Tripalladium(0) Sandwich Complexes with Nitrogen Based Ligands

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Abstract: The synthesis and characterization of a series of complexes based upon a central tripalladium ditropylium (Tr) unit $[\text{Pd}_3\text{Tr}_2]^{2+}$ containing different nitrogen-based ligands is reported. The complexes were synthesized in good yield and characterized by multi-nuclei NMR spectroscopy, elemental microanalysis and single-crystal X-ray crystallography. Variation in the equatorial ligand strongly influences Pd-N bond distances, but has only a minor effect on Pd-Pd distances. These complexes provide insight into the synthesis of materials of higher dimensionality.

Keywords: Tripalladium; Pyridine; Nitrile; Tropylium; Sandwich;

Introduction

In addition to their great diversity of applications in catalysis, palladium complexes are also of great interest in the formation of large multi-dimensional coordination systems. These unique systems range from the macrocyclic ring systems, self-assembled polyhedra and pseudo-infinite arrays based upon metal-organic frameworks (MOF's), and these systems can achieve great molecular diversity through the application of a variety of "node" and "linker" systems. New metal-containing systems make excellent nodes by possessing properties of stability to environmental conditions, multiple coordination sites and coordination motifs. Stang and coworkers have demonstrated the utility of mono-palladium complexes to act as the core of self-assembling metallomacrocycles.^{1,2}

The high surface areas and well-defined structures of MOF's make them promising molecular systems for a variety of applications including gas adsorption, gas storage, and catalysis. The key role of palladium in hydrogenation and other reactions (e.g. Suzuki-Miyaura coupling, Sonogashira coupling and other reactions) suggest that palladium MOF's may open a new window into catalytic active materials. Conventional sources of active palladium catalysts such as palladium stabilized by dibenzylideneacetone ligands $[\text{Pd}_2(\text{dba})_3]$ suffer from a number of drawbacks. Zero-valent palladium precursors are commonly sensitive to light, heat and oxidation and MOF's have been demonstrated to confer greater stability to environmental factors.^{3,4} The active zero-valent material undergoes rapid aggregation in solution with consequent loss of catalytic activity.^{5,6} Leaching of the catalytic material into the solution also requires additional clean up steps, and the ability to more effectively trap and stabilize the active metal catalyst would therefore provide a number of benefits.

We have extensively studied one particular system that may be utility in the formation of extended network systems. In 2006 the synthesis of a novel trimetallic palladium(0) sandwich complex $[\text{PPh}_4][\text{Pd}_3\text{Tr}_2\text{Cl}_3]$ was reported.⁷ This complex incorporated a triangular arrangement of palladium(0) atoms “sandwiched” between two tropylium (Tr) rings (C_7H_7^+). Although both triangular and linear tripalladium(II) complexes have been reported previously,⁸⁻¹¹ the stability and ease of ligand substitution on these sandwich complexes have given rise to the possibility of new substitution patterns and molecular motifs including the formation of network structures..

We have demonstrated that these complexes may incorporate a range of anionic and neutral ligands in the equatorial position, and may also utilize a wide range of counteranions.^{12,13} In addition, we have shown that these complexes give rise to one-dimensional polymers consisting of $[\text{Pd}_3\text{Tr}_2]^{2+}$ units linked by bridging anionic ligands. Since 2008 we have been interested in investigating the effect of ligand substitution on the $[\text{Pd}_3\text{Tr}_2]^{2+}$ motif, as well as expanding this structural system to include a variety of metal centers including platinum. Our group has reported trimetallic complexes of palladium and platinum could be formed using the same methodology.¹⁴ Murahashi and coworkers have also subsequently reported the synthesis and characterization of the $[\text{Pd}_x\text{Pt}_{3-x}\text{Tr}_2]^{2+}$ motif.¹⁵ Our group is interested in the formation of large network or dendrimeric structures that may also be possible after a greater understanding of the ligand binding motifs is developed.¹⁶⁻¹⁹ Herein we report the development of a series of zero-valent tripalladium sandwich complexes with nitrogen based ligand systems.

