

## Stabilisation of Monovalent Palladium by Tetra-aza Macrocycles

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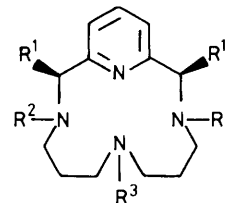
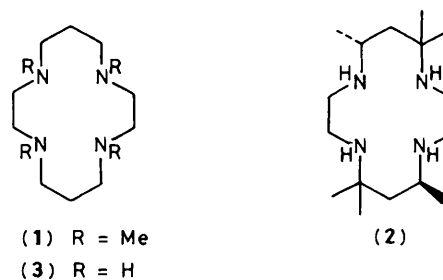
The single crystal X-ray structure of  $[\text{Pd}(\mathbf{1})](\text{PF}_6)_2 \cdot \text{MeNO}_2$  [ $\mathbf{1}$ ] = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclo-tetradecane] shows a square planar stereochemistry with an (*R,S,R,S*) conformation; electrochemical reduction at  $-1.65$  V vs.  $\text{Fc}/\text{Fc}^+$  ( $\text{Fc}$  = ferrocene) in MeCN affords a highly reactive  $d^9$  palladium(I) derivative.

The generation of low valent macrocyclic complexes and intermediates has been utilised for the catalytic and electrocatalytic reduction of substrates such as  $\text{CO}_2$ <sup>1</sup> and  $\text{O}_2$ .<sup>2</sup> As part of a study on macrocyclic complexes incorporating the platinum metals<sup>3</sup> we have been investigating the electrochemical activity of a range of palladium tetra-aza species with a view to the development of new electroactive precursors for the reduction of small molecule substrates. 1,4,8,11-Tetramethyl-1,4,8,11-tetra-azacyclotetradecane ( $\mathbf{1}$ ) (tmc) is a particularly attractive ligand for such work since oxidative dehydrogenation of the co-ordinated ligand is inhibited by the alkylated aza functions, and the rate of ligand exchange is relatively slow. Meyerstein and co-workers have recently shown<sup>4,5</sup> that ( $\mathbf{1}$ ) and related alkylated macrocycles successfully stabilise both nickel(I) and copper(I) oxidation states; we therefore reasoned that the stabilisation of low valent platinum group metal centres could be achieved using the same types of ligands.

Reaction of  $\text{Pd}(\text{OAc})_2$  with ( $\mathbf{1}$ ) at  $20^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$  for 24 h gave a solution of the complex cation  $[\text{Pd}(\mathbf{1})]^{2+}$ . Addition of  $\text{NH}_4\text{PF}_6$  afforded a pale cream precipitate which was recrystallised from  $\text{MeNO}_2$  to give crystals of  $[\text{Pd}(\mathbf{1})](\text{PF}_6)_2 \cdot \text{MeNO}_2$  in 85% yield.† The  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra of the product indicated the presence of only one isomer in solution with one resonance being observed for the methyl protons ( $\delta_{\text{H}}$  2.81,  $\text{CH}_3$ , 12H) and for the methyl carbons ( $\delta_{\text{C}}$  = 45.6,  $\text{CH}_3$ ) in  $\text{CD}_3\text{NO}_2$ . Close inspection of the resonances for the methylene protons could not differentiate conclusively between the possible (*R,S,R,S*) and (*R,S,S,R*) isomers. The isomerisation and conformations of  $[\text{Ni}(\mathbf{1})]^{2+}$  have been the subject of much debate.<sup>6</sup> To establish the configuration of the complex, and in view of the general paucity of structural data on palladium macrocycles, we undertook a single crystal X-ray analysis of our isolated product.

The single crystal X-ray structure‡ of the complex shows the

$[\text{Pd}(\mathbf{1})]^{2+}$  cation,  $\text{PF}_6^-$  anions, and  $\text{MeNO}_2$  solvent molecule all lying on crystallographic mirror planes. The cation, two views of which are given in Figure 1, therefore possesses *m* symmetry, with Pd co-ordinated by four N-donors N(1), N(4), and their mirror related equivalents N(1') and N(4'); Pd–N(1) 2.051(11), Pd–N(4) 2.066(11) Å,  $\angle\text{N}(1)\text{PdN}(4)$  88.0(4),  $\angle\text{N}(1)\text{PdN}(1')$  92.7(4),  $\angle\text{N}(1)\text{PdN}(4')$  175.5(4),  $\angle\text{N}(4)\text{PdN}(4')$  91.0(4)°. The Pd is displaced towards the N-bound methyl groups by 0.082 Å out of the plane of the four



- (4)  $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Me}$   
(5)  $\text{R}^1 = \text{R}^2 = \text{H}, \text{R}^3 = \text{Me}$   
(6)  $\text{R}^1 = \text{R}^3 = \text{Me}, \text{R}^2 = \text{H}$   
(7)  $\text{R}^1 = \text{Me}, \text{R}^2 = \text{R}^3 = \text{H}$

† All complexes have been characterised by elemental analysis, n.m.r., u.v.-visible, i.r., and fast atom bombardment mass spectroscopy and conductivity measurements.

