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Conformationally locked mixed aza–thioether macrocycles: synthesis and structures of complexes of Pd^{II}, Pt^{II} and Rh^{III} of 2,5,8-trithia-[9](2,9)-1,10-phenanthrolinophane

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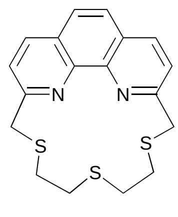
The complexation of the mixed aza–thioether crown 2,5,8-trithia[9](2,9)-1,10-phenanthrolinophane (L) with Pd^{II}, Pt^{II} and Rh^{III} has been investigated. The single-crystal structures of $[PdL][PF_6]_2$ and $[PtL][PF_6]_2$ confirm $[N_2S_2 + S]$ co-ordination in both complexes with the ligand adopting a folded conformation. Carbon-13 NMR spectroscopic studies, carried out in the solid state as well as in solution, indicated that only one form of each complex is present in solution, having $[N_2S_2 + S]$ co-ordination at Pd^{II} and Pt^{II} and octahedral co-ordination $[N_2S_3 + Cl^-]$ at Rh^{III} in $[RhL(Cl)]^{2+}$. The redox properties of $[ML][PF_6]_2$ (M = Pd or Pt) in MeCN are reported.

The co-ordination chemistry of homoleptic polyaza, polythia and mixed N, S-donor macrocyclic ligands has attracted the attention of several groups over the past few years.[1,2] These macrocycles show a remarkable ability to form stable and inert complexes with a wide range of metal ions, forcing the metal centre to adopt unusual co-ordination geometries and/or oxidation states.[3–11] The presence of rigid heterocyclic molecules such as pyridine, 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen), which carry hard N-donor atoms, as part of a macrocycle ligand has been shown to stabilize low-valent metal complexes as well as to have a marked influence on the co-ordination geometry at the metal centre.[12,13] Interest in complexes of substituted derivatives of bipy and phen is based mainly on their catalytic, redox and photoredox properties,[14] as well as on their use as building blocks for supramolecular devices.[15] We have recently reported the synthesis and co-ordinating properties of new mixed aza–thioether crowns incorporating the 1,10-phenanthroline sub-unit with Ni^{II}.[16] In particular, the pentadentate ligand 2,5,8-trithia[9](2,9)-1,10-phenanthrolinophane L has chelating properties strictly dependent on the conformational constraints imposed by the phenanthroline unit on the S-donor thioether linker of the ring. We report herein the results of our investigation on its co-ordination to platinum group metals, in particular Pd^{II}, Pt^{II} and Rh^{III}.


