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Synthesis and structures of half-sandwich palladium(II) complexes of 1,4,7-trithiacyclononane ([9]aneS$_3$) incorporating halide, phosphine and heterocyclic ligands

Alexander J. Blake, Yvonne V. Roberts and Martin Schröder *

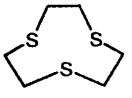
Department of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, UK

Reaction of $PdCl_2$ with [9]aneS$_3$ (1,4,7-trithiacyclononane) in MeCN–CH_2Cl_2 (3:1 v/v) afforded *cis*-[Pd([9]aneS$_3$)Cl$_2$] which can be converted into a range of half-sandwich palladium(II) complexes *cis*-[Pd([9]aneS$_3$)Cl(L)]PF_6 [L = PPh_3 or $P(C_6H_{11})_3$] and *cis*-[Pd([9]aneS$_3$)L][PF_6]$_2$ {L = 2PPh_3, $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2PPh_2$ (dppe), $(Ph_2PCH_2)_3CMe$, $(Ph_2PCH_2)_2[Ph_2P(O)CH_2]_2CMe$, 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)}. The single-crystal structures of *cis*-[Pd([9]aneS$_3$)Cl(PPh_3)]PF_6 and *cis*-[Pd([9]aneS$_3$)L][PF_6]$_2$ {L = 2PPh_3, dppm, $(Ph_2PCH_2)_2[Ph_2P(O)CH_2]CMe$, bipy or phen} have been determined. They all show square-planar co-ordination of Pd^{II} by L and two S-donors of [9]aneS$_3$, as well as an additional apical interaction with the third S-donor of [9]aneS$_3$, Pd · · · S_{ap} 2.990(2) Å for *cis*-[Pd([9]aneS$_3$)Cl(PPh_3)]PF_6, 2.948(13) Å for *cis*-[Pd([9]aneS$_3$)(phen)][PF_6]$_2$, 2.877(3) Å for *cis*-[Pd([9]aneS$_3$)(PPh_3)$_2$][PF_6]$_2$, 2.808(13) Å for *cis*-[Pd([9]aneS$_3$)(bipy)][PF_6]$_2$, 2.722(4) and 2.768(5) Å for the two independent molecules of *cis*-[Pd([9]aneS$_3$){$(Ph_2PCH_2)_2[Ph_2P(O)CH_2]CMe$}][$PF_6$]$_2$ and 2.698(3) Å for *cis*-[Pd([9]aneS$_3$)(dppm)][PF_6]$_2$. In the solid state there is, therefore, a general tendency for the third S-donor of [9]aneS$_3$ to form a long-range apical interaction giving overall five-co-ordination at Pd^{II}. The length of this interaction is influenced strongly by the electronic properties of the ligand L and by the overall charge of the complex cation. The redox properties of these complexes are discussed.

The tridentate thioether macrocycle [9]aneS$_3$ (1,4,7-trithiacyclononane) is well known to co-ordinate facially to a wide range of octahedral metal complexes.[1,2] The binding to Pd^{II}, however, gives products whose geometries are a compromise between the square-planar co-ordination preferred by the d^8 metal ion and the facial co-ordination preferred by the trithia crown. Thus, the single-crystal structures of $[Pd([9]aneS_3)_2]^{2+}$,[3,4] $[Pd([10]aneS_3)_2]^{2+}$ ([10]aneS$_3$ = 1,4,7-triathiacyclodecane),[5] $[Pd([18]aneS_6)]^{2+}$[6] ([18]aneS$_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane)[6] and $[Pd([9]aneNS_2)_2]^{2+}$[7] ([9]aneNS$_2$ = 1,4-dithia-7-azacyclononane) all show equatorial co-ordination to Pd^{II} with long-range interactions to the two remaining thioether S-donors at apical positions, Pd · · · S_{ap} 2.9–3.2 Å. Oxidation of these cations affords the corresponding mononuclear d^7 palladium(III) species which are stabilised by the hexadentate [4 + 2] co-ordination sphere imposed by the macrocyclic ligand(s).[1,3–6]

The complexes *cis*-[Pd([9]aneS$_3$)X$_2$] (X = Cl[8] or Br[4]) show [4 + 1] co-ordination at Pd^{II}, with square-planar co-ordination of two halides and two S-donors from [9]aneS$_3$. In each case the third S-donor of [9]aneS$_3$ occupies an apical site and interacts with the metal centre, Pd · · · S_{ap} 3.140(2) (X = Cl) and 3.125(1) Å (Br). The Pd · · · S_{ap} distances are noticeably longer for these neutral, half-sandwich complexes than for the cationic bis(sandwich) complexes $[Pd([9]aneS_3)_2]^{2+}$ [Pd · · · S_{ap} 2.952(4) Å],[3] $[Pd([10]aneS_3)_2]^{2+}$ [Pd · · · S_{ap} 3.11(1) Å][5] and $[Pd([9]aneNS_2)_2]^{2+}$ [Pd · · · S_{ap} 3.011(3) Å].[7]

We wished to determine whether [4 + 1] co-ordination to Pd^{II} in half-sandwich complexes was a general phenomenon, and were interested in studying five-co-ordinate complexes of this type since they also represent potential models for intermediates in associative substitution reactions at square-planar d^8 complexes. We report herein the synthesis, structure and electrochemistry of complexes of the type *cis*-$[Pd([9]aneS_3)L]^{n+}$ {L = 2PPh_3, $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2PPh_2$ (dppe), $(Ph_2PCH_2)_3CMe$, $(Ph_2PCH_2)_2[Ph_2P(O)CH_2]CMe$, 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)}.



[9]aneS$_3$

Results and Discussion

cis-[Pd([9]aneS$_3$)Cl$_2$]

Reaction of $PdCl_2$ with 1 molar equivalent of [9]aneS$_3$ in refluxing MeCN–CH_2Cl_2 (3:1 v/v) for 16 h yielded a red-brown precipitate. Recrystallisation of the product from $MeNO_2$ gave dark red crystals of [Pd([9]aneS$_3$)Cl$_2$]. The relative insolubility of this neutral compound in most common solvents inhibited its characterisation, although a ^{1}H NMR spectrum was obtained in $(CD_3)_2SO$. This showed a single broad resonance which could not be resolved at temperatures above 18.4 °C (the solvent freezing point). Mass spectrometry (FAB) and elemental analytical data confirmed the complex to be [Pd([9]aneS$_3$)Cl$_2$]. We have reported the crystal structure of this complex previously:[8] the palladium(II) ion occupies a distorted square plane of two mutually *cis* thia-donors *trans* to the two Cl^- ligands, with the third S atom occupying a remote apical site (see Table 1). The complex is isostructural with [Pd([9]aneS$_3$)Br$_2$] reported by Wieghardt *et al.*[4] Interestingly, the Pd · · · S_{ap} interaction in $[Pd([9]aneS_3)_2]^{2+}$[3] is much shorter than in either [Pd([9]aneS$_3$)X$_2$] (Table 1). The axial contraction in $[Pd([9]aneS_3)_2]^{2+}$ is at the expense of the Pd–S_{eq} bonds, which lengthen to 2.332(3), 2.311(3) Å compared to an average Pd–S_{eq} value of 2.25 Å for [Pd([9]aneS$_3$)X$_2$]. The differences seen in the Pd–S_{eq} and Pd · · · S_{ap} bond lengths may be a consequence of charge differences between [Pd([9]aneS$_3$)X$_2$] and $[Pd([9]aneS_3)_2]^{2+}$, coupled with the strongly π-donating effect of halides compared to the much weaker π interactions between Pd^{II} and thioethers.

Displacement of Cl^- ligands from [Pd([9]aneS$_3$)Cl$_2$] occurs

in refluxing $MeNO_2$ solution in the presence of other donor ligands L [L = $2PPh_3$, dppm, $(Ph_2PCH_2)_3CMe$, bipy or phen] followed by addition of 2 equivalents of NH_4PF_6 to yield $[Pd([9]aneS_3)L][PF_6]_2$. The asymmetric complexes $[Pd([9]aneS_3)Cl(L)][PF_6]$ were prepared by reaction of *cis*-$[Pd([9]aneS_3)Cl_2]$ with 1 equivalent of L [L = PPh_3 or $P(C_6H_{11})_3$]. The stoichiometry of each complex was confirmed by elemental analysis, infrared, NMR spectroscopy and by FAB mass spectrometry. Instead of the anticipated product $[Pd([9]aneS_3)\{(Ph_2PCH_2)_3CMe\}][PF_6]_2$ we obtained the complex in which oxidation of an unbound $RPPh_2$ arm had occurred giving $RP(O)Ph_2$.

$[Pd([9]aneS_3)(PPh_3)_2][PF_6]_2$

The complex *cis*-$[Pd([9]aneS_3)(PPh_3)_2]^{2+}$ was formed by reaction of $[Pd[9]aneS_3)Cl_2]$ with 2 equivalents of PPh_3 in refluxing $MeNO_2$. Addition of 2 equivalents of NH_4PF_6 caused precipitation of NH_4Cl which was filtered off. The product *cis*-$[Pd([9]aneS_3)(PPh_3)_2][PF_6]_2$ was isolated by addition of Et_2O to the filtrate, and recrystallised from MeOH. The ^1H NMR spectrum shows sharp multiplets at δ_H 2.79 and 2.38 which are assigned to the macrocyclic protons. The ^{13}C NMR spectrum, however, shows only a single resonance for the macrocycle at 293 K, suggesting that all carbon centres (and hence all three S-donors) are equivalent in solution. The multiplicity of the proton signals for co-ordinated $[9]aneS_3$ indicates inequivalence due to the spatial orientation of the macrocyclic protons. The fluxionality of thioether crowns at palladium and platinum centres has been confirmed and discussed previously.[9,10] In order to quantify the degree of interaction of Pd^{II} with the third S atom, a single-crystal structure determination was undertaken. Selected bond lengths and angles are given in Table 1, with a view of the cation shown in Fig. 1. The Pd sits in a distorted S_2P_2 square plane, Pd–S_{eq} 2.375(3), 2.407(3), Pd–P 2.317(3), 2.336(3) Å, the shorter Pd–S_{eq} bond being *trans* to the shorter Pd–P bond. The apical Pd···S_{ap} distance of 2.877(3) Å is shorter in $[Pd([9]aneS_3)(PPh_3)_2]^{2+}$ than in $[Pd([9]aneS_3)Cl_2]$. The PPh_3 ligands show a staggered conformation with interleaved phenyl rings.

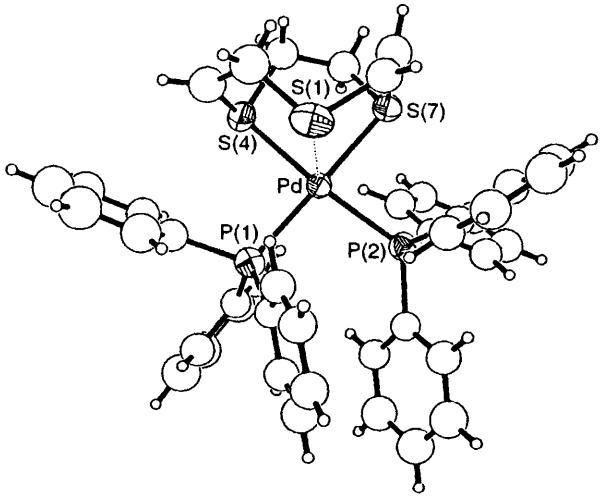


Fig. 1 View of the structure of the $[Pd([9]aneS_3)(PPh_3)_2]^{2+}$ cation with the numbering scheme adopted

We argued that the effects of phosphine size on the overall cation structure could be monitored by using smaller, PPh_nR_{3-n} (n = 0–2) or larger $[P(C_6H_{11})_3]$ tertiary phosphines. However, these tend to be more basic than PPh_3, and may have an additional electronic effect on any potential Pd···S_{ap} interaction. Attempts to produce pure samples of $[Pd([9]aneS_3)(PPh_2Me)_2][PF_6]_2$ were unsuccessful, elemental analytical data for the isolated product being low in both C and H. The ^1H NMR spectrum showed the target species had been formed [$(CD_3)_2CO$, 80 MHz, 298 K: δ_H 2.31, 2.42 (br, s, Me), 2.91–3.34 (m, SCH_2, 12 H) and 7.54–8.00 (m, PPh_2)] but with an unidentified impurity also present. The phosphine PMe_3 was also unsuitable for replacing Cl^- ligands in $[Pd([9]aneS_3)Cl_2]$. Nor was it possible to replace both Cl^- ligands with $P(C_6H_{11})_3$, probably because of the large cone angle of the latter. It was, however, possible to replace one Cl^- by treating the complex with only 1 equivalent of either PPh_3 or $P(C_6H_{11})_3$.