<Scheme 1>

Results and Discussion

Synthesis

Our group has previously reported the synthesis of a series of pnictogen complexes $[\text{Pd}_3\text{Tr}_2(\text{XPh}_3)_3][(\text{BF}_4)_2]$ ($\text{X} = \text{N}, \text{P}$ or Sb) via the reaction of $[\text{P-}n\text{-Bu}_4][\text{Pd}_3\text{Tr}_2\text{Br}_3]$ with AgBF_4 and an excess of XPh_3 in dichloromethane.²⁰ In certain reactions, use of silver tetrafluoroborate (AgBF_4) or silver triflate (AgSO_3CF_3) did not lead to the expected homoleptic product, but rather a system containing both neutral ligands and counter anions bound to the metal centre. A large excess of the silver salt was employed to drive displacement of the halide ligand. In the present study, a salt metathesis reaction was carried out in which $[\text{PBu}_4][\text{Pd}_3\text{Tr}_2\text{Br}_3]$ or $[\text{PPh}_4][\text{Pd}_3\text{Tr}_2\text{Br}_3]$ was reacted with AgBF_4 in neat pyridine to give a red-brown complex $[\text{Pd}_3\text{Tr}_2(\text{Py})_3][(\text{BF}_4)_2]$ ($\text{Py} = \text{pyridine}$) (**1a**) (Scheme 1). ^1H NMR in $\text{d}^6\text{-DMSO}$ confirmed the uptake of the pyridine ligand, and the absence of any of the original $[\text{PBu}_4]^+$ counter-cation. Reaction in either neat pyridine or pyridine diluted with dichloromethane gave identical products. The retention of the $[\text{Pd}_3\text{Tr}_2]^{2+}$ unit was confirmed by ^1H NMR with a shift in the tropylium resonance from 4.72 in the precursor complex to 4.81 ppm in **1a**. Peaks consistent with the presence of residual DMSO solvent (~ 2.48 ppm) and water (~ 3.30 ppm) were also observed. The integration between the signals of the pyridine and tropylium peaks varies between samples, but confirms the expected formulation. No signals consistent with unreacted tropylium (~ 9.2 ppm) were observed. The formation of the expected product was also confirmed by the absence of any signal in the ^{31}P NMR of the original phosphonium cation, and the appearance of the characteristic signal for the $[\text{BF}_4]^-$ anion at -155.3 ppm in the ^{19}F NMR. Replacement of AgBF_4 with AgSO_3CF_3 gave the analogous product $[\text{Pd}_3\text{Tr}_2(\text{Py})_3][(\text{SO}_3\text{CF}_3)_2]$ ($\text{Py} = \text{pyridine}$) (**1b**). The presence of the triflate counter-anion increased the solubility of the

product and permitted data collection from chloroform and dichloromethane solutions. This overall formula was confirmed by CHN microanalysis as $[\text{Pd}_3\text{Tr}_2(\text{Py})_3][(\text{BF}_4)_2]$ (Py = pyridine) (**1a**) and $[\text{Pd}_3\text{Tr}_2(\text{Py})_3][(\text{SO}_3\text{CF}_3)_2]$ (**1b**) respectively.

The ^1H NMR spectrum between 6 – 8 ppm in both **1a** and **1b** is similar to that of free pyridine, suggesting that in solution the pyridine ligands are labile and the available coordination sites contain weakly coordinated solvent molecules. The position of the tropylium peak occurs at 4.81 and 4.83 ppm in **1a** and **1b** respectively, indicating that there is minimal effect from the anion on the ^1H NMR spectra. Recrystallization from dichloromethane and diethyl ether gave single crystals suitable for X-ray diffraction studies. Attempts to recrystallize **1a** in acetonitrile for X-ray diffraction studies gave dark red plate-like crystals which were determined to be the acetonitrile substituted complex $[\text{Pd}_3\text{Tr}_2(\text{MeCN})_3][(\text{BF}_4)_2]$ (**2**) (*vide infra*). This unanticipated ligand exchange may provide a new synthetic pathway for the creation of extended systems. Unlike the halogen substituted complexes such as $[\text{Pd}_3\text{Tr}_2\text{Br}_3]^-$ no evidence of the parent ion of **1a** or **1b** was observed by ion-trap mass spectrometry.