L

Results and Discussion

Reaction of compound L with 1 molar equivalent of $PdCl_2$ in refluxing MeCN–water affords an orange solution. Addition of an excess of NH_4PF_6 and partial removal of the solvent gives a reddish product, which can be recrystallized from MeCN–Et_2O. The fast-atom bombardment (FAB) mass spectrum of the complex exhibits peaks with the correct isotopic distribution for $[PdL(PF_6)]^+$ ($m/z = 609$) and for $[PdL]^{2+}$ ($m/z = 463$). These data together with elemental analyses and IR spectroscopy confirm the formulation $[PdL][PF_6]_2$. A single-crystal structure determination was undertaken to ascertain the ligation and stereochemistry of this complex. The structure confirms the formation of the $[PdL]^{2+}$ cation (Fig. 1, Table 1) with the pentadentate macrocycle imposing a formal [4 + 1] co-ordination sphere at the Pd^{II}. The two N-donors of the phen unit, Pd–N 1.972(2) and 1.979(2) Å, and two of the three S-donors of the thioether linker, Pd–S 2.293(1) and 2.291(1) Å, are bound in a square-planar arrangement to the metal ion. The third S-donor occupies an apical site with a long-range interaction to the metal centre, $Pd\cdots S_{ap}$ 2.865(1) Å, and the Pd^{II} is displaced 0.115(1) Å out of the mean plane defined by the atoms S(1), S(2), N(1) and N(2) towards the apical sulfur atom S(3) [Fig. 1(*b*)]. Related long-range apical interactions to Pd^{II} ranging from 2.9 to 3.2 Å have been found in $[Pd([9]aneS_3)_2]^{2+}$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane),[4] $[Pd([10]aneS_3)_2]^{2+}$ ($[10]aneS_3$ = 1,4,7-trithiacyclodecane),[5] $[Pd([18]aneS_6)]^{2+}$ ($[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane),[1] $[Pd([9]aneNS_2)_2]^{2+}$ ($[9]aneNS_2$ = 1,4-dithia-7-azacyclononane)[3] and $[Pd\{(py)_2[9]aneN_2S\}]^{2+}$ $\{(py)_2[9]aneN_2S$ = 1-thia-4,7-bis(2-pyridylmethyl)-4,7-diazacyclononane$\}$[17] in which a [4 + 2] or [4 + 1] co-ordination sphere is imposed by the macrocyclic ligands. The structure of $[PdL]^{2+}$ is also similar to that of $[Pd([9]aneS_3)(phen)]^{2+}$[18] and is comparable to those reported for the palladium(II) half-sandwich complexes with $[9]aneS_3$ having a general formula $[Pd([9]aneS_3)L_2]^{n+}$ {L = Cl, Br, PPh_3, $\frac{1}{2}$bipy, $\frac{1}{2}$dppm ($Ph_2PCH_2PPh_2$), $\frac{1}{2}$dppe ($Ph_2PCH_2CH_2PPh_2$), $\frac{1}{2}(Ph_2PCH_2)_3CMe$ or $\frac{1}{2}(Ph_2PCH_2)_2[Ph_2P(O)CH_2]CMe$; $n = 0$, 1 or 2}.[18,19] For these last compounds the long-range apical $Pd\cdots S_{ap}$ interaction [2.698(3)–3.140(2) Å] increases with increasing overall charge of the complex cation and increasing π-acceptor ability of the ligand. However, in the present case, the Pd–N and $Pd\cdots S_{ap}$ distances are shorter than those found in $[Pd([9]aneS_3)(phen)]^{2+}$ [2.049(4), 2.053(4) Å for Pd–N and 2.948(13) Å for $Pd\cdots S_{ap}$] whereas the Pd–S_{eq} distances have very similar values. Interestingly, the S(1)–Pd–S(2) angle [109.37(2)°] is far higher than that observed for $[Pd([9]aneS_3)(phen)]^{2+}$ [88.83(11)°]. The basal angles, S(1)–Pd–N(2) and

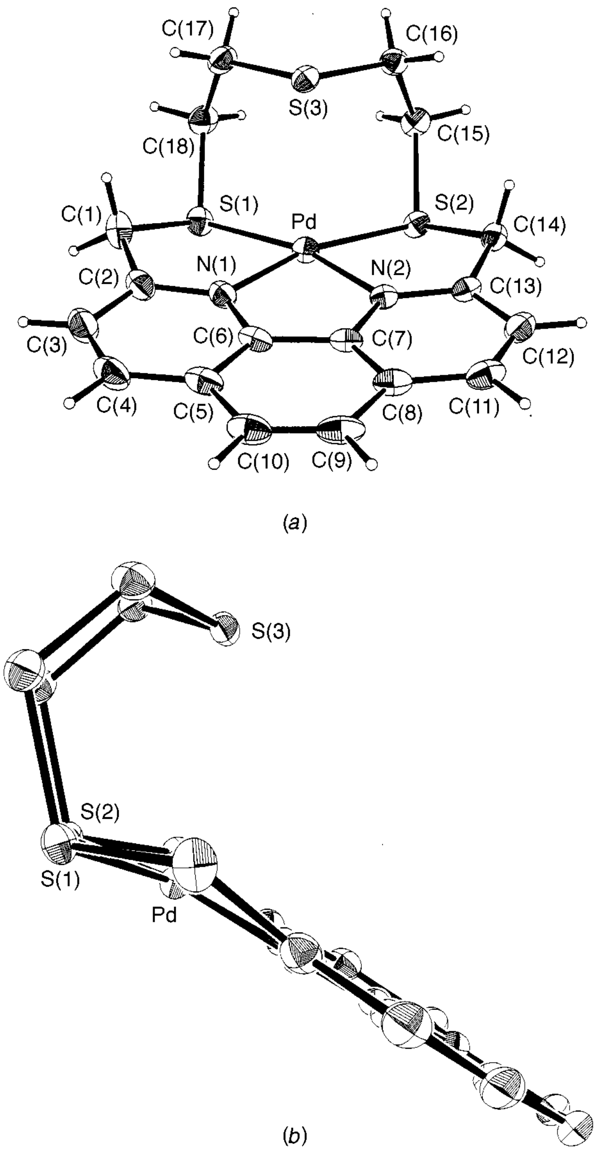


Fig. 1 Two views (*a*) and (*b*) of the $[PdL]^{2+}$ cation with the numbering scheme adopted. Thermal ellipsoids are drawn at 30% probability