‡ Crystal data:  $\text{C}_{14}\text{H}_{32}\text{N}_4\text{Pd}^{2+} \cdot 2\text{PF}_6^- \cdot \text{MeNO}_2$ , orthorhombic, space group *Pnam*,  $a = 18.325(5)$ ,  $b = 15.274(4)$ ,  $c = 9.768(5)$  Å,  $U = 2735$  Å<sup>3</sup>,  $D_c = 1.733$  g cm<sup>-3</sup>,  $Z = 4$ ; 5216 data measured to  $\theta = 25^\circ$ , 2466 unique; refinement based on 1814 data with  $F \geq 6\sigma(F)$ . At convergence,  $R, R_w = 0.0742, 0.0997$  respectively for 162 parameters. The Pd position was obtained from a Patterson synthesis and the remaining non-H atoms from iterative rounds of least-squares refinement and difference Fourier syntheses. The structure exhibits extensive disorder, affecting not only the  $\text{PF}_6^-$  ions but also  $[\text{Pd}(\mathbf{1})]^{2+}$ . We have attempted refinement of the structure in the corresponding non-centric space group *Pna2<sub>1</sub>* as well as investigating various models of disorder in *Pnam*. None of these offers any improvement over the essentially ordered structure described here. Hydrogen atoms were included in calculated positions and Pd, P, N, and O atoms were refined anisotropically, as were F atoms with at least one-half of the full occupancy for the relevant site.<sup>10</sup> At convergence, the difference map showed no feature above  $1.13 \text{ e}\text{\AA}^{-3}$ . Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1. Redox data for palladium(II) and nickel(II) complexes of tetra-aza macrocycles;  $[\text{M}(\text{L})]^{1+/2+/3+}$ , L = (1)–(7).

Complex	Reduction Potential, $E_p/\text{V}$ ( $\Delta E/\text{mV}$ )		Oxidation Potential, $E_p/\text{V}$ ( $\Delta E/\text{mV}$ )	
	Pd	Ni	Pd	Ni
$[\text{M}(\mathbf{1})]^{2+}$	-1.53 (65)	-1.25 (70)	—	+1.25 (106)
$[\text{M}(\mathbf{4})]^{2+}$	-1.53 (70)	-1.23 (75)	—	+1.19 (108)
$[\text{M}(\mathbf{5})]^{2+}$	-1.74 (i) <sup>a</sup>	-1.48 (70)	—	+0.95 (66)
$[\text{M}(\mathbf{6})]^{2+}$	-1.78 (qr) <sup>a</sup>	-1.47 (75)	—	+0.92 (78)
$[\text{M}(\mathbf{7})]^{2+}$	-1.82 (qr)	-1.56 (82)	—	+0.92 (81)
$[\text{M}(\mathbf{2})]^{2+}$	-1.99 (105)	-1.64 (95)	—	+0.81 (109)
$[\text{M}(\mathbf{3})]^{2+}$	-2.10 (82)	-1.80 (90)	—	+0.60 (75)

<sup>a</sup> i = irreversible, qr = quasi-reversible.