$[Pd([9]aneS_3)Cl(PPh_3)]PF_6$

Reaction of $[Pd([9]aneS_3)Cl_2]$ with 1 equivalent of each of PPh_3 and NH_4PF_6 affords the orange product $[Pd([9]aneS_3)Cl(PPh_3)]PF_6$ in 60–70% yield. The ^1H NMR spectrum shows a multiplet at δ_H 3.2–3.3 for $[9]aneS_3$, compared to a single resonance for the macrocycle in $[Pd([9]aneS_3)Cl_2]$, and two sets of multiplets for the macrocycle in $[Pd([9]aneS_3)(PPh_3)_2]^{2+}$. Although the protons of $[9]aneS_3$ in $[Pd([9]aneS_3)Cl(PPh_3)]^+$ are not equivalent, the ^{13}C NMR spectrum indicates that the macrocyclic carbon centres are equivalent in solution. A single-crystal structure determination of $[Pd([9]aneS_3)Cl(PPh_3)]^+$ was undertaken for comparison with $[Pd([9]aneS_3)Cl_2]$ and $[Pd([9]aneS_3)(PPh_3)_2]^{2+}$. Selected bond lengths and angles are given in Table 1 with a view of the cation shown in Fig. 2. The Pd is co-ordinated to one P-donor, a Cl^- and two S-donors of $[9]aneS_3$ in a square plane. The apical S atom [S(1)] in $[Pd([9]aneS_3)Cl(PPh_3)]^+$ sits 2.990(2) Å above the Pd and is angled away from the phosphine and towards S(7) [S(1)–Pd–S(4) 84.29(5), S(1)–Pd–S(7) 79.20(5)°].

$[Pd([9]aneS_3)Cl\{P(C_6H_{11})_3\}]PF_6$

Reaction of $[Pd([9]aneS_3)Cl_2]$ with 1 equivalent of $P(C_6H_{11})_3$

Table 1 Selected bond lengths (Å) and angles (°) for $[Pd([9]aneS_3)X(Y)]^{n+}$

	X, Y = $2Cl^-$ [8]	$2Br^-$ [4]	$2PPh_3$	Cl^-, PPh_3	dppm	$(Ph_2PCH_2)_2(Ph_2POCH_2)CMe$*		bipy	phen
Pd···S_{ap}	3.140(2)	3.125(1)	2.877(3)	2.990(2)	2.698(3)	2.722(4)	2.768(5)	2.808(13)	2.948(13)
Pd–S_{eq}	2.267(2)	2.275(2)	2.375(3)	2.2635(16)	2.375(3)	2.376(4)	2.393(4)	2.2696(13)	2.274(3)
	2.246(2)	2.257(2)	2.407(3)	2.3391(17)	2.379(3)	2.398(4)	2.385(4)	2.2906(13)	2.275(3)
Pd–X	2.332(2)	2.456(1)	2.317(3)	2.3285(17)	2.263(3)	2.280(4)	2.277(4)	2.058(4)	2.049(4)
Pd–Y	2.333(2)	2.468(1)	2.336(3)	2.2978(15)	2.275(3)	2.290(4)	2.276(4)	2.057(4)	2.053(4)
S_{eq}–Pd–S_{eq}	89.74(6)	89.3(1)	85.8(1)	88.38(6)	88.46(10)	87.97(14)	87.37(15)	87.92(5)	88.83(11)
X–Pd–Y	93.57(7)	93.4(1)	95.73(8)	89.85(6)	72.38(9)	92.98(14)	92.08(15)	79.62(16)	80.6(4)
S_{eq}–Pd–X	88.57(7)	87.5(1)	84.8(1)	88.09(4)	100.29(9)	87.34(14)	88.57(15)	94.92(12)	95.1(3)
S_{eq}–Pd–Y	87.58(7)	89.3(1)	92.8(1)	93.42(5)	97.40(9)	90.11(14)	89.85(15)	96.65(12)	94.6(3)
S_{eq}–Pd–S_{ap}	78.42(8)	78.7(1)	81.0(1)	84.29(5)	85.83(9)	83.83(13)	83.30(14)	85.71(14)	83.45(10)
	81.14(5)	81.7(1)	81.5(1)	79.20(5)	84.89(9)	83.16(13)	82.14(14)	86.15(4)	83.12(10)

* There are two cations and four anions per asymmetric unit.

and with NH_4PF_6 affords $[Pd([9]aneS_3)Cl\{P(C_6H_{11})_3\}]PF_6$ as an orange solid. The ^1H NMR spectrum at 293 K shows two multiplets in a 2:1 ratio for the macrocyclic protons {for $[Pd([9]aneS_3)Cl(PPh_3)]PF_6$ there is only one multiplet}, while the ^{13}C NMR spectrum shows a single resonance for the macrocycle. The $P(C_6H_{11})_3$ is larger than PPh_3 (Tolman angles 170 and 145°) and is also a poorer π acceptor.[11] Unfortunately, no solid-state structural information is available since crystals of X-ray-diffraction quality could not be prepared.

An alternative to small monodentate phosphines are chelating phosphines such as dppm, dppe and $(Ph_2PCH_2)_3CMe$. Variations in the chelate chain length and in the number of potential donors in species of type $[Pd([9]aneS_3)L]^{2+}$ (L = chelating phosphine) would be expected to alter the electronic nature of the Pd^{II}–$[9]aneS_3$ interactions.

$[Pd([9]aneS_3)(dppm)][PF_6]_2$

Reaction of $[Pd([9]aneS_3)Cl_2]$ with 1 molar equivalent of dppm followed by addition of NH_4PF_6 afforded an orange, crystalline precipitate of $[Pd([9]aneS_3)(dppm)][PF_6]_2$. Owing to the small bite angle of dppm, this ligand can act not only as a bidentate chelate to one palladium(II) centre, but can also bridge two such centres.[12] Elemental and IR spectral analysis would not necessarily differentiate between the two possibilities although FAB mass spectrometry did suggest the formation of a mononuclear species. Therefore, a crystal structure determination of the complex was carried out. Selected bond lengths and angles are given in Table 1, with a view of the cation shown in Fig. 3. The structure shows the Pd^{II} lying 0.185 Å out of an essentially planar S_2P_2 donor set. The Pd · · · S_{ap} distance is shorter than in $[Pd([9]aneS_3)(PPh_3)_2]^{2+}$, 2.698(3) compared to 2.877(3) Å, with no apparent lengthening of the Pd–S_{eq} bond lengths, 2.375(3) and 2.379(3) Å, compared to 2.375(3), 2.407(3) Å for $[Pd([9]aneS_3)(PPh_3)_2]^{2+}$. The shorter Pd–P bonds, 2.263(3) and 2.275(3) Å, compared to 2.317(3) and 2.336(3) Å for $[Pd([9]aneS_3)(PPh_3)_2]^{2+}$, are probably due to the greater basicity of dppm over PPh_3, and the restricted chelate 'bite' angle of dppm: P–Pd–P 72.38(9)° for $[Pd([9]aneS_3)(dppm)]^{2+}$ and 95.73(8)° for $[Pd([9]aneS_3)(PPh_3)_2]^{2+}$. It is interesting that the phenyl rings lie above the S_2P_2 plane on the same side as S(1) forming a pocket towards which the apical sulfur lone pairs point. On the opposite side of the S_2P_2 plane the phenyl rings are conversely angled.

$[Pd([9]aneS_3)(dppe)][PF_6]_2$

The synthesis of $[Pd([9]aneS_3)(dppe)][PF_6]_2$ was analogous to that for $[Pd([9]aneS_3)(dppm)][PF_6]_2$, using 1 molar equivalent of dppe in place of dppm. The ^1H NMR spectrum shows an AA'BB' pattern for the macrocyclic protons. Again, the ^{13}C NMR spectrum shows a single macrocyclic resonance. Unfortunately, no single crystals suitable for X-ray determination could be prepared.

Having examined some the effects of monodentate and chelating phosphines on Pd · · · S interactions, we wished to monitor the effect of a third phosphine donor: we argued that use of $(Ph_2PCH_2)_3CMe$ could lead to the formation of a potentially six-co-ordinate species $[Pd([9]aneS_3)\{(Ph_2PCH_2)_3CMe\}]^{2+}$.

$[Pd([9]aneS_3)\{(Ph_2PCH_2)_3CMe\}][PF_6]_2$

The complex $[Pd([9]aneS_3)\{(Ph_2PCH_2)_3CMe\}][PF_6]_2$ was prepared in an analogous manner to $[Pd([9]aneS_3)(dppm)][PF_6]_2$ by reaction of $[Pd([9]aneS_3)Cl_2]$ with $(Ph_2PCH_2)_3CMe$ followed by addition of NH_4PF_6. The resulting compound was crystallised by slow diffusion of Et_2O vapour into a solution of the complex in $MeNO_2$ at 0 °C. The IR spectrum and elemental analytical data were consistent with the formulation. However, the ^{31}P NMR spectrum clearly showed the presence of impurities identified as $[HPR_3]^+$ and free $(Ph_2PCH_2)_3CMe$. In addition, signals due to unbound and co-ordinated phosphorus centres were discernible. Similar resonances and impurities have been observed for samples of $[Ni([9]aneS_3)\{(Ph_2PCH_2)_3CMe\}]^{2+}$.[13] The FAB mass spectrum of the crystalline sample showed that for fragments containing the intact triphosphine ligand a corresponding fragment with 16 additional mass units was also present suggesting oxidation at a phosphorus atom during the prolonged period of crystallisation. Additionally, the IR spectrum of a crystalline sample showed a band at 1305 cm^{-1} assigned to the ν(P=O) stretching vibration. Addition of one oxygen to the molecular formula would not significantly alter the required elemental analysis. A crystal structure determination was undertaken on the crystalline product in order to ascertain whether oxidation had taken place at one or more of the P atoms. Selected bond lengths and angles are given in Table 1, with a view of the cation shown in Fig. 4.