Attempts to synthesize and characterize a series of pyridine substituted tripalladium complexes were generally unsuccessful. Reactions with a range of pyridine derivatives with electro-withdrawing substituents including 4-nitropyridine and 4-fluoropyridine were attempted. ^1H NMR studies indicated that the ligand were not present in the final product, but that the $[\text{Pd}_3\text{Tr}_2]^{2+}$ unit was retained. Competition between the nitrogen-containing ligand and the counteranion is expected to complicate isolation of such derivatives, given the known affinity for “non-coordinating” anions including BF_4^- and CF_3SO_3^- to bind to the $[\text{Pd}_3\text{Tr}_2]^{2+}$ unit.^{12,21}

To further investigate the role of changing Lewis base strength, a similar displacement reaction was undertaken with 4-dimethylaminopyridine (DMAP) in dichloromethane. DMAP is

a strong Lewis base which has significant utility in organic chemistry. Reaction of $[\text{PPh}_4][\text{Pd}_3\text{Tr}_2\text{Br}_3]$ with AgBF_4 and 4-dimethylaminopyridine in dichloromethane gave the new complex $[\text{Pd}_3\text{Tr}_2(\text{DMAP})_3][(\text{BF}_4)_2]$ (**3**), which was confirmed by CHN microanalysis and multi-nuclear NMR studies. Further investigations demonstrated that **3** could be also synthesized via an alternate synthetic route by reacting $[\text{Pd}_2(4\text{-MeO-dba})_3]$ (4-MeO-dba = 4-methoxy-dibenzylideneacetone) with $\text{Tr}\cdot\text{BF}_4$ and DMAP in dichloromethane at room temperature (Scheme 1).

^1H NMR studies on **3** indicate the presence of a single peak at 4.66 ppm that is attributed to the tropylium protons in the product. A large singlet at 3.00 ppm can be attributed to protons on the dimethylamino moiety. Two sets of signals were centered at 6.68 and 7.95 ppm, and were attributed to the two unique hydrogen environments on the 4-dimethylaminopyridine ring. The signals at 7.95 ppm were significantly broadened, which is not observed in free 4-dimethylaminopyridine in $\text{d}^6\text{-DMSO}$ solution (See supplementary information), and which may be attributed to the ligand environment upon coordination to the $[\text{Pd}_3\text{Tr}_2]^{2+}$ unit. The protons in this position are shifted upfield in comparison with the free ligand (8.08 ppm), but confirm the expected formulation. Such broadening is not observed in the ^1H NMR of the related complex $[\text{Pd}(\text{DMAP})_4][(\text{BF}_4)_2]$ in CD_3CN .²² ^{31}P NMR showed no residual phosphorous containing species within the limits of detection. The ^{19}F NMR showed a single peak at -148.3 ppm for the four equivalent fluorine atoms on the tetrafluoroborate ligands. Recrystallization from dichloromethane and diethyl ether gave single crystals suitable for X-ray diffraction studies.

The successful synthesis of **3**, suggested that reaction with other electron-donating ligands might be a useful direction. The ligand 4-dimethylaminobenzonitrile is structurally similar to DMAP but includes an extended pi-conjugated pathway through the nitrile group. Treatment of

[P-*n*-Bu₄][Pd₃Tr₂Br₃] with excess AgSO₃CF₃ and 4-(dimethylamino)benzonitrile in dichloromethane gave two distinct products, a colourless solid and a darker maroon-coloured precipitate **4**. The colourless solid was confirmed by multi-nuclear NMR to be [PPh₄][SO₃CF₃]. ¹H NMR studies on **4** indicate the presence of a single peak at 4.87 ppm that may be attributed to the tropylium environment in the product. Two sets of signals were centered at 6.74 and 7.52 ppm, and can be attributed to the two unique hydrogen environments on the 4-(dimethylamino)benzonitrile ring, however the peaks do not display the broadening observed in the ¹H NMR of **3**. The upfield shift that occurs in the ¹H NMR spectra of the tropylium peak of **3** in comparison with **4**, is in agreement with the stronger coordination of pyridine over nitrile ligands that has been observed in other palladium complexes.²³ Recrystallization from dichloromethane and diethyl ether gave single crystals of **4** suitable for X-ray diffraction studies. All of the above complexes were highly stable and gave clean NMR spectra even after several years of storage at room temperature.