S(2)–Pd–N(1), are 165.21(6) and 164.99(6)° respectively, in good agreement with that of 164° given by Rossi and Hoffmann[20] as optimum for a square-pyramidal geometry around a d^8 ion.

The reaction of compound L with 1 molar equivalent of $PtCl_2$ in refluxing MeCN–water affords a yellow product upon addition of an excess of NH_4PF_6. The crystal structure determination confirms the formation of $[PtL][PF_6]_2$ which is isostructural with $[PdL][PF_6]_2$. The main difference in the platinum(II) complex is the longer distance of the metal centre from the sulfur atom occupying the apical position of the elongated square-based pyramid [$Pt \cdots S_{ap}$ 2.938(1) Å] (Table 1). The Pt^{II} has a displacement of 0.096(1) Å out of the mean plane described by the basal donor atoms towards the apical sulfur atom. A [4 + 2] or [4 + 1] co-ordination sphere is also common among sandwich and half-sandwich complexes of Pt^{II} with facially co-ordinating macrocycles, $[9]aneS_3$[5] and $[10]aneS_3$,[6] reflecting the preference of a square-planar co-ordination by these d^8 metal ions.

The main structural parameters for the complexes $[M([9]aneS_3)(phen)]^{2+}$ and the $[ML]^{2+}$ (M = Pd or Pt) are compared in Table 2.[18,21] Quite intriguing is the opposite variation in the $M \cdots S_{ap}$ long-range interaction on passing from the complexes of Pd^{II} to those of Pt^{II}. According to Gray and co-workers,[21] for the complexes $[M([9]aneS_3)(phen)]^{2+}$ (M = Pd or Pt), the shorter $Pt \cdots S_{ap}$ distance should reflect the higher ability of Pt^{II} with respect to Pd^{II} back bonding of the d_{xz} and d_{yz} electrons into the diimine π^* orbitals; the consequent enhanced positive charge at the metal centre will increase the interaction with the apical σ S-donor atom. It is likely that for $[ML]^{2+}$ (M = Pd or Pt) the geometrical constraints imposed by the phen unit on the thioether linker might work against the expected electronic effects, causing an increase in the $Pt \cdots S_{ap}$ distance instead of a decrease with respect to the analogous palladium(II) complex. The crucial role played by the conformational constraints is clearly reflected in the opening of the S(1)–M–S(2) angles and the shortening of the M–N bonds in $[ML]^{2+}$ (M = Pd or Pt) with respect to $[M([9]aneS_3)(phen)]^{2+}$ (M = Pd or Pt).

Table 1 Selected interatomic distances (Å), angles and torsions (°) for $[ML][PF_6]_2$ (M = Pd or Pt)

	M = Pd	M = Pt
M–S(1)	2.293(1)	2.277(1)
M–S(2)	2.291(1)	2.274(1)
M–N(1)	1.972(2)	1.977(3)
M–N(2)	1.979(2)	1.985(3)
$M \cdots S(3)$	2.865(1)	2.938(1)
S(1)–M–S(2)	109.37(2)	109.04(4)
S(1)–M–N(1)	83.94(6)	84.3(1)
S(1)–M–N(2)	165.21(6)	165.7(1)
S(2)–M–N(1)	164.99(6)	165.5(1)
S(2)–M–N(2)	83.71(6)	84.0(1)
N(1)–M–N(2)	82.30(8)	82.2(1)
M–S(1)–C(18)–C(17)	−42.2(3)	−42.4(5)
S(1)–C(18)–C(17)–S(3)	45.1(3)	44.4(6)
C(18)–C(17)–S(3)–C(16)	76.0(3)	75.4(5)
C(17)–S(3)–C(16)–C(15)	−74.8(3)	−73.2(4)
S(3)–C(16)–C(15)–S(2)	−46.4(3)	−46.7(5)
C(16)–C(15)–S(2)–M	42.1(2)	42.3(4)
C(15)–S(2)–M–S(1)	63.2(1)	62.4(2)
S(2)–M–S(1)–C(18)	−62.7(1)	−61.8(2)

The reaction of compound L with $RhCl_3$ in refluxing MeCN–water affords a yellow microcrystalline powder after addition of an excess of NH_4PF_6; analytical data, IR and FAB mass spectroscopy suggest the formulation $[RhL(Cl)][PF_6]_2 \cdot MeCN$, but no single crystals suitable for X-ray studies have been obtained.

