Oxidative Dimerisation of an Anilido-complex of Platinum; *X*-Ray Structure of $[Pt_2Cl_2(PEt_3)_4N_2C_{12}H_{10}]^+[PF_6]^-$

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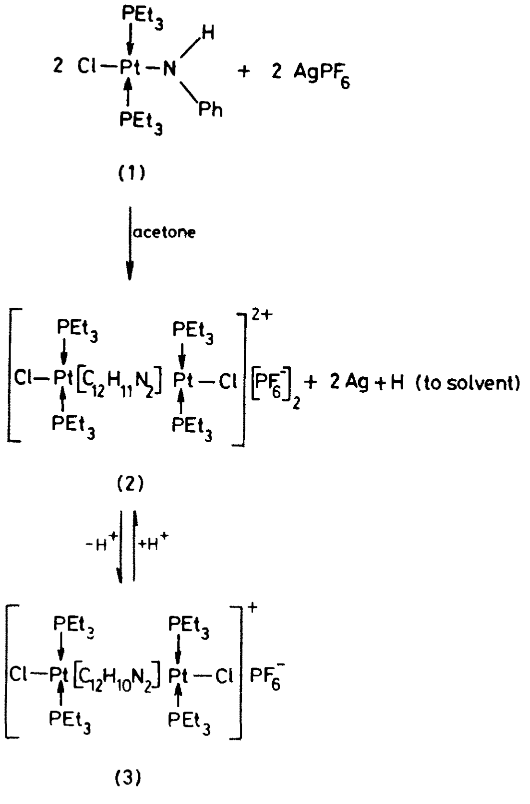
Summary The reaction of $(PhNH)Pt(PEt_3)_2Cl$ with $AgPF_6$ gives a weakly paramagnetic benzidine (4,4'-diaminobiphenyl) complex, which undergoes reversible deprotonation, an *X*-ray crystal structure of the deprotonated complex shows that the benzidine ligand has a marked quinonoid character

Although the chemistry of amine and alkyl complexes of platinum has been studied extensively, the corresponding amides have attracted far less attention.[1] We decided to examine the reaction of the anilido-complex[2] (**1**) with silver ion, as similar reactions in the alkyl series have given cationic complexes of high reactivity.[3] The reaction of (**1**) with silver hexafluorophosphate in acetone takes place quickly in normal light to give a red solution. After removal of metallic silver by filtration, the addition of ether causes the precipitation of (**2**) as a red solid; it is the only platinum-containing product and is formed in moderate yield. Reaction of (**2**) with potassium hydroxide in methanol followed by the addition of water and extraction into dichloromethane gives a deep green hexafluorophosphate salt (**3**) (Scheme).‡ On reaction with potassium cyanide in aqueous methanol, both (**2**) and (**3**) decompose giving benzidine (4,4′-diaminobiphenyl), but no aniline. Both (**2**) and (**3**) are weakly paramagnetic and show N–H stretching absorption in their i.r. spectra, but spectroscopic techniques failed to provide an unequivocal structure and so (**3**) was examined by *X*-ray diffraction.

Crystal data: $C_{36}H_{70}Cl_2F_6N_2P_5Pt_2$, $M = 1261$, orthorhombic, space group *Pnnm*, $a = 13{\cdot}431(2)$, $b = 14{\cdot}470(3)$, $c = 13{\cdot}033(2)$ Å, $U = 2532{\cdot}8(7)$, $Z = 2$. Four circle diffractometry, 2854 reflections $[I/\sigma(I) > 3{\cdot}0]$, anisotropic temperature factors for non-hydrogen atoms, current R 0·024.§

The single crystal *X*-ray structure shows that dimerisation of the anilido-ligand has occurred to give a benzidine complex (Figure). The dimeric complex has also undergone a one-electron oxidation to produce a free radical cation of $2/m$ symmetry. Not surprisingly for a benzidine radical cation, the aromatic group shows marked quinonoid character in its bond lengths (Figure).



Scheme

The oxidative coupling observed here is analogous to the known oxidation of dimethylaniline to tetramethylbenzidine. Tetramethylbenzidine may be converted into a free radical cation by electrolytic or chemical oxidation or by photolysis and, in common with (**3**), the organic radical is green in colour.[4] Both (**2**) and (**3**) gave e.s.r. signals in

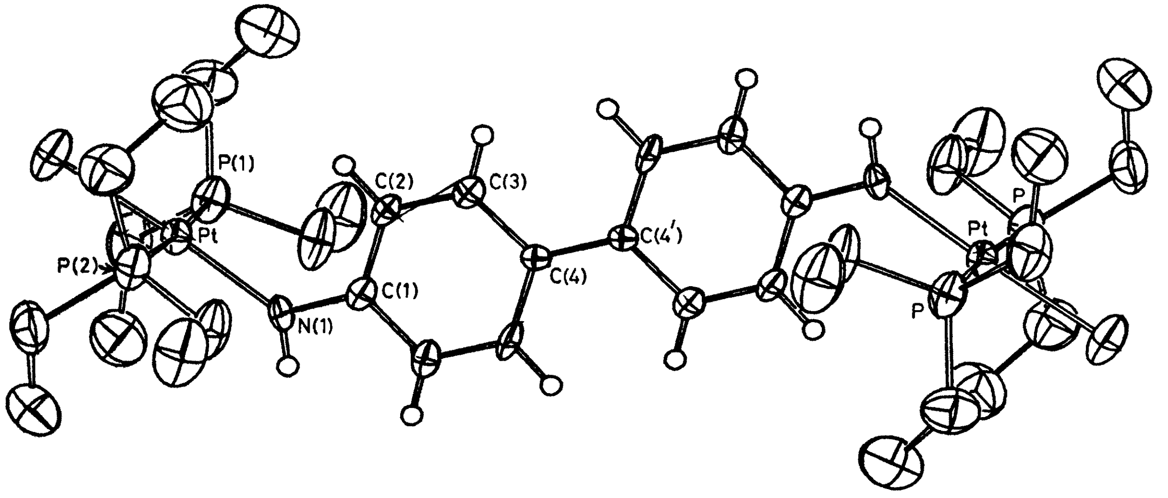


Figure. The cation $[Pt_2Cl_2(PEt_3)_4N_2C_{12}H_{10}]^+$ (**3**); side chain protons are omitted for clarity. Bond lengths (average values): C(1)–C(2) 1·427(5), C(2)–C(3) 1·355 (5), C(3)–C(4) 1·423(5), C(4)–C(4′) 1·431(6), Pt–Cl 2·319(1), Pt–P 2·309(1), and Pt–N 2·003(4) Å, the latter three are within the ranges expected (M. A. Bennett, Ho-Kin Chee, J. C. Jeffrey, and G. B. Robertson, *Inorg. Chem.*, 1979, **18**, 1071; J. W. Lauther and J. A. Ibers, *ibid.*, 1975, **14**, 640). Bond angle Pt–N(1)–C(1) 129·7(3)°.

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‡ Satisfactory elemental analyses have been obtained for both (**2**) and (**3**).

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

agreement with our formulation The e s r spectra of substituted benzidine-cations have been studied in some detail,[5,6] but the low symmetry of our system and the incomplete resolution of the spectra make analysis difficult The deprotonation of (**2**) to give (**3**) is reversible and virtually instantaneous in both directions, but the site of protonation in (**2**) is not known These results are of relevance to recent attempts to use benzidine derivatives[7] and dinuclear metal complexes[8] for the photolysis of water

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