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STRUCTURAL AND ELECTROCHEMICAL STUDIES ON TRITHIA MACROCYCLIC COMPLEXES OF PALLADIUM

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Summary

The single crystal X-ray structure of $[Pd(\mathbf{1})_2](PF_6)_2$ ($\mathbf{1}$ = 1,4,7-trithiacyclononane) shows a crystallographically centrosymmetric cation with a distorted octahedral stereochemistry about the Pd^{II} centre with $Pd{-}S_{eq}$ 2.332(3) and 2.311(3) Å for the equatorial thia donors, and $Pd{-}S_{ax}$ 2.952(4) Å for the two apically coordinated donors. The crystals have space group $C2/c$, with a 17.879(8), b 15.627(13), c 11.476(8) Å, β 125.92(4)° and $Z = 4$. Least squares refinement gave $R = 0.0565$ for 1153 unique observed reflections measured by counter diffractometry using Mo-K_α radiation. This green complex undergoes a chemically reversible, one-electron oxidation in CH_3CN, $E_{pa} = +0.65$V, $E_{pc} = +0.56$ V vs. Fc/Fc^+, $\Delta E_p = 84$ mV. Oxidation of $[Pd(\mathbf{1})_2](PF_6)_2$ by controlled potential electrolysis at +0.7 V affords an orange, ESR active product which may be tentatively assigned to the corresponding palladium(III) species. These results are contrasted with data for the related homoleptic thia complexes $[Pd(L)]^{2+}$ (L = 1,4,8,11-tetrathiacyclotetradecane ($\mathbf{2}$), 1,4,7,10,13,16-hexathiacyclooctadecane ($\mathbf{3}$)). The syntheses of the complexes *cis*-$[Pd(\mathbf{1})Cl_2]$, *cis*-$[Pt(\mathbf{1})Cl_2]$, *cis*-$[Pd(\mathbf{1})(PPh_3)_2](PF_6)_2$ and *cis*-$[Pt(\mathbf{1})(PPh_3)_2](PF_6)_2$ are also described.

Introduction

During the past few years we have been investigating the synthesis of macrocyclic complexes incorporating platinum metal ions [1–4]. Of particular interest to us has been the incorporation of these metal centres into ligand structures that do not necessarily have the correct hole size, conformational characteristics, or stereochemical features for the metal ion. We reasoned that this might confer unusual coordination and/or redox properties to the resulting complexes leading to selectivily activated metal species which may be reactive towards small molecules and organic substrates.

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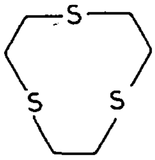
We report herein the binding of the tridentate thia macrocycle 1,4,7-trithiacyclononane (**1**) to palladium(II) to give the bis-macrocyclic complex $[Pd(\mathbf{1})_2]^{2+}$, and the related 1 : 1 species *cis*-$[M(\mathbf{1})Cl_2]$ and *cis*-$[M(\mathbf{1})(PPh_3)_2]^{2+}$ (M = Pd, Pt).

Results

Reaction of $K_2[PdCl_4]$ with two molar equivalents of 1,4,7-trithiacyclononane (**1**) in refluxing water/methanol (1/1 v/v) rapidly gave a blue solution from which the complex cation $[Pd(\mathbf{1})_2]^{2+}$ could be isolated as its BF_4^- or PF_6^- salt. Recrystallisation from water afforded green crystals of $[Pd(\mathbf{1})_2](BF_4)_2$ and $[Pd(\mathbf{1})_2](PF_6)_2$.



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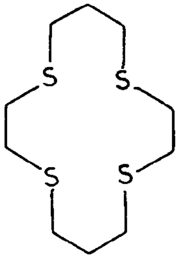

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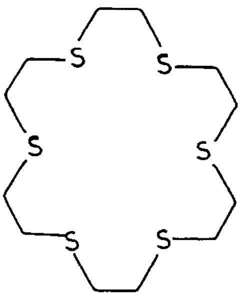

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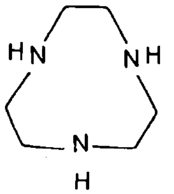

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The ^1H NMR spectrum of the products in CD_3CN at 293 K showed only a singlet resonance for the methylene protons of the macrocycle suggesting a fluxional coordination in solution; the ^1H NMR spectrum remained unchanged down to