The structure shows planar S_2P_2 co-ordination to Pd^{II} with the third S-donor of $[9]aneS_3$ sitting above the Pd at an apical site [Pd · · · S 2.722(4) Å for molecule 1, 2.768(5) Å for molecule 2]. The third phosphine has been oxidised to a phosphine oxide, which is not bound and is remote from the Pd in each molecule. The two molecules of the asymmetric unit differ in the spatial arrangements of the oxygen atom. The arrangement of the

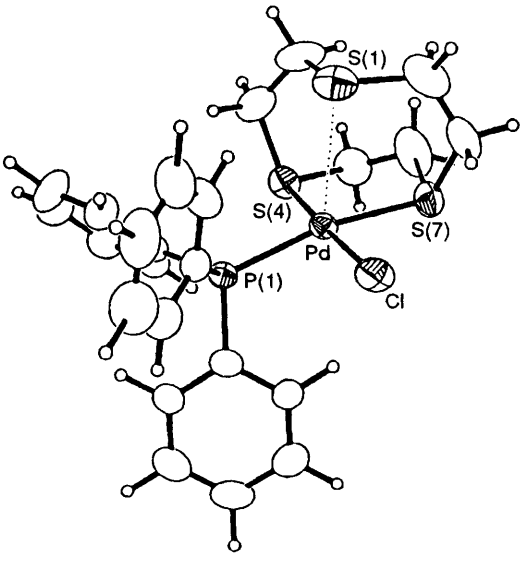


Fig. 2 View of the structure of the $[Pd([9]aneS_3)Cl(PPh_3)]^+$ cation with the numbering scheme adopted

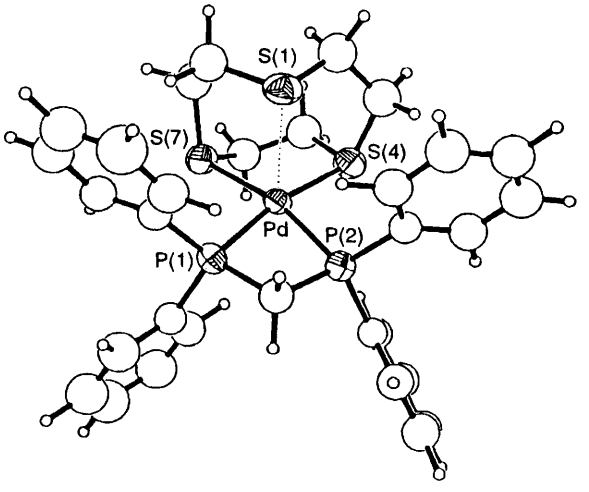


Fig. 3 View of the structure of the $[Pd([9]aneS_3)(dppm)]^{2+}$ cation with the numbering scheme adopted

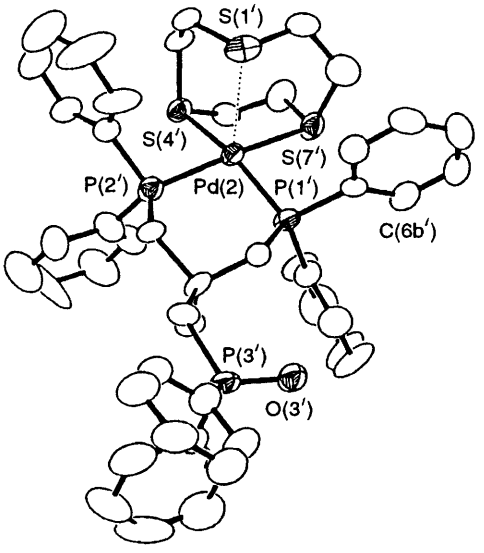


Fig. 4 View of the structure of one of the $[Pd([9]aneS_3)\{(Ph_2PCH_2)_2[Ph_2P(O)CH_2]CMe\}]^{2+}$ cations with the numbering scheme adopted. Owing to the complexity of this structure, hydrogen atoms have been omitted for clarity

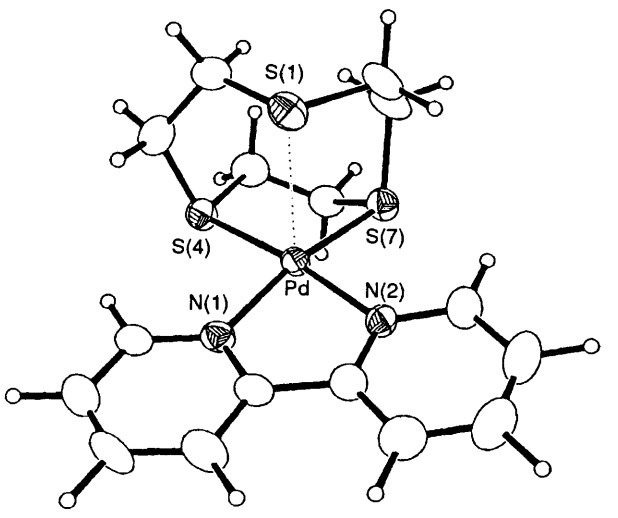


Fig. 5 View of the structure of the $[Pd([9]aneS_3)(bipy)]^{2+}$ cation with the numbering scheme adopted

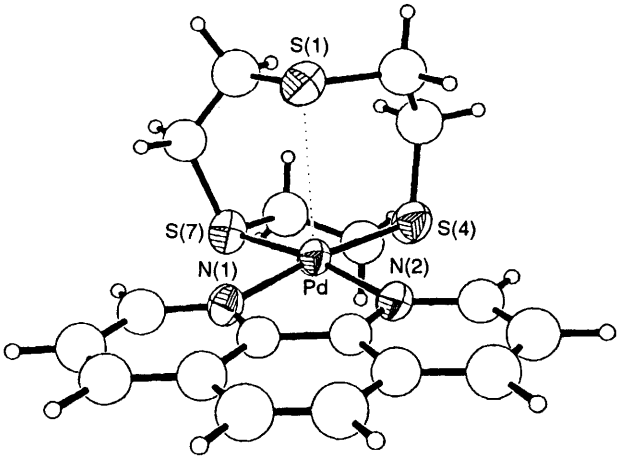


Fig. 6 View of the structure of the $[Pd([9]aneS_3)(phen)]^{2+}$ cation with the numbering scheme adopted

phenyl rings again provides pockets not only for the apical sulfur lone pairs but also for the methyl group on the pivotal C atom of the phosphine oxide ligand. This may be contrasted with the analogous nickel(II) complex $[Ni([9]aneS_3)\{(Ph_2P-CH_2)_3CMe\}][PF_6]_2$ in which no phosphine oxidation has taken place.[13]

In the $[Pd([9]aneS_3)L]^{2+}$ complexes discussed so far it has been observed that π-accepting ligands such as phosphines lead to shorter Pd · · · S_{ap} distances than do π-donating ligands such as Cl^-. This led us to investigate whether the [4 + 1] five-co-ordination seen in the above complexes might be enhanced in the presence of other π-accepting chelates such as 2,2′-bipyridine and 1,10-phenanthroline.

$[Pd([9]aneS_3)(bipy)][PF_6]_2$

Reaction of $[Pd([9]aneS_3)Cl_2]$ with 1 molar equivalent of bipy in $MeNO_2$ afforded a yellow suspension, which changed to a pink solution on addition of NH_4PF_6. Removal of NH_4Cl and precipitation of the product with Et_2O yielded a pinkish brown powder which was recrystallised from $MeNO_2$ to give purple blocks. The first point of interest is the pinkish purple colour of the final product, $[Pd([9]aneS_3)(bipy)][PF_6]_2$ (λ_{max} = 508 nm), rather than the orange or yellow of the analogous phosphine complexes (λ_{max} < 480 nm). This colouration is almost identical to that of $[Pd([15]aneS_5)]^{2+}$ ([15]$aneS_5$ = 1,4,7,10,13-pentathiacyclopentadecane), which is known to be five co-ordinate in the solid state, Pd–S 2.278(8), 2.294(12), 2.336(11), 2.532(11) and 2.540(11) Å.[1,14] The ^1H NMR spectrum of $[Pd([9]aneS_3)(bipy)]^{2+}$ at 293 K shows, in addition to resonances due to co-ordinated bipy, a single sharp resonance for [9]$aneS_3$. The ^{13}C NMR spectrum also shows a single macrocyclic resonance. Since the available information indicated that the complex might be truly five-co-ordinate (at least in solution), a crystal structure determination was undertaken to allow a comparison with the solid-state structure. Selected bond lengths and angles are given in Table 1, with a view of the cation shown in Fig. 5.

The structure of $[Pd([9]aneS_3)(bipy)][PF_6]_2$ shows the Pd^{II} co-ordinated to a distorted square plane defined by two S-donors of the [9]$aneS_3$ and both N-donors of bipy. The third S-donor again shows an apical interaction with the metal ion [Pd · · · S_{ap} 2.808(13) Å]. The bipy ligand is not absolutely planar; in order to accommodate [4 + 1] co-ordination at the $Pd([9]aneS_3)^{2+}$ fragment, it has 'bowed', not twisted, by approximately 4°, N–Pd–S_{ap} 104.52(12) and 99.87(11)°. In order to gauge the effects of the bowing of the N-chelate ligand on Pd–N and Pd · · · S_{ap} bonding, the phen derivative was prepared. Phenanthroline is more rigid than bipy and would therefore be expected to resist deformation from an overall planar structure.

$[Pd([9]aneS_3)(phen)][PF_6]_2$

The complex $[Pd([9]aneS_3)(phen)][PF_6]_2$ was prepared in an analogous fashion to the bipy complex, with similar colour changes during the reaction. Crystals of $[Pd([9]aneS_3)(phen)][PF_6]_2$ appear redder than those of $[Pd([9]aneS_3)(bipy)][PF_6]_2$, but in solution the UV/VIS spectrum of the two are virtually identical (λ_{max} = 507 for phen, 508 nm for bipy). The ^1H NMR spectrum also shows a single resonance for [9]$aneS_3$. In order to gauge the effect of the increased chelate rigidity on the overall [9]$aneS_3$ bonding in the solid state, a single-crystal structure determination was undertaken. Selected bond lengths and angles are given in Table 1, with a view of the cation shown in Fig. 6.

The structure is very similar to that of the bipy analogue, the major difference being the Pd · · · S_{ap} distance, which is longer by 0.140 Å (see Table 1). The planes of the outer rings are both angled slightly inward, unexpectedly bowing the ligand in a similar manner to that observed for the bipy ligand in $[Pd([9]aneS_3)(bipy)]^{2+}$.

The trithia macrocycle [9]aneS$_3$ can be regarded as six-electron σ donor. However, it seems increasingly likely that it also has a limited π-donor/acceptor capacity.[15] This possible M–L π interaction may explain why the Pd · · · S$_{ap}$ interaction in [Pd([9]aneS$_3$)L]$^{n+}$ is affected by changes in charge and the π-donor/acceptor properties of L. A comparison of relevant bond lengths and angles (Table 1) shows that π-acceptor ligands encourage greater Pd · · · S$_{ap}$ interaction in [Pd([9]aneS$_3$)L]$^{n+}$ than do π donors or strong σ donors. It is not surprising that π-acceptor ligands cause shortening of the Pd · · · S$_{ap}$ bond lengths; the third thia donor is in an ideal position to balance the electron density at the metal centre by σ and π interactions. Indeed, if one considers the [Pd([9]aneS$_3$)L]$^{n+}$ system as being five-co-ordinate, square-based pyramidal, then Rossi and Hoffmann[16] have shown that strong σ donors (L) would, on the basis of molecular orbital calculations for d^8 low-spin metal centres, be expected to lie in basal positions. Furthermore, a weak σ donor would be expected to occupy the axial position. The greatest basal π interaction in square-based pyramidal complexes comes with a ligand orbital parallel to the pseudo-C_{4v} axis (ba$_{\parallel}$).[16] This is also the preferred orientation for π acceptors. A π donor would prefer a ba$_{\perp}$ orientation and would have less interaction with the metal centre. It is noticeable that most five-co-ordinate low-spin d^8 metal systems are trigonal bipyramidal {*e.g.* [Fe(CO)$_5$], [Pt(SnCl$_3$)$_5$]$^{3-}$ and [Co(CNMe)$_5$]$^+$[16]}. Even [Ni(CN)$_5$]$^{3-}$, which does have a square-based pyramidal form, co-exists with a form intermediate between trigonal bipyramidal and square-based pyramidal.[17]

In conclusion, it has been found from the crystal structures of [Pd([9]aneS$_3$)L]$^{n+}$ and [Pd([9]aneS$_3$)L$_2$]$^{n+}$ that *all* the complexes show long-range apical Pd · · · S interactions in the solid state. The use of chelating ligands L and increasing positive charge of the complex both lead to shorter Pd · · · S$_{ax}$ distances. Additionally, the structures of [Pd([9]aneS$_3$)(bipy)]$^{2+}$ and [Pd([9]aneS$_3$)(phen)]$^{2+}$ show non-planarity of the N-heterocycles. There is a precedent for bowing or twisting of bipy bound to Pd^{II}.[18] However, both ligands exhibit bow deformations of 4–5°. These complexes have been monitored by ^{1}H and ^{13}C NMR spectroscopy and found to be fluxional with fast intramolecular S-atom exchange occurring in solution, presumably *via* 1,4-metallotropic shifts as described previously by Abel *et al.*[9] and Bennett *et al.*[10]

