

Structure and reactivity of palladium and platinum arylazooximates

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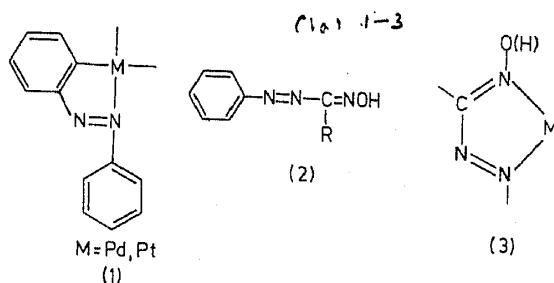
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Abstract. The structure and selected reactions of the title compounds are reviewed. Some highlights are as follows (L = conjugate base of phenylazoacetaldoxime). While PtL_2 exist in *cis* and *trans* forms, PdL_2 occurs only in the *trans* form. In the crystalline state *cis*- PtL_2 consists of weakly held dimers ($Pt \dots Pt$ 3.151 Å) but *trans*- PtL_2 consists of stacks of discrete molecules in the solid state. *Trans*- PdL_2 displays a surprisingly large tetrahedral distortion. The different metal-ligand bonds undergo selective cleavage by different reagents. Thus HCl and tertiary phosphines respectively cleave the $M-N$ (oxime) and $M-N$ (azo) bonds. Phosphine cleavage leads to interesting situations such as cone angle-dependent equilibria and fluxional behaviour. A rich redox chemistry consisting of successive reductions of the azo groups and of the metal are revealed electrochemically. *Cis*- PtL_2 unlike *trans*- PtL_2 undergoes a facile one-electron oxidation at low potentials. Another very curious reaction of *cis*- PtL_2 is the process in which an aromatic ring is thermally hydroxylated at the expense of an oximate oxygen atom. The meaning and significance of the observations are discussed.

Keywords. Palladium arylazooximates; platinum arylazooximates; selective bond cleavage; cone angles; fluxional behaviour; aromatic hydroxylation.

1. Introduction

The *ortho*-metallation of azobenzene (as in (1)) was discovered in the mid-sixties and the gate for many subsequent activities around this novel reaction became open (Cope and Sickman 1965; Omae 1979 and references therein). It is in this background that we initially examined whether the benzene ring would compete effectively with the oxime function when arylazooximes (2) (Kalia and Chakravorty 1970) are metallated with palladium and platinum. In practice binding was found to occur exclusively at azo- and oxime-nitrogens as in (3) (Kalia and Chakravorty 1969). The major features of the structure and reactivity of palladium and platinum arylazooximates are outlined in this article. All discussions are limited to the case $R=Me$ and the corresponding ligand phenylazoacetaldoxime is abbreviated as HL .



2. Parent species and their structures

2.1 *Cis*- and *trans*- PtL_2 : weak $Pt \dots Pt$ bond in the *cis* isomer

The *bis* complex PtL_2 exists in *cis* and *trans* isomeric forms, the structures of which are

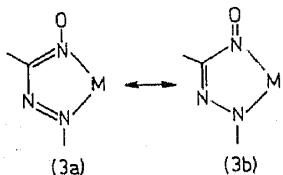
accurately known from x-ray data. In both cases azo- and oxime-nitrogen atoms are coordinated affording grossly planar MN_4 coordination spheres and five-membered chelate rings as in (3).

The *cis* and *trans* forms are furnished respectively by reacting HL with K_2PtCl_4 under acidic and basic conditions (Bandyopadhyay *et al* 1983a). The solvated proton is believed to have a role in favouring the *cis* form by a cooperative template effect of the metal and the proton whereby two oximato functions are brought together in a *cis* position *via* hydrogen bonding in the course of the chelatative reaction.

The *cis*- PtL_2 molecules are arranged in an unexpected way in the crystalline state. The asymmetric unit consists of two crystallographically independent molecules which have almost identical internal dimensions and are close enough ($Pt \dots Pt$, 3.151 Å) to each other to constitute a loose dimer. The two coordination planes *i.e.* the mean planes of the four coordinated nitrogen atoms in the dimer are nearly parallel forming a dihedral angle of 16.4°. Each platinum atom is located slightly out of its coordination plane by a distance of ~ 0.1 Å. The directions of these displacements are such that the two platinum atoms approach each other (Bandyopadhyay *et al* 1983a). While $Pt(II)-Pt(II)$ interaction in chelates is documented in literature (Hollis and Lippard 1983; Simonsen and Toftlund 1981) well characterized examples are not common.

