# The Oxidative Dimerization of Arylamido Complexes of Platinum revisited: Protonation/Deprotonation or Oxidation/Reduction?

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A study of the products of oxidative dimerization of arylamido complexes of platinum using cyclic voltammetry and rotating-electrode techniques has demonstrated that the first compound isolated from the oxidation of *trans*-$[Pt(NHPh)Cl(PEt_3)_2]$ is $[\{PtCl(PEt_3)_2\}_2(\mu\text{-}N_2C_{12}H_{10})][PF_6]_2$, rather than $[\{PtCl(PEt_3)_2\}_2(\mu\text{-}N_2C_{12}H_{11})][PF_6]_2$. Consequently, its transformation to $[\{PtCl(PEt_3)_2\}_2(\mu\text{-}N_2C_{12}H_{10})]PF_6$ is a one-electron reduction rather than a deprotonation.

In the course of our current research on the redox behaviour of some binuclear orthopalladated complexes derived from *N*-phenylhydrazones described recently[1] we have found an oxidative coupling of the dimers to give tetramers.[2] A precedent for this is the oxidative coupling of arylamido complexes of platinum, reported to occur as shown in Scheme 1.[3,4] While the nature of the products (**3**) and (**4**) is well established, that of complex (**2a**) is somewhat obscure since it is stated[3] that 'elemental analysis shows that the radical (**2a**) is a dication derived from (**3**) by protonation, though the site of protonation is not known.' Also the initial oxidation is unclear since it 'is shown as occurring with a 2:3 molar ratio of (**1a**) to silver ion. An alternative stoicheiometry, involving a 1:1 ratio is also possible....'.[3] As the initial oxidation and product (**2a**) are very relevant to our work on palladium complexes, we decided to reinvestigate the reactions in Scheme 1 using cyclic voltammetry (c.v.) and rotating electrode (r.e.) techniques in order to gain insight into the true nature of (**2a**) and the processes in which it is involved.

## Results and Discussion

The results of the c.v. and r.e. experiments on complex (**2a**) show (Figure 1) that the dication undergoes two successive reversible monoelectronic reductions leading stepwise to the monocation (**3**) and the neutral complex (**4**). Similar experiments on (**3**) prepared chemically (Figure 2) reproduce exactly the potentials obtained for (**2a**). Furthermore, controlled-potential electrolysis (c.p.e.) of the green complex (**3**) at 0.3 V (referred to the saturated calomel electrode, s.c.e.) in electrochemical grade dichloromethane and $NBu_4PF_6$ as electrolyte gives a red-orange solution, and c.v. and r.e. experiments on this solution again reproduce Figure 1.

Hence the complexes (**2a**), (**3**), and (**4**) are all related by redox processes. The reaction of (**2a**) with MeOH–KOH is not a deprotonation but a reduction; likewise the reaction of (**3**) with acid ($H^+$) to give (**2a**) is a monoelectronic oxidation rather than a protonation. Consequently, complex (**2a**) must be formulated without the 'unlocalized' hydrogen atom, as shown in Scheme 2 for (**5**).

In contrast to the reported 'failure of attempts to measure the n.m.r. spectra of (**2a**)' we had no difficulty in recording such spectra; this suggests that the failure of earlier attempts and the 'weak paramagnetism' reported for complex (**2a**) were most likely due to the presence of some paramagnetic (**3**) contaminant, since (**2a**) [correctly formulated as (**5**)] must be diamagnetic. The $^{31}P$ n.m.r. spectrum of (**5**) in $CDCl_3$ shows a singlet with $^{195}Pt$ satellites at δ 15.24 p.p.m. (reference 85% $H_3PO_4$) with $^1J(^{195}Pt\text{–}^{31}P) = 2\,326.28$ Hz. Its $^1H$ n.m.r. spectrum in hexadeuterioacetone shows the signals of the $PEt_3$ ligands (1.19, pseudoquintet, $CH_3$, 36 H; 1.95, m, $CH_2$, 24 H, partially overlapped by the $CD_3COCD_2H$ signals), the NH groups (10.9, hump, 2 H), and the aromatic hydrogens; the latter integrate for 8 H (thus demonstrating the lack of any unlocalized hydrogen atom) and appear as two AB systems in accordance with the chemical inequivalence of the four hydrogens in each ring [$\delta_A = 8.57$, $\delta_B = 7.72$, $J_{AB} = 9.6$ Hz; $\delta_{A'} = 8.10$, $\delta_{B'} = 7.33$, $J(A'B') = 9.6$ Hz].