The redox chemistry of these half-sandwich complexes was investigated. Cyclic voltammetry in MeCN at platinum electrodes confirms that [Pd([9]aneS$_3$)(PPh$_3$)$_2$]$^{2+}$, [Pd([9]aneS$_3$)Cl(PPh$_3$)]$^+$ and [Pd([9]aneS$_3$)Cl{P(C$_6$H$_{11}$)$_3$}]$^+$ show irreversible reductions at E_p = −0.79, −0.96 and −1.10 V *vs.* ferrocene–ferrocenium respectively at a scan rate of 160 mV s^{-1} at 293 K. These processes do not become reversible at lower temperatures. In contrast, at 240 K the complexes [Pd([9]aneS$_3$)(dppm)]$^{2+}$, [Pd([9]aneS$_3$)(dppe)]$^{2+}$ and [Pd([9]aneS$_3$){(Ph$_2$PCH$_2$)$_2$[Ph$_2$P(O)CH$_2$]CMe}]$^{2+}$ show quasi-reversible reductions at $E_{\frac{1}{2}}$ (ΔE_p) = −1.04 (63), −1.23 (61) and −1.15 V (124 mV) respectively, while [Pd([9]aneS$_3$)(bipy)]$^{2+}$ and [Pd([9]aneS$_3$)(phen)]$^{2+}$ show reversible processes at 240 K at $E_{\frac{1}{2}}$ (ΔE_p) = −0.86(68) and −0.83 (72 mV), respectively. Controlled-potential electrolysis of the last two complexes suggested one-electron processes. *In situ* reduction of [Pd([9]aneS$_3$)(bipy)]$^{2+}$ [λ_{max} = 508 (ε_{max} = 11.8), 321 (4100), 303 (4100), 242 (9200) and 214 nm (12 000 dm^3 mol^{-1} cm^{-1})] at 235 K afforded a reduction product isosbestically [λ_{max} = 455 (ε_{max} = 3800), 380 (85 000) and 280 nm (14 800 dm^3 mol^{-1} cm^{-1}), λ_{iso} = 325, 296 and 270 nm], as did reduction of [Pd([9]aneS$_3$)(phen)]$^{2+}$ [λ_{max} = 507 (ε_{max} = 120), 278 (18 000) and 217 (21 000); product, λ_{max} = 400 (ε_{max} = 510 broad), 261 (3800) and 228 nm (44 000 dm^3 mol^{-1} cm^{-1}); λ_{iso} = 290, 265 and 221 nm]. Reoxidation afforded the starting palladium(II) complexes although some decomposition was observed. The precise nature of these reduction products is not yet established. They appear to be ESR inactive with only very weak signals being observed for electrogenerated solutions. This is consistent with the expected high reactivity of the redox product, the redox process being irreversible at room temperature and reversible only at greatly reduced temperatures. We are currently investigating in more detail the reductive redox processes for these and related complexes of Pd^{II} and Pt^{II} of thioether crowns, the potential formation of M^{I}–M^{I} dimers being of particular interest.

Experimental

Infrared spectra were recorded over the range 200–4000 cm^{-1} as KBr discs using Perkin-Elmer 598 and Lambda 9 spectrometers. Microanalyses were performed by the Edinburgh University Chemistry Department Microanalytical Service. Electronic spectra were recorded in quartz cells using a Philips Scientific SP8-400 spectrophotometer, FAB mass spectra on a Kratos MS50TC spectrometer, ^{1}H NMR spectra on Bruker WP80, WP200 and WH360 instruments, operating at 80.13, 200.13 and 360.13 MHz respectively; ^{13}C [DEPT (distortionless enhancement of polarisation transfer) and broad-band ^{1}H-decoupled] spectra were recorded at 50.32 MHz on the Bruker WP200 instrument and ^{31}P (^{1}H-decoupled) spectra on the same instrument at 81.02 MHz. Electrochemical measurements were carried out on a Bruker E310 Universal Polarograph. All readings were taken using a three-electrode system in MeCN using 0.1 mol dm^{-3} NBu$^n_4$PF$_6$ as base electrolyte.

Syntheses

***cis*-[Pd([9]aneS$_3$)(PPh$_3$)$_2$][PF$_6$]$_2$.** The complex [Pd([9]aneS$_3$)Cl$_2$] (0.03 g, 8.39 × 10^{-5} mol) was treated with PPh$_3$ (0.04 g, 1.68 × 10^{-4} mol) in MeNO$_2$ (15 cm^3) under reflux for 1 h and NH$_4$PF$_6$ (0.027 g, 1.68 × 10^{-4} mol) was added. The reaction mixture was refluxed for 30 min, after which the solution was cooled and the NH$_4$Cl precipitate filtered off. Addition of Et$_2$O to the filtrate yielded [Pd([9]aneS$_3$)(PPh$_3$)$_2$][PF$_6$]$_2$ as an orange precipitate which was recrystallised from MeOH. Yield 70% (Found: C, 45.6; H, 3.75. Calc. for C$_{42}$H$_{42}$F$_{12}$P$_4$PdS$_3$: C, 45.8; H, 3.85%). IR: 1480, 1435, 1412, 1305, 1185, 1092, 840, 750, 739, 704, 692, 555, 529 and 514 cm^{-1}. ^{1}H NMR (CD$_3$NO$_2$, 80 MHz, 293 K): δ 2.38 (m, 6 H, CH$_2$), 2.79 (m, 6 H, CH$_2$) and 7.37 (m, 30 H, PPh$_3$). FAB mass spectrum: *m*/*z* = 955, [Pd([9]aneS$_3$)(PPh$_3$)$_2$(PF$_6$)]$^+$; 810, [Pd([9]aneS$_3$)(PPh$_3$)$_2$]$^+$ and 368, [Pd(PPh$_3$)]$^+$. Electronic spectrum (MeNO$_2$); λ_{max} = 472 (ε_{max} = 485) and 356 nm (9460 dm^3 mol^{-1} cm^{-1}).

***cis*-[Pd([9]aneS$_3$)Cl(PPh$_3$)]PF$_6$.** The complex *cis*-[Pd([9]aneS$_3$)Cl(PPh$_3$)]PF$_6$ was prepared by reaction of [Pd([9]aneS$_3$)Cl$_2$] (0.03 g, 8.39 × 10^{-5} mol) with 1 molar equivalent of PPh$_3$ (0.023 g, 8.4 × 10^{-5} mol) and NH$_4$PF$_6$ (0.014 g, 8.4 × 10^{-5} mol). Recrystallisation by slow vapour diffusion of Et$_2$O into a solution of the complex in MeNO$_2$ gave red crystals of [Pd([9]aneS$_3$)Cl(PPh$_3$)]PF$_6$·1.5MeNO$_2$ in 60% yield (Found: C, 37.1; H, 3.85; N, 2.60. Calc.: C, 37.3; H, 3.85; N, 2.55%). IR: 3050, 2980, 2945, 1548, 1479, 1432, 1400, 1375, 1282, 1250, 1184, 1158, 1094, 1025, 995, 945, 935, 840, 748, 708, 692, 655, 555, 527, 509, 495, 428, 350 and 280 cm^{-1}. NMR [(CD$_3$)$_2$CO, 298 K]: ^{1}H (200 MHz), δ 3.2–3.3 (m, 12 H, CH$_2$) and 7.5–7.9 (m, 15 H, PPh$_3$); ^{13}C (DEPT, 50.3 MHz), δ 34.9 (s, 6 C, CH$_2$), 127.8 (d, 6 C, PPh$_3$), 128.5 (s, 3 C, PPh$_3$) and 133.5 (d, 6 C, PPh$_3$); ^{31}P (81.02 MHz), δ 28.9. Mass spectrum (FAB): *m*/*z* = 585, [Pd([9]aneS$_3$)Cl(PPh$_3$)]$^+$; 547, [Pd([9]aneS$_3$)(PPh$_3$)]$^+$ and 368, [Pd(PPh$_3$)]$^+$.

***cis*-[Pd([9]aneS$_3$)Cl{P(C$_6$H$_{11}$)$_3$}]PF$_6$.** This complex was prepared as above, using P(C$_6$H$_{11}$)$_3$ (0.024 g, 8.4 × 10^{-5} mol) in place of PPh$_3$. Yield 40% (Found: C, 38.7; H, 6.20. Calc.: C, 38.6; H, 6.05%). IR: 2920, 2845, 1442, 1408, 1320, 1296,

Table 2 Summary of crystal data for $[Pd([9]aneS_3)X(Y)]^{n+}$

	X(Y) = 2PPh$_3$	Cl, PPh$_3$	dppm	$(Ph_2PCH_2)_2[Ph_2P(O)CH_2]CMe$	bipy	phen
Formula	$C_{42}H_{42}F_{12}P_4PdS_3$	$C_{24}H_{27}ClF_6P_2PdS_3 \cdot 2MeNO_2$	$C_{34}H_{34}F_{12}P_4PdS_3 \cdot 0.5Et_2O$	$2C_{47}H_{51}F_{12}OP_5PdS_3 \cdot 3MeNO_2 \cdot 2Et_2O$	$C_{16}H_{20}F_{12}N_2P_2PdS_3$	$C_{18}H_{20}F_{12}N_2P_2PdS_3 \cdot MeNO_2$
Crystal size/mm	0.27 × 0.24 × 0.10	0.096 × 0.35 × 0.54	0.70 × 0.70 × 0.60	0.46 × 0.46 × 0.77	0.17 × 0.27 × 0.39	0.62 × 0.62 × 0.27
Crystal appearance	Orange plate	Red plate	Orange block	Yellow column	Purple tablet	Red tablet
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$C2/c$	$Pn2_1a$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	20.9756(8)	29.2330(15)	14.4478(5)	19.482(4)	10.370(2)	7.6243(10)
b/Å	10.4489(5)	8.2902(5)	14.9574(7)	28.720(4)	10.808(2)	10.168 0(14)
c/Å	21.3262(7)	27.2890(13)	20.0948(7)	22.252(5)	10.897(2)	19.173(3)
α/°					84.338(15)	105.333(11)
β/°	101.720(3)	93.96(1)		109.23(9)	87.276(13)	93.624(10)
γ/°					84.843(14)	97.014(10)
U/Å^3	4576.6	6597.6	4342.5	11.755	1209.5	1415.7
M	1101.3	851.5	998.01	2669.2	732.7	817.8
D_c/g cm^{-3}	1.598	1.714	1.526	1.508	2.012	1.918
Z	4	8	4	4	2	2
T/K	298	298	298	173	298	293
μ(Mo-Kα)/mm^{-1}		0.982	0.778	0.578	1.237	
μ(Cu-Kα)/mm^{-1}	6.685					9.561
F(000)	2224	3440	2012	5472	724	812
$2\theta_{max}$/°	120	45	45	45	45	95
hkl Ranges	−23 to 23, 0–11, 0–23	−31 to 31, 0–8, 0–29	0–15, 0–16, 0–21	−20 to 19, 0–30, 0–22	−8 to 10, −7 to 11, −4 to 11	−7 to 7, −3 to 9, 0–18
Unique reflections	5669	3988	2888	12 755	2973	2557
Observed [$I \geqslant 3\sigma(I)$]	5066	3176	2591	9130	2778	2414
Parameters refined	487	390	283	1116	326	288
Weighting scheme						
g In $w^{-1} = \sigma^2(F) + gF^2$	0.0002	0.0006	0.001	0.025	0.007	0.0004
R	0.0752	0.0411	0.0472	0.0984	0.0426	0.0764
R'	0.0936	0.0526	0.0659	0.1207	0.0656	0.0835
S	1.111	1.109	1.099	1.000	0.827	1.089
Mininum and maximum residues in final ΔF synthesis/e Å^{-3}	+1.60, −1.13	+0.66, −0.48	+0.66, −0.38	+1.33, −1.23	+0.52, −1.43	+1.06, −0.68

Common parameters: Stoe Stadi-4 four-circle diffractometer; Cu-Kα radiation for first and last structures, Mo-Kα radiation for the remainder; ω–2θ scans; structures solved from Patterson syntheses (Pd);[19] other non-H atoms found after iterative cycles of least-squares refinement (on F)[19] and Fourier-difference synthesis. Except where stated otherwise, non-H atoms were refined anisotropically and H atoms were introduced at calculated positions. Phenyl rings, where present, were refined as idealised hexagons.