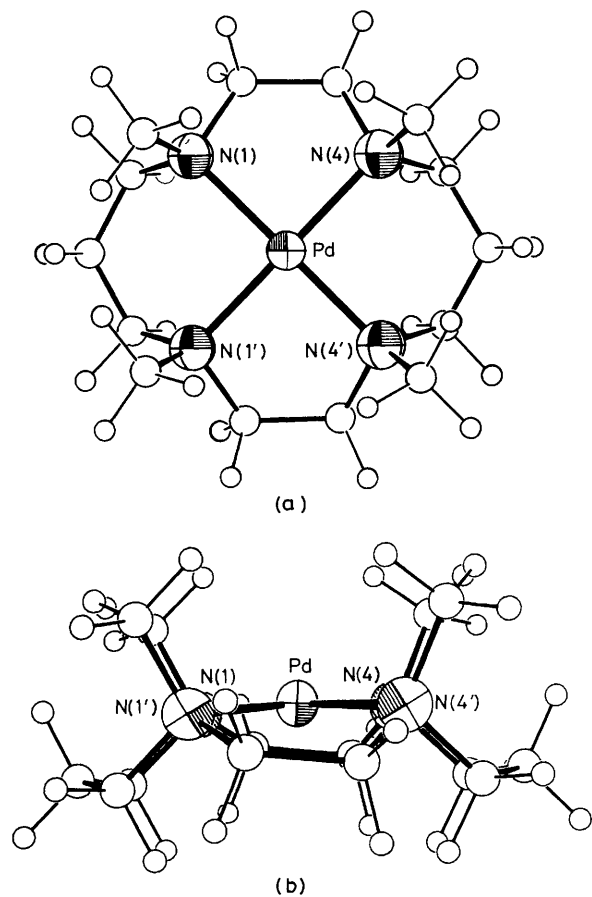


Figure 1. The single crystal X-ray structure of  $[\text{Pd}(\text{1})]^{2+}$ .

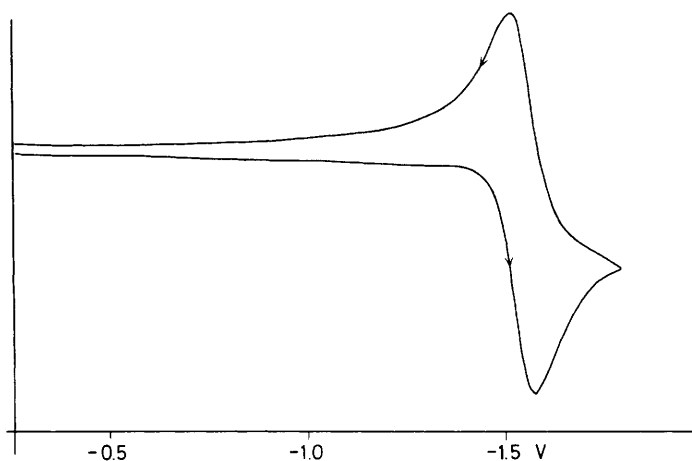


Figure 2. Cyclic voltammogram of  $[\text{Pd}(\text{1})](\text{PF}_6)_2$  in MeCN (0.1 M  $\text{Bu}^n_4\text{NPF}_6$ ) at 20°C at platinum electrodes. Scan rate = 100  $\text{mV s}^{-1}$ . Potentials vs.  $\text{Fc}/\text{Fc}^+$ .

N atoms. The  $\text{N}_4$  donor set is essentially planar, but only approximately a square,  $\text{N}(1) \cdots \text{N}(4)$  2.860(16),  $\text{N}(1) \cdots \text{N}(1')$  2.968(15),  $\text{N}(4) \cdots \text{N}(4')$  2.946(17) Å. The crystal structure confirms that the four methyl groups lie on the same side of the  $\text{N}_4$  plane in an (*R,S,R,S*) configuration, the same configuration as found for  $[\text{Ni}(\text{1})]^{2+}$  prepared in strongly co-ordinating solvents.

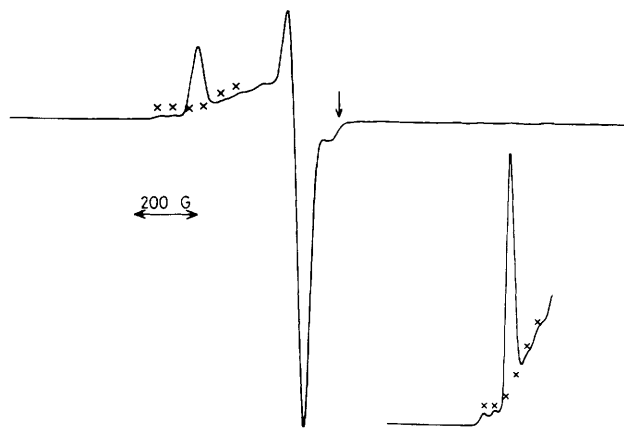


Figure 3. X-Band e.s.r. spectrum of  $[\text{Pd}(\text{1})]^+$  generated electrochemically, measured at 77 K in MeCN glass in the presence of 0.1 M  $\text{Bu}^n_4\text{NPF}_6$  including expansion to show hyperfine coupling to  $^{105}\text{Pd}$ .