In crystals of *trans*- PtL_2 the molecular arrangement is entirely different. Discrete molecules are stacked parallel to the b axis at intervals of 3.956 Å. Each molecule is centrosymmetric. The metal atom and the eight other atoms forming the two chelate rings define an excellent plane of C_{2h} symmetry. The deviation of each atom from the best plane is < 0.08 Å (Bandyopadhyay *et al* 1984).

Some selected average bond distance data are in table 1. These are consistent with the resonance (3a) \leftrightarrow (3b). The free ligand structure is also known and it has pure azoimine ($-N=N-C=N-O$) character (Roy and Sengupta 1980).



2.2 *Trans-PdL₂*: unprecedented tetrahedral distortion

Unlike PtL_2 , PdL_2 occurs in only one isomeric form (Bandyopadhyay *et al* 1981) now

Table 1. Selected average distances (Å)

Bond	<i>trans</i> - PdL_2	<i>trans</i> - PtL_2	<i>cis</i> - PtL_2
M-N(O)	2.027 (3)	2.015 (6)	1.954 (6)
M-N(Ph)	2.033 (3)	2.020 (6)	2.018 (7)
N-O	1.268 (4)	1.261 (8)	1.342 (19)
N(O)-C	1.339 (5)	1.348 (9)	1.322 (2)
(R)C-N	1.352 (5)	1.338 (9)	1.356 (6)
N=N	1.283 (4)	1.294 (9)	1.326 (5)

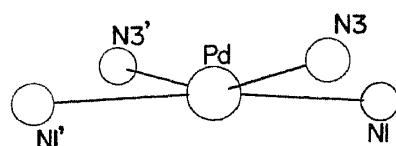


Figure 1. A view of the Pd coordination shell geometry in *trans*-PdL₂, showing the distortion from planarity towards tetrahedral geometry.

shown to be the *trans* form. However the crystals of *trans*-PtL₂ and *trans*-PdL₂ are *not* isomorphous. Discrete molecules are present in both cases but the molecular geometry and packing are dissimilar. There is no sort of stacking in *trans*-PdL₂ and the shortest Pd...Pd distance is 6.636 Å (Bandyopadhyay *et al* 1984).

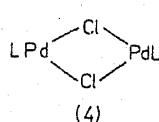
Each chelate ring is planar to within 0.06 Å. Even though the gross relative orientation of the two chelate rings is *trans*, the deviation of the PdN₄ coordination sphere from planarity towards the tetrahedral configuration is large (figure 1). The dihedral angle between the two planar chelate rings is 25.6°. The bond distances (and angles) within the chelate rings are similar in the palladium and platinum compounds (table 1).

The origin of the distortion in *trans*-PdL₂ and of the lack of it in *trans*-PtL₂ are unclear at present. Interplay of the following factors could be important: (i) stronger preference of platinum(II) for planar tetracoordination, (ii) gain in conjugation as the dihedral angle of the phenyl ring to the chelate ring decreases and (iii) increase in the steric repulsion between the phenyl ring and oxime oxygen of the adjacent ligand under conditions defined in (ii). The following observations are significant in this context: (i) the dihedral angle of the phenyl ring with the corresponding chelate ring is much smaller (24.8°) in *trans*-PdL₂ than in *trans*-PtL₂ (43.8°); (ii) in high boiling solvents PtL₂ undergoes (see below) an internal redox transformation in which an oximato oxygen atom migrates to the adjacent phenyl ring; and (iii) in tetrahedral Cu^I(HL)(L) the dihedral angle of the phenyl ring to the corresponding chelate ring is only ~ 1° (Dickman and Doedens 1980).