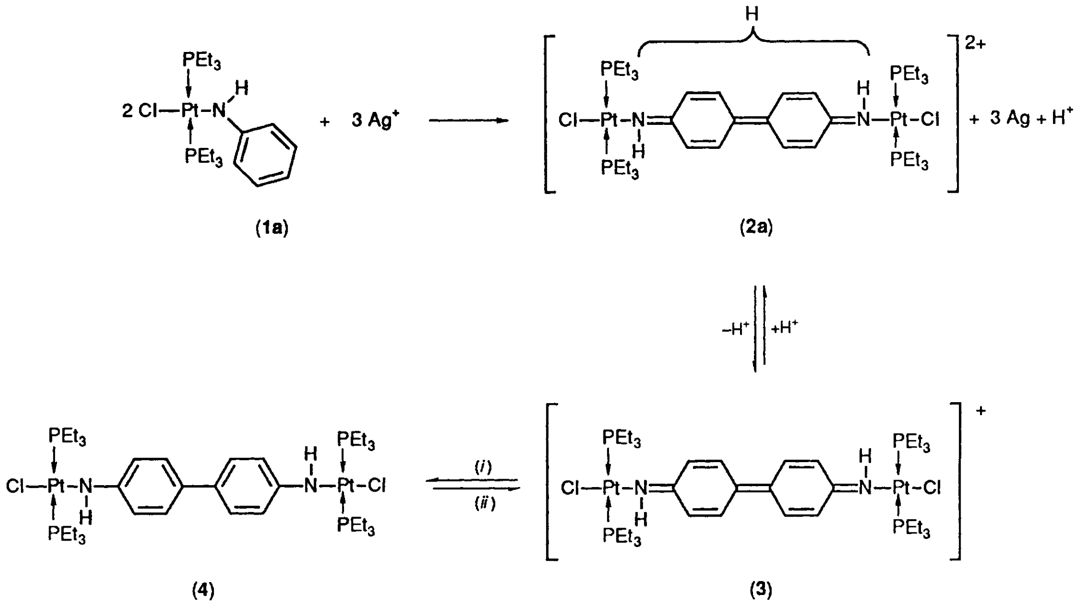
With the true nature of complex (**2a**) in mind, some reactions need to be reconsidered. Thus, the initial oxidative coupling leading to (**2a**) [now (**5**)] can be balanced as shown in equation (1). The formation of hydrogen may be obscured by the fact that it can be oxidized by $Ag^+$ to $H^+$ and if this oxidation were fully efficient the reaction should be balanced as in equation (2). In our studies on palladium complexes[2] we have found that some hydrogen is evolved but also some is oxidized. Thus, any stoicheiometry between those in equations (1) and (2) is possible, depending on the efficiency of the oxidation of $H_2$ by $Ag^+$, and this explains the uncertainty about the stoicheiometry of this process pointed out by the authors in the original paper.[3]

$$2[Pt(NHPh)Cl(PEt_3)_2] + 2Ag^+ \longrightarrow [\{PtCl(PEt_3)_2\}_2(\mu\text{-}N_2C_{12}H_{10})]^{2+} + 2Ag + H_2 \quad (1)$$

$$2[Pt(NHPh)Cl(PEt_3)_2] + 4Ag^+ \longrightarrow [\{PtCl(PEt_3)_2\}_2(\mu\text{-}N_2C_{12}H_{10})]^{2+} + 4Ag + 2H^+ \quad (2)$$

The 'deprotonation' of complex (**2a**) to (**3**) shown in Scheme 1 is really a one-electron reduction of (**5**) to (**3**) by the methanol used as solvent [equation (3)] under the conditions described in ref. 3 (10 $cm^3$ MeOH and 0.1 g of KOH), whereas the reverse 'protonation' is a one-electron oxidation by $H^+$ [equation (4)].