Five-co-ordinate d^8 metal ion complexes containing a weakly bonded ligand represent useful models for the transition state in associative substitution reactions at square-planar Pd^{II} and Pt^{II}. Sandwich and half-sandwich complexes of these metal ions with $[9]aneS_3$ have been found to be fluxional in solution with a fast S-atom exchange presumably *via* 1-4 metallotropic shifts.[18,21,22] In our view, for $[ML]^{2+}$ (M = Pd or Pt) in solution, the most likely intramolecular S-atom shift around the metal centre could be the flipping of the S_{ap} atom between a bonded and a non-bonded situation.

The ^{13}C NMR chemical shifts for the complexes $[ML]^{2+}$ (M = Pd or Pt) and $[RhL(Cl)]^{2+}$ in CD_3CN solution are reported in Table 3 and are compared with those for the free macrocycle[16] (the crystal structure numbering scheme has been adopted for their assignment). Only six peaks for the aromatic region and three for the thioether one are observed in ^{13}C NMR spectra; this suggests that the three complexes exist in solution in only one form having a C_s symmetry with a plane of reflection passing through the metal and the S(3) atoms and bisecting the N(1)–M–N(2) angle. With respect to the free macrocycle, the carbon atoms next to S(1) and S(2) are deshielded whereas those next to S(3) are shielded for the complexes of Pd^{II} and Pt^{II}; the situation is different for Rh^{III} in which all the carbon atoms are deshielded. The ^{13}C NMR chemical shifts do not change upon cooling to 238 K. Furthermore, the ^{13}C NMR spectra recorded in the solid state on the three complexes

Table 2 Main structural features for the complexes $[ML]^{2+}$ and $[M([9]aneS_3)(phen)]^{2+}$ (M = Pd or Pt)

	$[PdL]^{2+}$ This work	$[PtL]^{2+}$ This work	$[Pd([9]aneS_3)(phen)]^{2+}$ Ref. 18	$[Pt([9]aneS_3)(phen)]^{2+}$ Ref. 21
$M\cdots S_{ap}$/Å	2.865(1)	2.938(1)	2.948(13)	2.821(3)
$M-S_{eq}$/Å	2.293(1), 2.291(1)	2.274(1), 2.277(1)	2.274(3), 2.275(3)	2.272(3), 2.279(3)
M–N/Å	1.972(2), 1.979(2)	1.977(3), 1.985(3)	2.049(4), 2.053(4)	2.070(9), 2.074(10)
$S_{eq}-M-S_{eq}$/°	109.37(2)	109.04(4)	88.83(11)	88.5(1)
N–M–N/°	82.30(8)	82.2(1)	80.6(4)	82.1(5)

Table 3 ^{13}C NMR chemical shifts (δ) for the complexes of Pd^{II}, Pt^{II} and Rh^{III} with L in CD_3CN solution

Compound	C(1)/C(14)	C(18)/C(15)	C(17)/C(16)	C(2)/C(13)	C(3)/C(12)	C(4)/C(11)	C(5)/C(8)	C(6)/C(7)	C(10)/C(9)
L [a]	37.1	33.7	32.0	159.5	122.6	137.1	127.3	144.6	125.8
$[PdL]^{2+}$ [b]	49.5	40.8	27.7	164.3	125.3	141.1	131.2	147.3	128.6
$[PtL]^{2+}$ [b]	50.8	41.6	27.3	164.1	124.8	141.3	131.3	146.3	128.7
$[RhL(Cl)]^{2+}$ [b]	51.6	40.7	39.6	161.5	126.3	141.0	132.0	146.4	128.8

[a] Ref. 16. [b] This work.

exhibit the same pattern as those in solution, with good agreement between the chemical shifts. These data are consistent with a [4 + 1] co-ordination sphere being imposed at the Pd^{II} and Pt^{II} in the solid state as well as in solution with the S(3)-donor atom weakly interacting with the metal centres. For $[RhL(Cl)]^{2+}$ the tendency of Rh^{III} to adopt an octahedral co-ordination sphere causes the S(3) atom to be strongly co-ordinated both in solution and in the solid state with a chloride completing the octahedral environment.