There have been several unsuccessful attempts in the past to utilize interligand steric crowding to introduce tetrahedral distortion in four coordinate *bis*-chelates of palladium(II). Good examples are certain salicylaldimines (Braun and Lingafelter 1967; Day *et al* 1968) and dipyrromethenes (March *et al* 1971). In both cases the metal coordination sphere retained planarity at the expense of intraligand bending. The tetrahedral distortion in *trans*-PdL₂ is unique and unprecedented for palladium(II).

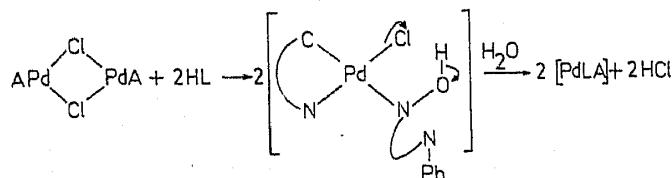
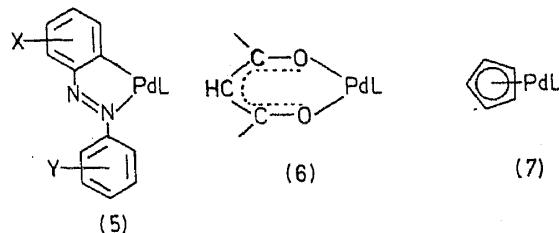
2.3 Halo-bridged dimers

Addition of HL to PdCl₄²⁻ or Pd(NCPh)₂Cl₂ in aqueous ethanol affords the violet dimer (4) which is converted to green-coloured *trans*-PdL₂ on further addition of HL. The corresponding bromo species are similarly made and the platinum analogue of (4) is also known (Kalia and Chakravorty 1969; Mascharak and Chakravorty 1979a, 1980).



2.4 Mixed ligand species including organometallics

Violet complexes of type PdLA (5) are made by cleaving the halo-bridge in $\text{Pd}_2\text{Cl}_2\text{A}_2$ ($\text{A} = \text{ortho-metallated azobenzene}$ as in (5) by HL. The reaction medium is a mixture of benzene and water. The latter acts as a base in the dehydrohalogenation reaction (scheme I). In effect the halo-bridge is split by the oxime-N atom of HL with subsequent elimination of HCl and chelate ring closure (Bandyopadhyay *et al* 1982).



Scheme 1.

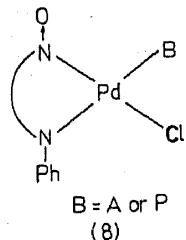
The PdLA species occur as isomeric mixtures whose compositions are conveniently established with the help of ^1H NMR data. The isomerism originates from different modes of *ortho*-metallation with respect to X and Y and is carried over to PdLA from the precursor complex $\text{Pd}_2\text{Cl}_2\text{A}_2$. Substituent (X and Y) effects on isomer population are consistent with the electrophilic nature of the palladation reaction but the steric factor also plays an important role. A simple and accurate ^1H NMR method for isomer population analysis in the precursor complex $\text{Pd}_2\text{Cl}_2\text{A}_2$ has been based on bridge splitting and solubilisation by PPh_3 (Bandyopadhyay *et al* 1982).

Species of type (6) and (7) have also been synthesised but remains unreported so far (Bandyopadhyay and Chakravorty).

3. Selective cleavage of metal-ligand bonds

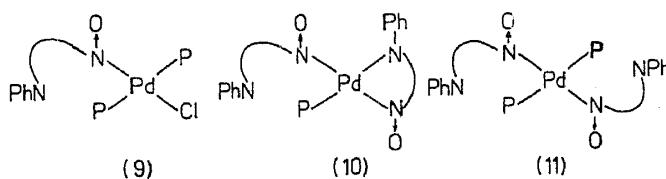
3.1 Bridge-splitting

A common reaction of halo-bridged species is the facile cleavage of the bridge by Lewis bases. The arylazooximates are no exceptions and adducts of type (8) are readily isolated by reacting (4) with amines (A) or tertiary phosphines (P) (Kalia and Chakravorty 1969; Mascharak *et al* 1977; Mascharak and Chakravorty 1979b, 1980).

