C–H Activation in a Co-ordinated Catenand: *ortho*-Metallation of Cat30 by Palladium(II)

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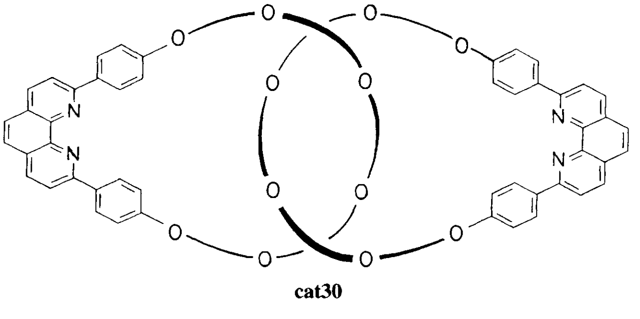
Insertion of Pd^{2+} into the catenand ligand cat30 yields the monocation $[Pd^{II}(cat30–H)]^+$ *via* ortho-metallation of one of the ligand phenyl rings to give square planar co-ordination by an N_3C donor set, Pd–N(1) = 2.139(11), Pd–N(3) = 2.286(10), Pd–N(4) = 1.961(10), Pd–C(71) = 2.017(7) Å; the N-atom N(2) associated with the phenanthroline (phen) chelate incorporating N(1) lies 2.559(11) Å from the metal centre making this phen moiety monodentate to the Pd^{II} centre.

The insertion of Ni^{II},[1] Cu^{I},[2] Zn^{II}, Co^{II}, Li^{I},[3] and H^+ (ref. 4) into the catenand ligand cat30 has been reported previously.[5] In all of these complexes cat30 imposes a distorted tetrahedral stereochemistry upon the metal centre. Thus, d^{10} Cu^{I} is well suited to this co-ordination, and oxidation of $[Cu^{I}(cat30)]^+$ to the corresponding Cu^{II} complex occurs at particularly high potential.[2] The same stereochemical constraints operate in the Ni^{II} complex $[Ni^{II}(cat30)]^{2+}$.[1] This results in a very accessible $Ni^{II/I}$ redox couple at $E_{1/2}$ = +0.105 (*vs.* Ag/Ag^+) and the generation of an air-stable d^9 Ni^{I} complex $[Ni(cat30)]^+$.[1]

The generation of d^9 Pd^{I} has been achieved recently using tetra-aza macrocyclic ligands.[6—8] The stabilisation of these Pd^{I} species is related to the extent of the tetrahedral distortion at the metal centre.[7] We argued that insertion of Pd^{II} into cat30 might impose a tetrahedral stereochemistry at the metal centre.

Reaction of $Pd(OAc)_2$ with cat30 in refluxing CH_2Cl_2 for 4 days affords an orange solution. Addition of NH_4PF_6 gives in 60% yield an orange diamagnetic product which, on the basis of elemental analysis and fast atom bombardment (f.a.b.) mass spectrometry, was formulated as $[Pd(cat30–H)]PF_6$. It



