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Hemilabile bonding of 1-oxa-4,7-dithiacyclononane in cyclometallated palladium(II) complexes†

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The synthesis and characterization of a series of cyclometallated complexes of Pd(II) incorporating the mixed donor ligand 1-oxa-4,7-dithiacyclononane ([9]aneS₂O) are presented in this study. Complexes of the form [Pd(C^N)([9]aneS₂O)](PF₆) (C^N = 2-phenylpyridine (ppy) **1b**, 4-(2-pyridyl)benzaldehyde (ppyCHO) **2b**, 7,8-benzoquinoline (bzq) **3b**, 2-benzothienylpyridine (btp) **4b**, 2-phenylbenzothiazole (pbt) **5b**), were obtained in high-yield from a simple two-step synthetic scheme. All of these complexes were fully characterized by NMR, ESI-MS, IR, combustion analyses, and most (**1b**, **2b**, **4b**, **5b**) by X-ray crystallography. Solution ¹H and ¹³C NMR studies of [Pd(C^N)([9]aneS₂O)](PF₆) complexes demonstrate complicated [9]aneS₂O behavior at room temperature. Variable temperature NMR reveals dynamic bonding of the [9]aneS₂O ligand consistent with the presence of both endodentate and exodentate bonding modes. This is in stark contrast to the related [9]aneS₃ (1,4,7-trithiacyclononane) cogeners that demonstrate fluxional endodentate bonding only in solution. X-ray structures reveal only exodentate [9]aneS₂O bonding in this series, unlike the related [9]aneS₃ complexes that show endodentate bonding with an axial Pd...S interaction. DFT calculations performed on *endo* and *exo* [9]aneS₂O bonding forms of **4b**, as well as a transition state calculation for interconversion, suggest reasonable access to both bonding forms based on the energy barrier. Natural bond order calculations provide further evidence for a weak axial Pd...O interaction in the *endo* form of **4b**.

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Introduction

Palladium catalysts used for a variety of organic transformations including C–H bond activation^{1,2} and oxidative cross-coupling reactions³ rely on the Pd^{II/IV} redox couple and the coordination preferences of each oxidation state. More recently, cyclometallated palladium systems have shown evidence suggesting the Pd(III) oxidation state can play an important role in catalysis.^{4–7} Our previous studies of cyclometallated Pd(II) complexes with [9]aneS₃ (1,4,7-trithiacyclononane) have shown unusual well-defined sequential 1-e-reversible

Pd^{II/III} and Pd^{III/IV} electrochemistry, suggesting some stability of a potentially five-coordinate Pd(III) species^{8,9}. Solid-state structural evidence also suggests axial Pd...S interactions of [9]aneS₃ play a key role in this behavior. The vast majority of structures of d⁸ metal complexes with [9]aneS₃ demonstrate that the ligand forms two M–S bonds with a third M...S interaction longer than a bond but significantly shorter than the sum of van der Waals radii. The disparity between the electronic preferences of square planar d⁸ ions and the endodentate geometric preference of the [9]aneS₃ ligand permits stabilization of related complexes in unusual oxidation states such as Pd(III),¹⁰ Pt(III),¹¹ and Au(II).¹²

While the coordination chemistry of [9]aneS₃ has been studied widely, reports of metal complexes of related mixed donor tridentate macrocyclic ligands such as [9]aneS₂N ([9]aneS₂N = 1-aza-4,7-dithiacyclononane)¹³ and [9]aneS₂O ([9]aneS₂O = 1-oxa-4,7-dithiacyclononane) are sparse. Several bis-homoleptic complexes of [9]aneS₂O with first-row transition metals are reported (Co(II),¹⁴ Ni(II),¹⁵ Cu(I),¹⁴ Cu(II)¹⁵) as well as 4d and 5d metals (Hg(II),¹⁶ Cd(II),¹⁶ Au(I),¹⁷ Au(II),¹⁷ Au(III),¹⁷ Pt(II),¹⁸ and Pd(II)¹⁸). Very few heteroleptic metal complexes of [9]aneS₂O are reported. Unlike complexes of [9]aneS₃ which almost exclusively display endodentate ligand

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conformations, [9]aneS₂O can bind in both exodentate and endodentate fashion. While the *endo/exo* preference of bonding [9]aneS₂O to transition metals likely involves the coordination number and stereochemical preferences of the metal and hard/soft compatibility, d⁸ metal complexes present additional complexity with the possibility of axial interactions. Of particular interest are the complexes Pt([9]aneS₂O)Cl₂ and Pd([9]aneS₂O)Cl₂.¹⁹ Both of these complexes have been crystallographically characterized in a form with endodentate [9]aneS₂O coordination and another form with an exodentate [9]aneS₂O ligand conformation. As minimally higher crystal growth temperatures favored the exodentate conformations in each complex (lacking an axial M...O interaction), the presence of oxygen atom interactions with the d⁸ metal center for the thermodynamically more stable endodentate conformation suggests a subtle interplay between preferred ligand conformation and the strength of the M...O interaction. Heteroditopic ligands, including [9]aneS₂O, can be considered hemilabile and this behavior could be exploited in complexes for catalysis.^{20,21}

As Pd(III) is expected to prefer hard Lewis base donor atoms compared with Pd(II), we postulated that a mixed donor macrocycle of the same size that includes softer sulfur donors and a harder oxygen donor might provide enhanced stability for a potentially stabilized Pd^{III} species. In an effort to probe these potential axial donor effects, we studied a series of heteroleptic palladium complexes of the form [Pd(C[^]N)([9]aneS₂O)](PF₆) (C[^]N = cyclometalating ligand with carbonanion and nitrogen donors) with a variety of C[^]N ligands including 2-phenylpyridine (ppy), 7,8-benzoquinoline (bzq), 2-benzothienylpyridine (btp), 2-phenylbenzothiazole (pbt), and 4-(2-pyridyl)benzaldehyde (ppyCHO) (Scheme 1).

Some of these potentially cyclometallating ligands were chosen so comparisons could be made between [9]aneS₂O and previously studied [9]aneS₃ palladium complexes.^{8,9} Also, all these cyclometallating ligands are planar, preventing the introduction of further steric effects, and are all commercially available. While cyclometallation chemistry of most of these ligands is common, Pd(II) chemistry with thienylpyridine^{22–24} ligands is relatively rare. Study of cyclometallated ppyCHO is unknown at Pd(II), but limited examples of Pt(II),²⁵ Ir(III),²⁶ and Ru(II)²⁷ complexes are reported.

Scheme 1

Results and discussion

Syntheses

The synthesis of cyclometallated palladium(II) complexes with [9]aneS₂O proceeds by a two-step method we have developed previously⁸ for analogous [9]aneS₃ complexes, shown in Scheme 2.

The mild low-temperature route for C–H activation of the neutral protonated form of the potentially cyclometallating ligand with palladium(II) acetate in CH₂Cl₂ proceeds cleanly in high yields to form binuclear bis-μ-acetato-bridged complexes. We previously reported the preparation of the complexes [Pd(C[^]N)(μ-O₂CCH₃)₂] (where C[^]N = ppy, bzq, btp, and pbt).⁸ This study extends this synthetic scheme to include the preparation of [Pd(C[^]N)(μ-O₂CCH₃)₂] (where C[^]N = ppyCHO (**2a**), fpp (**6a**); ppyCHO = 4-(2-pyridyl)benzaldehyde; fpp = 2-[4-(trifluoromethyl)phenyl]pyridine). It is clear that this synthetic method is tolerant of both moderate and strongly electron-withdrawing functional groups as demonstrated with the aldehyde group of ppyCHO and the trifluoromethyl group of fpp. A combination of combustion analyses, X-ray crystal structures, and NMR characterization confirmed the dimeric composition of complexes **2a** and **6a**. To our knowledge, **6a** is the first report of a cyclometallated fpp complex of Pd(II).

Ligand substitution reactions of appropriate acetate bridged dimers (or [Pd(ppy)Cl]₂ for ppy ligand) with [9]aneS₂O in a 1 : 2 molar ratio at room temperature in CH₃CN followed by anion metathesis using hexafluorophosphate affords the complexes [Pd(C[^]N)([9]aneS₂O)](PF₆) (C[^]N = ppy (**1b**), ppyCHO (**2b**), bzq (**3b**), btp (**4b**), pbt (**5b**)) for all cyclometallating ligands of this study except fpp. The complexes **1b–5b** were all obtained in high yields. No product of the form [Pd(fpp)([9]aneS₂O)](PF₆) was either isolated or detected spectroscopically (NMR, ESI-MS) in solution. Further attempts to produce [Pd(fpp)([9]aneS₂O)](PF₆) including longer reaction times and heat were also not successful. The same problems were encountered in attempts to synthesize the [9]aneS₃ analog using **6a**, resulting in no evidence of the formation of [Pd(fpp)([9]aneS₃)](PF₆). While crude products **1b–5b** were obtained in high purity, further purification was achieved by recrystallization using nitromethane/diethyl ether or slow evaporation from acetonitrile. For comparison with the [9]aneS₂O complex

Scheme 2

2b, the complex $[\text{Pd}(\text{ppyCHO})([\text{9}] \text{aneS}_3)](\text{PF}_6)$ **2c** was prepared using the same procedure except for using the solvent CH_3NO_2 . Complexes **1b–5b** and **2c** were fully characterized by combustion analyses, ATR-IR, and ESI-MS. The identity of the molecular monocation of each complex was confirmed by observation of the expected mass and isotopic pattern based on the predicted formulas.

