with a pyridine is well established[2] and the ^1H n.m.r. data for the ethylene ligands in complexes (III) and *trans*-$[PtCl_2(C_2H_4)$(collidine)],[2b] (IV), and for the pyridine groups in complexes (I), (III), and (IV) support the *trans* configuration assignment of complexes (III) and (I).

Despite the frequent statement that *trans* square-planar complexes of platinum(II) show only one i.r. (Pt–Cl) stretching frequency[3] this is not a necessary condition for non-centrosymmetric complexes. The asymmetric band or doublets that we observe for our unsymmetrical chelated complexes are similar to those observed for some *trans*-$[PtCl_2$(olefin)(pyridine)] complexes.[4]†

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† For the complexes *trans*-$[PtCl_2$(olefin)(pyridine)], with ethylene and 2,4- and 2,6-dimethylpyridine or quinoline we observe shoulders at shorter frequency on the main band at *ca.* 350 cm^{-1}; with ethylene or pent-1-ene and 2,4,6-trimethylpyridine we observe the main band at 350 cm^{-1} and a medium band at 325 cm^{-1}.

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