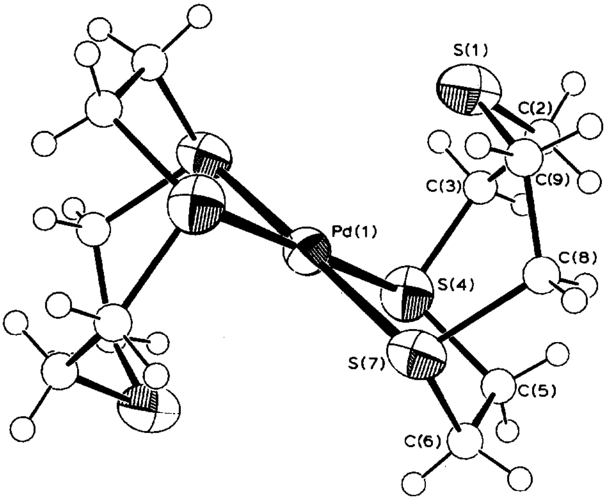

Fig. 1. Single crystal X-ray structure of $[Pd(\mathbf{1})_2]^{2+}$.

238 K. The complexes are soluble in polar solvents such as acetonitrile, acetone and nitromethane to give blue solutions (λ_{max} 615 nm; ε 54 M^{-1} cm^{-1} in CH_3CN); this unusual absorption spectrum for a palladium(II) complex is not consistent with simple square planar coordination around the metal centre, and an X-ray structure determination was therefore undertaken on a crystal obtained from aqueous solution.

A view of the $[Pd(\mathbf{1})_2]^{2+}$ cation is shown in Fig. 1. The X-ray diffraction study shows the Pd^{II} cation occupying an inversion centre and coordinated primarily by an approximate square plane of four thia donors from two centrosymmetrically related molecules of **1** ($Pd{-}S_{eq}$ 2.332(3), 2.311(3) Å, $< S_{eq}PdS_{eq}$ 88.63(11)°). The remaining similarly related S atoms participate in significant apical interactions to give, overall, a distorted octahedral stereochemistry around Pd^{II}; ($Pd \cdots S_{ax}$ 2.952(4) Å, $< S_{ax}PdS_{eq}$ 83.13(10), 83.24(11)°). This constrasts markedly with the analogous platinum(II) complex $[Pt(\mathbf{1})_2](PF_6)_2$ which is yellow (λ_{max} 432 nm, ε 95 M^{-1} cm^{-1}) and which shows an interaction with only *one* apical thia donor in the solid state to yield a square-based pyramidal stereochemistry ($Pt \cdots S_{ax}$ 2.88 Å) [3]. The quasi-octahedral stereochemistry established for $[Pd(\mathbf{1})_2]^{2+}$ is presumably the basis for the unusual visible spectrum observed for this complex cation since the related essentially square planar complexes $[Pd(L)]^{2+}$ (L = 1,4,8,11-tetrathiacyclotetradecane (**2**) [4], 1,4,7,10,13,16-hexathiacyclooctadecane (**3**) [2]) are yellow/brown and do not show absorptions near 600 nm. The single crystal structure of the latter complex shows [2] it to involve a square-planar metal centre with two dangling or very weakly interacting thia donors at 3.27 Å from the metal centre (0.31 Å longer than for $[Pd(\mathbf{1})_2]^{2+}$), $< S_{ax}PdS_{eq} \simeq 75°$; this suggests that the thia crown **3** is too small to fully encapsulate the palladium(II) centre octahedrally.

In view of the unexpected structural results obtained for these homoleptic thia complexes of palladium [5], it was clearly important to monitor their redox activity. Cyclic voltammetry of $[Pd(\mathbf{1})_2](PF_6)_2$ in CH_3CN (0.1 M $^nBu_4NPF_6$ at 20°C) showed a reversible one-electron oxidation with $E_{pa} = +0.65$ V and $E_{pc} = +0.56$ V,