NMR spectroscopy

$[\text{Pd}(\text{C}^{\wedge}\text{N})(\mu\text{-O}_2\text{CCH}_3)_2]$ complexes. Proton and carbon NMR spectroscopy confirmed cyclometallation and assembly of the $[\text{Pd}(\text{C}^{\wedge}\text{N})(\mu\text{-O}_2\text{CCH}_3)_2]$ complexes **2a** and **6a**. Fig. S1 and S2† show the ^1H NMR spectra of **2a** and **6a**, respectively. The cyclometallation is confirmed as each aromatic ligand displays one less ^1H resonance than the corresponding free ligand and downfield coordination induced chemical shifts are typical to those previously observed.⁸ Two sets of aromatic peaks are present, as expected for *syn* and *anti* isomers of these dimers (Scheme S1†). The major isomer present in solution is the *anti* isomer, as confirmed by the larger integration of the two equivalent acetate methyl groups compared with the sum of the integration of the inequivalent acetate methyl groups of the *syn* isomer. Based on the acetate resonances, the *anti/syn* ratio is about 5 : 1 for **2a** and 10 : 1 for **6a**. Carbon NMR of **2a** and **6a** (Fig. S3 & S4,† respectively) and fluorine NMR of **6a** (Fig. S5†) are consistent with the presence of two isomers with a predominance of the *anti* isomer. The lower symmetry of the bridging acetate groups of the *syn* isomer is seen in both the carboxylate and methyl carbons of the ^{13}C spectrum. The low solubility of **6a** in CD_2Cl_2 precluded acquisition of a high-quality ^{13}C spectrum.

$[\text{Pd}(\text{C}^{\wedge}\text{N})([\text{9}] \text{aneS}_2\text{O})](\text{PF}_6)$ complexes. Room temperature ^1H NMR of the complexes $[\text{Pd}(\text{C}^{\wedge}\text{N})([\text{9}] \text{aneS}_2\text{O})](\text{PF}_6)$ clearly demonstrates the bonded cyclometallating ligand is retained with small but significant changes in the aromatic region associated with ligand exchange of acetate for $[\text{9}] \text{aneS}_2\text{O}$. Proton resonances in the region of the coordinated $[\text{9}] \text{aneS}_2\text{O}$ ligand are shifted relative to the free ligand (3.88 ppm ($-\text{CH}_2\text{OCH}_2-$), 3.02 ppm ($-\text{SCH}_2\text{CH}_2\text{S}-$), 2.77 ppm ($-\text{OCH}_2\text{CH}_2\text{S}-$) in CD_3NO_2) but show complicated behavior. Fig. 1 shows the ^1H NMR spectrum of **2b** as a typical example. The spectrum shows seven inequivalent aromatic protons of the coordinated ppyCHO ligand with integration, chemical shifts, peak widths, and spin-spin splitting as expected. The singlet at 7.91 ppm partially overlaps with a doublet at 7.94 ppm. The aldehyde proton appears as a single peak with a chemical shift further downfield (9.93 ppm). Comparison with the aliphatic region indicates complicated behavior of the coordinated $[\text{9}] \text{aneS}_2\text{O}$, with the presence of peaks with large variable widths. A simple interpretation of the narrowest peaks in this region (4.45, 4.00, 3.38 ppm) might suggest these represent an exodentate conformation of the coordinated $[\text{9}] \text{aneS}_2\text{O}$ (Scheme 3).

The resonance at 4.45 ppm is assigned as the four hydrogens of carbons 2 and 9 of the macrocycle and is shifted downfield compared to the analogous peak of the free ligand

Fig. 1 ^1H NMR of $[\text{Pd}(\text{ppyCHO})([\text{9}] \text{aneS}_2\text{O})](\text{PF}_6)$ (**2b**), in CD_3NO_2 at 23 °C. Top: Aromatic region. Bottom: Coordinated $[\text{9}] \text{aneS}_2\text{O}$ region. Both plots retain the same ppm and intensity scales. * indicates peaks associated with residual CD_2HNO_2 .

Scheme 3 Endodentate/exodentate equilibrium behavior of $[\text{9}] \text{aneS}_2\text{O}$ contrasted with fluxional behavior of $[\text{9}] \text{aneS}_3$ in palladium(II) cyclometallated complexes.

(3.88 ppm). The resonance at 4.00 ppm is assigned as the four hydrogens of carbons 3 and 8 of the macrocycle ligand and is shifted considerably downfield compared to the free ligand (2.77 ppm). The resonance at 3.38 ppm is assigned as the four hydrogens of carbons 5 and 6 of the macrocycle is shifted least downfield of the coordinated $[\text{9}] \text{aneS}_2\text{O}$ ligand compared to the resonance of the free ligand (3.02 ppm). Exodentate coordination of $[\text{9}] \text{aneS}_2\text{O}$ in **2b** contrasts with the previous report of $\text{Pd}([\text{9}] \text{aneS}_2\text{O})\text{Cl}_2$ ¹⁴ where the solution macrocycle conformation was assigned as endodentate, consistent with the only X-ray structure known at the time of publication. A simple ana-

lysis of the spin–spin splitting patterns of these peaks in **2b** are also not consistent with this assignment. However, metal complexes of mixed donor macrocycles such as [9]aneS₂O have been shown to exhibit one of several ligand conformation possibilities in X-ray structural data.²⁸ Allowing for dynamic ligand conformers as well as observation of large peak widths suggest dynamics are present in the ethylene straps of the coordinated [9]aneS₂O. Selective proton decoupling experiments confirmed coupling of the resonances at 4.45 ppm and 4.00 ppm and no coupling of either of these with the resonance at 3.38 ppm. This interpretation does not account for the extremely broad signal in the 3.45–3.95 ppm region or the broad resonance at 3.27 ppm. Integration of the three assigned resonances of an exodentate form of [9]aneS₂O in **2b** account for 50% of the population of the sample (6H of 12H) based on comparison with the aromatic region (each nonequivalent aromatic resonance as one proton). If the broad regions integrations are summed, they account for the remaining 6 protons for the expected btp:[9]aneS₂O stoichiometry of the compound.

Carbon NMR at room temperature (Fig. 2) showed analogous behavior with the presence of the expected number of peaks in the aromatic region (11 inequivalent resonances) and

an aldehyde carbon peak at 194.04 ppm. The aliphatic [9]aneS₂O portion of the spectrum shows six broad peaks shifted downfield relative to the free ligand (74.93 ppm, 35.81 ppm, 34.26 ppm). To be consistent with the ¹H NMR interpretation of exodentate [9]aneS₂O, the two broad resonances near 77 ppm, and four broad resonances between 36–46 ppm would be assigned as the carbons in the 2 and 9 positions, and 3,5,6,8 positions, respectively. The large peak widths again indicate the possibility of dynamics in the bound [9]aneS₂O ligand. The six broad carbon peaks could be consistent with one of two possible explanations. The presence of six peaks could be the result of a single solution species bearing a coordinated [9]aneS₂O ligand with the lack of axial symmetry enforced by the cyclometallating ppyCHO ligand or the presence of two nonidentical similar dynamic species in similar population, each with 3 unique ¹³C environments for the [9]aneS₂O ligand. The second explanation could account for the presence of both *endo* and *exo* conformers.

Variable temperature NMR of [Pd(C[^]N)([9]aneS₂O)](PF₆) complexes

To further investigate the dynamic behavior of the [9]aneS₂O ligand, we performed a variable temperature ¹H NMR study. Fig. 3 displays the aliphatic region of the ¹H NMR of complex **2b** in CD₃NO₂ in a range from –15 °C to 70 °C.

Small chemical shift changes are observed for all aromatic proton resonances, but the number of peaks, integrations, and splitting remain the same across all temperatures, with some reasonable broadening at higher temperatures. The aliphatic region, however, shows large changes in this temperature range. Assuming the interpretation that peaks near 4.45, 4.00, and 3.40 represent an exodentate form of the bonded [9]aneS₂O ligand, these resonances appear to show small monotonic chemical shift changes with temperature, broaden at temperatures below 23 °C, then demonstrate more complexity with inequivalence present in a more rigid exodentate metal complex at –15 °C. The remaining peaks at 70 °C, in the region near 3.64 ppm and 3.25 ppm, are assigned as an endodentate conformation of the bound ligand [9]aneS₂O. These peaks account for the integration of 4 and 2 hydrogens, respectively. The complex symmetric peak centered at 3.64 ppm (70 °C) broadens, coalesces near 23 °C, then splits into two resonances at 3.80 ppm and 3.48 ppm. The peak at 3.25 ppm (70 °C) coalesces near the same temperature, splitting into a complicated feature near 3.19 and 3.32 ppm. This temperature dependent behavior of the endodentate conformation is interpreted as fast fluxional behavior of the *endodentate* [9]aneS₂O at higher temperatures, coalescence at temperatures near room temperature as the barrier to 1,4-metallotropic shifts is approached, and a nonfluxional endodentate conformation is observed at the lowest temperatures.

The dynamic behavior of endodentate [9]aneS₂O has not been observed previously. Only two other relevant examples of palladium [9]aneS₂O complexes exist. The NMR of the homoleptic bis complex [Pd([9]aneS₂O)₂](PF₆)₂¹⁸ is reported as consistent with the exodentate X-ray structure, though the authors

Fig. 2 ¹³C NMR of [Pd(ppyCHO)([9]aneS₂O)](PF₆) (**2b**), in CD₃NO₂ at 23 °C. Top: Aromatic region. Two nearly overlapping peaks near 154 ppm. Bottom: Coordinated [9]aneS₂O region. Both plots retain the same ppm and intensity scales. * indicates peaks associated with residual CD₂HNO₂.

Fig. 3 Variable temperature ^1H NMR of $[\text{Pd}(\text{ppyCHO})([9]\text{aneS}_2\text{O})](\text{PF}_6)$ (**2b**), in CD_3NO_2 , aliphatic region. * indicates peaks associated with residual CD_2HNO_2 .

also note that ^1H NMR cannot differentiate between exodentate and endodentate coordination modes. This may be true for bis homoleptic complexes of $[9]\text{aneS}_2\text{O}$ but not in general. The complex $\text{Pd}([9]\text{aneS}_2\text{O})\text{Cl}_2$, of which polymorphs of endodentate and exodentate forms are now known,¹⁹ is reported as consistent with the endodentate $[9]\text{aneS}_2\text{O}$ geometry of the only known structure at that time.¹⁴ As the growth of endodentate and exodentate $\text{Pd}([9]\text{aneS}_2\text{O})\text{Cl}_2$ polymorphs is controlled by small changes in crystal growth temperature (higher temperature favors exodentate form), simultaneous thermodynamic access to both bound ligand conformations is possible. If the barrier in fact to interconversion between *exo-2b* and *endo-2b* is sufficiently low, at equilibrium, the population of the two conformers should change as a function of temperature, assuming one conformer is more stable than the other as expected. Based on integration of the ^1H NMR, the population of the *endo* and *exo* forms of **2b** are essentially unchanged and nearly equal across the temperature range. To explain this apparent temperature insensitivity to equilibrium population in this temperature range, both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are required to be small. Subtle intramolecular geometry differences between the *endo* and *exo* forms and flexibility of the nine-membered macrocycle ring could justify a small $\Delta S^\ddagger$. A small $\Delta H^\ddagger$ for *endo/exo* conversion is also reasonable as the enthalpy required to overcome the expected weak axial $\text{Pd}\cdots\text{O}$ interaction present in the *endo* form to reach the *exo* form should be minimal.