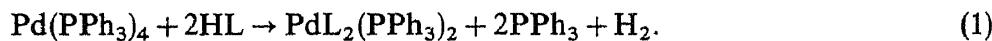


3.2 *Pd–N (azo) cleavage*

In the case of P further addition of base leads to selective cleavage of the chelate ring at the azo end leading to the formation of (9) which occurs in the solid state and displays interesting equilibria (see below) in solution. There are two major spectroscopic differences between (8) and (9). In (8) an allowed $d(Pd) \rightarrow \pi^*$ (chelated azoimine) transition occurs at ~ 520 nm ($\epsilon \sim 5000$); when the chelate ring is cleaved at the azo end (as in (9)) or at the oxime end (see below) this band disappears. The 1H NMR $\delta(Me)$ of L in (8) is ~ 2 ppm while in (9) it is 0.87 ppm due to the location of the methyl group well into the shielding cone of P (Mascharak and Chakravorty 1980).

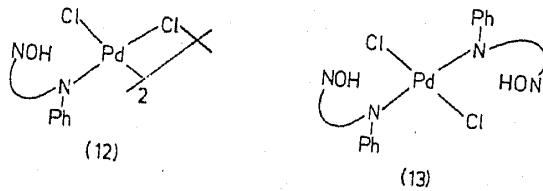


Tertiary phosphines also cleave the azo end of one or both rings in *trans*-PdL₂ affording (10) or (11), the latter being stable only in the solid state going over of (10) + P in solution. An alternative route to (11) is the oxidative addition of HL to Pd(PPh₃)₄ (Bandyopadhyay *et al* 1981)



3.3 *Pd–N(oxime) cleavage*

Selective cleavage of the oxime end is brought about by hydrogen chloride. The neutral oxime function is a weaker donor than the oximato anion (Chakravorty 1974). Hydrogen chloride first protonates the oximato function and the resultant chloride ion then displaces the Pd–N(oxime) bond. Thus from (4) red crystals of (12) arise. Interestingly the same product is furnished by hydrohalogenation of *trans* PdL₂. Here displacement of the Pd–N(oxime) bond by chloride ion with the formation of the postulated intermediate (13) is followed by partial ligand elimination and dimerisation. Crystals of (12) readily lose hydrogen chloride to regenerate (4) in the presence of bases including moisture (Mascharak and Chakravorty 1980; Bandyopadhyay *et al* 1981).



By the successive application of HCl and P in any order the chelate ring gets cleaved at both ends leading to ligand elimination and formation of PdCl₂P₂.

3.4 *Case of platinum*

Whereas cleavage reactions of platinum arylazooximates have not been studied as thoroughly as those of palladium analogues, the known reactions (Mascharak and Chakravorty 1979a) are essentially analogous. A point of special interest is the isolation

Table 2. Cone angle (θ , degree) and equilibrium constant (K, mole⁻¹ lit) at 298 K

Phosphine	θ	10^{-2} K
PM ₂ Ph	122	2310 ± 50
PM ₂ Ph ₂	136	670 ± 20
PPh ₃	145	28 ± 2
P(<i>p</i> -tolyl) ₃	145	70 ± 2
P(cyclohexyl) ₃	170	0.5*
P(<i>o</i> -tolyl) ₃	194	0.006*

* Estimated value.

of the platinum analogue of postulated intermediate (13) in pure form. This strengthens the proposed mechanism for the conversion of *trans*-PdL₂ to (4) under hydrohalogenation in the presence of moisture.

3.5 Reversible binding of phosphines: cone angle correlations

We return to reconsider the species (8) and (9). The various phosphines(P) of interest are in table 2. When P is added to a solution of (8) in eg benzene, the 520 nm band progressively loses intensity. Variable concentration spectra display a well-defined isosbestic point. All results are in agreement with the presence of the equilibrium (2).



Equilibrium constant data obtained from spectral intensity data are in table 2.

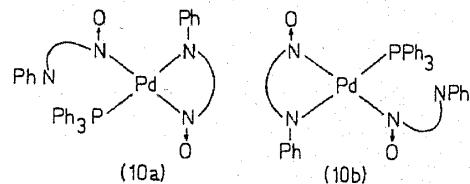
The observed trend in K values has been rationalised (Bandyopadhyay *et al* 1980). A measure of the steric demand of P is its cone angle (Tolman 1977). In case of predominant steric control of a reaction of the general type (3) the equilibrium constant usually decreases with increase in cone angle (θ) of P .