$$2[\{PtCl(PEt_3)_2\}_2(\mu\text{-}N_2C_{12}H_{10})][PF_6]_2 + KOMe + KOH \longrightarrow 2\,[\{PtCl(PEt_3)_2\}_2(\mu\text{-}N_2C_{12}H_{10})]PF_6 + CH_2O + H_2O + 2KPF_6 \quad (3)$$



Scheme 1. (*i*) $Na_2S_2O_4$–OH; (*ii*) $Ag^+$

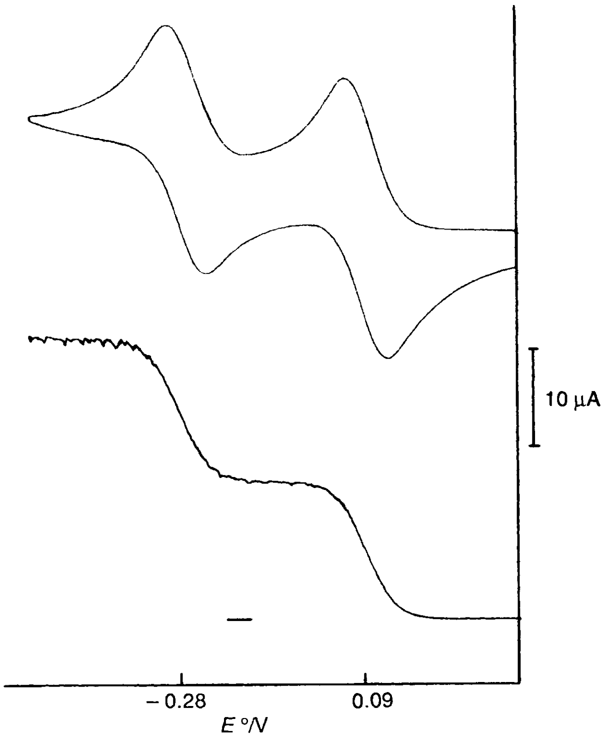


**Figure 1.** C.v. and r.e. curves of complex (**2a**) [(**5**)] at a platinum-bead electrode. Bar represents zero current

$$2[\{PtCl(PEt_3)_2\}_2(\mu\text{-}N_2C_{12}H_{10})]PF_6 + 2HPF_6 \longrightarrow 2[\{PtCl(PEt_3)_2\}_2(\mu\text{-}N_2C_{12}H_{10})][PF_6]_2 + H_2 \quad (4)$$

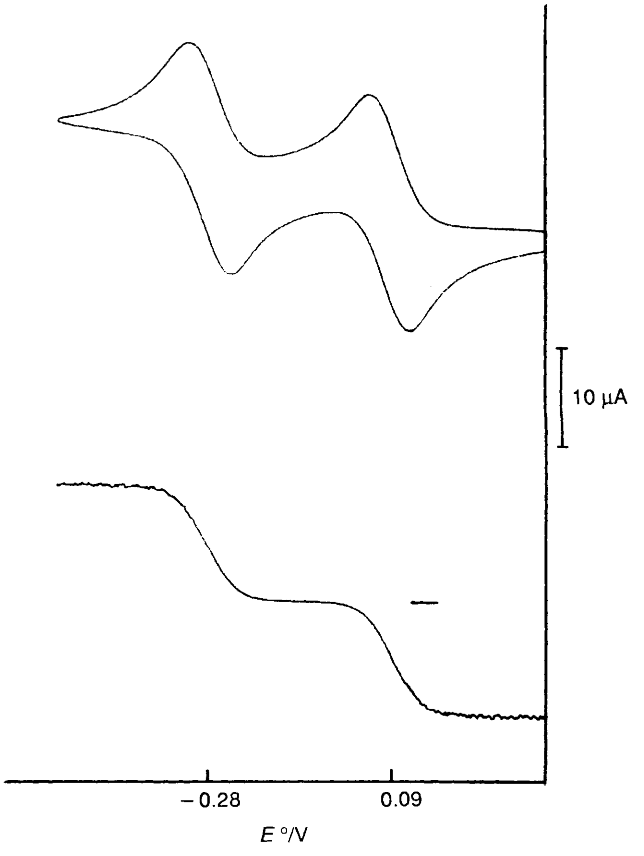
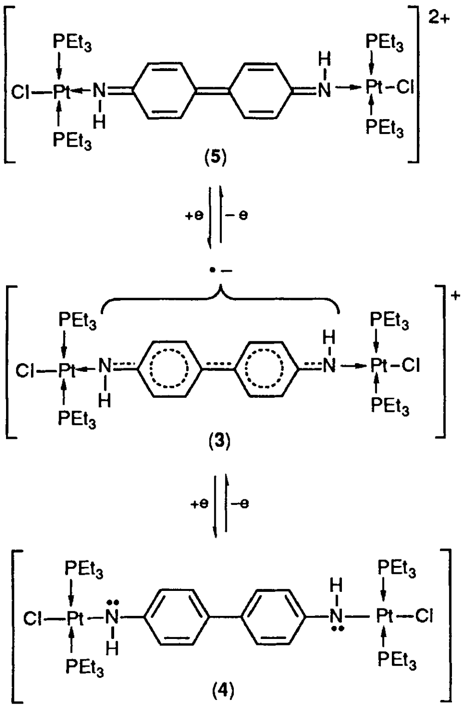