Table 3 Atomic coordinates for *cis*-[Pd([9]aneS$_3$)(PPh$_3$)$_2$][PF$_6$]$_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd	0.2264(1)	0.0801(1)	−0.0159(1)	C(2A2)	0.3903	−0.0871	0.1098
S(1)	0.0885(1)	0.0391(3)	−0.0311(2)	C(2A3)	0.4329	−0.1786	0.1425
C(2)	0.0626(7)	0.0882(15)	−0.1135(6)	C(2A4)	0.4185	−0.2398	0.1960
C(3)	0.1120(6)	0.0836(14)	−0.1546(6)	C(2A5)	0.3615	−0.2096	0.2169
S(4)	0.1929(1)	0.1458(3)	−0.1258(1)	C(2A6)	0.3188	−0.1181	0.1842
C(5)	0.1759(6)	0.3176(11)	−0.1222(6)	C(2B1)	0.2206(3)	0.0966(7)	0.1367(3)
C(6)	0.2073(6)	0.3815(12)	−0.0603(5)	C(2B2)	0.1757	−0.0022	0.1362
S(7)	0.1961(1)	0.2894(3)	0.0103(1)	C(2B3)	0.1241	0.0130	0.1677
C(8)	0.1088(6)	0.2986(12)	0.0012(6)	C(2B4)	0.1173	0.1270	0.1998
C(9)	0.0725(6)	0.1780(12)	0.0114(6)	C(2B5)	0.1621	0.2258	0.2003
P(1)	0.2602(1)	−0.1192(3)	−0.0439(1)	C(2B6)	0.2138	0.2106	0.1688
C(1A1)	0.2228(4)	−0.1627(8)	−0.1260(3)	C(2C1)	0.3408(3)	0.2050(6)	0.1052(3)
C(1A2)	0.1695	−0.2448	−0.1415	C(2C2)	0.3562	0.2756	0.0549
C(1A3)	0.1414	−0.2683	−0.2055	C(2C3)	0.4009	0.3760	0.0676
C(1A4)	0.1665	−0.2098	−0.2540	C(2C4)	0.4300	0.4057	0.1306
C(1A5)	0.2199	−0.1277	−0.2385	C(2C5)	0.4145	0.3351	0.1810
C(1A6)	0.2480	−0.1042	−0.1745	C(2C6)	0.3699	0.2347	0.1683
C(1B1)	0.3439(3)	−0.1306(7)	−0.0501(3)	P(3)	0.3757(2)	0.3498(4)	0.8605(2)
C(1B2)	0.3691	−0.2482	−0.0643	F(1)	0.3315(5)	0.2602(9)	0.8942(4)
C(1B3)	0.4308	−0.2545	−0.0792	F(2)	0.3165(5)	0.3703(12)	0.8047(4)
C(1B4)	0.4673	−0.1431	−0.0799	F(3)	0.4168(6)	0.4347(15)	0.8262(7)
C(1B5)	0.4422	−0.0255	−0.0656	F(4)	0.3539(6)	0.4611(10)	0.9001(6)
C(1B6)	0.3805	−0.0192	−0.0508	F(5)	0.3976(6)	0.2335(13)	0.8250(5)
C(1C1)	0.2391(3)	−0.2431(7)	0.0084(3)	F(6)	0.4340(5)	0.3206(17)	0.9164(5)
C(1C2)	0.1737	−0.2533	0.0123	P(4)	−0.0066(2)	0.5231(4)	0.8545(2)
C(1C3)	0.1545	−0.3440	0.0528	F(7)	0.0694(4)	0.5250(9)	0.8759(5)
C(1C4)	0.2007	−0.4245	0.0893	F(8)	−0.0085(8)	0.6612(15)	0.8690(10)
C(1C5)	0.2661	−0.4142	0.0854	F(9)	−0.0816(4)	0.5209(12)	0.8346(7)
C(1C6)	0.2853	−0.3236	0.0449	F(10)	−0.0039(7)	0.3818(12)	0.8490(12)
P(2)	0.2831(1)	0.0729(3)	0.0904(1)	F(11)	−0.0050(6)	0.5630(23)	0.7904(5)
C(2A1)	0.3332(3)	−0.0569(7)	0.1306(3)	F(12)	−0.0086(7)	0.4897(29)	0.9218(8)

Table 4 Atomic coordinates for [Pd([9]aneS$_3$)Cl(PPh$_3$)]PF$_6$·2MeNO$_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd	0.083 110(10)	0.057 16(5)	0.114 92(2)	C(4C)	0.178 63(12)	−0.304 2(4)	−0.033 64(11)
S(1)	0.045 24(7)	0.217 65(23)	0.022 72(7)	C(5C)	0.151 82(12)	−0.164 9(4)	−0.033 69(11)
C(2)	0.066 1(3)	0.414 6(8)	0.042 6(3)	C(6C)	0.144 45(12)	−0.087 5(4)	0.010 46(11)
C(3)	0.107 81(25)	0.414 7(8)	0.079 0(3)	P(2)	0.124 39(6)	0.182 7(3)	0.300 06(8)
S(4)	0.106 15(5)	0.309 04(18)	0.137 09(6)	F(1)	0.158 1(3)	0.034 9(9)	0.292 1(4)
C(5)	0.058 00(23)	0.397 9(8)	0.166 5(3)	F(2)	0.147 2(3)	0.272 7(12)	0.258 6(4)
C(6)	0.011 90(24)	0.340 1(9)	0.149 9(3)	F(3)	0.091 2(3)	0.085 5(13)	0.263 2(6)
S(7)	0.009 54(5)	0.125 17(22)	0.136 65(6)	F(4)	0.164 2(4)	0.236 0(16)	0.338 1(4)
C(8)	−0.025 98(22)	0.116 8(11)	0.080 9(3)	F(5)	0.105 6(5)	0.099 0(19)	0.345 7(4)
C(9)	−0.014 17(25)	0.218 4(10)	0.038 9(3)	F(6)	0.090 3(3)	0.324 2(11)	0.293 5(4)
Cl	0.055 18(5)	−0.199 06(18)	0.094 66(7)	O(1)	0.422 2(4)	0.034 9(10)	0.078 8(3)
P(1)	0.156 79(5)	−0.035 30(18)	0.110 31(5)	O(2)	0.373 3(3)	0.196 9(11)	0.057 2(4)
C(1A)	0.202 04(11)	0.116 1(4)	0.111 23(13)	N(1)	0.397 8(3)	0.141 6(10)	0.088 9(4)
C(2A)	0.212 46(11)	0.203 2(4)	0.154 29(13)	C(1S)	0.392 6(6)	0.187 7(15)	0.140 1(5)
C(3A)	0.246 37(11)	0.321 9(4)	0.155 63(13)	O(3)	0.528 3(5)	0.119 5(15)	0.259 9(6)
C(4A)	0.269 83(11)	0.353 4(4)	0.113 89(13)	N(2)	0.5	0.205 8(13)	0.25
C(5A)	0.259 43(11)	0.266 3(4)	0.070 81(13)	F(1′)	0.097 5(8)	0.040 5(21)	0.318 4(10)
C(6A)	0.225 50(11)	0.147 7(4)	0.069 48(13)	F(2′)	0.076 2(6)	0.171 6(20)	0.276 5(7)
C(1B)	0.173 68(11)	−0.162 8(4)	0.162 70(12)	F(3′)	0.137 7(7)	0.157 2(20)	0.249 4(8)
C(2B)	0.139 92(11)	−0.234 8(4)	0.189 02(12)	F(4′)	0.157 6(6)	0.329 6(18)	0.313 7(8)
C(3B)	0.152 34(11)	−0.338 4(4)	0.227 99(12)	F(5′)	0.102 6(5)	0.259 4(17)	0.347 1(6)
C(4B)	0.198 55(11)	−0.369 8(4)	0.240 60(12)	F(6′)	0.161 1(7)	0.102 3(21)	0.327 2(8)
C(5B)	0.232 31(11)	−0.297 8(4)	0.214 26(12)	O(1′)	0.432 3(18)	0.114(3)	0.096 3(18)
C(6B)	0.219 87(11)	−0.194 2(4)	0.175 31(12)	O(2′)	0.382 4(12)	0.273 4(24)	0.069 2(13)
C(1C)	0.163 88(12)	−0.149 4(4)	0.054 67(11)	C(1S′)	0.369 5(17)	0.133(3)	0.137 7(20)
C(2C)	0.190 67(12)	−0.288 6(4)	0.054 71(11)	C(2S)	0.5	0.372 5(21)	0.25
C(3C)	0.198 06(12)	−0.366 0(4)	0.010 54(11)				

1268, 1200, 1172, 1132, 1002, 840, 738, 555, 515, 497, 393, 343, 315 and 270 cm^{-1}. NMR [(CD$_3$)$_2$CO, 298 K]: ^{1}H (200 MHz), δ 1.35–1.79 (m, 33 H, PCH$_2$), 2.54, 3.38 (m, 12 H, SCH$_2$); ^{13}C (50.32 MHz), δ 25.17 [s, 4 C, P(C$_6$H$_{11}$)$_3$], 26.36 [d, 6 C, $^2J_{PC}$ = 11, P(C$_6$H$_{11}$)$_3$], 29.23 [d, 6 C, $^3J_{PC}$ = 6 Hz, P(C$_6$H$_{11}$)$_3$] and 35.24 (s, 6 C, SCH$_2$); ^{31}P (81.02 MHz), δ 49.63. FAB mass spectrum: *m*/*z* = 603, [Pd([9]aneS$_3$)Cl{P(C$_6$H$_{11}$)$_3$}]$^+$; 566, [Pd([9]aneS$_3$){P(C$_6$H$_{11}$)$_3$}]$^+$ and 387, [Pd{P(C$_6$H$_{11}$)$_3$}]$^+$.

[Pd([9]aneS$_3$)(dppm)][PF$_6$]$_2$. The complex [Pd([9]aneS$_3$)Cl$_2$] (0.04 g, 1.12 × 10^{-4} mol) was refluxed in MeNO$_2$ (15 cm^3) with dppm (0.043 g, 1.12 × 10^{-4} mol) for 1 h, then NH$_4$PF$_6$ (0.037 g, 2.24 × 10^{-4} mol) was added and the solution refluxed for 30 min. The reaction mixture was cooled and filtered: addition of Et$_2$O to the filtrate yielded [Pd([9]aneS$_3$)(dppm)][PF$_6$]$_2$ as bright orange crystals which were recrystallised from MeNO$_2$ by slow diffusion of Et$_2$O vapour. Yield 50% (Found: C, 39.0; H, 3.85. Calc: C, 38.7; H, 3.55%).