A barrier for the dynamic fluxional behavior of endodentate **2b** can be estimated from the coalescence temperatures of the

endo $[9]\text{aneS}_2\text{O}$ NMR resonances according to the equation $\Delta G^\ddagger = RT_c[22.96 + \ln(T_c/\delta\nu)]$ in J mol^{-1} .²⁹ The free energy of activation calculated from the NMR at the coalescence temperatures suggests a barrier of approximately 12 kcal mol^{-1} . A lower barrier of approximately 9 kcal mol^{-1} has been estimated for the fluxional endodentate behavior of $[9]\text{aneS}_3$ in the complex $[\text{Pt}(\text{phen})([9]\text{aneS}_3)](\text{PF}_6)_2$ with an even lower barrier for $[\text{Pd}(\text{bpy})([9]\text{aneS}_3)](\text{PF}_6)_2$.³⁰

Further NMR studies were performed to determine if the NMR behavior of **2b** is similar to others in this series of $[9]\text{aneS}_2\text{O}$ complexes. Variable temperature ^1H NMR spectra were acquired for the complex $[\text{Pd}(\text{pbt})([9]\text{aneS}_2\text{O})](\text{PF}_6)$ (**5b**) in the range of 5°C to 50°C (Fig. S6†). Similar behavior is observed, consistent with the interpretation of the VT-NMR of **2b**. As several peaks of $[9]\text{aneS}_2\text{O}$ overlap with solvent of crystallization and NMR solvent, and peaks attributed to *endo* and *exo* forms overlap, further analysis including integration of peaks to determine populations of the two forms is precluded. Variable temperature proton NMR spectra of **3b** were recorded in the range of 22°C to 75°C (Fig. S7†). While the 22°C spectrum **3b** is difficult to interpret with overlapping broad $[9]\text{aneS}_2\text{O}$ peaks, the high-temperature spectrum of **3b** is quite similar to that of **2b**. In a series of variable temperature ^1H NMR spectra collected of **4b** (0°C to 50°C , Fig. S8†) all peaks of the $[9]\text{aneS}_2\text{O}$ region are very broad near room temperature. This behavior is in contrast with complexes **2b**, **3b**, and **5b**. Interesting changes are also observed in the $[9]\text{aneS}_2\text{O}$ region of the ^{13}C NMR of **4b** with changes in temperature (Fig. S9†). The carbon NMR of **4b** shows a progression from a six peak

Table 1 Crystal data, data collection, and refinement parameters for [Pd(ppy)([9]aneS₂O)](PF₆) (**1b**), [Pd(ppyCHO)([9]aneS₂O)](PF₆) (**2b**), [Pd(btp)([9]aneS₂O)](PF₆) (**4b**), and [Pd(pbt)([9]aneS₂O)](PF₆) (**5b**)

Compound	1b	2b	4b ·CH ₃ NO ₂	4b ·CH ₃ CN	5b ·CH ₃ NO ₂
Formula	C ₁₇ H ₂₀ F ₆ NOPPdS ₂	C ₁₈ H ₂₀ F ₆ NO ₂ PPdS ₂	C ₁₉ H ₂₀ F ₆ NOPdS ₃ ·CH ₃ NO ₂	C ₁₉ H ₂₀ F ₆ NOPdS ₃ ·CH ₃ CN	C ₁₉ H ₂₀ F ₆ NOPdS ₃ ·CH ₃ NO ₂
Lattice type	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1̄	<i>P</i> 1̄	<i>P</i> 1̄
<i>a</i> , Å	14.9321(11)	14.3588(14)	8.1573(8)	8.200(3)	8.3654(11)
<i>b</i> , Å	11.8841(9)	12.2238(13)	11.5199(12)	11.574(5)	11.5711(15)
<i>c</i> , Å	12.3550(9)	13.3861(14)	14.1783(14)	13.934(5)	14.3794(19)
α , °	90	90	80.646(6)	81.388(6)	95.561(7)
β , °	110.699(8)	114.020(8)	73.894(5)	73.532(5)	105.629(7)
γ , °	90	90	77.935(6)	79.026(6)	106.146(8)
<i>V</i> , Å ³	2050.9(3)	2146.1(4)	1244.0(2)	1238.5(8)	1265.1(3)
<i>Z</i>	4	4	2	2	2
<i>F</i> _{wt} , g mol ^{−1}	569.84	597.85	686.96	666.97	686.96
<i>D</i> _c , Mg m ^{−3}	1.845	1.850	1.834	1.788	1.803
Total reffs.	20 724	21 879	13 061	12 954	12 850
Unique reffs.	4698 (<i>R</i> _{int} = 0.029)	4926 (<i>R</i> _{int} = 0.052)	5700 (<i>R</i> _{int} = 0.025)	5653 (<i>R</i> _{int} = 0.023)	5752 (<i>R</i> _{int} = 0.035)
Data, rest., param.	4698/0/262	4926/21/302	5700/0/326	5653/0/317	5752/47/381
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0325, 0.0682	0.0473, 0.1073	0.0326, 0.0818	0.0292, 0.0714	0.0729, 0.1449
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0416/0.0717	0.0674, 0.1170	0.0371, 0.0842	0.0328, 0.732	0.0843, 0.1495
Goodness-of-fit (<i>F</i> ²)	1.038	1.037	1.080	1.075	1.185

spectrum of broad line widths at 0 °C, to broader peaks at 22 °C, and finally to the absence of [9]aneS₂O peaks at 50 °C. At least small differences in fluxional endodentate [9]aneS₂O and/or endodentate/exodentate equilibria are expected as a function of the cyclometallated ligand. In the case of **4b**, the temperature dependent ¹H and ¹³C NMR are consistent with similar barriers for both types of processes.

[Pd(ppyCHO)([9]aneS₃)](PF₆). The NMR of cyclometallated [9]aneS₃ complexes of Pd(II) and Pt(II) have been reported by our group previously.^{8,9} As a means for direct comparison with the complex [Pd(ppyCHO)([9]aneS₂O)](PF₆) **2b**, we synthesized the [9]aneS₃ analog [Pd(ppyCHO)([9]aneS₃)](PF₆) **2c** and present the ¹H and ¹³C NMR in Fig. S10.† The ¹H NMR of **2c** in the aliphatic region shows a highly symmetric AA'BB' peak pattern consistent with a fluxional endodentate [9]aneS₃ ligand. No evidence of an exodentate form is present. The ¹³C NMR of **2c** displays a single peak for the six equivalent methylene carbons of the fluxional endodentate [9]aneS₃ ligand. Assignment of the endodentate conformation of [9]aneS₃ is consistent with the X-ray structure of **2c** as well. All other reported complexes of Pt and Pd with [9]aneS₃ and cyclometallated ligands and related diimine ligands^{30–36} show the same solution behavior in ¹H and ¹³C NMR. We have noted that the lack of axial mirror symmetry in this cyclometallated complex (and previously reported complexes) is not manifested in lower symmetry of the fluxional [9]aneS₃ as the ¹³C NMR spectrum indicates only a single averaged ¹³C environment. Lack of any solution NMR evidence of exodentate [9]aneS₃ compared with [9]aneS₂O suggests that axial Pd...S interactions may be stronger than analogous axial Pd...O interactions.

X-ray structures

A summary of data collection and refinement for five X-ray structures collected on complexes of the form [Pd(C^N)([9]aneS₂O)](PF₆) (**1b**, **2b**, **4b**·CH₃CN, **4b**·CH₃NO₂, **5b**·CH₃NO₂) are

presented in Table 1. Table S1† includes data collection and refinement for X-ray structures of the acetate bridged-dimers **2a** and **6a**, as well as the [9]aneS₃ complex **2c**.

[Pd(C^N)(μ-O₂CCH₃)]₂ complexes. The structures of [Pd(ppyCHO)(μ-O₂CCH₃)]₂ (**2a**) and [Pd(fpp)(μ-O₂CCH₃)]₂ (**6a**) were collected as synthetic intermediates in the preparation of subsequent [9]aneS₂O complexes. An anisotropic thermal displacement ellipsoid diagrams of **2a** is shown in Fig. 4 (**6a** in Fig. S11†).

These dimer structures consist of two four-coordinate approximately square pyramidal Pd(II) centers, each with a chelating cyclometallating ligand, two bridging acetate groups, and a short axial Pd...Pd interaction. The *anti* isomer is

Fig. 4 Thermal ellipsoid perspective of [Pd(ppyCHO)(μ-O₂CCH₃)]₂ (**2a**) (50% probability, H atoms omitted for clarity).

observed exclusively in each structure, where the cyclometallating ligands of a dimer are related by a non-crystallographic 2-fold axis. The *anti* isomer is commonly observed for these types of cyclometallated dimers. In the case of **2a** and **6a**, these structures additionally have steric constraints arising from the substituents in the 4-position of the phenyl ring of the cyclometallating ligands, consistent with the observed *anti* isomer in the solid-state. In the structure of **6a**, the aldehyde groups are nearly planar with the phenylpyridine ligands (torsion angles C22–C21–C24–O2 = $-1.9(9)^\circ$, C10–C9–C12–O1 = $5.3(8)^\circ$) and carbonyl groups are directed toward the Pd in the coordination plane. Typical Pd–N and Pd–C bond lengths are observed for μ -acetate bridged complexes of this type. The pattern of longer Pd–N bonds and shorter Pd–C bonds is reasonable given the carbanionic character of the Pd bonded carbon atoms of these ligands. The Pd–C bonds of **6a** (Pd1–C11 = 1.959(7) Å, Pd2–C23 = 1.948(5) Å) are quite similar to those of **2a** (Pd1–C11 = 1.955(4) Å, Pd2–C23 = 1.970(4) Å). These Pd–C bond lengths are also analogous to other cyclometallated Pd complexes, suggesting minimal effects on the Pd–C bonds of the strong electron-withdrawing CF₃ and moderately electron-withdrawing aldehyde groups. Likewise, the Pd–O bonds *trans* to the stronger σ -donor Pd–C bonds are slightly longer (≈ 0.1 Å) than the Pd–O bonds *trans* to the Pd–N bonds. As these dimers adopt a sandwich-type structure, short intramolecular Pd...Pd contacts are present. The Pd...Pd separations (**6a** = 2.8673(7) Å, **2a** = 2.8553(5) Å) are shorter than the van der Waals radii sum for two Pd atoms (3.26 Å). The angle between least-squares planes of the cyclometallating ligands (**6a** = 14.5° , **2a** = 17.9°) and shorter Pd...Pd separation of **2a** allow for a short intramolecular contact in **2a** (C22...C1 = 3.400 Å) and intradimer aromatic ring centroid distances (N1, C1–C5 centroid...C18–C23 centroid distance = 3.80 Å, N2, C13–C17 centroid...C6–C11 centroid distance = 3.84 Å) consistent with π – π stacking interactions described previously.³⁷