**Figure 2.** C.v. and r.e. curves of complex (**3**) at a platinum-bead electrode. Bar represents zero current

In conclusion, the reactions (**5**) ⟶ (**3**) ⟶ (**4**) should be seen as reversible ligand-based one-electron reductions in which, as depicted in Scheme 2, the bridging ligand changes from a co-ordinated 4,4′-biphenylene quinone di-imine in (**5**) to its corresponding radical monoanion in (**3**) (with the unpaired electron delocalized within the system), and to a benzidine diamido complex in (**4**); the number of electrons (including the lone electrons on the nitrogen atoms) changes from 14 in (**5**), to 15 in (**3**), and to 16 in (**4**). It is worth remarking that although this process is closely related to the oxidative coupling of aromatic amines[5] and also to the well known oxidation of dihydroxybenzenes to quinones through semiquinones,[6] the fact that the organic moiety is co-ordinated to a metal apparently excludes some alternative reactions occurring on the free organic compounds and makes the electrochemical studies particularly clean and clear.



Scheme 2.

Finally, although we have not studied the system with the *para* position blocked, leading to *ortho* coupling,[3] it is obvious that also complex (**2b**) in that paper should be formulated without the unlocalized hydrogen atom.

## Experimental

Electrochemical studies were carried out using an AMEL 551 potentiostat-amperostat and a Tacussel GSTP signal generator in conjunction with a three-electrode cell. For c.v. the working electrode was a platinum bead, the auxiliary electrode a platinum wire, and the reference an aqueous s.c.e. separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. In r.e. experiments the same platinum-bead electrode was used rotating at 500 revolutions min$^{-1}$. The solutions in $CH_2Cl_2$ were $0.5 \times 10^{-3}$ mol dm$^{-3}$ in complex and 0.1 mol dm$^{-3}$ in $NBu_4PF_6$ as supporting electrolyte. Under the conditions described above, the $E^\circ$ value of the couple used as reference, $[Fe(\eta^5\text{-}C_5H_5)_2]^+\text{–}[Fe(\eta^5\text{-}C_5H_5)_2]$, is 0.47 V.

Proton n.m.r. spectra were recorded on a Bruker AC-80 spectrometer at 80 MHz.

Compounds (**2a**) [(**5**)] and (**3**) were prepared as described.[3] Alternatively, (**5**) was prepared as follows. To a solution of $[Pt(NHPh)Cl(PEt_3)_2]$ (0.5 g, 0.89 mmol) in $CH_2Cl_2$ (20 cm$^3$) was added $[Fe(\eta^5\text{-}C_5H_5)_2]PF_6$ (0.295 g, 0.89 mmol). After stirring for 30 min the mixture was filtered and the solution was reduced *in vacuo* to small volume. Addition of diethyl ether afforded complex (**5**) as a red solid in 42% yield (Found: C, 30.6; H, 5.2; N, 2.1. $C_{36}H_{70}Cl_2F_{12}N_2P_6Pt_2$ requires C, 30.8; H, 5.0; N, 2.0%).

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