Spectroscopic characterization

The ultra-violet and visible spectra (800 and 350 nm) of compounds **1** - **4** are dominated by a strong ($\epsilon \sim 10^4$) feature with a λ_{max} at approximately 401 nm with a shoulder near 450 nm. This is consistent across the series and is independent of the ligand substituent. This is in contrast to the precursor series [Y][Pd₃Tr₂X₃] (Y = NBu₄, PBu₄ or PPh₄, X = Cl, Br or I,) where the ultra-violet and visible spectra is characterized by two major absorption peaks around 481 and 417 nm. Comparison of the ultra-violet and visible absorption spectra for select complexes and the precursor [PBu₄][Pd₃Tr₂Br₃] is shown in Figure 1. The 417 nm absorption in [PBu₄][Pd₃Tr₂Br₃] is attributed to electronic absorption within the [Pd₃Tr₂]²⁺ unit. In the newly reported series of

complexes this peak undergoes a blue-shift upon replacement of the halide anions with the neutrally charged nitrogen-containing species. Comparison of the UV-visible spectrum of **1a** and **1b** demonstrate the minimal influence of the counter anion on the absorption spectra.

In [PPh₄][Pd₃Tr₂Cl₃] the lower energy peak at 481 nm is attributed to electronic transfer between the [Pd₃Tr₂]²⁺ unit and the negatively charged anionic species.⁷ Previous studies in which the electron-rich halides were replaced with neutral pnictogen ligands also led a shift of λ_{max} to higher energies. In the current series, this peak is also blue-shifted, consistent with the presence of the more electron-poor nitrogen-containing ligands. The ultra-violet and visible spectrum for **3** in a range of solvents of different polarity indicates no significant solvatochromic effects (Figure 2). None of the complexes in the present study demonstrated any evidence of fluorescent properties.

<Figure 1 and Figure 2>

X-ray diffraction studies

The results of single crystal X-ray diffraction studies on compounds **1a**, **2** and **4** are summarized in Table 1 and selected bond lengths and angles are collected in Table 2.

<Table 1 and Table 2>

<Figure 3>

<Figure 4>

<Figure 5>

Previous work on the tripalladium ditropylium motif has revealed interesting structural characteristics, and the compounds described here are no exception. In compounds **1b**, **2** and **4** the triangular [Pd₃Tr₂]²⁺ core is retained and the tropylium ring is planar in all the complexes

characteristic of the expected aromaticity. In the $[\text{Pd}_3\text{Tr}_2(\text{Py})_3][(\text{SO}_3\text{CF}_3)_2]$ complex **1b** the tripalladium unit lays on a twofold rotation axis and thus the complete formula is twice the asymmetric unit. Interestingly the pyridine rings are oriented approximately planar to the plane of the palladium triangle with rotation away by 23.32° for the two symmetry related pyridine ligands and 8.22° for the remaining ligand. The Pd-Pd bond lengths are 2.7374(8) and 2.7857(6) Å, shorter than in the previously studied pnictogen series. The Pd-N bond lengths are 2.202(3) and 2.208(4) Å, slightly longer than in related structures of Pd(0). The internal Pd-Pd-Pd angles are all close to 60° due to the homoleptic ligand substitution pattern.

Displacement of the pyridine ligands in **1a** by recrystallization in acetonitrile gave the structure of $[\text{Pd}_3\text{Tr}_2(\text{MeCN})_3][(\text{BF}_4)_2]$ **2** which has previously been reported.²⁴ Both structures of **2** show similar unit cell parameters, packing motif and similar R_1 values. The Pd-Pd distances (2.7692, 2.7404 and 2.7526 Å) and angles (59.507 , 59.945 and 60.548°) are also similar. The Pd-N distances are similar (2.186, 2.145 and 2.155 Å) and longer than those in related Pd(II) acetonitrile complexes (1.956 Å).²⁵ The overall crystal packing in **2** shows evidence of aromatic stacking interactions that stabilize the overall structure.

The structure of **4** was also characterized by single crystal diffraction study. As shown in Figure 5, **4** possesses an internal $[\text{Pd}_3\text{Tr}_2]^{2+}$ unit mostly identical to that of the comparative structures. The Pd-Pd distances (2.7678, 2.7534 and 2.7626 Å) and angles (60.05 , 59.72 and 60.24°) in **4** are comparable to the pyridine (**1b**) and acetonitrile (**2**) derivatives (*vide supra*). In comparison however the Pd-N distances are significantly shorter (2.180, 2.149 and 2.150 Å) than the pyridine derivative, and are comparable with those of the acetonitrile complex. This suggests that the relative type of ligand (e.g. nitrile, benzonitrile or pyridine) may not influence the structural parameters as much as the nature of the substituent on ligands of the same family. Also

of interest is the relative orientation of the 4-(dimethylamino)benzonitrile ligands. In the structure of **1b**, two of the ligands are orientated close to planarity with the Pd₃ unit, and this is also the case in **4**. Unlike **1b** however, **4** crystallizes in space group P-1 and thus the ligands are not related by symmetry. In all three 4-(dimethylamino)benzonitrile ligands the dimethylamino substituent is essentially coplanar with the aromatic ring. With respect to the Pd₃ plane, ligand A (formed by atoms N1 to C23) is twisted by 13.33(3)°, ligand B (formed by atoms N2 to C32) is twisted by 15.68(2)° and ligand C (formed by atoms N3 to C41) is twisted by 83.79(15)°.