$\Delta E_p = 84$ mV, $E_{1/2} = +0.605$ V vs. Fc/Fc$^+$ (Fig. 2). This oxidation potential compares with values of $E_{1/2}$ of +0.99 (irrev), +0.97 and +0.39 V for the oxidation of **1**, $[Ni(\mathbf{1})_2]^{2+}$ [6] and $[Pt(\mathbf{1})_2]^{2+}$ [3] respectively, and suggested that the redox process for the palladium complex may be essentially metal-based. Controlled potential electrolysis at +0.7 V yielded an orange solution (λ_{max} 475 nm, ε 3000 M^{-1} cm^{-1}), the ESR spectrum of which as a frozen glass at 77 K (Fig. 3a) showed an anisotropic, broad signal with $g_{\parallel} = 2.008$, $g_{\perp} = 2.048$, $g_{av} = 2.032$. A similar ESR spectrum has been reported [7] previously for the nickel(III) species $[Ni(\mathbf{4})_2]^{3+}$ (**4** = 1,4,7-triazacyclononane); this, together with the cyclic voltammetric data suggest that the positive charge in the cation $[Pd(\mathbf{1})_2]^{3+}$ resides predominantly on the metal centre. We have recently proposed a similar redox activation to afford the platinum(III) species $[Pt(\mathbf{1})_2]^{3+}$ [3]. The cation $[Pd(\mathbf{1})_2]^{3+}$ could also be generated by chemical oxidation with Ce^{4+}, $S_2O_8{}^{2-}$ or $HClO_4$. The ESR spectrum of the product generated by chemical oxidation with $HClO_4$ under aqueous conditions (Fig. 3b) shows $g_{\parallel} = 2.009$, $g_{\perp} = 2.049$ with possible coupling to ^{105}Pd ($I = 5/2$, 20%) $A_{\perp}$20, $A_{\parallel} \simeq 5$ G.

The stabilisation of palladium(III) (and platinum(III)) by homoleptic sulphur coordination is intriguing and must reflect the electronic and stereochemical characteristics of the trithia crown ligand. Thia crowns would be expected, relative to the triaza analogue, to destabilise higher oxidation state metal species; for example, the $[Co(\mathbf{1})_2]^{2+/3+}$ and $[Fe(\mathbf{1})_2]^{2+/3+}$ redox couples occur at −0.013 and at +0.98 V vs. Fc/Fc$^+$ respectively [6], as compared with values of −0.41 and +0.13 V vs. NHE for the $[Co(\mathbf{4})_2]^{2+/3+}$ and $[Fe(\mathbf{4})_2]^{2+/3+}$ couples [8,9]. Presumably the metal(IV) oxidation state for our platinum and palladium complexes is therefore destabilised by the soft thia coordination sphere, thereby deactivating the system towards disproportionation of metal(III) to metal(II) and (IV). Stereochemically, the trithia crowns would be expected to destabilise palladium and platinum(II) via the apical

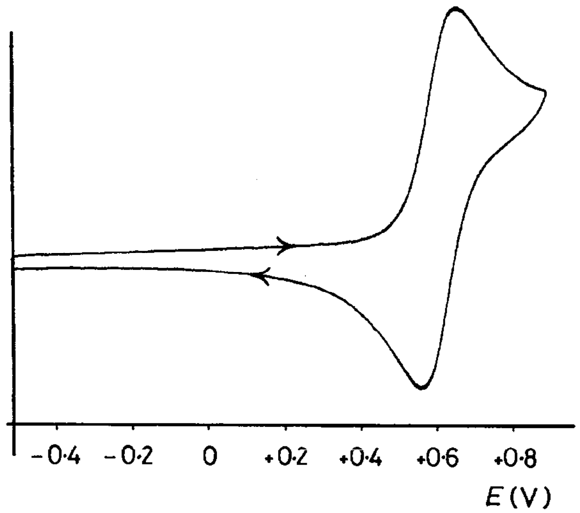

Fig. 2. Cyclic voltammogram of $[Pd(\mathbf{1})_2](PF_6)_2$ in CH_3CN (0.1 M $^nBu_4NPF_6$) at Pt electrodes at 20° C. Scan rate 100 mV s^{-1}. Potential vs. Fc/Fc$^+$.