Notable intermolecular features are also present in the structures of **2a** and **6a**. Both structures pack as pairs of intramolecular dimers (Fig. S12 & S13†). Two nearest intramolecular dimers are related by inversion, with short inter-dimer Pd...Pd distances of 3.3606(6) Å and 3.4115(7) Å for **2a** and **6a**, respectively. The packing geometry prevents significant intermolecular π overlap of the ppy ligand moieties in both structures (shortest intermolecular pyridine...pyridine and pyridine...phenyl ring centroid distances = 6.88, 5.31 Å (**2a**), 7.41, 5.43 Å (**6a**)). However, the distances between neighboring inter-dimer parallel least-squares planes (atoms of coordination Pd sphere; **2a**, 3.16 Å; **6a**, 3.12 Å) as well as the Pd1–Pd2...Pd2 angles (**2a**, $167.16(2)^\circ$; **6a**, $170.47(1)^\circ$) suggests these inter-dimer interactions are important contributions to the packing in **2a** and **6a**. Each pair of dimers has neighboring dimer pairs at further distances that pack with geometry for minimal ppy moiety π overlap (shortest intermolecular pyridine...pyridine and pyridine...phenyl centroid distances = 4.12, 4.90 Å (**2a**); 5.05, 4.02 Å (**6a**)) indicative of significant lateral π slippage with longer Pd...Pd separations (**2a**, 5.7143(9) Å; **6a**, 5.1003(8) Å).

Fig. 5 Thermal ellipsoid perspective of the cation of [Pd(ppy)([9]aneS₂O)](PF₆) (**1b**, top) and [Pd(btp)([9]aneS₂O)](PF₆) (**4b**·CH₃NO₂, bottom) (50% probability, H atoms, anions, and solvent omitted for clarity).

[Pd(C[^]N)([9]aneS₂O)](PF₆) complexes. Anisotropic thermal displacement ellipsoid diagrams are presented for **1b** and **4b** in Fig. 5. In each of the related structures **1b**, **2b**, **4b**·CH₃NO₂, and **4b**·CH₃CN, and **5b**·CH₃NO₂, the molecular cation consists of a square planar Pd(II) center with a chelating cyclometallating ligand and an exodentate bound [9]aneS₂O ligand with two typical length Pd–S bonds. As observed in related structures of cyclometallated Pd [9]aneS₃ complexes, the Pd–N bonds are consistently slightly shorter than the Pd–C bonds. Likewise, the Pd–S bond *trans* to the Pd–N bond is about 0.1 Å shorter than the Pd–S *trans* to the Pd–C bond. The aldehyde functional group of the ligand in **2b** is oriented nearly in the ppy plane (O2–C18–C15–C16 = $176.5(5)^\circ$) pointed away from the Pd. Only the exodentate binding motif is observed for the [9]aneS₂O complexes of this study. This exodentate bonding is clear from the intramolecular Pd...O distances, which vary only slightly across this series (3.48–3.53 Å, Table 2). The oxygen atom of [9]aneS₂O is beyond van der Waals radii contact and oriented in a manner that precludes intramolecular interaction with Pd.

While [9]aneS₂O has been shown to bind in both *endo* and *exo* fashion, depending on the metal, within Pd complexes, only one example of endodentate [9]aneS₂O is reported (Pd([9]aneS₂O)Cl₂).¹⁴ One could envision either intramolecular or intermolecular factors favoring *exo* or *endo* bonding of [9]aneS₂O. Intramolecular features favoring exodentate bonding

Table 2 Selected intramolecular distances (Å), van der Waals radii sum comparisons, and macrocycle ligand binding descriptors for related heteroleptic Pd complexes of [9]aneS₂O and [9]aneS₃

Coligand(s)	[9]aneS ₂ O					[9]aneS ₃				
	Pd...O distance	vdW radii ^b sum – dist.	<i>Exo</i> or <i>Endo</i>	Macrocycle conformation	Ref.	Pd...S distance	vdW radii sum – dist.	<i>Exo</i> or <i>Endo</i>	Macrocycle conformation	Ref.
ppy	3.530(3)	+0.38	<i>exo</i>	[234]	^a	2.871(1)	–0.56	<i>endo</i>	[333]	9
ppyCHO	3.476(5)	+0.33	<i>exo</i>	[234]	^a	2.888(1)	–0.54	<i>endo</i>	[333]	^a
btp	3.481(2)	+0.33	<i>exo</i>	[234]	^{a,c}	2.909(2)	–0.52	<i>endo</i>	[333]	8
btp	3.454(2)	+0.30	<i>exo</i>	[234]	^{a,d}					
pbt	3.487(5)	+0.34	<i>exo</i>	[234]	^a	2.894(2)	–0.54	<i>endo</i>	[333]	8
bzq	NA	NA	NA	NA	NA	3.007(1)	–0.42	<i>endo</i>	[234], [333]	9
2Cl	2.957(1)	–0.19	<i>endo</i>	[234]	64	3.140(2)	–0.29	<i>endo</i>	[234]	65
2Cl	3.406(2)	+0.19	<i>exo</i>	[234]	64					
Homoleptic	3.379(5)	+0.23	<i>exo, exo</i>	[234], [234]	64	2.957(2)	–0.47	<i>endo, endo</i>	[333], [333]	66

^a This study. ^b van der Waals radii values S = 1.8 Å, Pd = 1.63 Å, O = 1.52 Å obtained from A. Bondi.⁶³ NA = not available. ^c CH₃NO₂ solvate. ^d CH₃CN solvate.

could include the macrocycle conformation. The bonded [9]aneS₂O macrocycle conformation observed in each of these structures is the [234] conformer, in the modified Dale notation.³⁸ The same conformation is observed in both the *endo* and *exo* polymorphs of Pd([9]aneS₂O)Cl₂ as well as the homoleptic complex [Pd([9]aneS₂O)₂](PF₆)₂¹⁸ (Table 2). Previous studies, using molecular mechanics calculations, have shown that strain energies for [9]aneS₃ complexes are significantly less for the [333] conformer compared with the [234] conformer.³⁹ The only [9]aneS₂O Pd complexes reported outside this study also exhibit the [234] conformer. This is consistent with smaller calculated conformer strain energy differences for mixed donor macrocycles (such as [9]aneS₂N) compared with macrocycles of a single donor atom type.³⁹ The lower symmetry [234] conformation may be favored for lower symmetry mixed donor macrocycles (such as [9]aneS₂O) as the C–O–C angle of [9]aneS₂O (~117°) is considerably larger than the C–S–C angle (101–105°), and a more asymmetric binding conformation can accommodate these significant angle differences. Another contribution that may help favor the exodentate conformation lies in a persistent short intramacrocyclic contact. A short [9]aneS₂O oxygen...H–C(position 5) contact (2.30–2.49 Å) less than van der Waals radii sum (average = –0.35 Å) is found in each of the structures of this study (Fig. S15†). While this C–H...O interaction is not expected to be a strong intramolecular feature, this contact could contribute to the stability of the exodentate conformation observed crystallographically. This interaction is also observed in the X-ray structures of the *exo* forms of M([9]aneS₂O)Cl₂ and [M([9]aneS₂O)₂](PF₆)₂, (M = Pd, Pt).

Intermolecular features were examined to identify potential influence on the preferred exodentate [9]aneS₂O bonding. The π -stacking interactions observed are discussed here in the context of formerly described motifs.³⁴ The structure of **1b** packs as isolated π -dimers in an out-out motif with a ppy ligand π - π parallel least-squares plane separation of 3.38 Å, with no intermolecular contacts involving oxygen (Fig. S16†). The packing of **2b** differs in that while π dimers are present with significant π overlap and close parallel separation (3.32 Å), each dimer has four additional nearly parallel dimers

with close aldehyde...pyridine π contacts (C18...O11 3.28 Å) (Fig. S17†). The oxygen of [9]aneS₂O in **2b** also has a short intermolecular contacts with a C–H bond of a nearby bonded [9]aneS₂O (O1...H6Aa = 2.67 Å). The aldehyde oxygen of the ppyCHO also has a short intermolecular contact with a C–H of nearby bonded [9]aneS₂O (O2...H5B = 2.63 Å). The structure of **4b-CH₃NO₂** has no [9]aneS₂O intermolecular oxygen contacts, and packs in an slipped infinite π -stack with an alternating out-out/in-in motif, at interplanar separations of 3.39 Å (out-out) and 3.46 Å (in-in) (Fig. S18†). The acetonitrile solvate **4b-CH₃CN** has similar intermolecular oxygen...hydrogen contact as **2b** (2.64 Å), and a π -stacking motif nearly identical to the nitromethane solvate structure (3.40 Å out-out, 3.46 Å in-in) (Fig. S18†). The structure of the pbt analog **5b-CH₃NO₂** is very similar to that of **4b-CH₃CN** with the same π -stacking motif (3.39 Å out-out, 3.60 Å in-in) and intermolecular oxygen...hydrogen contact (2.55 Å) (Fig. S19†). Any direct relationship between the cyclometallated ligand and the resulting π -stacking motif adopted is unclear. While the anion remains the same across this series of structures, the presence or absence of solvent (none, CH₃NO₂, CH₃CN) and temperature effects (173 K for **1b**, **4b-CH₃NO₂**, **4b-CH₃CN**, **5b-CH₃NO₂**; 293 K for **2b**) could play a role in the observed solid-state π -stacking motif. While π -stacking is found in all these solid-state structures, neither π -interactions nor the intermolecular C–H...O interactions found in some (not all) of the structures in this series are not expected to strongly influence *exo/endo* preferences of this series, as they are not particularly short.