Table 5 Atomic coordinates for $[Pd([9]aneS_3)(dppm)][PF_6]_2 \cdot 0.5Et_2O$

Atom	*x*	*y*	*z*
Pd	0.194 22(3)	0.75	0.079 19(4)
S(1)	0.184 14(15)	0.893 75(21)	−0.035 20(20)
S(4)	0.301 24(12)	0.726 11(22)	0.015 97(18)
S(7)	0.148 52(14)	0.661 27(20)	−0.039 93(17)
P(1)	0.100 60(11)	0.760 62(20)	0.162 68(15)
P(2)	0.223 02(12)	0.811 99(18)	0.213 57(16)
C(2)	0.262 6(6)	0.881 5(9)	−0.092 6(8)
C(3)	0.318 3(6)	0.838 1(9)	−0.036 9(8)
C(5)	0.285 1(6)	0.648 5(8)	−0.079 0(7)
C(6)	0.222 1(6)	0.594 6(8)	−0.071 7(7)
C(8)	0.137 4(5)	0.739 3(8)	−0.133 9(7)
C(9)	0.128 0(6)	0.838 3(8)	−0.111 8(8)
C(1A)	0.070 1(3)	0.652 8(4)	0.207 2(4)
C(2A)	0.007 3(3)	0.648 1(4)	0.246 9(4)
C(3A)	−0.016 5(3)	0.563 8(4)	0.278 9(4)
C(4A)	0.022 3(3)	0.484 1(4)	0.271 2(4)
C(5A)	0.085 0(3)	0.488 8(4)	0.231 5(4)
C(6A)	0.108 9(3)	0.573 2(4)	0.199 4(4)
C(1B)	0.033 91(24)	0.820 9(4)	0.110 4(3)
C(2B)	0.025 95(24)	0.916 2(4)	0.120 8(3)
C(3B)	−0.022 57(24)	0.963 1(4)	0.071 8(3)
C(4B)	−0.063 12(24)	0.914 6(4)	0.012 3(3)
C(5B)	−0.055 16(24)	0.819 3(4)	0.001 9(3)
C(6B)	−0.006 62(24)	0.772 4(4)	0.050 9(3)
C(1C)	0.264 08(24)	0.743 4(4)	0.296 1(3)
C(2C)	0.298 12(24)	0.662 6(4)	0.273 2(3)
C(3C)	0.330 83(24)	0.611 6(4)	0.339 1(3)
C(4C)	0.329 49(24)	0.641 3(4)	0.427 9(3)
C(5C)	0.295 40(24)	0.722 1(4)	0.450 7(3)
C(6C)	0.262 71(24)	0.773 1(4)	0.384 9(3)
C(1D)	0.265 79(25)	0.921 3(4)	0.206 9(4)
C(2D)	0.334 02(25)	0.923 4(4)	0.223 9(4)
C(3D)	0.369 73(25)	1.005 1(4)	0.211 0(4)
C(4D)	0.337 23(25)	1.084 7(4)	0.181 2(4)
C(5D)	0.268 99(25)	1.082 5(4)	0.164 2(4)
C(6D)	0.233 27(25)	1.000 7(4)	0.177 0(4)
C(1E)	0.138 0(5)	0.828 8(7)	0.252 4(6)

IR: 3050, 2964, 2924, 1480, 1435, 1409, 1308, 1187, 1099, 998, 840, 742, 718, 688, 555, 543, 502, and 478 cm^{-1}. NMR (CD_3NO_2, 298 K): ^1H (200 MHz), δ 2.85, 3.07 (m, 12 H, SCH_2), 5.02 (t, 2 H, $^2J_{HP}$ = 11.5, PCH_2) and 7.69–7.86 (m, 20 H, PPh_2); ^{13}C (50.32 MHz), δ 33.12 (s, 6 C, SCH_2), 35.34 (t, 1 C, $^1J_{PC}$ = 29, PCH_2), 129.01 (d, 8 C, $^2J_{PC}$ = 12, PPh_2), 132.03 (d, 8 C, $^3J_{PC}$ = 3 Hz, PPh_2) and 132.65 (s, 4 C, PPh_2); ^{31}P (81.02 MHz), δ −37.73.

$[Pd([9]aneS_3)(dppe)][PF_6]_2$. This complex was produced from $[Pd([9]aneS_3)Cl_2]$ in a similar manner to the dppm complex, except for the use of dppe (0.045 g, 1.12 × 10^{-4} mol). The yellow-orange product was recrystallised from Me_2CO–Et_2O to give $[Pd([9]aneS_3)(dppe)][PF_6]_2$ in 68% yield. (Found: C, 39.8; H, 3.70. Calc.: C, 39.4; H, 3.70%). IR: 1475, 1434, 1408, 1308, 1185, 995, 838, 750, 720, 708, 692, 655, 555, 528, 485 and 427 cm^{-1}. NMR [$(CD_3)_2CO$, 298 K]: ^1H (360 MHz), δ 2.54 (m, 6 H, SCH_2), 3.15 (m, 6 H, SCH_2), 3.56 (m, 4 H, PCH_2) and 7.67–8.00 (m, 20 H, PPh_2); ^{13}C (50.32 MHz), δ 29.37 (dd, 2 C, $^2J_{PC}$ = 11, $^1J_{CP}$ = 24), 32.80 (s, 6 C, SCH_2), 129.40 (d, 8 C, $^2J_{PC}$ = 12, PPh_2), 131.97 (d, 8 C, $^3J_{PC}$ = 11 Hz, PPh_2) and 133.03 (s, 4 C, PPh_2). FAB mass spectrum: *m*/*z* = 683, $[Pd([9]aneS_3)(dppe)]^+$; 504, $[Pd(dppe)]^+$ and 475, $[Pd(PPh_2)_2]^+$. Electronic spectrum ($MeNO_2$): λ_{max} = 430 (ε_{max} = 448) and 346 nm (1900 $dm^3\ mol^{-1}\ cm^{-1}$).

$[Pd([9]aneS_3)\{(Ph_2PCH_2)_2[Ph_2P(O)CH_2]CMe\}][PF_6]_2$. The complex $[Pd([9]aneS_3)Cl_2]$ (0.03 g, 8.39 × 10^{-5} mol) and $(Ph_2PCH_2)_3CMe$ (0.053 g, 8.39 × 10^{-5} mol) were refluxed in $MeNO_2$ (15 cm^3) under N_2 for 1 h. Addition of NH_4PF_6 (0.037 g, 1.68 × 10^{-4} mol) and further refluxing afforded a pale, yellow solution, which was cooled and filtered to remove NH_4Cl. Addition of Et_2O to the filtrate gave a yellow precipitate which was recrystallised from $MeNO_2$ solution by slow diffusion of Et_2O vapour. Yield 55% (Found: C, 46.2; H, 4.20. Calc. for $C_{47}H_{51}F_{12}P_5PdS_3$: C, 47.0; H, 4.30. Calc. for

Table 6 Atomic coordinates for $[Pd([9]aneS_3)\{(Ph_2PCH_2)_2[Ph_2P(O)CH_2]CMe\}][PF_6]_2 \cdot 1.5MeNO_2 \cdot Et_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd	0.089 66(6)	0.263 94(4)	0.058 00(5)	C(2F′)	0.872 2(4)	0.016 6(3)	0.078 0(4)
S(1)	0.116 52(20)	0.200 82(14)	0.154 27(19)	C(3F′)	0.856 1(4)	−0.029 3(3)	0.058 0(4)
C(2)	0.037 4(8)	0.214 0(6)	0.176 9(7)	C(4F′)	0.854 1(4)	−0.063 6(3)	0.101 8(4)
C(3)	−0.035 1(7)	0.221 4(5)	0.124 1(6)	C(5F′)	0.868 3(4)	−0.052 0(3)	0.165 6(4)
S(4)	−0.029 89(19)	0.263 79(14)	0.063 97(17)	C(6F′)	0.884 4(4)	−0.006 0(3)	0.185 6(4)
C(5)	−0.077 7(7)	0.233 1(5)	−0.009 8(6)	C(1H)	0.776 5(7)	0.171 4(5)	0.117 4(6)
C(6)	−0.040 2(7)	0.187 7(5)	−0.015 7(8)	C(2H)	0.714 4(8)	0.139 4(5)	0.190 2(7)
S(7)	0.057 00(20)	0.195 90(13)	−0.007 72(19)	C(3H)	0.835 1(7)	0.110 5(5)	0.196 3(7)
C(8)	0.096 8(7)	0.146 9(5)	0.044 3(7)	C(2Z)	0.763 7(7)	0.125 3(5)	0.147 0(7)
C(9)	0.089 0(8)	0.146 4(6)	0.108 9(7)	C(2M)	0.728 6(8)	0.086 9(5)	0.100 9(8)
P(1)	0.193 74(19)	0.270 89(13)	0.033 14(18)	P(4)	0.873 3(3)	0.240 54(19)	0.304 72(22)
C(1A)	0.179 9(4)	0.283 1(3)	−0.049 6(3)	F(1)	0.803 5(6)	0.245 5(4)	0.244 4(4)
C(2A)	0.109 9(4)	0.287 8(3)	−0.093 1(3)	F(2)	0.827 8(5)	0.257 8(5)	0.349 6(4)
C(3A)	0.100 2(4)	0.300 3(3)	−0.156 0(3)	F(3)	0.946 3(9)	0.242 2(9)	0.362 9(8)
C(4A)	0.160 4(4)	0.308 1(3)	−0.175 3(3)	F(4)	0.916 5(6)	0.222 1(5)	0.260 4(5)
C(5A)	0.230 4(4)	0.303 3(3)	−0.131 8(3)	F(5)	0.850 1(7)	0.189 3(4)	0.313 9(7)
C(6A)	0.240 1(4)	0.290 8(3)	−0.068 9(3)	P(5)	0.769 7(3)	0.010 61(17)	0.313 16(24)
C(1B)	0.244 0(4)	0.217 25(25)	0.050 0(4)	F(7)	0.797 1(6)	−0.007 0(4)	0.385 7(5)
C(2B)	0.276 3(4)	0.203 18(25)	0.113 0(4)	F(8)	0.744 1(6)	0.026 2(3)	0.239 1(5)
C(3B)	0.314 9(4)	0.161 40(25)	0.126 6(4)	F(9)	0.690 8(6)	−0.006 7(5)	0.303 7(6)
C(4B)	0.321 1(4)	0.133 66(25)	0.077 2(4)	F(10)	0.789 5(7)	−0.037 7(4)	0.293 5(5)
C(5B)	0.288 7(4)	0.147 73(25)	0.014 2(4)	F(12)	0.848 1(7)	0.028 8(6)	0.323 2(6)
C(6B)	0.250 2(4)	0.189 50(25)	0.000 6(4)	P(6)	0.363 3(3)	0.289 41(19)	0.283 87(21)
P(2)	0.103 33(20)	0.336 68(13)	0.102 62(18)	F(13)	0.323 5(6)	0.298 3(4)	0.334 7(5)
C(1C)	0.084 1(4)	0.333 85(25)	0.177 2(3)	F(14)	0.377 7(5)	0.235 9(4)	0.306 3(5)
C(2C)	0.138 4(4)	0.319 80(25)	0.232 7(3)	F(15)	0.287 5(6)	0.274 1(4)	0.232 9(5)
C(3C)	0.122 9(4)	0.315 18(25)	0.289 3(3)	F(16)	0.439 3(6)	0.302 7(4)	0.335 1(5)
C(4C)	0.053 1(4)	0.324 60(25)	0.290 4(3)	F(17)	0.401 8(6)	0.280 3(5)	0.232 6(5)
C(5C)	−0.001 2(4)	0.338 68(25)	0.234 9(3)	F(18)	0.346 3(7)	0.341 9(4)	0.262 4(6)
C(6C)	0.014 3(4)	0.343 31(25)	0.178 3(3)	P(7)	0.247 1(4)	0.034 6(3)	0.171 8(4)
C(1D)	0.036 9(4)	0.376 95(25)	0.054 4(4)	F(19)	0.221 4(7)	0.057 1(5)	0.105 0(5)
C(2D)	−0.010 1(4)	0.364 02(25)	−0.005 4(4)	F(20)	0.167 0(7)	0.035 6(5)	0.172 5(7)
C(3D)	−0.062 2(4)	0.395 42(25)	−0.041 3(4)	F(21)	0.325 5(9)	0.040 4(10)	0.176 5(9)