We considered the possibility that there may be an approximate linear correlation of free energy change or simply $\ln K$ with θ . Analysis of literature data indeed showed this to be true. The K data (table 2) of equilibrium (2) follows the linear $\ln K$ - θ relationship very well. The trend of this equilibrium with these phosphines is therefore set by phosphine bulk. Tricyclohexyl and tri-*o*-tolyl phosphines are too bulky to react ($K \sim 0$, table 2).

3.6 Phosphine binding and fluxional behaviour

This pertains to complexes of type (10) and we shall consider specifically the case of $\text{PdL}_2(\text{PPh}_3)$ (Bandyopadhyay *et al* 1981). The $\delta(\text{Me})$ value (^1H NMR in CDCl_3) for



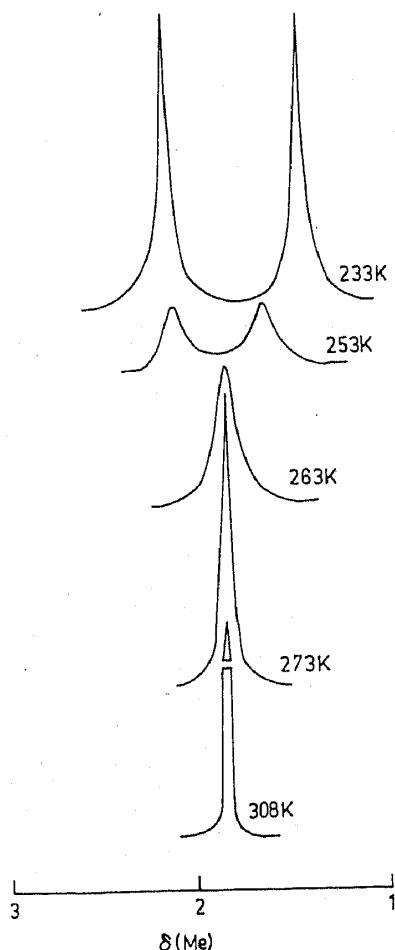


Figure 2. Temperature dependence of the ^1H methyl NMR signals of $\text{PdL}_2(\text{PPh}_3)$ in CDCl_3 ; recording amplitudes varies from temperature to temperature.

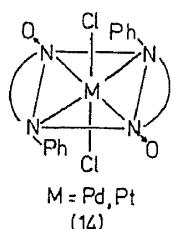
trans- PdL_2 is 2.13 ppm. At room temperature $\text{PdL}_2(\text{PPh}_3)$ also has a single sharp Me signal but with $\delta = 1.82$ ppm. Rapid scrambling of the chelated and unidentate ligands via fast interconversion of (10a) and (10b) is implicated. On cooling below 293 K, the Me signal broadens progressively and around 253 K splitting into two signals occurs (figure 2). These sharpen on further cooling and finally at 233 K two well-defined sharp signals of equal intensity remain (δ 2.16 and 1.44 ppm) confirming that the instantaneous structure is indeed (10). The signal at higher field is assigned to unidentate L since here ligand flexibility can bring the methyl group within the shielding cone of the phosphine.

A probable mechanism for the fluxional behaviour is intramolecular nucleophilic attack (S_Ni) by the pendant azo-group resulting in displacement of the bound azo function. While the S_Ni path is documented in the displacement of phosphine by a free azo group (Cross and Tennent 1974), process (4) is unique in that both the forward and the backward reactions must have identical S_Ni dynamics since the attacking and leaving groups are identical.

4. Redox reactions

4.1 Oxidative addition of dihalogen: platinum(IV) and palladium(IV)

Both *trans*- and *cis*- PtL_2 react with dichlorine to afford the same PtL_2Cl_2 product



which has $^1\text{H} \delta_{\text{Me}}$ of 2.33 ppm. The halide ligands are *trans* (single ν_{PtCl} 324 cm^{-1}) and the vibration spectrum is more akin to that *trans*- PtL_2 than to *cis*- PtL_2 . The likely structure of PtL_2Cl_2 is (14). A *cis* \rightarrow *trans* rearrangement of the PtL_2 moiety, therefore, occurs when Cl_2 reacts with *cis*- PtL_2 (Bandyopadhyay *et al* 1983a).