Structure of [Pd(ppyCHO)([9]aneS₃)](PF₆) (2c). A careful comparison of the structure of **2c** with the analogous [9]aneS₂O structure of **2b** gives insight into structural effects induced by the macrocyclic ligand, as neither structure contains solvent, both have the same anion, and crystal growth conditions were identical. The molecular cation of **2c** consists of a square pyramidal Pd(II) center with a chelating cyclometalating ligand; an endodentate bound [9]aneS₃ ligand with two typical Pd–S bonds, and a longer intramolecular Pd...S axial interaction (2.888(1) Å). Anisotropic thermal displacement ellipsoid diagrams are presented for **2b** and **2c** in Fig. 6. The

Fig. 6 Thermal ellipsoid perspective of the cation of [Pd(ppyCHO)([9]aneS₂O)](PF₆) (**2b**, top) and [Pd(ppyCHO)([9]aneS₃)](PF₆) (**2c**, bottom) (50% probability, H atoms, and anions omitted for clarity). Larger thermal parameters for **2b** are due to 293 K data collection (**2c** collected at 173 K).

aldehyde functional group of the ligand in **2c** is oriented nearly in the ppy plane (O2–C18–C15–C14 = 178.0(3)°) but is pointed toward the Pd. Most intramolecular features of **2b** and **2c**, including the Pd–C, Pd–N, and Pd–S bonds, exhibit remarkably similar metrics such as the pattern and magnitudes of bond lengths. However, the structure of **2c** shows a displacement of the Pd of 0.14 Å from the plane formed by the coordinated atoms in the direction of the axial Pd...S interaction, while **2b** shows a smaller such distortion (0.04 Å). The endodentate axial sulfur atom in **2c** lies 0.54 Å closer to Pd than the Pd/S van der Waals radii sum and in an orientation for favorable orbital overlap with a Pd d_{z^2} orbital. The Pd...S axial interaction distance falls squarely in the range observed for similar Pd cyclometallated complexes (Table 2). This endodentate bonding of [9]aneS₃ is consistent with the appearance of a fluxional [9]aneS₃ observed in solution by ¹H and ¹³C NMR of **2c** and the observation that essentially all Pd structures involving [9]aneS₃ (92 structures⁴⁰) demonstrate endodentate bonding. The single report of an exodentate bonded [9]aneS₃ at Pd for the complex [Pd([9]aneS₃)(κ¹-O₂CCH₃)₂] surprisingly yields an NMR consistent with fluxional endodentate [9]aneS₃ in room temperature CD₃NO₂ solution.⁴¹ While

specific intermolecular packing forces may be the cause for the exodentate binding in this specific solid-state structure of [Pd([9]aneS₃)(κ¹-O₂CCH₃)₂], the barrier to *endo/exo* conversion must not be large for facile access of both bonding modes.

The intermolecular features of **2c** are significantly different from those of **2b**. The structure of **2c** packs as isolated π -dimers with an in-in motif and an intradimer interplanar separation of 3.37 Å (Fig. S20†). While nearby dimers also stack in a parallel layered fashion (interdimer planar separation of 2.92 Å), displacement of neighboring ppy ligands prevents infinite π -stacking. Also, within each inversion-related π -dimer there is a pair of close CH...S contacts at 2.89 Å involving the axial sulfur and C–H bond of the ppyCHO ligand.

DFT calculations

DFT calculations were carried out on **4b** to help understand features of the electronic structure and the low-lying excited states of this compound. Comparison of the crystal structure geometry of the cation of **4b** with that of the geometry minimized structure demonstrates they are remarkably similar (Fig. S21,† RMS deviation of 25 atom coordinate pairs = 0.131). The frontier orbitals of **4b** from DFT calculation were examined to better understand the electronic structure of the molecular cation. The calculated HOMO and LUMO of **4b** are shown in Fig. 7.

The HOMO of **4b** has orbital contributions from the d_{xz} orbital of Pd (along C–Pd–S bonding vector) as well $p\pi$ btp ligand orbitals. The LUMO of **4b** consists mainly of the σ bonding framework of the Pd coordination sphere with contributions from bonded N, C, and S atoms with the $d_{x^2-y^2}$ orbital at Pd. As expected from the bonded exodentate geometry of the [9]aneS₂O ligand, no significant interaction of the oxygen atom of the ligand with the Pd orbitals is present. This is in

Fig. 7 DFT calculated HOMO (left column) and LUMO (right column), of complex **4b**, [Pd(btp)([9]aneS₂O)]⁺. Upper perspective perpendicular to coordination plane, lower perspective parallel to coordination plane. Plots at isovalue 0.03, density 0.0004.

stark contrast with previous calculations on the related $[\text{Pd}(\text{ppy})([9]\text{aneS}_3)]^+$ complex⁹ where the Pd d_{z^2} orbital and a p orbital of the axial sulfur of the endodentate $[9]\text{aneS}_3$ showed significant orbital contributions in the HOMO. The LUMO, however, is remarkably similar for both **4b** and $[\text{Pd}(\text{ppy})([9]\text{aneS}_3)]^+$.

In an effort to help explain the variable temperature NMR results for **2b**, free energies were calculated for both *endo* and *exo* forms of the related complex **4b**. These *endo* and *exo* bonding mode geometries were then used in a calculation to determine a transition state geometry and energy barrier to conversion between these complexes (Fig. 8). DFT calculations on related systems have been used previously to study the relative energies of energies of *endo* and exodentate bonding modes of 9-membered tridentate macrocycles and the effects of axial donor atoms.^{42,43}

The thermodynamically more stable *exo* form is consistent with the obtained X-ray structure of **4b** (exodentate). The *endo* conformer, however, is less stable by only 2.2 kcal mol⁻¹. This difference in calculated energies is reversed in a study of the *endo/exo* forms of $\text{Pd}([9]\text{aneS}_2\text{O})\text{Cl}_2$ (*endo* 4.6 kcal mol⁻¹ lower in energy than *exo*).⁴³ The calculated barrier to interconversion from *exo-4b* to *endo-4b*, 10.6 kcal mol⁻¹, suggests that a significant population of the less stable *endo* form is reasonable near room temperature. The significant presence of both *endo* and *exo* forms of **4b** and a relatively low barrier to interconversion is also consistent with previous work on the related compound $\text{Pd}([9]\text{aneS}_2\text{O})\text{Cl}_2$, for which X-ray crystal structures were obtained for both *endo* and *exo* forms. In this crystallographic study of $\text{Pd}([9]\text{aneS}_2\text{O})\text{Cl}_2$, the *endo* form was favored at lower crystal growth temperatures, had a higher density, and calculations of total and cohesive energies supported the *endo* form as more stable than the *exo* form.¹⁹ An explanation for this reversal in favored bonding mode for **4b** lies in the coligand donor/acceptor properties. As the benzothienylpyridine carbanion of **4b** is both a strong σ -donor and π -acceptor, electron density at the metal is enhanced relative to the chloride π -donor ligands of $\text{Pd}([9]\text{aneS}_2\text{O})\text{Cl}_2$. This could account for the increased stability of the *endo* form for the more electron

poor Pd center of $\text{Pd}([9]\text{aneS}_2\text{O})\text{Cl}_2$ where the axial oxygen donor supplies electron density in the *endo* form at a distance appropriate for orbital overlap with the metal. Related work^{31,44} on Pt, suggests that increased electron density at the metal provided by coligands leads to longer axial d⁸ metal...sulfur distances in $[9]\text{aneS}_3$ complexes. Longer Pd...O distances will by definition diminish the electron donation capacity of the axial oxygen. In the complex **4b**, the cyclometalating btp ligand provides an electron-rich metal center that does not significantly effect the stability of an *exo* form (as no close oxygen interaction is possible) but rather diminishes the need for donation by an *endo* oxygen, resulting in less stability of the *endo* bonding mode.

In an attempt to quantify any Pd...O interactions in the *endo* and *exo* forms of **4b**, a Natural Bond Order Analysis⁴⁵ was carried out on each form. Using the natural population analysis,⁴⁶ calculated atomic charges (Table S2†) on Pd are positive values (~ 0.51 au) with smaller positive values for $[9]\text{aneS}_2\text{O}$ sulfur atoms (~ 0.35 au). Ligated C19 bears a small negative charge (~ -0.05 au), while nitrogen (~ -0.48 au) and oxygen (~ -0.62 au) bear a greater negative charge. A close comparison of changes in atomic charges between *endo* and *exo* forms reveals small changes in atomic charge involving oxygen (*endo* = -0.612 au; *exo* = -0.634 au) while the ligated atoms show little change. The difference between the Pd/O charges for the *endo* form (1.13 au) is similar to the difference for the *exo* form (1.14 au), suggesting little to no interaction. If significant electron donation of the oxygen through a lone pair to the Pd atom was present in the *endo* form, less negative charge on the oxygen atom and less positive charge at the Pd might be observed. In the case of calculations on the *endo* and *exo* forms of $\text{Pd}([9]\text{aneS}_2\text{O})\text{Cl}_2$, a larger decrease in charge difference was observed in the *endo* form than the *exo* form compared with the atomic charges in our system.⁴³ Results obtained from calculating atomic charges using the CHELPG scheme (Charges from Electrostatic Potentials using a Grid based method) showed similar effects, with no strong evidence for charge transfer in the *endo* form.

Through atomic charges do not indicate significant interactions in the *endo* form of **4b**, we looked for evidence of an axial interaction in the second-order perturbative estimates of 'donor-acceptor' interactions in the NBO basis. A few very weak interactions were found involving filled oxygen Lewis-type lone pair orbitals acting as donors to empty antibonding non-Lewis Pd orbitals (Table S3†). No such donor-acceptor interactions involving oxygen lone pairs and Pd orbitals are present in the *exo* form. As a control, we compared these results to the $[9]\text{aneS}_3$ analogue, $[\text{Pd}(\text{btp})([9]\text{aneS}_3)]^+$. A significant interaction (8.5 kcal mol⁻¹) is found here between the axial sulfur and Pd in this complex where the $[9]\text{aneS}_3$ binds in an endodentate fashion. A persistent axial Pd...S interaction in $[\text{Pd}(\text{btp})([9]\text{aneS}_3)]^+$ is consistent with exclusive fluxional endodentate $[9]\text{aneS}_3$ NMR results of this complex, and a short Pd...S axial distance in the crystal structure.