The ^1H NMR spectra of the three complexes in CD_3CN solution exhibit three distinct groups of aliphatic protons the assignments of which have been made on the basis of two-dimensional correlation (COSY 45) and $^1H-^{13}C$ heteronuclear correlation (HETCOR) experiments (see Experimental section). The absence of any observed coalescence in the range 320–238 K for any of the peaks is further evidence that these complexes are not fluxional in solution. An AB sub-spectrum for each pair of protons on C(1) and C(14) suggests that they assume inequivalent dispositions (up and down with respect to the plane of the phenanthroline moiety) as a consequence of complexation. The same behaviour has been observed for the protons of the methylene group in the pendant arms of the ligand in $[Pd\{(py)_2[9]aneN_2S\}]^{2+}$.[17] For this latter complex also, no fluxional processes have been observed by NMR techniques, with the axial S atom of the ligand bonded to the metal centre in solution as well as in the solid state.

The redox properties of $[ML]^{2+}$ (M = Pd or Pt) have been monitored by cyclic voltammetry in MeCN solution (0.1 mol dm^{-3} $NBu^n{}_4BF_4$) in the range +1.8 to −1.8 V *vs.* ferrocene–ferrocenium where the free macrocycle is electrochemically inactive. Both reductive and oxidative cyclic voltammetry (scan rate 0.1 V s^{-1} at 298 K) show the complexes to be characterized by one irreversible oxidation and two irreversible reductions ($E_{pa} = +1.268$, $E_{pc} = -0.733$ and −1.201 V for Pd^{II}, $E_{pa} = +0.989$, $E_{pc} = -1.174$ and −1.520 V for Pt^{II}). In the case of $[PdL]^{2+}$ the first irreversible reduction becomes quasi-reversible if the cyclic voltammogram scanned in the cathodic direction is reversed at −0.9 V ($\Delta E_p = 0.090$ V at a scan rate of 0.1 V s^{-1}). A similar behaviour has been reported for the complex $[Pd(Me_2[18]aneN_2S_4)]^{2+}$ ($Me_2[18]aneN_2S_4$ = 7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclooctadecane), the first example of a thioether complex exhibiting a reversible Pd^{II}–Pd^{I} couple (−0.74 V *vs.* ferrocene–ferrocenium at 298 K).[7] A reversible reduction at −0.83 V, tentatively assigned to the Pd^{II}–Pd^{I} couple, has also been observed for the complex $[Pd([9]aneS_3)(phen)]^{2+}$.[18] Coulometric measurements in MeCN upon the first reduction indicate that this is a one-electron process for $[ML]^{2+}$ (M = Pd or Pt): it is assigned tentatively to the couples Pd^{II}–Pd^{I} and Pt^{II}– Pt^{I} respectively. Attempts to establish the precise nature of the reduction products have not been successful, presumably because of their high reactivity. Mononuclear palladium(I) and platinum(I) co-ordination compounds are highly unusual and dimerization involving metal–metal bond formation has been described as the dominant quenching process.[23,24] The locked [4 + 1] co-ordination sphere that L can impose on the Pd^{II} and Pt^{II} as well as the nature of its donor atom set seem to be responsible for the stabilization of the corresponding low-valent complexes Pd^{I} and Pt^{I}. This, together with the possibility for the encapsulated metal centre to reach an octahedral stereochemistry by interaction with an additional ligand, might confer on the system interesting catalytic properties.