Green solutions of *trans*- PdL_2 in benzene on treatment with one equivalent of X_2 ($\text{X} = \text{Cl, Br}$) change colour to deep red. In the red solution diamagnetic species with δ_{Me} 2.33 ($\text{X} = \text{Cl}$) or 2.40 ($\text{X} = \text{Br}$) are present. It has not been possible to isolate such species—believed to be palladium(IV) species of type (14)—in the solid state because of their relative instability which is not unexpected (Mursinik and Pross 1978). Ethanol reduces the red solution affording $\text{Pd}_2\text{Cl}_2\text{L}_2$ (4) in good yield (Bandyopadhyay *et al* 1981).

4.2 Reductive electrochemical reactions

In general the arylazooximates display voltammetric responses corresponding to reductions of ligand and metal. The situation is illustrated (figure 3) with the case PdLA (5, $\text{X} = \text{Y} = \text{H}$). The complex displays three reversible to quasireversible cyclic

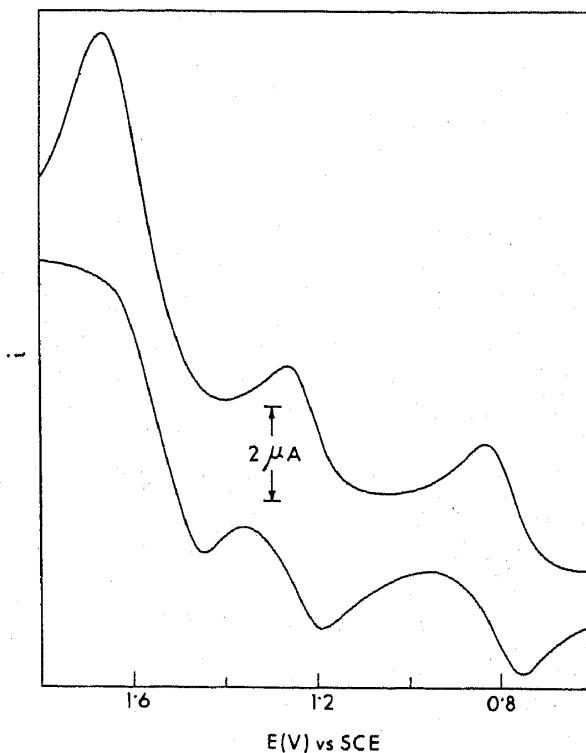


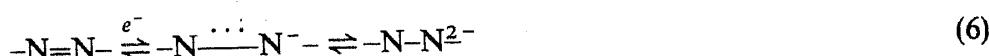
Figure 3. Cyclic voltammogram of PdLA in acetonitrile (0.1 M tetraethylammonium perchlorate) at hanging mercury drop electrode at 50 mVs^{-1} scan rate.

voltammetric responses in acetonitrile solution corresponding to formal potentials of -0.76 , -1.19 and -1.46 V vs saturated calomel electrode (Bandyopadhyay *et al* 1982).

At -0.76 and -1.19 V the processes are respectively (4) and (5) corresponding to ligand reduction primarily at the azo functions.



It is known that the azo group can undergo the following successive one-electron reductions, equation (6), in aprotic solvents (Loufty and Sharp 1977). On the basis of our unpublished electrochemical studies on species of type PdLD and PdAD where \mathbf{D} is an electroinert bidentate ligand we have concluded that \mathbf{L} is reduced more readily



than \mathbf{A} . The two one-electron reductions in PdLA are therefore due to addition of one electron to the azo group of \mathbf{L} (couple (4)) and one electron to that of \mathbf{A} (couple (5)). At potentials more negative of couple (5) one more electron could in principle be added to each of the two $-\text{N}-\cdots-\text{N}-$ groups. However, metal reduction intervenes before this level of reduction is achieved.

In the case of the couple at -1.46 V, the cathodic peak height corresponds to the transfer of two electrons. The anodic peak is smaller than the cathodic peak. These are good reasons to believe that processes (7) and (8) are involved. The direct conversion of



Pd^{II} to Pd^0 is documented in phosphine complexes in aprotic media (Martelli *et al* 1974). There is no evidence that the Pd^1 intermediate is formed.