The lack (*exo*) or presence (*endo*) of an axial oxygen is not likely the sole contributor to the stability of these two forms.

Fig. 8 Calculated free energy diagram of *endo* and *exo* bonding modes of $[\text{Pd}(\text{btp})([9]\text{aneS}_2\text{O})]^+$ (**4b**).

Others factors need to be considered. There is a possibility that ring conformers preferred for endodentate and exodentate coordination may differ significantly, leading to a metal complex macrocycle preference for conformation solely based on the ligand. Previously reported DFT calculations performed suggest the unligated [9]aneS₂O exodentate form is lower in energy than the endodentate geometry by 3.5 kcal mol⁻¹.⁴³ While a barrier for interconversion of these geometries was not calculated, this difference in *endo/exo* stabilities is similar to the difference calculated for the conformers of **4b**. Even within endodentate and exodentate metal bonding modes, several common conformers differing by arrangements of *gauche* torsions are observed amongst complexes of [9]aneS₃ and [9]aneS₂O, including the [234], [333], and [12 222] conformers, which also differ in energy. X-ray structural data for cyclometallated Pd complexes suggests that [9]aneS₃ is the preferred [333] endodentate conformation, while [234] is most common for exodentate [9]aneS₂O. Solvent incorporation in a crystal structure or intermolecular solid-state packing forces could also influence the stability of endodentate *vs.* exodentate ligand binding. In the case of the two solvatomorphs of **4b**, the solvent seems to play a negligible role as the exodentate bonding mode and [234] conformer are the same for both structures, and intermolecular packing is nearly identical.

The transition state geometry calculated for the *exo/endo* bonding interconversion of **4b** is shown in Fig. 9, overlapped with the coordinates of the energy minimized calculated *endo* and *exo* bonding geometries. The overall geometry at Pd and the btp ligand is virtually unchanged. The calculated intra-molecular Pd...O distances (*exo* = 3.65 Å, *endo* = 2.93 Å) agree well with experimental values for *exo-4b* (3.481(2) Å, 3.454(2) Å) and the Pd([9]aneS₂O)Cl₂ *endo* polymorph (2.957(1) Å). The transition state geometry indicates a swing of the oxygen atom through the cavity of the [9]aneS₂O macrocycle, achieving a shorter Pd...O distance in the transition state (2.83 Å) than in the *endo* form, rather than outside and away from the Pd. This relatively minor geometry change accompanying the *endo/exo* interconversion is consistent with a small entropy change proposed to help explain the dynamic NMR results. Also, comparison of simple van der Waals surface volume calculations of these *exo*, transition state, and *endo* forms of **4b** are consistent with small overall geometric changes (*endo* = 457.6 Å³, t.s. = 468.4 Å³, *exo* 458.1 Å³). Accompanying this large change in the Pd...O distance is a significant bond angle change at the oxygen. The C–O–C bond angle changes from 117.8° in the *exo* form, to 124.7° in the transition state, and settling at 116.7° in the *endo* form, with negligible change in the C–O bond lengths. This may hint at why dynamic *endo/exo* conversion has not been observed for [9]aneS₃. The C–S bonds in [9]aneS₃ are considerably longer compared with C–O bonds in [9]aneS₂O (average C–S length 1.80 Å; average C–O length = 1.42 Å). If a similar mechanism is invoked in a [9]aneS₃ d⁸ metal complex, the swing of the axial S through the macrocycle ring could yield a prohibitive barrier for interconversion as the sulfur would pass even closer to the metal. Alternately, the axial metal...S interaction is simply stronger (than metal...O),

Fig. 9 Overlap of DFT calculated geometries of *endo* (green), *exo* (red), and transition state (blue) of [Pd(btp)([9]aneS₂O)](PF₆) (**4b**). Oxygen atoms of [9]aneS₂O ligands shown as spheres. Above: Side view of changes in [9]aneS₂O geometry. Below: View perpendicular to the coordination plane.

and regardless of barrier to interconversion, the endodentate conformer is highly favored through sulfur lone pair overlap with the d_{z²} metal orbital. Further computational studies are underway to better understand the strength and nature of these types of axial interactions.

Conclusions

A series of cyclometallated complexes of Pd(II) with [9]aneS₂O were prepared in a synthetic fashion similar to their [9]aneS₃ derivatives. Marked differences, however, are observed in their solution behavior and solid-state structures. NMR spectra of these [9]aneS₂O complexes indicate the presence of both exodentate and endodentate bonding modes of this macrocycle. X-ray crystal structures demonstrate only exodentate bonding of [9]aneS₂O with no Pd...O axial interactions in the solid-state. Only weak intermolecular π -stacking interactions dominate the packing in the crystal structures. DFT calculations support the NMR interpretation of *endo/exo* interconversion, the crystallography results suggesting greater stability of the

exodentate bonding mode, and provide evidence for weak Pd...O bonding in the endodentate form of [9]aneS₂O. Likely contributors to the differences between related [9]aneS₃ and [9]aneS₂O cyclometallated Pd(II) complexes include ring conformer bonding preferences, relative energy ordering of free ligand *endo* and *exo* forms, other intramolecular intramacro-cyclic interactions, and the strength of the donor-acceptor interaction of S vs. O with Pd.

Experimental

Materials and measurements

All materials were used as received. The ligands [9]aneS₃, btp, pbt, as well as NH₄PF₆ were purchased from Sigma-Aldrich. The ligand [9]aneS₂O was prepared as previously reported.¹⁴ Palladium(II) acetate was purchased from Strem. The ligands fpp, bzq, and ppyCHO were purchased from TCI. Cyclometallated acetate dimers used in the preparation of **1b**, **3b**, **4b**, and **5b** were prepared as previously reported.⁸ [Pd(ppy)Cl]₂ was prepared by the reported method.⁴⁷ All synthetic manipulations were carried out in air. Elemental analyses were performed by Atlantic Microlab. Fourier transform IR spectra were obtained for solid samples using a PerkinElmer Spectrum One FTIR with diamond ATR accessory. Proton and carbon-13 NMR spectra were obtained on a JEOL 400 MHz NMR spectrometer using residual solvent for both the deuterium lock and reference. Variable temperature measurements were performed using a JEOL temperature-controlled probe. Samples were held at each temperature for 10 min prior to acquisition of each spectrum. After spectra were collected at the lowest and highest temperatures recorded, room temperature spectra were recollected and compared with the initial room temperature spectra to ensure equilibrium NMR measurements were acquired. Mass spectra were acquired using a Thermo LCQ Fleet ESI-MS.

DFT Calculations

All quantum mechanical calculations were performed using the Gaussian 09 program suite.⁴⁸ Density functional theory calculations were performed using the B3LYP functional.^{49,50} The Hay and Wadl effective core potential basis set (termed LANL2DZ⁵¹ in Gaussian) was used to describe the Pd atoms whereas the 6-311+G(d,p) was used for the remaining atoms (except for the first geometry minimization steps, as specified below). All DFT calculations were performed using PCM (Polarizable Continuum Model),⁵² choosing acetonitrile as the implicit solvent. DFT calculations were performed using X-ray structural data as a starting point for geometry minimizations and excluded the PF₆[−] anion in all calculations. Geometry minimizations were performed by first minimizing using LANL2DZ/6-31G* basis set with “fine” integration grid, followed by minimization with LANL2DZ/6-311+G(d,p) with “ultrafine” integration grid, followed by a more accurate minimization, with new calculation of force constants at every step, through the “calcall” keyword. CHELPG⁵³ charges were calcu-

lated using Gaussian09, taking Bondi radii as the van der Waals radii for all atoms: H 1.20 pm, O 1.52 pm, C 1.70 pm, S 1.80 pm, N 1.55 pm, Pd 1.63. NBO charges were obtained using standalone NBO 7.0,⁵⁴ from input generated by Gaussian09 through its embedded NBO version 3.1. For all calculations, singlet species of overall charge +1 were considered. The optimized geometry of exodentate [Pd([9]aneS₂O)(btp)]⁺ using acetonitrile solvent (using the Polarizable Continuum Model) was calculated with the X-ray structural data obtained as a starting point. For the endodentate form, the optimized geometry (using acetonitrile solvent) was obtained by starting with the X-ray structural coordinates of [Pd([9]aneS₃)(btp)]⁺ with the axial sulfur reassigned as oxygen (coordinates obtained from a previously collected published structure⁸). A transition state between these *endo* and *exo* forms was obtained using the Synchronous Transit-Guided Quasi-Newton method,⁵⁵ followed by a transition state search using the opt = (ts,calcall) keywords.⁵⁶ The transition state geometry was verified by the presence of a single imaginary frequency. Calculated free energies are reported as the sum of electronic and thermal free energies. The program Multiwfn⁵⁷ was used to calculate the molecular van der Waals volume.

X-ray crystallography

Tables 1 and S1† contain crystal data, collection parameters, and refinement criteria for the crystal structures of **1b**, **2b**, **4b-CH₃CN**, **4b-CH₃NO₂**, **5b-CH₃NO₂** and **2a**, **6a**, **2c**, respectively. Crystals were mounted on the tip of MiTeGen micro-mount and X-ray intensity data were measured at low temperature using an Oxford Cryosystems desktop cooler⁵⁸ (173(2) K for all structures except **2b** (293(2) K)) with graphite monochromated Mo K α radiation (λ = 0.71073 Å) on a Rigaku XtaLAB mini diffractometer.⁵⁹ A preliminary set of cell constants was calculated from reflections harvested from 12 frames. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of at least 0.80 Å. Three major sections of frames were collected with 1.0° steps in ω at three different φ settings. The intensity data were corrected for absorption⁶⁰ and decay using CrystalClear.⁵⁹ Final cell constants were calculated from the xyz centroids of strong reflections from the actual data collection after integration using CrystalClear.