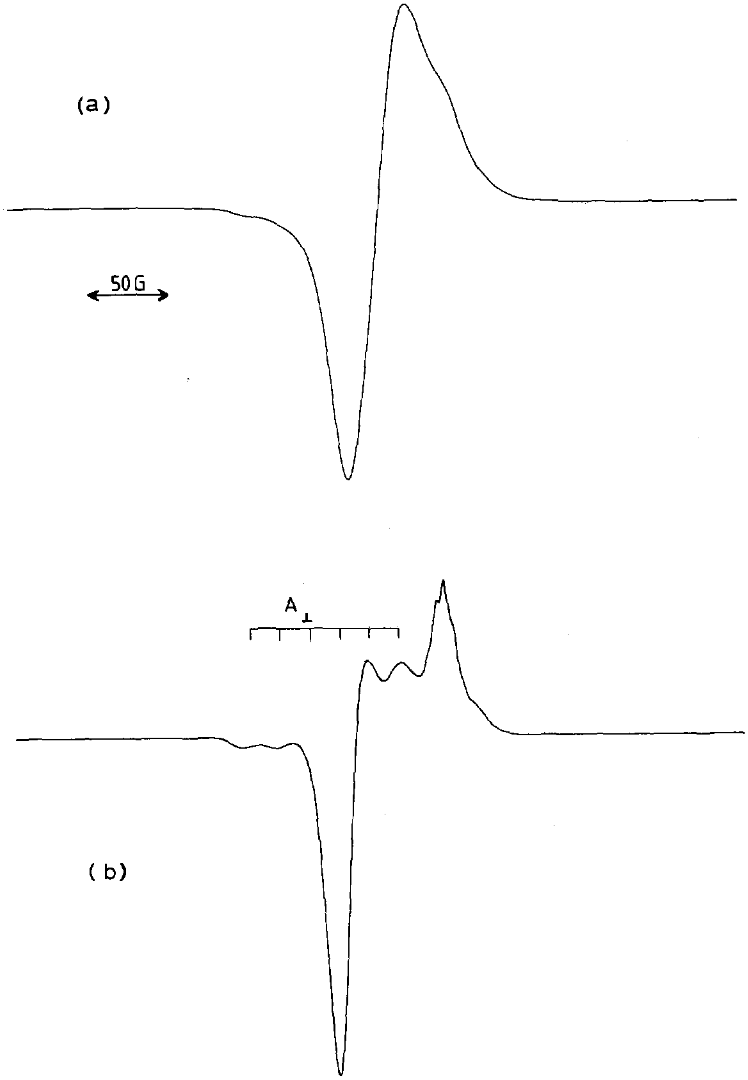

Fig. 3. X-Band ESR spectrum of $[Pd(\mathbf{1})_2]^{3+}$; (a) as a frozen glass in CH_3CN (0.1 M $^nBu_4NPF_6$) (77 K) formed by electrochemical oxidation, (b) as a frozen glass in aqueous $HClO_4$ (77 K).

coordination that we have observed in our structural studies, but could readily accommodate octahedral or distorted octahedral stereochemistries around a d^7 centre. The overall importance of the stereochemical flexibility of **1** on coordination to palladium(II)/(III) is reflected by the oxidative inactivity of the palladium complexes of **2** and **3** in which octahedral coordination cannot be achieved. Very few examples of monomeric palladium(III) have been reported in the literature [10–12]. In our system it is likely that positive charge is delocalised onto the thia donors thus conferring stability to the oxidised product.

Parallel to this work we have also been studying the redox properties of the corresponding triaza complexes. Thus $[Pd(\mathbf{4})_2]^{2+}$ (**4** = 1,4,7-triazacyclononane) shows a reversible oxidation at $E_{1/2} = -0.03$ V vs. Fc/Fc$^+$ which may be assigned to a palladium(II)/(III) couple *. This redox couple occurs at substantially lower potential than for the trithia system described above and reflects the expected difference in hardness/softness between amine and thia ligation.

Experimental

Infrared spectra were measured as Nujol mulls, KBr and CsI discs using a Perkin–Elmer 598 spectrometer over the range 200–4000 cm^{-1}. UV-VIS spectra were measured in quartz cells using a Pye Unicam SP8-400 spectrophotometer. Microanalyses were performed by the Edinburgh University Chemistry Department micro-analytical service. ESR spectra were recorded as solids or as frozen glasses down to 77 K using a Bruker ER200D X-band spectrometer. Electrochemical measurements were performed on a Bruker E310 Universal Modular Polarograph. All readings were taken using a three-electrode potentiostatic system in acetonitrile containing 0.1 M ^{n}Bu$_4$NPF$_6$ or ^{n}Bu$_4$NBF$_4$ as supporting electrolyte. Cyclic voltammetric measurements were carried out using a double platinum electrode and a Ag/Ag$^+$ reference electrode. All potentials are quoted vs. ferrocene/ferrocinium, Fc/Fc$^+$. Mass spectra were run by electron impact on a Kratos MS 902 and by fast atom bombardment on a Kratos MS 50TC spectrometer in a glycerol/dmf matrix.

1,4,7-trithiacyclononane (**1**) was prepared by the method described by Sellman and Zapf [13]. Instead of using $(Me_4N^+)_2(^-SCH_2CH_2SCH_2CH_2S^-)$, the disodium salt was used by reaction of the parent dithiol with NaOEt. At no stage in the reaction were the air-sensitive products isolated; filtering of the solution was performed on formation of the air stable [Mo(CO)$_3$(**1**)]. Yield 50%. ^{1}H NMR (CDCl$_3$, 80 MHz, 293 K): δ 3.12 ppm (CH_2).