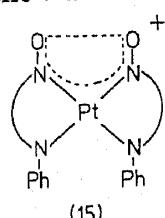
4.3 The curious behaviour of cis-PtL_2

*Trans-PtL*₂ shows successive azo reductions at -0.39 and -1.77 V. The corresponding reductions in *cis-PtL*₂ are at -0.27 and -1.76 V respectively. In addition the *cis* isomer shows a reversible one-electron oxidative response at $+0.43$ V. The *trans* isomer does not show this response (Bandyopadhyay *et al* 1983a).

The oxidation of *cis-PtL*₂ is believed to be due to the process (9)



in which the metal is oxidised. A plausible, though speculative, explanation for the relative ease with which the *cis* isomer (but not the *trans* isomer) can be oxidised is that delocalisation can occur over the *cis*-nitroxide system (15). No analogous possibility exists for the *trans* isomer.

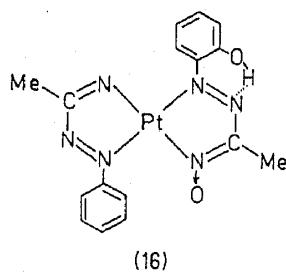


Significantly preparations of *cis*-PtL₂ invariably contains a small concentration of a paramagnetic species such that *cis*-PtL₂ is EPR-active but shows no ¹H NMR lines. The EPR spectrum is axial ($g_{\parallel} 1.946$, $g_{\perp} 1.988$; powder 77 K) with the expected ¹⁹⁵Pt hyperfine structure. Since $g_{\perp} > g_{\parallel}$ the paramagnetic species could have a d^7 configuration. It could be PtL₂⁺ itself (Bandyopadhyay *et al* 1983a).

4.4 *A novel case of aromatic hydroxylation*

When a suspension of *cis*-PtL₂ is boiled in xylene for a few hours a deep blue solution results from which blue crystals are obtainable. The deep blue colour is due to an intense absorption in the red (635 nm; $\epsilon = 22500$).

The elemental composition of the blue complex is the same as that of PtL₂. Proton NMR in CD₂Cl₂ shows the presence of two equally intense methyl signals (2.50 and 2.54 ppm) and a phenolic OH signal (11.00 ppm) apart from highly structured aromatic resonances (6.9–7.8 ppm). The complex true to its phenolic nature dissolves in aqueous alkali giving a deep blue solution. The blue complex has been examined x-ray crystallographically. Unfortunately there is the complication of crystallographic disorder. It is however clear that the crystal consists of monomolecular molecules of type (16) (Bandyopadhyay *et al* 1983b).



The central platinum atom resides on a site of mm symmetry and the ligands are disordered. The five-membered chelate ring and the platinum coordination sphere are planar. The O(H) ... NN₂Pt distance of 2.60(3) Å is indicative of hydrogen bonding which is also reflected in the broadness of the OH NMR signal.

In the reaction *cis*-PtL₂ → (16) an oximate oxygen may have been utilised to hydroxylate an adjacent aromatic ring, although convincing proof of an intramolecular redox transformation is lacking at present. In any case the observed reaction is of an unprecedented type.

Lastly, the blue colour of the medicinally relevant 'platinum blues' are usually associated with a polynuclear mixed valence core (Lippard 1982). The present work as well as other recent work (Overbosch *et al* 1982) show that a deep blue colour in platinum complexes can arise for different reasons in different cases. In the case of (16) the blue colour is no doubt due to charge transfer transitions involving both ligand and metal orbitals.

5. *Concluding remarks*

The arylazooximates under review display an impressive array of structure and reactivity patterns some of which are quite unusual. The phenomenon of aromatic hydroxylation is probably the most exciting development. The scope and mechanism of

this fascinating reaction is being closely investigated. We have no answer as yet to questions such as 'does such a reaction occur in PdL_2 also?', 'does a real oxygen play a role?' etc.

We conclude by noting that arylazooximates of a number of transition metals other than palladium and platinum have also been studied in our laboratories and a very brief summary appeared recently (Bandyopadhyay *et al* 1983a). Metal arylazooximates invariably have something interesting to display.

Acknowledgements

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