The crystal packing contains a mix of weak hydrogen bonding and aromatic stacking interactions. Figure 3 shows some edge-face and face-face $\pi\cdots\pi$ interactions. Close face-face stacking is found between adjacent cyclopentatrienyl ligands, as are edge-face interactions between the edge of the cyclopentatrienyl ligands and the face of adjacent 4-(dimethylamino)benzonitrile ligands. Further overlapping face-face stacking between adjacent 4-(dimethylamino)benzonitrile ligands generates a three-dimensional framework supported entirely by aromatic stacking interactions (Figure 4). Such stacking interaction may be a useful method by which to stabilize large multi-dimensional arrays composed of [Pd₃Tr₂]²⁺ derivatives.

During the synthesis of **3** small red crystals were isolated after repeated recrystallization attempts. The crystallographic data set was complete and of good resolution and redundancy. Structure solution and refinement initially suggested the previously unreported complex [Pd(DMAP)₂][(BF₄)] (**5a**) (Figure 6). Although tetrakis substituted complexes of palladium with DMAP have been reported previously,^{26,27} no such comparable structure has been determined. A search of the Cambridge Structural Database showed no similar structures. None of the metal to nitrogen bond distances in the unit cell were significantly different (2.100 – 2.118 Å), indicating similar electronic environments around the metal centers in the asymmetric unit. Although Pd(I)-

Pd(I) complexes have been reported previously, including $[\text{Pd}_2(\text{MeCN})_6][(\text{BF}_4)_2]$,²⁸ these have been stabilized by relatively strong palladium-palladium interactions. The presence of AgBF_4 in the reaction supports an alternate hypothesis that the structure may potentially be $[\text{Ag}(\text{DMAP})_2][(\text{BF}_4)]$ (**5b**) the synthesis of which was recently reported.²⁹ The bond lengths and angles for **5b** are very similar to that of the related complex $[\text{Ag}(\text{DMAP})_2](\text{NO}_3) \cdot 2\text{H}_2\text{O}$.³⁰ Within the unit cell the Ag(2)-Ag(2) bond length of 3.0347(5) Å is very close to that previously reported for $[\text{Ag}(\text{DMAP})_2](4\text{-bromophenylacetate}) \cdot \text{H}_2\text{O}$ (3.0395(12) Å).³¹ In the current structure the complex has distorted linear coordination geometry around the metal ion, with two molecules in the asymmetric unit. The closest metal-metal contact is 3.035 Å suggestive of weak interaction and which causes distortion of the metal atom out of the plane defined by the ligands.

Refinement of the metal centers as palladium gives R_1 of 3.27% and wR_2 of 6.65%. Subsequent refinement of the occupancies gives occupancies for Pd(1) of 0.98845 and Pd(2) to 0.98337. Changing the metal element to silver then refines Ag(1) with an occupancy of 0.9633 while Ag(2) is 0.9581 ($R_1 = 3.30\%$, $wR_2 = 6.90\%$) However, if the Ag occupancies are set to 1 this produces R_1 of 3.42% and $wR_2 = 7.55\%$. Disorder modelling of the tetrafluoroborate counterions gives a decrease in the R values for both metal atoms, but does not significantly alter the relative values. This suggests that from a purely crystallographic point of view the metals are palladium and not silver. Comparison with related structures and the presence of AgBF_4 in the reaction mixture nevertheless leads us to consider the central metal atom to be silver. The ambiguity of atomic centers with similar atomic masses is a well known issue in crystallography,³² and further studies are underway to determine unambiguously the nature of the metal atoms.