cat30

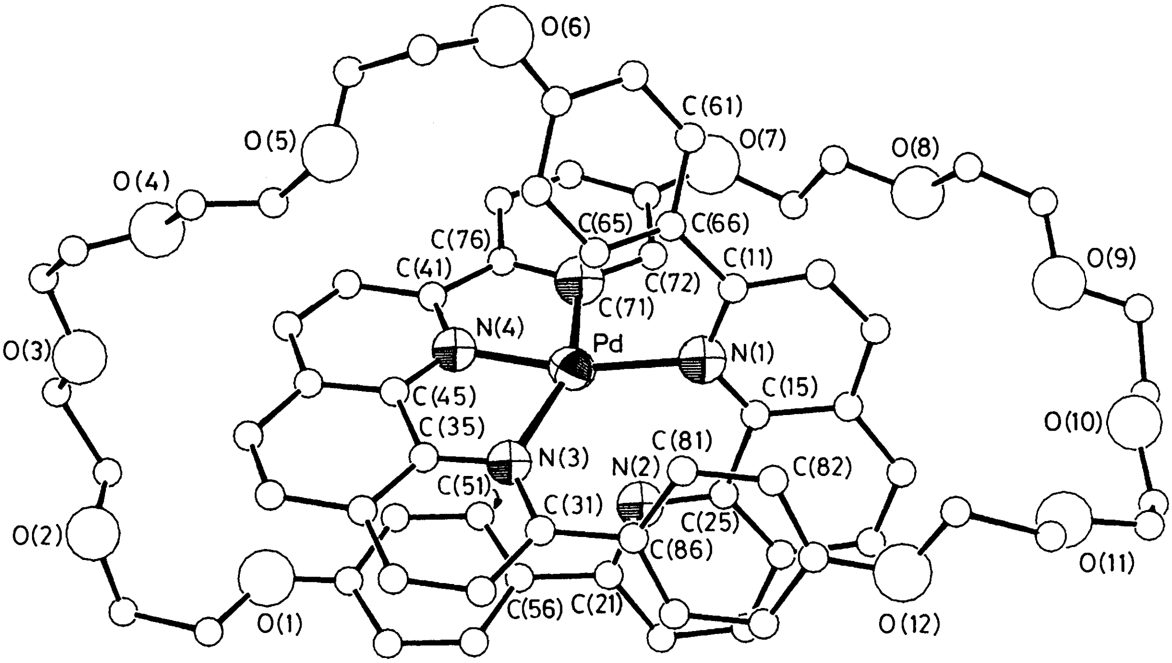


Figure 1. Structure of [Pd(cat30–H)]$^+$ with numbering scheme adopted.

was clear that the isolated complex did not incorporate a tetrahedral Pd^{II} centre and in order to determine its structure we undertook a single crystal *X*-ray crystallographic study. Suitable crystals were obtained by diffusion of Et_2O vapour into a solution of the complex in MeCN.

The structure determination† reveals a [Pd(cat30–H)]$^+$ cation with N_3C co-ordination about Pd^{II} (Figure 1). The Pd^{II} centre is bound to both N-donors of one phenanthroline (phen) unit, Pd–N(3) = 2.286(10), Pd–N(4) = 1.961(10) Å. In addition, *ortho*-metallation of one of the phenyl rings associated with this phen chelate is observed, Pd–C(71) = 2.017(7) Å, consistent with the overall 1+ charge of the cation. Interestingly, the second phen moiety is bound only in a monodentate fashion, Pd–N(1) = 2.139(11) Å, with N(2) lying 2.559(11) Å from the Pd^{II} centre. The stereochemistry about Pd^{II} is therefore distorted square planar (Figure 2) and the dihedral angle between the two phen units is 68.6°.

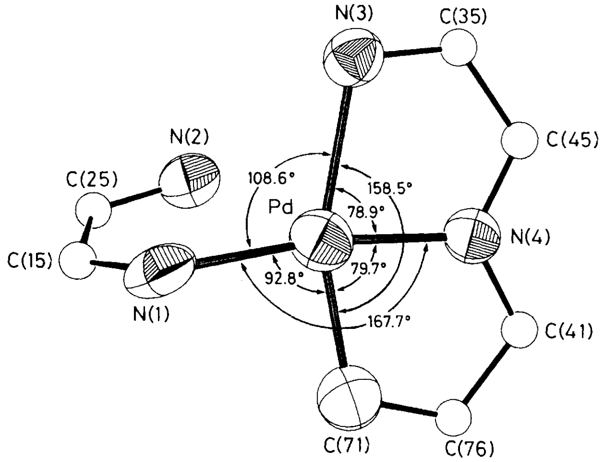


Figure 2. Co-ordination geometry at the Pd^{II} centre in [Pd(cat30–H)]$^+$ with numbering scheme adopted.