Experimental

All melting points are uncorrected. The NMR spectra were recorded on a Varian VXR300 spectrometer operating at 75.47 MHz; the assignment of the ^1H chemical shifts has been done on the basis of two-dimensional COSY 45 and $^1H-^{13}C$ HETCOR experiments. Cross polarization magic angle spinning solid-state ^{13}C NMR spectra were recorded on a Varian Unity Inova 400 MHz instrument operating at 100.5 MHz with samples packed into a zirconium oxide rotor. The 90° pulse time was 4.6 μs and the cycle time 45 s. The ^{13}C chemical shifts were calibrated indirectly through the adamantane peaks (δ 38.3, 29.2) relative to $SiMe_4$. Mass spectra (3-nitrobenzyl alcohol matrix) were recorded at the EPSRC National Service for Mass Spectrometry at Swansea, UK. The spectrophotometric measurements were carried out at 25 °C using a Varian model Cary 5 UV/VIS/NIR spectrophotometer. Microanalytical data were obtained by using a Fisons EA 1108 CHNS-O instrument (T = 1000 °C). Infrared spectra were taken in the range 3500–200 cm^{-1} using a Perkin-Elmer 983 instrument connected to a 7500 data station. Cyclic voltammetry was performed using a conventional three-electrode cell, with a platinum double-bead electrode and a Ag–AgCl reference electrode. All measurements were taken in a 0.1 mol dm^{-3} solution of tetra-*n*-butylammonium tetrafluoroborate in acetonitrile, which was freshly distilled from CaH_2 prior to use. Compound L was synthesized according to the procedure previously reported[16] and all the metal salts and solvents used in the synthesis of the complexes (Aldrich) were used without further purification.

Preparations

$[PdL][PF_6]_2$. A mixture of compound L (100 mg, 0.28 mmol) and $PdCl_2$ (49.6 mg, 0.28 mmol) in MeCN–water (1 : 1 v/v, 80 cm^3) was refluxed under N_2 for 6 h. Addition of a large excess

Table 4 Summary of crystallographic data *

	$[PdL][PF_6]_2$	$[PtL][PF_6]_2$
Formula	$C_{18}H_{18}F_{12}N_2P_2PdS_3$	$C_{18}H_{18}F_{12}N_2P_2PtS_3$
M	754.88	843.57
a/Å	10.212(1)	10.227(2)
b/Å	11.421(1)	11.428(3)
c/Å	11.554(2)	11.593(2)
α/°	98.05(1)	97.87(2)
β/°	101.46(1)	101.69(2)
γ/°	107.20(1)	107.06(2)
U/Å^3	1232.8(3)	1240.2(5)
D_c/g cm^{-3}	2.033	2.259
μ(Mo-Kα)/cm^{-1}	12.2	61.9
F(000)	744	808
Absorption correction range	0.94–1.00	0.56–1.00
Measured reflections	4664	4628
Unique reflections with $I > 3\sigma(I)$	3793	3818
Final R and R'	0.025, 0.039	0.024, 0.033
No. variables	343	343
Goodness of fit	1.620	1.376

* Details in common: triclinic, space group $P\bar{1}$; $Z = 2$; scan mode ω; ω-scan width 0.90 + 0.35 tan θ; θ range 3–25°; *hkl* ranges 0–12, −13 to 13, −13 to 13; $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$; $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$; goodness of fit = $[\Sigma w(F_o - k|F_c|)^2/(N_{observations} - N_{variables})]^{\frac{1}{2}}$.

of NH_4PF_6 and reduction of the volume under reduced pressure afforded a reddish microcrystalline powder. Recrystallization by slow diffusion of diethyl ether into a MeCN solution of the solid product gave orange-brown needle-shaped crystals of $[PdL][PF_6]_2$ (137.4 mg, 65% yield). M.p. 200 °C with decomposition [Found (Calc. for $C_{18}H_{18}F_{12}N_2P_2PdS_3$): C, 28.8 (28.7); H, 2.5 (2.4); N, 4.0 (3.7); S, 13.1 (12.7)%]. FAB mass spectrum: *m*/*z* 609, 463; calc. for $[^{106}PdL(PF_6)]^+$ and $[^{106}PdL]^{2+}$ 609 and 464 respectively. IR (KBr pellet): ν 3086w, 3013w, 2950w, 1585m, 1484m, 1420m, 1391m, 1285m, 1175m, 1083m, 941w, 838s, 739w, 694m and 558s cm^{-1}. Electronic spectrum (MeCN): $\lambda_{max} = 280$ ($\varepsilon_{max} = 32\,230$), 376 (2150) and 491 nm (312 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR (CD_3CN, 300 MHz): δ 8.88 [2 H, d, $J = 8.9$, H(3)/H(12)], 8.27 [2 H, s, H(10)/H(9)], 8.10 [2 H, d, $J = 8.8$, H(4)/H(11)], 5.26 [2 H, d, $J = 18.8$, H(1a)/H(14a) or H(1b)/H(14b)], 4.86 [2 H, d, $J = 18.8$ Hz, H(1b)/H(14b) or H(1a)/H(14a)], 3.6–3.4 [4 H, m, H(18)/H(15)], 3.08–3.0 and 2.98–2.90 [4 H, m, H(17)/H(16)]. ^{13}C-{^{1}H} NMR (CD_3CN, 75.4 MHz): δ 49.5 [t, $J = 147.0$, C(1)/C(14)], 40.8 [t, $J = 145.4$, C(18)/C(15)], 27.7 [t, $J = 144.6$, C(17)/C(16)], 164.3 [s, C(2)/C(13)], 125.3 [d, $J = 173.5$, C(3)/C(12)], 141.1 [d, $J = 171.0$, C(4)/C(11)], 131.2 [s, C(5)/C(8)], 147.3 [s, C(6)/C(7)] and 128.6 [d, $J = 169.4$ Hz, C(10)/C(9)].