1,4,8,11-tetrathiacyclotetradecane (**2**) was purchased from Aldrich Co; 1,4,7,10,13,16-hexathiacyclooctadecane (**3**) [2,14] and 1,4,7-triazacyclononane (**4**) [15] were prepared by published methods.

Synthesis of [Pd(1)$_2$](PF$_6$)$_2$

K$_2$[PdCl$_4$] (0.15 g, 4.6×10^{-4} M) was treated with **1** (0.17 g, 9.4×10^{-4} M) in water/methanol (30 cm^3, 1/1 v/v) under reflux for 30 min to yield a dark blue solution of the complex cation. Addition of an excess of NH$_4$PF$_6$ followed by cooling of the solution gave a green precipitate which could be recrystallised from water to give green crystals of [Pd(**1**)$_2$](PF$_6$)$_2$ in 80% yield. Elemental analysis: Found: C, 18.9; H, 3.1; [Pd(**1**)$_2$](PF$_6$)$_2$ calc: C, 19.0; H, 3.2%. Infrared spectrum: 2982, 2960, 1441, 1413, 1407, 1303, 1287, 1193, 1152, 1129 and 840 cm^{-1}. Mass spectrum: $m/e = 610$ [Pd(**1**)$_2$](PF$_6$)$^+$, 465 [Pd(**1**)$_2$]$^+$ (FAB-MS). Electronic spectrum: λ_{max} 615 nm, ϵ 54 M^{-1} cm^{-1} (CH$_3$CN). ^{1}H NMR. (CD$_3$CN, 80 MHz, 273 K): δ 3.3 ppm. (CH_2). Conductivity (CH$_3$NO$_2$): plot of $\Lambda_e - \Lambda_0$ vs. $C_e^{1/2}$ gives a slope of 485, $\Lambda_0 = 96.3$ consistent for a 2 : 1 electrolyte.

The BF$_4^-$ salt was prepared in a similar manner by use of NaBF$_4$ in place of NH$_4$PF$_6$. Elemental analysis: Found: C, 22.1; H, 3.8; [Pd(**1**)$_2$](BF$_4$)$_2$ calc: C, 22.5;

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* During the course of this work, McAuley and coworkers reported the oxidation of [Pd(**4**)$_2$]$^{2+}$ to afford a palladium(III) product: D. Fortier, A. McAuley, S. Subramanian and T. Whitcombe, 30th. International Congress of Pure and Applied Chemistry, September 1985, Manchester, UK.

H, 3.8%. Recrystallisation of $[Pd(\mathbf{1})_2](PF_6)_2$ from nitromethane gave blue crystals of $[Pd(\mathbf{1})_2](PF_6)_2 \cdot (CH_3NO_2)_2$. Elemental analysis: Found: C, 18.7; H, 3.4; N, 3.3; $[Pd(\mathbf{1})_2](PF_6)_2 \cdot (CH_3NO_2)_2$ calc: C, 19.1; H, 3.4; N, 3.2%.

Crystal structure determination of $[Pd(1)_2](PF_6)_2$

Crystal data. $C_{12}H_{24}PdS_6{}^{2+} \cdot 2PF_6^-$, $M = 1513.8$, monoclinic, a 17.879(8), b 15.627(13), c 11.476(8) Å, β 125.92(4)°, U 2597 Å^3, $Z = 4$, λ(Mo-K_α) 0.71069 Å, μ 13.77 cm^{-1}, D_x 1.936 g cm^{-3}, space group $C2/c$ (No. 15), crystal dimensions $0.08 \times 0.10 \times 0.42$ mm.

Data collection and processing. The crystal was mounted on a Stoe-Siemens AED2 four-circle diffractometer. After determination of an accurate orientation matrix, 1771 independent data (h $-19 \rightarrow 19$, k $0 \rightarrow 16$, l $0 \rightarrow 12$) were collected to $2\theta = 45°$ using ω–θ scans. Two standard reflections showed no significant crystal movement or decay over 35 X-ray h. Data reduction yielded 1153 reflections with $|F| \geqslant 2\sigma(F)$ which were used for solution and refinement of the structure.