Although examples of Pd–C bonded complexes of metallated phen and bipyridine derivatives have been reported,[9] these do not incorporate such a strained chelation as observed for [Pd(cat30–H)]$^+$. *ortho*-Metallation of the C(71)—C(76) ring results in a narrow angle N(4)–C(41)–C(76) of 113.4(11)° compared with N(3)–C(31)–C(86), N(2)–C(21)–C(56), and N(1)–C(11)–C(66) angles of 121.0(11), 118.6(11), and 125.1(12)° respectively. The dihedral angle between the *ortho*-metallated phenyl ring and the adjacent phen is 4.3°, making this unit almost planar. This compares with a dihedral angle of 36° between the C(61)—C(66) phenyl ring and the N(1), N(2) phen ring. Efficient packing of the C(81)—C(86)

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† *Crystal data* for $C_{68}H_{67}N_4O_{12}Pd^+ \cdot PF_6^- \cdot 0.57C_4H_{10}O$: $M = 1424.4$, monoclinic, space group $P2_1/a$, $a = 15.082(3)$, $b = 23.882(5)$, $c = 20.361(5)$ Å, $\beta = 108.706(19)°$, $U = 6946.4$ Å^3, [from 2θ values of 40 reflections measured at $\pm\omega$ ($2\theta = 28$—$30°$, $\bar{\lambda} = 1.54184$ Å), $T = 293$ K], $Z = 4$, $D_c = 1.362$ g cm^{-3}, $\mu(\text{Cu-}K_\alpha) = 3.08$ mm^{-1}. An orange lath (0.175 × 0.25 × 1.25 mm) was sealed in a Lindemann glass capillary tube and mounted on a Stoë STADI-4 four-circle diffractometer. Data collection using Cu-K_α *X*-radiation ($\bar{\lambda} = 1.54184$ Å), ω–2θ scans, and the learnt-profile method[10] gave 5792 absorption-corrected reflections ($2\theta_{max.}$ 90°), of which 4056 with $F \geqslant 4\sigma(F)$ were used in all calculations. A Patterson synthesis located the Pd and iterative cycles of least-squares refinement and difference Fourier synthesis[11] located all remaining non-H atoms. Disorder in the polyether chains was modelled by allowing two orientations for each chain: C–C bonds and C–O bonds were constrained to have common lengths, which refined to 1.47 and 1.52 Å respectively; and angles around the C and O atoms in the disordered regions were constrained to be tetrahedral. In each chain, the major orientation had an occupancy about twice that of the minor. Disorder models were also successfully developed for the PF_6^- anion and the partly-occupied diethyl ether solvate. At isotropic convergence, final correction for absorption was made using DIFABS.[12] Excepting those of the disordered polyether chains, H atoms were included in fixed, calculated positions.[11] At final convergence, $R = 0.0973$, $R_w = 0.1270$, $S = 1.246$ for 537 parameters and the final ΔF synthesis showed, with the exception of one peak of 1.47 eÅ^{-3} near the metal, no feature above 0.71 eÅ^{-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.

phenyl ring above the N(1), N(2) phen ring (3.29 Å between their centres of gravity with a dihedral angle of 8.9°) and of the C(51)—C(56) ring above the N(3), N(4) phen ring (3.35 Å between their centres of gravity and a dihedral angle of 8.6°) is observed. An intriguing long-range interaction of 2.431(7) Å is observed between Pd and H(65) in the solid state although no evidence for an agostic H-interaction can be deduced from the solution ^{1}H n.m.r. spectrum. Both ^{1}H and ^{13}C n.m.r. spectra are fully consistent with the *ortho*-metallated solid state structure.

[Pd(cat30–H)]$^+$ shows a reversible oxidation at $E_{1/2}$ = +0.55 V *vs.* Fc$^+$/Fc (Fc = ferrocene) assigned tentatively to a Pd$^{II/III}$ couple. By comparison, the Ni^{II} catenate cannot be oxidised before damaging the ligand [for Ni$^{II/III}$ $E_{1/2} > +1.5$ V] showing the dramatic differences in electronic properties between the square planar arrangement of the *ortho*-metallated species and the pseudo-tetrahedral co-ordination in more classical catenates like [Ni(cat30)]$^{2+}$.[1] Two reversible reductions are also observed for [Pd(cat30–H)]$^+$ at extreme cathodic potentials, $E_{1/2} = -1.95$ and -2.23 V *vs.* Fc$^+$/Fc.

The structure of [Pd(cat30–H)]$^+$ is a compromise between the stereochemical and conformational preferences of metal and ligand where the disparity between the requirements of square planar Pd^{II} and tetrahedral cat30 is resolved by *ortho*-metallation.

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