Each structure was solved and refined using SHELXL-2013⁶¹ within the CrystalStructure program suite.⁶² A direct-methods solution was calculated that provided most of the non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed that located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All of the hydrogen atoms in each structure were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

Crystals of **2a** and **6a** were grown by vapor diffusion of hexanes into a concentrated CH₂Cl₂ solution at room temperature. Both structures **2a** and **6a** consist of one entire dimer in the asymmetric unit, with all atoms on general positions. One

CF₃ group of the dimer in **6a** was modeled with positional disorder over two positions differing by rotation around the bond C24–C21 with freely refined occupancies of 66/34.

Crystals of **1b**, **2b**, **4b-CH₃NO₂**, and **5b-CH₃NO₂** were grown by vapor diffusion of diethyl ether into concentrated CH₃NO₂ solutions at room temperature. Crystals of **4b-CH₃CN** were grown by slow evaporation of an CH₃CN solution at room temperature. In the structures of **1b** and **2b**, the asymmetric unit is composed one cation/anion pair, with all atoms on general positions. The structures of **4b-CH₃NO₂**, **4b-CH₃CN**, and **5b-CH₃NO₂** similarly contain one cation/anion pair and one solvent molecule in the asymmetric unit, with all atoms on general positions. In the structure of **2b**, one PF₆[−] anion was modeled with positional disorder over two locations with freely refined occupancies of 37/63 and pairwise thermal parameter constraints. Disorder in the structure of **5b** was modeled for Pd and the entire pbt ligand over two unique sets of positions in the same plane that involve swapping of ligated rings coordinated to the metal. The final model freely refined with occupancies of 79/21 for the two sets of Pd/pbt positions using the SAME restraint and accompanied by appropriate pairwise thermal parameter constraints. Numerous lower quality X-ray data sets were collected on crystals grown of **5b** at both room temperature, and 5 °C and all showed evidence of this disorder.

Crystals of **2c-CH₃NO₂** were grown by vapor diffusion of diethyl ether into a concentrated CH₃NO₂ solution at room temperature. The asymmetric unit of **2c** is composed one cation/anion pair and one solvent molecule, with all atoms on general positions.

Syntheses of [Pd(C[^]N)(μ-O₂CCH₃)]₂ Complexes

Preparation of [Pd(fpp)(μ-O₂CCH₃)]₂ (6a**).** To a solution of fpp (0.216 g, 0.963 mmol) in CH₂Cl₂ (30 mL) was added solid palladium(II) acetate (0.15 g, 0.6 mmol). The solution was heated at reflux for 12 h, changing to a bright orange product. The reaction was diluted with CH₂Cl₂ (40 mL) and washed with water (2 × 25 mL). The CH₂Cl₂ was removed under reduced pressure yielding a bright orange precipitate. The product was recrystallized from CH₂Cl₂/hexanes. Yield: 0.286 g, 0.369 mmol, 77%. Anal. Calc. for C₂₈H₂₀F₆N₂O₄Pd₂: C, 43.38, H, 2.60, N, 3.61. Found: C, 43.39, H, 2.52, N, 3.57. ¹H-NMR (400 MHz, CD₂Cl₂, *only major isomer reported): δ = 7.92 (d, *J* = 5.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.13–6.97 (m, 3H), 6.72 (t, *J* = 8.0 Hz, 1H), 2.25 (s, 3H). ¹⁹F-NMR (376 MHz, CD₂Cl₂, *indicates minor isomer): δ = −62.98, −63.29*. ATR-IR (diamond): ν/cm^{−1} = 3082, 2929, 2633, 2361, 1608, 1596, 1565, 1487, 1411, 1388, 151, 1316, 1272, 1257, 1235, 1154, 1130, 1116, 1105, 1073, 1034, 902, 897, 823, 814, 775, 746, 739, 734, 718, 685, 661, 648, 624, 544, 466. Isomers present in 90/10 *anti/syn* ratio.

Preparation of [Pd(ppyCHO)(μ-O₂CCH₃)]₂ (2a**).** To a solution of 4-(2-pyridyl)benzaldehyde (0.148 g, 0.66 mmol) in CH₂Cl₂ (20 mL) was added solid palladium(II) acetate (0.15 g, 0.67 mmol). The solution was heated at reflux for 6 h and monitored by TLC (silica gel, CH₂Cl₂), changing to a deep

yellow/orange product. The reaction was diluted with CH₂Cl₂ (40 mL) and washed with water (2 × 25 mL). The CH₂Cl₂ was removed under reduced pressure yielding a light yellow/orange precipitate. The product was recrystallized from CH₂Cl₂/hexanes. Yield: 0.159 g, 0.229 mmol, 69%. Anal. Calc. for C₂₈H₂₂F₆N₂O₆Pd₂: C, 48.37, H, 3.19, N, 4.03. Found: C, 48.27, H, 3.10, N, 3.94. ¹H-NMR (400 MHz, CD₂Cl₂, *only major isomer reported): δ = 9.81 (s, 1H), 7.93 (d, *J* = 5.0 Hz, 1H), 7.48 (td, *J* = 7.8, 1.4 Hz, 1H), 7.33 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.29 (s, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.67 (td, *J* = 8.0, 0.8 Hz, 1H), 2.28 (s, 3H). ¹³C-NMR (101 MHz, CD₂Cl₂, *only major isomer reported): δ = 192.92, 182.76, 163.62, 152.72, 150.68, 139.21, 136.10, 134.26, 125.52, 123.46, 123.43, 119.65, 25.39. ATR-IR (diamond): ν/cm^{−1} = 3075, 2925, 2829, 2730, 2360, 1680, 1605, 1559, 1481, 1345, 1408, 1371, 1343, 1311, 1269, 1236, 1180, 1164, 1109, 1062, 1033, 879, 818, 769, 746, 709, 684, 675, 655, 625, 557, 481. Isomers present in 82/18 *anti/syn* ratio.

Syntheses of [Pd(C[^]N)([9]aneS₂O)](PF₆) complexes

Preparation of [Pd(ppy)([9]aneS₂O)](PF₆) (1b**).** To a solution of [Pd(ppy)(Cl)]₂ (0.100 g, 0.169 mmol) in CH₃CN (10 mL) was added [9]aneS₂O (0.056 g, 0.338 mmol) dissolved in CH₃CN (2 mL). A pale yellow precipitate formed almost immediately. The reaction mixture was stirred 23 h at rt. The solvent removed under reduced pressure, and the residue was redissolved in CH₃OH (20 mL). Solid NH₄PF₆ (0.0550 g, 0.338 mmol) was added and precipitate formed gradually. After stirring 24 hours, the pale yellow solid was collected, rinsed with Et₂O (3 × 5 mL), and dried *in vacuo*. Yield: 0.121 g, 0.218 mmol, 65%. Anal. Calc. for C₁₇H₂₀NPdOS₂PF₆: C, 35.83, H, 3.54, N, 2.46. Found: C, 35.86, H, 3.42, N, 2.54. ¹H-NMR (400 MHz, CD₃NO₂): δ = 8.59 (d, *J* = 5.0 Hz, 1H), 8.14 (td, *J* = 8.0, 4.0 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.76 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.43 (m, 2H), 7.31 (td, *J* = 8.0, 1.2 Hz, 1H), 7.22 (td, *J* = 8.0, 1H), 4.57–4.42 (m, 2H), 4.11–3.97 (m, 2H), 3.91–3.42 (m (broad), 4H), 3.41–3.30 (m 2H), 3.29–3.10 (m, 2H). ¹³C-NMR (101 MHz, CD₃NO₂): δ = 160.58, 151.21, 147.06, 142.09, 136.38, 130.55, 126.30, 122.24, 120.66, 119.80, 115.61, 73.81–71.01 (2C), 37.98–30.43 (4C). ATR-IR (diamond): ν/cm^{−1} = 3210, 2867, 2360, 1909, 1606, 1577, 1488, 1469, 1437, 1423, 1414, 1297, 1262, 1240, 1172, 1131, 1017, 1004, 885, 828, 754, 733, 663, 649, 629, 615, 555, 503, 478, 463, 455. ESI-MS (rel. ab. %): [Pd(ppy)([9]aneS₂O)]⁺ *m/z* 424.08 (100%).

Preparation of [Pd(ppyCHO)([9]aneS₂O)](PF₆) (2b**).** To a solution of [Pd(ppyCHO)(μ-O₂CCH₃)]₂ (0.100 g, 0.144 mmol) in CH₃CN (25 mL) was added [9]aneS₂O (0.047 g, 0.288 mmol) dissolved in CH₃CN (1 mL). The reaction mixture was stirred 16 h at rt. The solvent removed under reduced pressure and the residue was redissolved in CH₃OH (3 mL). Solid NH₄PF₆ (0.047 g, 0.288 mmol) was added and a pale yellow precipitate formed immediately. After stirring 30 min, the solid was collected, rinsed with Et₂O (3 × 5 mL), and dried *in vacuo*. Yield: 0.150 g, 0.251 mmol, 87%. Anal. Calc. for C₁₈H₂₀NO₂PdS₂PF₆·0.15CH₃NO₂: C, 35.91, H, 3.40, N, 2.65. Found: C, 36.08, H, 3.58, N, 2.83. ¹H-NMR (400 MHz,

CD_3NO_2): δ = 9.94 (s, 1H), 8.62 (d, J = 5.0 Hz, 1H), 8.20 (m, 2H), 8.12 (d, J = 7.8 Hz, 1H), 7.93 (s, 1H), 7.90 (d, J = 6.4, 1H), 7.80 (d, J = 6.4, 1H), 7.53 (m, 1H), 4.46 (br d, 12 Hz), 4.02 (br dd, 12 Hz, 12 Hz), 3.95–3.45 (br), 3.39 (br d, 16 Hz), 3.33–3.15 (br). ^{13}C -NMR (101 MHz, CD_3NO_2): δ = 194.04, 164.96, 156.73, 153.48, 153.38, 142.66, 138.49, 136.50, 129.44, 127.11, 126.76, 122.80, 77.28 (br), 77.10 (br), 43.61 (br), 40.82 (br), 39.50 (br), 37.59 (br). ATR-IR (diamond): ν/cm^{-1} = 2929, 2869, 1683, 1603, 1569, 1558, 1487, 1435, 1410, 1314, 1242, 1197, 1128, 1031, 1001, 877, 825, 774, 747, 709, 693, 659, 555. ESI-MS (rel. ab. %): $[\text{Pd}(\text{ppyCHO})([\text{9}] \text{aneS}_2\text{O})]^+ m/z$ 452.17 (100%).