Cyclic voltammetry of  $[\text{Pd}(\text{1})](\text{PF}_6)_2$  in MeCN (0.1 M  $\text{Bu}^n_4\text{NPF}_6$ ) at platinum electrodes shows a fully reversible reduction at  $E_{\frac{1}{2}} = -1.53$  V vs.  $\text{Fc}/\text{Fc}^+$  ( $\text{Fc}$  = ferrocene),  $\Delta E_p = 65$  mV,  $I_{pa}/I_{pc} = 1.0$ , at a scan rate of 100  $\text{mV s}^{-1}$  (Figure 2). Controlled potential electrolysis of  $[\text{Pd}(\text{1})]^{2+}$  at a platinum gauze in MeCN at  $-1.65$  V under a stream of Ar at 20°C affords a highly air-sensitive, reactive species, the e.s.r. spectrum of which at 77 K as a frozen glass (Figure 3) shows an anisotropic signal with axial symmetry  $g_{\parallel} 2.302$ ,  $g_{\perp} 2.076$ . These spectral features are consistent with the formation of a  $d^9$  palladium(I) species  $[\text{Pd}(\text{1})]^+$ ; the isoelectronic nickel(I) complex  $[\text{Ni}(\text{1})]^+$  shows similar e.s.r. features.<sup>4,7</sup> Further confirmation for a predominantly metal based redox process is obtained from the observation of hyperfine coupling to  $^{105}\text{Pd}$  ( $I = \frac{5}{2}$ , 22.2%)  $A_{\parallel} = 53$  G,  $A_{\perp} = 40$  G ( $1 \text{ G} = 10^{-4} \text{ T}$ ). We have measured the e.s.r. spectrum of a sample of  $^{61}\text{Ni}$  ( $I = \frac{3}{2}$ ) enriched  $[\text{Ni}(\text{1})]^+$  at 77 K and have observed hyperfine coupling to the metal centre with  $A_{\parallel} = 62$  G, and  $A_{\perp} = 27$  G.

We have prepared a range of palladium(II) complexes incorporating the tetra-aza macrocyclic ligands (2)–(7).† These species show reductions by cyclic voltammetry at more negative potentials than both  $[\text{Pd}(\text{1})]^{2+}$  and the analogous nickel(II) complexes (Table 1). Attempts to generate electrochemically the reduction products of the palladium complexes of (2)–(7) at 20°C and identify them by e.s.r. spectroscopy have been thus far unsuccessful owing to their very high reactivity. The relative stability of  $[\text{Pd}(\text{1})]^+$  is reflected by the lower negative potential at which this species is generated and may also be due to steric inhibition of dimerisation. These results are consistent with the work of Meyerstein<sup>4</sup> on the stabilisation of nickel(I) with (1) (Table 1). However, the full characterisation of  $[\text{Pd}(\text{1})]^+$  is impeded by its high reactivity in solution, the complex having a half-life of  $t_{\frac{1}{2}}$  ca. 5 min under the conditions of electrogeneration in MeCN at 20°C; we have been unable to isolate this species in the solid state. Very few examples of palladium(I) species have been reported in the literature. The electrogeneration of the  $\pi$ -complex  $[\text{Pd}(\text{C}_5\text{Ph}_5)(\text{cod})]$  ( $\text{cod}$  = cyclo-octa-1,5-diene) has been described recently,<sup>8</sup> the complex showing satellites in the e.s.r. spectrum due to coupling to  $^{105}\text{Pd}$  ( $A = 25$  G). It is of interest to note that, in contrast with their nickel(II) analogues which show nickel(II)/(III) redox couples in the range  $E_{\frac{1}{2}} = +0.6$  to  $+1.25$  V (Table 1), none of the tetra-aza complexes of palladium described herein show oxidative activity up to  $+2.2$  V in MeCN.

We are currently investigating the reactivity of  $[\text{Pd}(\text{I})]^+$  with small molecules. Thus  $[\text{Pd}(\text{I})]^+$  binds CO strongly as measured by cyclic voltammetry to give presumably a transient five co-ordinate species  $[\text{Pd}(\text{I})\text{CO}]^+$ , while reaction with  $\text{O}_2$  would be likely to yield palladium(II)-superoxy species  $[\text{Pd}(\text{I})(\text{O}_2)]^+$ . Such superoxy species have been proposed as active intermediates for the epoxidation of alkenes.<sup>9</sup>

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