Table 6 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(4D)	−0.067 2(4)	0.439 74(25)	−0.017 4(4)	F(22)	0.256 5(11)	0.091 0(8)	0.200 8(10)
C(5D)	−0.020 1(4)	0.452 66(25)	0.042 4(4)	F(23)	0.251 7(11)	−0.010 2(8)	0.155 7(10)
C(6D)	0.032 0(4)	0.421 27(25)	0.078 3(4)	F(24)	0.244 2(16)	0.002 7(11)	0.229 4(12)
P(3)	0.365 64(21)	0.401 47(15)	0.065 13(23)	C(1E)	0.446 7(6)	0.427 6(4)	0.122 2(6)
O(3)	0.382 2(5)	0.358 5(4)	0.034 9(6)	C(2E)	0.499 3(6)	0.443 6(4)	0.097 2(6)
C(1G)	0.261 1(7)	0.313 2(5)	0.075 8(7)	C(3E)	0.566 7(6)	0.458 5(4)	0.138 1(6)
C(2G)	0.191 1(7)	0.366 0(5)	0.126 9(6)	C(4E)	0.581 5(6)	0.457 4(4)	0.203 8(6)
C(3G)	0.304 4(7)	0.394 0(5)	0.109 8(7)	C(5E)	0.528 9(6)	0.441 4(4)	0.228 7(6)
C(1Z)	0.237 1(7)	0.364 2(5)	0.079 3(7)	C(6E)	0.461 4(6)	0.426 5(4)	0.187 9(6)
C(1M)	0.191 0(7)	0.383 9(5)	0.015 0(7)	C(1E*)	0.439 0(21)	0.426 9(14)	0.086 7(19)
Pd(2)	0.596 74(6)	0.212 26(4)	0.073 79(5)	C(2E*)	0.495 5(21)	0.451 0(14)	0.063 8(19)
S(1′)	0.599 28(23)	0.294 81(15)	0.138 68(22)	C(3E*)	0.560 4(21)	0.470 5(14)	0.104 6(19)
C(2′)	0.517 0(8)	0.286 2(5)	0.156 2(7)	C(4E*)	0.573 8(21)	0.460 7(14)	0.167 8(19)
C(3′)	0.454 1(7)	0.262 8(5)	0.106 5(7)	C(5E*)	0.527 7(21)	0.420 0(14)	0.194 3(19)
S(4′)	0.472 46(20)	0.210 36(14)	0.069 68(19)	C(6E*)	0.459 5(21)	0.424 7(14)	0.158 5(19)
C(5′)	0.430 3(8)	0.222 5(5)	−0.013 1(7)	C(1F)	0.331 2(8)	0.442 2(5)	0.004 7(7)
C(6′)	0.458 7(8)	0.264 5(6)	−0.037 0(7)	C(2F)	0.324 7(8)	0.431 4(5)	−0.058 0(7)
S(7′)	0.558 96(22)	0.262 56(15)	−0.016 50(19)	C(3F)	0.294 0(8)	0.463 5(5)	−0.106 5(7)
C(8′)	0.586 9(9)	0.319 8(6)	0.013 9(9)	C(4F)	0.269 8(8)	0.506 4(5)	−0.092 2(7)
C(9′)	0.567 6(9)	0.334 6(5)	0.072 2(8)	C(5F)	0.276 2(8)	0.517 3(5)	−0.029 5(7)
P(1′)	0.702 82(20)	0.198 31(13)	0.054 82(18)	C(6F)	0.306 9(8)	0.485 2(5)	0.019 0(7)
C(1A′)	0.689 6(4)	0.163 8(3)	−0.016 1(4)	C(1F*)	0.325 0(12)	0.452 4(8)	0.012 2(11)
C(2A′)	0.750 1(4)	0.147 0(3)	−0.029 5(4)	C(2F*)	0.317 1(12)	0.439 4(8)	−0.056 0(11)
C(3A′)	0.741 1(4)	0.123 0(3)	−0.086 1(4)	C(3F*)	0.293 4(12)	0.476 6(8)	−0.104 3(11)
C(4A′)	0.671 5(4)	0.115 8(3)	−0.129 3(4)	C(4F*)	0.276 3(12)	0.484 9(8)	−0.085 2(11)
C(5A′)	0.610 9(4)	0.132 6(3)	−0.115 9(4)	C(5F*)	0.300 0(12)	0.533 0(8)	0.019 4(11)
C(6A′)	0.620 0(4)	0.156 6(3)	−0.059 3(4)	C(6F*)	0.321 4(12)	0.498 0(8)	0.059 9(11)
C(1B′)	0.742 4(4)	0.252 73(24)	0.041 4(4)	F(3′)	0.933 9(21)	0.223 1(13)	0.367 7(20)
C(2B′)	0.774 3(4)	0.282 10(24)	0.093 1(4)	F(6)	0.893 6(8)	0.291 6(5)	0.298 8(7)
C(3B′)	0.803 1(4)	0.324 87(24)	0.083 6(4)	F(11)	0.760 5(9)	0.059 3(7)	0.333 7(9)
C(4B′)	0.799 9(4)	0.338 32(24)	0.022 5(4)	F(11′)	0.281 8(21)	−0.056 9(16)	−0.324 5(20)
C(5B′)	0.768 1(4)	0.308 95(24)	−0.029 1(4)	F(23′)	0.280 2(11)	0.027 4(8)	0.248 1(10)
C(6B′)	0.739 3(4)	0.266 17(24)	−0.019 6(4)	F(24′)	0.205 9(14)	−0.018 9(9)	0.123 7(13)
P(2′)	0.621 85(21)	0.156 99(14)	0.151 33(19)	O(1S)	0.400 6(6)	0.385 0(4)	0.424 9(6)
C(1C′)	0.598 9(5)	0.181 0(3)	0.216 9(4)	O(2S)	0.450 1(6)	0.413 1(4)	0.359 5(6)
C(2C′)	0.647 1(5)	0.212 0(3)	0.258 1(4)	N(1S)	0.396 8(6)	0.409 3(4)	0.377 9(6)
C(3C′)	0.628 1(5)	0.233 8(3)	0.306 4(4)	C(1S)	0.324 9(6)	0.425 7(4)	0.336 2(6)
C(4C′)	0.560 9(5)	0.224 6(3)	0.313 5(4)	O(10)	0.837 8(5)	0.410 8(3)	0.204 8(5)
C(5C′)	0.512 7(5)	0.193 6(3)	0.272 4(4)	C(10)	0.808 3(5)	0.400 7(3)	0.254 8(5)
C(6C′)	0.531 7(5)	0.171 8(3)	0.224 0(4)	C(11)	0.742 3(5)	0.368 0(3)	0.229 6(5)
C(1D′)	0.570 4(4)	0.104 8(3)	0.130 4(4)	C(10′)	0.894 8(5)	0.444 9(3)	0.227 0(5)
C(2D′)	0.526 1(4)	0.095 9(3)	0.068 0(4)	C(11′)	0.925 5(5)	0.457 0(3)	0.173 3(5)
C(3D′)	0.487 1(4)	0.054 3(3)	0.053 4(4)	O(20)	0.504 9(9)	0.107 0(5)	0.377 3(7)
C(4D′)	0.492 4(4)	0.021 7(3)	0.101 2(4)	C(20)	0.435 1(9)	0.099 0(5)	0.329 8(7)
C(5D′)	0.536 8(4)	0.030 6(3)	0.163 5(4)	C(21)	0.377 9(9)	0.131 5(5)	0.341 4(7)
C(6D′)	0.575 8(4)	0.072 2(3)	0.178 1(4)	C(20′)	0.558 8(9)	0.078 5(5)	0.363 7(7)
P(3′)	0.906 55(22)	0.087 97(15)	0.167 45(21)	C(21′)	0.632 4(9)	0.104 1(5)	0.384 0(7)
O(3′)	0.918 8(5)	0.117 3(4)	0.116 0(5)	O(3S)	0.375 7(16)	−0.017 0(12)	−0.031 9(15)
C(1E′)	0.985 8(4)	0.084 5(3)	0.239 0(4)	N(2S)	0.338 7(16)	0.002 3(12)	−0.003 2(15)
C(2E′)	1.052 2(4)	0.076 3(3)	0.230 0(4)	C(2S)	0.317 3(16)	0.051 6(12)	−0.017 1(15)
C(3E′)	1.115 4(4)	0.071 7(3)	0.282 4(4)	O(5S)	0.977 0(8)	0.068 9(6)	−0.006 3(8)
C(4E′)	1.112 1(4)	0.075 3(3)	0.343 9(4)	O(6S)	0.967 1(8)	0.093 4(6)	−0.100 1(8)
C(5E′)	1.045 6(4)	0.083 5(3)	0.353 0(4)	N(3S)	0.961 1(8)	0.061 8(6)	−0.064 3(8)
C(6E′)	0.982 5(4)	0.088 0(3)	0.300 6(4)	C(3S)	0.950 3(8)	0.013 3(6)	−0.088 3(8)
C(1F′)	0.886 3(4)	0.028 3(3)	0.141 8(4)				

$C_{47}H_{51}F_{12}OP_5PdS_3$: C, 46.4; H, 4.20%). IR: 1478, 1432, 1408, 1382, 1305 [ν(P=O)], 1186, 1095, 1051, 1032, 997, 930, 840, 741, 728, 694, 555, 512, 480 and 450 cm^{-1}. NMR (CD_3NO_2, 298 K): ^1H (200 MHz), δ 0.64 (s, 3 H, Me), 2.29 (m, 6 H, SCH_2), 2.84 (m, 6 H, SCH_2), 2.15 (m, 2 H, PCH_2), 3.13 (m, 4 H, PCH_2), and 7.14–7.94 (m, 30 H, PPh_2); ^{13}C (50.32 MHz), δ 32.9 (s, 6 H, SCH_2), 128.2 (m, PPh_2), 129.5 (s, PPh_2), 132.0 (m, PPh_2) and 134.0 (m, PPh_2); CH_3 group not observed, PCH_2 signals weak and hidden by those due to [9]aneS$_3$; ^{31}P (81.02 MHz), δ −29.20 (free triphosphine), 16.46 (s, 1 P, PPh_2), 18.08 (s, 2 P, PPh_2) and 28.17 $[HPR_3]^+$. FAB mass spectrum: *m*/*z* = 910, $[Pd([9]aneS_3)\{(Ph_2PCH_2)_3CMe\}]^+$ (908); 729, $[Pd\{(Ph_2PCH_2)_3CMe\}]^+$ (731); 544, $[Pd\{(Ph_2PCH_2)_2CMe\}]^+$. Electronic spectrum ($MeNO_2$): λ_{max} = 429 (ε_{max} = 288) and 348 nm (3300 $dm^3\ mol^{-1}\ cm^{-1}$).