Structure analysis and refinement. The position of the Pd was obtained from a Patterson synthesis and subsequent iterative least-squares cycles and difference Fourier syntheses yielded the remaining non-hydrogen atoms. Although the $[Pd(\mathbf{1})_2]^{2+}$ cation is ordered, there is disorder in one of the PF_6^- counterions which lie on two-fold axes. Hydrogen atoms were included at fixed, idealised positions (C–H 1.08 Å). Carbon atoms were refined with isotropic thermal parameters while all Pd, S, P and F atoms were refined anisotropically with $w^{-1} = \sigma^2(F) + 0.00268F^2$ [16]. At convergence, R, $R_w = 0.0565$, 0.0654, $S = 1.301$, maximum shift/error in final cycle was 0.01. A final ΔF synthesis gave maximum peak and minimum trough of 0.82 and -0.54 eÅ^{-3} respectively. Scattering factors for Pd were taken from ref. 17 and were otherwise inlaid. Other computer programs used were CALC [18] and ORTEP [19]. Bond lengths, interbond angles and torsion angles are given in Table 1–3. Final positional parameters for non-hydrogen atoms are listed in Table 4. Tables of calculated hydrogen positions and anisotropic thermal parameters, and lists of observed and calculated structure factors are available from the authors.

Synthesis of cis-$[Pd(1)Cl_2]$

$PdCl_2$ (0.08 g, 4.5×10^{-4} M) was treated with **1** (0.08 g, 4.4×10^{-4} M) in refluxing nitromethane/dichloromethane (60 cm^3, 3/1 v/v) for 24 h under N_2 to give an orange/brown precipitate. The product was collected and dissolved in a minimum amount of hot nitromethane. The solution was allowed to cool and was reduced in volume to afford orange crystals of *cis*-$[Pd(\mathbf{1})Cl_2]$ which were dried in vacuo. Yield 60%. Elemental analysis: Found: C, 19.7; H, 3.2, *cis*-$[Pd(1)Cl_2]$ calc:

TABLE 1

BOND LENGTHS (Å) FOR $[Pd(1)_2](PF_6)_2$ (with standard deviations)

Pd(1)–S(1)	2.952(4)	C(3)–S(4)	1.854(14)
Pd(1)–S(4)	2.332(3)	S(4)–C(5)	1.812(13)
Pd(1)–S(7)	2.311(3)	C(5)–C(6)	1.491(19)
S(1)–C(2)	1.799(14)	C(6)–S(7)	1.837(15)
S(1)–C(9)	1.809(15)	S(7)–C(8)	1.795(14)
C(2)–C(3)	1.467(19)	C(8)–C(9)	1.515(20)

TABLE 2

INTERBOND ANGLES (°) FOR $[\mathrm{Pd}(\mathbf{1})_2](\mathrm{PF}_6)_2$ (with standard deviations)

S(1)-Pd(1)-S(4)	83.13(10)	Pd(1)-S(4)-C(5)	99.5(4)
S(1)-Pd(1)-S(7)	83.24(11)	C(3)-S(4)-C(5)	100.6(6)
S(4)-Pd(1)-S(7)	88.63(11)	S(4)-C(5)-C(6)	114.2(9)
Pd(1)-S(1)-C(2)	90.3(5)	C(5)-C(6)-S(7)	112.5(10)
Pd(1)-S(1)-C(9)	94.6(5)	Pd(1)-S(7)-C(6)	104.5(5)
C(2)-S(1)-C(9)	105.4(7)	Pd(1)-S(7)-C(8)	104.5(5)
S(1)-C(2)-C(3)	118.8(10)	C(6)-S(7)-C(8)	103.3(6)
C(2)-C(3)-S(4)	114.8(10)	S(7)-C(8)-C(9)	119.9(10)
Pd(1)-S(4)-C(3)	108.2(4)	S(1)-C(9)-C(8)	114.6(10)

TABLE 3

TORSION ANGLES (°) FOR $[\mathrm{Pd}(\mathbf{1})_2](\mathrm{PF}_6)_2$ (with standard deviations)