$[PtL][PF_6]_2$. A procedure similar to that for the palladium complex was employed. A mixture of L (100 mg, 0.28 mmol) and $PtCl_2$ (74.5 mg, 0.28 mmol) in MeCN–water (1 : 1 v/v, 80 cm^3) was refluxed under N_2 for 12 h. An excess of NH_4PF_6 was added to the resulting yellow solution and the solvent partially removed in vacuum to give a yellow microcrystalline powder. This was recrystallized from MeCN by diethyl ether diffusion to yield yellow needles of $[PtL][PF_6]_2$ (161 mg, 68% yield). M.p. 200 °C with decomposition [Found (Calc. for $C_{18}H_{18}F_{12}N_2P_2PtS_3$): C, 26.0 (25.6); H, 2.0 (2.2); N, 3.5 (3.3); S, 11.8 (11.4)%]. FAB mass spectrum: *m*/*z* 698, 552; calc. for $[^{195}PtL(PF_6)]^+$ and $[^{195}PtL]^{2+}$ 698 and 553 respectively. IR (KBr pellet): ν 3087w, 3015w, 2954w, 2936w, 1608w, 1584m, 1496w, 1486m, 1441w, 1420m, 1391m, 1286m, 1157m, 841s, 738m, 696m, 558s and 538m cm^{-1}. Electronic spectrum (MeCN): $\lambda_{max} = 284$ ($\varepsilon_{max} = 18\,110$), 362 (1840) and 400 nm (1700 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR (CD_3CN, 300 MHz): δ 8.99 [2 H, d, $J = 8.4$, H(3)/H(12)], 8.31 [2 H, s, H(10)/H(9)], 8.24 [2 H, d, $J = 8.5$, H(4)/H(11)], 5.44 [2 H, d, $J = 18.8$, H(1a)/H(14a) or H(1b)/H(14b)], 5.03 [2 H, d, $J = 18.8$ Hz, H(1b)/H(14b) or H(1a)/H(14a)], 3.74–3.70 [4 H, m, H(18)/H(15)], 3.10–3.0 and 2.98–2.90 [4 H, m, H(17)/H(16)]. ^{13}C-{^{1}H} NMR (CD_3CN, 75.4 MHz): δ 50.8 [t, $J = 146.6$, C(1)/C(14)], 41.6 [t, $J = 147.0$, C(18)/C(15)], 27.3 [t, $J = 144.7$, C(17)/C(16)], 164.1 [s, C(2)/C(13)], 124.8 [d, $J = 174.7$, C(3)/C(12)], 141.3 [d, $J = 171.2$, C(4)/C(11)], 131.3 [s, C(5)/C(8)], 146.3 [s, C(6)/C(7)] and 128.7 [d, $J = 170.2$ Hz, C(10)/C(9)].