Preparation of $[\text{Pd}(\text{bzq})([\text{9}] \text{aneS}_2\text{O})](\text{PF}_6)$ (3b). To a solution of $[\text{Pd}(\text{bzq})(\mu\text{-O}_2\text{CCH}_3)]_2$ (0.100 g, 0.145 mmol) in CH_3CN (15 mL) was added $[\text{9}] \text{aneS}_2\text{O}$ (0.0478 g, 0.291 mmol) dissolved in CH_3CN (2 mL). The reaction mixture was stirred 18 h at rt. The solvent removed under reduced pressure, and the residue was redissolved in CH_3OH (20 mL). Solid NH_4PF_6 (0.0474 g, 0.291 mmol) was added and light yellow precipitate formed immediately. After stirring 5 h, the solid was collected, rinsed with Et_2O (3×5 mL), and dried *in vacuo*. Yield: 0.159 g, 0.274 mmol, 94%. Anal. Calc. for $\text{C}_{19}\text{H}_{20}\text{NPdOS}_3\text{PF}_6$: C, 38.43, H, 3.39, N, 2.36. Found: C, 38.58, H, 3.36, N, 2.54. ^1H -NMR (400 MHz, CD_3NO_2): δ = 8.82 (dd, J = 5.0, 0.9 Hz, 1H), 8.61 (dd, J = 8.2, 0.9 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.73 (dd, J = 8.2, 5.0 Hz, 1H), 7.63 (d, J = 4.0 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 4.57–4.42 (m, 2H), 4.11–3.97 (m, 2H), 3.92–3.41 (m, 4H), 3.41–3.30 (m, 2H), 3.10–3.29 (m, 2H). ^{13}C -NMR (101 MHz, CD_3NO_2): δ = 149.66, 146.11, 136.93, 134.84, 130.33, 127.95, 125.34, 124.81, 123.34, 120.83, 119.99, 118.70, 73.30, 71.32, 38.55, 35.97, 33.85, 32.10. ATR-IR (diamond): ν/cm^{-1} = 3326, 2904, 2867, 2360, 1878, 1626, 1607, 1570, 1469, 1453, 1407, 1327, 1293, 1220, 1144, 1130, 1051, 1033, 1026, 1003, 923, 878, 828, 785, 753, 741, 711, 651, 555, 506. ESI-MS (rel. ab. %): $[\text{Pd}(\text{bzq})([\text{9}] \text{aneS}_2\text{O})]^+ m/z$ 448.08 (100%).

Preparation of $[\text{Pd}(\text{btp})([\text{9}] \text{aneS}_2\text{O})](\text{PF}_6)$ (4b). To a solution of $[\text{Pd}(\text{btp})(\mu\text{-O}_2\text{CCH}_3)]_2$ (0.100 g, 0.133 mmol) in CH_3CN (25 mL) was added $[\text{9}] \text{aneS}_2\text{O}$ (0.0437 g, 0.266 mmol) dissolved in CH_3CN (2 mL). The reaction mixture was bright yellow stirred 22 h at rt. The solvent removed under reduced pressure and the residue was redissolved in CH_3OH (30 mL). Solid NH_4PF_6 (0.0435 g, 0.266 mmol) was added and a yellow precipitate formed immediately. After stirring 14 h, the solid was collected, rinsed with Et_2O (4×5 mL), and dried *in vacuo*. Yield: 0.133 g, 0.213 mmol, 80%. Anal. Calc. for $\text{C}_{19}\text{H}_{20}\text{NPdS}_3\text{O}_2\text{PF}_6 \cdot 0.5\text{CH}_3\text{NO}_2$: C, 35.68, H, 3.30, N, 3.20. Found: C, 35.60, H, 3.20, N, 3.37. ^1H -NMR (400 MHz, CD_3NO_2): δ = 8.55 (m, 1H), 8.36 (m, 1H), 8.12 (t, J = 8.0 Hz, 1H), 7.99 (m, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.46 (m, 2H), 7.36 (t, J = 6.4 Hz, 1H), 4.41 (s broad, 2H), 3.92 (s, broad, 3H), 3.69 (s, broad, 1H), 3.38 (m 6H). ^{13}C -NMR (101 MHz, CD_3NO_2): δ = 156.89, 149.40, 147.04, 140.46, 137.90, 137.64, 136.05, 122.10, 121.57, 121.51, 119.42, 119.19, 116.39, 73.73, 71.70, 41.15, 36.69, 34.59, 30.82. ATR-IR (diamond): ν/cm^{-1} = 3218, 2981, 2911, 2361, 1902, 1604, 1546, 1497, 1470, 1449, 1415, 1379, 1293, 1261, 1236, 1162, 1127, 1063, 1033, 1001, 879, 828, 746,

721, 677, 655, 556, 497, 468. ESI-MS (rel. ab. %): $[\text{Pd}(\text{btp})([\text{9}] \text{aneS}_2\text{O})]^+ m/z$ 480.00 (100%).

Preparation of $[\text{Pd}(\text{pbt})([\text{9}] \text{aneS}_2\text{O})](\text{PF}_6)$ (5b). To a solution of $[\text{Pd}(\text{pbt})(\mu\text{-O}_2\text{CCH}_3)]_2$ (0.100 g, 0.133 mmol) in CH_3CN (23 mL) was added $[\text{9}] \text{aneS}_2\text{O}$ (0.0437 g, 0.266 mmol) dissolved in CH_3CN (2 mL). The reaction mixture was stirred 16 h at rt. The solvent removed under reduced pressure, and the residue was redissolved in CH_3OH (20 mL). Solid NH_4PF_6 (0.0435 g, 0.266 mmol) was added, but no significant amount of precipitate formed. Cooling to -10°C facilitate precipitation. The yellow solid was collected and rinsed with Et_2O (3×5 mL) and dried *in vacuo*. Yield: 0.159 g, 0.253 mmol, 95%. Anal. Calc. for $\text{C}_{19}\text{H}_{20}\text{NPdO}_3\text{S}_3\text{PF}_6 \cdot \text{CH}_3\text{NO}_2$: C, 34.97, H, 3.37, N, 4.08. Found: C, 35.16, H, 3.29, N, 4.02. ^1H -NMR (400 MHz, CD_3NO_2): δ = 8.11 (d, J = 8.2, 2H), 7.74 (dd, J = 7.1, 1.6 Hz 1H), 7.71 (t, J = 7.8 Hz, 1 Hz), 7.59 (m, 2H), 7.35 (m, 2H), 4.40 (s (broad), 2H), 3.91 (td, J = 11.6, 3.0 Hz, 2H), 3.67, (s (broad), 2H), 3.60–3.43 (m, 2H), 3.37–3.19 (m, 4H). ^{13}C -NMR (101 MHz, CD_3NO_2): δ = 148.40, 145.27, 136.39, 129.72, 127.59, 126.78, 123.91, 122.68, 122.41, 121.92, 118.88, 115.10, 73.14–71.68 (2C), 37.45–32.21 (4C). ATR-IR (diamond): ν/cm^{-1} = 3307, 2902, 2863, 2360, 1918, 1551, 1482, 1449, 1415, 1378, 1294, 1273, 1128, 1053, 1033, 1003, 992, 937, 920, 879, 829, 749, 710, 679, 654, 626, 556, 478. ESI-MS (rel. ab. %): $[\text{Pd}(\text{pbt})([\text{9}] \text{aneS}_2\text{O})]^+ m/z$ 480.00 (100%).

Syntheses of $[\text{Pd}(\text{C}^{\wedge}\text{N})([\text{9}] \text{aneS}_3)](\text{PF}_6)$ complex

Preparation of $[\text{Pd}(\text{ppyCHO})([\text{9}] \text{aneS}_3)](\text{PF}_6)$ (2c). To a solution of $[\text{Pd}(\text{ppyCHO})(\mu\text{-O}_2\text{CCH}_3)]_2$ (0.0704 g, 0.100 mmol) in CH_3CN (15 mL) was added $[\text{9}] \text{aneS}_3$ (0.036 g, 0.200 mmol). The reaction mixture was stirred 16 h at rt. The solvent removed under reduced pressure and the residue was redissolved in CH_3OH (10 mL). Solid NH_4PF_6 (0.036 g, 0.208 mmol) was added and a bright yellow precipitate formed immediately. The solid was collected and dried *in vacuo*. Yield: 0.116 g, 0.189 mmol, 94%. Anal. Calc. for $\text{C}_{18}\text{H}_{20}\text{NOPdS}_3\text{PF}_6 \cdot 0.5\text{H}_2\text{O}$: C, 34.71, H, 3.40, N, 2.25. Found: C, 34.57, H, 3.16, N, 2.31. ^1H -NMR (400 MHz, CD_3NO_2): δ = 9.92 (s, 1H), 8.60 (d, J = 5.5 Hz, 1H), 8.14 (m, 2H), 7.93 (d, J = 7.8 Hz, 1H), 7.81 (s, 1H), 7.75 (d, J = 7.8, 1H), 7.48 (td, J = 6.0, 2.3 Hz, 1H), 3.26 (m, 12H, $[\text{9}] \text{aneS}_3$). ^{13}C -NMR (101 MHz, CD_3NO_2): δ = 188.27, 159.21, 152.64, 147.01, 146.34, 135.80, 132.13, 129.63, 122.47, 120.67, 120.49, 116.87, 27.86 ($[\text{9}] \text{aneS}_3$). ATR-IR (diamond): ν/cm^{-1} = 3333, 2982, 2360, 2003, 1682, 1603, 1582, 1482, 1436, 1409, 1379, 1272, 1242, 1187, 1113, 1058, 1030, 1009, 882, 823, 774, 741, 709, 669, 648, 555, 472. ESI-MS (rel. ab. %): $[\text{Pd}(\text{ppyCHO})([\text{9}] \text{aneS}_3)]^+ m/z$ 424.08 (100%).

Conflicts of interest

There are no conflicts of interest to declare.

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