S(4)-Pd(1)-S(1)-C(2)	18.0(5)	Pd(1)-S(1)-C(9)-C(8)	-29.2(10)
S(4)-Pd(1)-S(1)-C(9)	-87.5(5)	C(2)-S(1)-C(9)-C(8)	-120.8(10)
S(7)-Pd(1)-S(1)-C(2)	107.4(5)	S(1)-C(2)-C(3)-S(4)	62.1(13)
S(7)-Pd(1)-S(1)-C(9)	2.0(5)	C(2)-C(3)-S(4)-Pd(1)	-34.1(11)
S(1)-Pd(1)-S(4)-C(3)	4.0(5)	C(2)-C(3)-S(4)-C(5)	137.8(10)
S(1)-Pd(1)-S(4)-C(5)	108.5(4)	Pd(1)-S(4)-C(5)-C(6)	-48.2(10)
S(7)-Pd(1)-S(4)-C(3)	-79.4(5)	C(3)-S(4)-C(5)-C(6)	62.5(11)
S(7)-Pd(1)-S(4)-C(5)	25.2(4)	S(4)-C(5)-C(6)-S(7)	48.6(12)
S(1)-Pd(1)-S(7)-C(6)	-88.5(5)	C(5)-C(6)-S(7)-Pd(1)	-22.1(10)
S(1)-Pd(1)-S(7)-C(8)	19.7(5)	C(5)-C(6)-S(7)-C(8)	-131.2(10)
S(4)-Pd(1)-S(7)-C(6)	-5.3(5)	Pd(1)-S(7)-C(8)-C(9)	-51.2(11)
S(4)-Pd(1)-S(7)-C(8)	102.9(5)	C(6)-S(7)-C(8)-C(9)	57.9(12)
Pd(1)-S(1)-C(2)-C(3)	-47.3(11)	S(7)-C(8)-C(9)-S(1)	58.5(13)
C(9)-S(1)-C(2)-C(3)	47.5(12)		

TABLE 4

POSITIONAL PARAMETERS FOR NONHYDROGEN ATOMS IN $[\mathrm{Pd}(\mathbf{1})_2](\mathrm{PF}_6)_2$ (with estimated standard deviations)

Atom	x	y	z	U_{eq}
Pd(1)	0.25	0.25	0.5	0.0466(9)
S(1)	0.41920(19)	0.25947(21)	0.7976(3)	0.0695(24)
C(2)	0.4163(8)	0.1454(7)	0.8157(13)	0.064(3)
C(3)	0.3289(8)	0.1050(8)	0.7695(12)	0.060(3)
S(4)	0.23432(19)	0.11696(17)	0.5753(3)	0.0561(22)
C(5)	0.1380(8)	0.1400(7)	0.5831(11)	0.053(3)
C(6)	0.1483(9)	0.2206(7)	0.6606(14)	0.063(3)
S(7)	0.18258(21)	0.31171(17)	0.6005(3)	0.0609(23)
C(8)	0.2773(8)	0.3579(7)	0.7659(12)	0.060(3)
C(9)	0.3615(9)	0.3041(7)	0.8707(14)	0.065(3)
P(1)	0.5	0.0928(3)	0.25	0.089(5)
F(11)	0.4419(8)	0.0215(6)	0.1385(10)	0.144(10)
F(12)	0.5642(9)	0.0895(7)	0.1994(14)	0.198(15)
F(13)	0.4440(11)	0.1626(6)	0.1343(12)	0.205(15)
P(2)	0.5	0.5339(3)	0.75	0.072(4)
F(21)	0.4611(8)	0.5336(5)	0.5875(9)	0.150(10)
F(22)	0.5300(16)	0.6249(11)	0.7429(25)	0.14(3)
F(22′)	0.6038(15)	0.5612(21)	0.811(3)	0.14(3)
F(23)	0.5581(12)	0.4603(11)	0.7656(14)	0.257(19)

C, 20.1; H, 3.4%. Infrared spectrum: 2958, 2930, 1437, 1403, 1308, 1300, 1282, 1263, 1247, 1180, 1144, 935, 887, 805, 332 and 312 cm^{-1}. ^{1}H NMR (dmso-d_6, 80 MHz, 293 K): δ 3.3 ppm (br. s., CH_2).

*Synthesis of cis-[Pd(**1**)(PPh$_3$)$_2$](PF$_6$)$_2$*

cis-[Pd(**1**)Cl$_2$] (0.65 g, 1.82×10^{-4} *M*) was treated with an excess of PPh$_3$ (0.1 g, 3.82×10^{-4} *M*) in refluxing nitromethane (15 cm^3) for 30 min. Addition of NH$_4$PF$_6$ to the cooled orange solution, followed by addition of diethyl ether (40 cm^3) gave the required complex as an orange precipitate. The pure crystalline salt was obtained by recrystallisation from nitromethane/methanol. Yield 80%. Elemental analysis: Found: C, 45.1; H, 4.1; *cis*-[Pd(**1**)(PPh$_3$)$_2$](PF$_6$)$_2$ calc: C, 45.8; H, 3.8%. Infrared spectrum: 1480, 1435, 1412, 1305, 1185, 1092, 998, 840, 750, 739, 704, 692, 529 and 514 cm^{-1}. Electronic spectrum: λ_{max} 478 nm. ^{1}H NMR. (CD$_3$NO$_2$, 80 MHz, 293 K): δ 2.74 (m, CH_2, 12H), 7.3–7.7 ppm (m, PPh_3, 30H).