$[RhL(Cl)][PF_6]_2 \cdot MeCN$. A mixture of compound L (50 mg, 0.14 mmol) and $RhCl_3$ (29 mg, 0.14 mmol) in MeCN–water (1 : 1 v/v, 30 cm^3) was refluxed under N_2 for 5 h. Addition of a large excess of NH_4PF_6 caused the formation of a reddish brown solid that was filtered off and discarded. The yellow solution was concentrated under vacuum to give a yellow microcrystalline powder of the desired product. Recrystallization by slow diffusion of diethyl ether into a MeCN solution of the product gave yellow needle-shaped crystals (33 mg, 30% yield) of $[RhL(Cl)][PF_6]_2 \cdot MeCN$. M.p. 243–245 °C [Found (Calc. for $C_{20}H_{21}ClF_{12}N_3P_2RhS_3$): C, 28.8 (29.0); H, 2.4 (2.6); N, 4.7 (5.1); S, 11.6 (11.6)%]. FAB mass spectrum: *m*/*z* 641, 495; calc. for $[^{103}RhL(Cl)(PF_6)]^+$ and $[^{103}RhL(Cl)]^{2+}$ 642 and 497 respectively. IR (KBr pellet): ν 3090w, 2980w, 2920w, 2120m (CN), 1605w, 1582m, 1498m, 1480m, 1420m, 1380m, 1180w, 1155w, 990w, 930m, 830s, 745m, 720w, 690w, 555s, 540m and 345m cm^{-1} (Rh–Cl). Electronic spectrum (MeCN): $\lambda_{max} = 281$ ($\varepsilon_{max} = 21\,960$), 306 (3680), 339 (2480) and 357 nm (59 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR (CD_3CN, 300 MHz): δ 8.844 [2 H, d, $J = 8.8$, H(3)/H(12)], 7.87 [2 H, s, H(10)/H(9)], 7.77 [2 H, d, $J = 8.8$, H(4)/H(11)], 4.96 [2 H, d, $J = 18.8$, H(1a)/H(14a) or H(1b)/H(14b)], 4.65 [2 H, d, $J = 18.8$ Hz, H(1b)/H(14b) or H(1a)/H(14a)], 3.4–3.2 [2 H, m, H(18a)/H(15a) or H(18b)/H(15b)], 3.00–2.70 [6 H, m, H(18b)/H(15b) or H(18a)/H(15a) and H(17)/H(16)]. ^{13}C-{^{1}H} NMR (CD_3CN, 75.4 MHz): δ 51.6 [t, $J = 147.0$, C(1)/C(14)], 40.7 [t, $J = 149.0$, C(18)/C(15)], 39.6 [t, $J = 148.0$, C(17)/C(16)], 161.5 [s, C(2)/C(13)], 126.3 [d, $J = 174.3$, C(3)/C(12)], 141.0 [d, $J = 170.8$, C(4)/C(11)], 132.0 [s, C(5)/C(8)], 146.4 [s, C(6)/C(7)] and 128.8 [d, $J = 170.4$ Hz, C(10)/C(9)].

Crystallography

Details of the data collection and refinement of the structures are reported in Table 4. Crystals of both compounds were mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with graphite-monochromatized Mo-Kα radiation (λ 0.710 73 Å) on an Enraf-Nonius CAD4 computer-controlled κ axis diffractometer. Cell constants and an orientation matrix for data collection were obtained for least-squares refinement, using the setting angles of 25 reflections. The data were collected at room temperature using a variable scan rate (2 to 20° min^{-1} in ω). Three representative reflections were measured every hour to check the stability of the crystals under X-ray exposure; these measurements revealed no decay of the scattering power of the crystal. Lorentz-polarization and semiempirical absorption[25] corrections were applied to the data. The structures were solved by a combination of Patterson and Fourier-difference syntheses, and refined in full-matrix least squares, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$. Individual weights were assigned as $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = \sigma(F_o{}^2)/2F_o$, $\sigma(F_o{}^2) = [\sigma^2(I) + (iI)^2]^{\frac{1}{2}}/L_p$, where i, the 'ignorance factor', is equal to 0.04. All non-H atoms were refined anisotropically and all the hydrogen atoms were introduced in the structure model at calculated positions (C–H 0.95 Å) and not refined. Scattering factors were taken from Cromer and Waber.[26]

Anomalous dispersion effects were included in F_c; the values for $\delta f'$ and $\delta f''$ were those of Cromer.[27] The final Fourier-difference synthesis showed maximum residuals of 0.43 and 0.97 e Å^{-3} for $[PdL][PF_6]_2$ and $[PtL][PF_6]_2$ respectively, close to the metal atoms. All calculations were performed on a 80486/33 computer using Personal SDP software.[28]

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