$[Pd([9]aneS_3)(bipy)][PF_6]_2$. 2,2′-Bipyridine (0.013 g, 8.39 × 10^{-5} mol) was treated with $[Pd([9]aneS_3)Cl_2]$ (0.03 g, 8.39 × 10^{-5} mol) in refluxing $MeNO_2$, followed by the addition of NH_4PF_6 (0.037 g, 1.68 × 10^{-4} mol). After removal of NH_4Cl by filtration, $[Pd([9]aneS_3)(bipy)][PF_6]_2$ was isolated as a pinkish brown precipitate which was recrystallised by slow diffusion of Et_2O vapour into a solution in $MeNO_2$, giving purple blocks. Yield 50% (Found: C, 26.0; H, 2.70; N, 3.80. Calc.: C, 26.2; H, 2.75; N, 3.80%). IR: 3110, 3080, 2960, 2920, 1600, 1495, 1472, 1445, 1425, 1405, 1380, 1315, 1285, 1245, 1175, 1162, 1150, 1120, 1105, 1081, 1070, 1037, 1020, 950, 900, 840, 808, 768, 740, 722, 661, 647, 610, 555, 482 and 412 cm^{-1}. NMR (298 K): ^1H [$(CD_3)_2CO$, 80 MHz], δ 3.68 (s, 12 H, SCH_2) and 7.9–8.9 (m, 8 H, bipy); ^{13}C (CD_3NO_2, 50.32 MHz), δ 32.80 (s, 6 C, SCH_2), 123.92 [s, 2 C, bipy C(6), C(6′)], 127.66

[s, 2 C, bipy C(4), C(4′)], 141.50 [s, 2 C, bipy C(5), C(5′)] and 149.35 [s, 2 C, bipy C(3), C(3′)]. FAB mass spectrum: m/z = 442, $[Pd([9]aneS_3)(bipy)]^+$; 364, $[Pd([9]aneS_3)(C_5H_4N)]^+$; 285, $[Pd([9]aneS_3)]^+$; and 262, $[Pd(bipy)]^+$. Electronic spectrum (MeCN): λ_{max} = 508 (ε_{max} = 11.8), 321 (4100), 303 (4100), 242 (9200) and 214 nm (12 000 $dm^3\ mol^{-1}\ cm^{-1}$).

$[Pd([9]aneS_3)(phen)][PF_6]_2$. This was synthesised in a similar manner to the above, using 1,10-phenanthroline (0.015 g, 8.39×10^{-5} mol) instead of 2,2′-bipyridine. The pink-brown precipitate formed was recrystallised in the same way. Yield 40% (Found: C, 28.3; H, 2.65; N, 3.70. Calc: C, 28.6; H, 2.65; N, 3.70%). IR: 1518, 1447, 1430, 1410, 1348, 1312, 1288, 1222, 1151, 1110, 840, 742, 725, 716, 558, 482 and 432 cm^{-1}. NMR (298 K): ^1H [$(CD_3)_2CO$, 80 MHz], δ 3.73 (s, 12 H, SCH_2), 8.17–8.48, 9.11–9.34 (m, 8 H, phen); ^{13}C (CD_3NO_2, 50.32 MHz), δ 32.97 (s, 6 C, SCH_2), 125.68 [phen C(5), C(6)], 127.24 [phen C(3), C(8)], 140.44 [phen C(4), C(7)] and 149.83 [phen C(2), C(9)]. FAB mass spectrum: m/z = 467, $[Pd([9]aneS_3)(phen)]^+$; 287, $[Pd([9]aneS_3)]^+$ or $[Pd(1,10\text{-phen})]^+$. Electronic spectrum (MeCN): λ_{max} = 507 (ε_{max} = 120), 278 (18 000) and 217 nm (21 000 $dm^3\ mol^{-1}\ cm^{-1}$).

Table 7 Atomic coordinates for $[Pd([9]aneS_3)(bipy)][PF_6]_2$

Atom	x	y	z
Pd	0.161 48(3)	0.276 50(3)	0.247 90(3)
S(1)	0.368 02(13)	0.308 84(12)	0.395 91(11)
C(2)	0.495 2(5)	0.274 0(5)	0.281 2(5)
C(3)	0.456 2(5)	0.305 7(5)	0.148 7(5)
S(4)	0.316 22(11)	0.237 49(12)	0.099 00(11)
C(5)	0.363 0(5)	0.070 7(5)	0.115 3(5)
C(6)	0.252 1(5)	0.000 8(5)	0.178 6(5)
S(7)	0.189 49(12)	0.069 51(11)	0.318 55(11)
C(8)	0.332 9(5)	0.048 8(5)	0.413 2(5)
C(9)	0.351 5(6)	0.159 9(5)	0.483 2(5)
N(1)	0.104 2(4)	0.453 5(4)	0.171 5(4)
C(b2)	0.001 2(4)	0.510 1(5)	0.227 4(4)
C(b3)	−0.045 9(6)	0.630 5(5)	0.187 8(5)
C(b4)	0.015 4(6)	0.693 8(5)	0.084 0(5)
C(b5)	0.117 5(5)	0.634 6(5)	0.028 0(5)
C(b6)	0.161 0(5)	0.515 0(5)	0.070 6(5)
N(2)	0.007 7(4)	0.322 8(4)	0.365 8(4)
C(b2′)	−0.055 1(5)	0.436 3(5)	0.334 6(4)
C(b3′)	−0.164 6(6)	0.477 1(6)	0.401 1(6)
C(b4′)	−0.208 5(6)	0.401 8(6)	0.503 1(6)
C(b5′)	−0.142 6(6)	0.292 1(6)	0.534 3(6)
C(b6′)	−0.033 5(5)	0.251 4(5)	0.465 4(5)
P(1)	−0.190 63(14)	0.036 45(14)	0.205 67(14)
F(11)	0.732 7(4)	0.115 4(4)	0.097 7(4)
F(12)	0.672 7(4)	0.005 5(4)	0.269 7(4)
F(13)	0.942 6(4)	0.073 2(6)	0.143 7(5)
F(14)	0.809 0(5)	−0.079 9(5)	0.129 8(6)
F(15)	0.883 5(5)	−0.046 9(8)	0.308 1(5)
F(16)	0.805 1(5)	0.157 0(6)	0.273 9(6)
P(2)	−0.501 38(13)	0.673 34(13)	0.230 86(12)
F(21)	0.364 3(3)	0.288 2(4)	0.736 9(4)
F(22)	0.432 2(4)	0.417 1(3)	0.863 8(3)
F(23)	0.489 7(4)	0.438 3(3)	0.663 3(3)
F(24)	0.569 1(3)	0.237 7(4)	0.673 3(3)
F(25)	0.513 8(4)	0.213 6(4)	0.874 2(3)
F(26)	0.638 1(4)	0.367 0(6)	0.797 2(5)

Crystal structure determinations

A summary of the crystal and experimental data for all six structures is given in Table 2: only special features of individual determinations are noted here.

***cis*-$[Pd([9]aneS_3)(PPh_3)_2][PF_6]_2$.** Absorption corrections (minimum 0.070, maximum 0.303) were applied by means of ψ scans. Atomic coordinates are given in Table 3.

$[Pd([9]aneS_3)Cl(PPh_3)]PF_6 \cdot 2MeNO_2$. One $MeNO_2$ molecule lies on a crystallographic two-fold axis. Solvent H atoms were not included in the refinement model. Atomic coordinates are given in Table 4.

$[Pd([9]aneS_3)(dppm)][PF_6]_2 \cdot 0.5Et_2O$. The unconventional setting $Pn2_1a$ was used because the structure analysis was initiated in the corresponding centrosymmetric space group *Pnma*. The Pd, F, P and S atoms were refined anisotropically. Disorder in the PF_6^- was treated by allowing each F atom of the ion to occupy two positions. The solvent molecule was refined as a rigid group. No H atoms were included for the half-occupied solvent molecule. Atomic coordinates are given in Table 5.

$[Pd([9]aneS_3)\{(Ph_2PCH_2)_2[Ph_2P(O)CH_2]CMe\}][PF_6]_2 \cdot 1.5MeNO_2 \cdot Et_2O$. The crystal was cooled to 173 K using an Oxford Cryosystems low-temperature device.[20] All cation non-H atoms were refined anisotropically. Disorder in two rings of the phosphine oxide group in one molecule was treated by allowing alternative positions for each ring. The PF_6^- groups were each disordered over multiple sites. Solvent H atoms were not included. Atomic coordinates are given in Table 6.

Table 8 Atomic coordinates for $[Pd([9]aneS_3)(phen)][PF_6]_2 \cdot MeNO_2$

Atom	x	y	z	Atom	x	y	z
Pd	0.419 26(9)	0.371 61(7)	0.260 69(4)	O(1S)	0.307 9(14)	0.371 1(14)	0.803 7(7)
S(1)	0.301 5(4)	0.500 4(3)	0.194 40(18)	O(2S)	0.373 1(17)	0.172 5(16)	0.792 4(7)
S(4)	0.350 3(4)	0.184 8(3)	0.162 58(17)	C(2)	0.328 5(16)	0.399 5(13)	0.101 2(7)
S(7)	0.046 4(4)	0.301 4(3)	0.286 03(17)	C(3)	0.272 7(17)	0.250 0(14)	0.089 0(7)
N(1)	0.554 8(11)	0.271 4(9)	0.321 4(5)	C(5)	0.151 9(14)	0.087 4(12)	0.180 8(7)
N(2)	0.522 8(11)	0.536 0(9)	0.347 1(5)	C(6)	−0.003 7(16)	0.157 9(14)	0.206 6(7)
P(1)	0.121 9(4)	−0.098 5(3)	0.355 24(18)	C(8)	−0.016 1(16)	0.447 2(13)	0.258 2(7)
F(10)	0.130 9(16)	0.057 5(10)	0.353 5(6)	C(9)	0.061 9(16)	0.476 9(14)	0.191 6(7)
F(11)	0.124 4(13)	−0.248 9(8)	0.360 4(7)	C(12)	0.580 0(15)	0.138 1(13)	0.305 5(7)
F(12)	−0.013 6(16)	−0.133 7(15)	0.290 2(7)	C(13)	0.672 5(15)	0.085 5(13)	0.355 0(7)
F(13)	0.276 9(16)	−0.116 3(13)	0.305 5(7)	C(14)	0.738 7(15)	0.162 9(13)	0.418 3(7)
F(14)	−0.015 9(15)	−0.071 8(15)	0.409 5(7)	C(14A)	0.720 7(14)	0.306 7(12)	0.438 9(6)
F(15)	0.271 5(16)	−0.055 1(11)	0.423 2(6)	C(15)	0.789 1(17)	0.402 3(14)	0.505 6(7)
P(2)	0.254 8(4)	0.750 9(4)	0.012 23(20)	C(16)	0.772 6(16)	0.535 0(14)	0.519 4(7)
F(20)	0.421 5(15)	0.863 6(13)	0.035 1(7)	C(16A)	0.686 8(15)	0.588 4(12)	0.466 9(6)
F(21)	0.278 3(12)	0.737 6(11)	−0.071 1(5)	C(17)	0.673 2(16)	0.727 8(14)	0.477 0(7)
F(22)	0.377 2(13)	0.639 1(11)	0.012 1(6)	C(18)	0.583 0(16)	0.767 7(14)	0.423 0(7)
F(23)	0.227 6(13)	0.762 0(13)	0.093 9(5)	C(19)	0.509 6(14)	0.670 6(12)	0.358 8(6)
F(24)	0.130 5(15)	0.864 5(14)	0.012 4(6)	C(21)	0.610 1(13)	0.494 9(11)	0.400 5(6)
F(25)	0.085 8(13)	0.640 3(12)	−0.011 6(6)	C(22)	0.628 1(13)	0.355 8(11)	0.386 6(6)
N(1S)	0.307 7(14)	0.263 3(16)	0.823 2(7)	C(1S)	0.215 4(21)	0.261 9(21)	0.885 7(11)

[Pd([9]aneS$_3$)(bipy)][PF$_6$]$_2$. Atomic coordinates are given in Table 7.

[Pd([9]aneS$_3$)(phen)][PF$_6$]$_2$·MeNO$_2$. At isotropic convergence, final corrections for absorption (minimum 0.718, maximum 1.348) were applied empirically using DIFABS.[21] The Pd, F, N, P and S atoms were refined anisotropically. The CH_3 group of the $MeNO_2$ solvate was allowed to rotate about the C–N bond. Disorder in the PF_6^- groups was modelled by allowing partial occupancies for the F atoms. Atomic coordinates are given in Table 8.

Illustrations were generated by SHELXTL-PC[22] and molecular geometry calculations utilised CALC.[23] Scattering factors were inlaid or taken from ref. 24.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue. 1

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