*Synthesis of cis-[Pt(**1**)Cl$_2$]*

PtCl$_2$ (0.12 g, 4.5×10^{-4} *M*) was treated with **1** (0.08 g, 4.4×10^{-4} *M*) in refluxing acetonitrile/dichloromethane (60 cm^3, 3/1 v/v) for 24 h under N$_2$. The yellow solution was filtered hot and allowed to cool; addition of diethyl ether afforded *cis*-[Pt(**1**)Cl$_2$] as a yellow solid. Recrystallisation from nitromethane yielded orange crystals which were dried in vacuo. Yield 60%. Elemental analysis: Found: C, 16.0; H, 2.7; [Pt(**1**)Cl$_2$] calc: C, 16.1; H, 2.7%. Infrared spectrum: 2960, 2930, 1438, 1404, 1305, 1281, 1266, 1248, 1182, 1144, 932, 886, 806, 318 and 304 cm^{-1}. ^{1}H NMR (dmso-d_6 80 MHz, 293 K): 3.28 ppm (br. s., CH_2).

*Synthesis of cis-[Pt(**1**)PPh$_3$)$_2$](PF$_6$)$_2$*

[Pt(**1**)Cl$_2$] (0.08 g, 1.79×10^{-4} *M*) was treated with PPh$_3$ (0.094 g, 3.6×10^{-4} *M*) in refluxing acetonitrile (20 cm^3) for 30 min to yield an orange solution. The mixture was filtered and evaporated to dryness and redissolved in the minimum of methanol. Addition of excess of NH$_4$PF$_6$ afforded yellow crystals of [Pt(**1**)-(PPh$_3$)$_2$](PF$_6$)$_2$ in 70% yield. Elemental analysis: Found: C, 42.1; H, 3.5%; [Pt(**1**)-(PPh$_3$)$_2$](PF$_6$)$_2$ calc: C, 42.4; H, 3.6%. Infrared spectrum: 3080, 1480, 1435, 1410, 1095, 995, 840, 753, 745, 597, 554, 539, 522, 510 and 493 cm^{-1}. ^{1}H NMR (CD$_3$CN, 80 MHz, 293 K): δ 7.4–7.5 (m, PPh_3, 30H), 2.2–2.8 ppm (m, CH_2, 12H).

*Synthesis of [Pd(**2**)](PF$_6$)$_2$*

Reaction of K$_2$[PdCl$_4$] (0.1 g, 3.1×10^{-4} *M*) with **2** (0.09 g, 3.4×10^{-4} *M*) in refluxing acetonitrile/dichloromethane (20 cm^3, 3/1 v/v) for 4 h resulted in the formation of the yellow dichloride salt [Pd(**2**)]Cl$_2$. This product was collected, washed with cold water, methanol and finally dichloromethane. The complex was dissolved in hot water and converted into the PF$_6^-$ salt by addition of an excess of NH$_4$PF$_6$ and allowing the solution to cool. Yellow crystals of [Pd(**2**)](PF$_6$)$_2$ were obtained on further recrystallisation from water. Yield 75%. Elemental analysis: Found: C, 17.9; H, 3.0; [Pd(**2**)](PF$_6$)$_2$ calc: C, 18.1; H, 3.0%. Infrared spectrum: 2998, 2938, 2910, 2886, 1428, 1410, 1307, 1284, 1253, 1208, 1170, 1136, 1028 and 840 cm^{-1}. Mass spectrum: $m/e = 519$ [Pd(**2**)](PF$_6$)$^+$, 374 [Pd(**2**)]$^+$ (FAB-MS).

Synthesis of $[Pd(4)_2](PF_6)_2$

Reaction of $PdCl_2$ (0.08 g, 4.5×10^{-4} *M* with **4** (0.21 g, 9.3×10^{-4} *M*) in refluxing methanol (30 cm^3) for 3 h yielded a yellow solution; addition of NH_4PF_6 gave $[Pd(\mathbf{4})_2](PF_6)_2$ in 80% yield. Elemental analysis: Found: C, 21.6; H, 4.56; N, 13.0; $[Pd(\mathbf{4})_2](PF_6)_2$ calc: C, 22.2; H, 4.7; N, 13.0%. ^1H NMR (CD_3CN, 200 MHz, 293 K): δ 2.8–3.3 ppm. (AA'BB', CH_2), at 233 K (v.br.d). ^{13}C NMR ($(CD_3)_2CO$, 60 MHz, 293 K) δ 106.6 ppm. (t., CH_2).

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