< Figure 6 >

Conclusions

This series of complexes demonstrates a range of nitrogen-based ligands bound to the tripalladium ditropylium complex $[\text{Pd}_3\text{Tr}_2]^{2+}$. NMR and single-crystal diffraction studies have helped in understanding the influence of the ligand substituent on the structure-property relationships. New ligand systems including substituted cycloheptatrienes and multidentate nitrogen systems will extend the variety of unusual metal coordination motifs.³³ The coordination of the nitrogen lone pair in an “end-on” configuration suggests that the complex may have significant potential to form extended multi-dimensional systems as well as possessing catalytic activity in carbon-carbon bond forming reactions. In order to gain further insight into potential molecular configurations, studies involving multidentate ligands including cyanopyridine and pyrazine are currently underway.

General Methods

All experiments were performed under an Ar atmosphere using standard Schlenk techniques. ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, and ^{19}F NMR spectra were recorded on a 400 MHz (Varian Mercury) instrument, and the chemical shifts were referenced to the residual resonances of the deuterated solvents. Electronic spectra were recorded using a Bruker Cary50 UV–VIS spectrophotometer. Fluorescence spectra were recorded using a Agilent spectrophotometer. Elemental analyses were performed by Robertson Microlit Laboratories Inc. of Madison, New Jersey, and the School of Oceanography at the University of Rhode Island. CH_2Cl_2 , CH_3Cl , CH_3CN , hexanes, pyridine and Et_2O were purified according to standard procedures. $[\text{P-}n\text{-Bu}_4][\text{Pd}_3\text{Tr}_2\text{Br}_3]$ was prepared according to the method of Babbini *et al.*²⁰ The chemicals 4-dimethylaminopyridine (DMAP), 4-dimethylaminobenzonitrile (DMAB), AgBF_4 , and AgSO_3CF_3 were purchased from the Sigma Aldrich Corporation and used without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratories.

Synthesis of $[\text{Pd}_3\text{Tr}_2(\text{Py})_3](\text{BF}_4)_2$ (1a) To a solution of $[\text{P-n-Bu}_4][\text{Pd}_3\text{Tr}_2\text{Br}_3]$ (106.2 mg, 0.106 mmol) in pyridine (15 mL), AgBF_4 (127.1 mg, 0.653 mmol) was added and the solution was stirred for 1 h. The solution was filtered leaving a dark burgundy colored precipitate and a clear filtrate. The precipitate was collected by filtration and washed with small quantities of diethyl ether (2 x 20 mL) and then dried in vacuo. The product was then crystallized via vapor diffusion of diethyl ether into CH_2Cl_2 . Yield: 51.3 mg (53 %). Anal. Calcd. For $\text{C}_{29}\text{H}_{29}\text{B}_2\text{F}_8\text{N}_3\text{Pd}_3$: C, 38.17; H, 3.20; N, 4.61. Found: C, 38.36; H, 3.61; N, 4.88. ^1H NMR (400 MHz, d^6 -DMSO, 25 $^\circ\text{C}$): δ 4.81 (s, 14H, H_1), 7.38 – 7.45 (m, 6H, H_3), 7.79 – 7.84 (m, 3H, H_4), 8.51 – 8.54 (m, 3H, H_2). ^{19}F (376.2 MHz, d^6 -DMSO, 25 $^\circ\text{C}$): δ -148.3 (s, F_1). UV-Visible [CH_2Cl_2 λ_{max} (nm) 400.9 (6.1 x 10³)].

Synthesis of $[\text{Pd}_3\text{Tr}_2(\text{Py})_3](\text{SO}_3\text{CF}_3)_2$ (1b**)** To a solution of $[\text{PPh}_4][\text{Pd}_3\text{Tr}_2\text{Br}_3]$ (105.4 mg, 0.0975 mmol) in dichloromethane (30 mL) and pyridine (0.3 mL), AgSO_3CF_3 (245.3 mg, 0.955 mmol) was added and the solution was stirred for 1 h. The solution was filtered leaving a dark burgundy colored precipitate and a clear filtrate. The precipitate was collected by filtration and washed with small quantities of diethyl ether (2 x 25 mL) and then dried in vacuo. The product was then crystallized via vapor diffusion of diethyl ether into CH_2Cl_2 . Yield: 78.9 mg (78 %).
 Anal. Calcd. For $\text{C}_{31}\text{H}_{29}\text{F}_6\text{N}_3\text{O}_6\text{Pd}_3\text{S}_2$: C, 35.91; H, 2.82; N, 4.05. Found: C, 35.76; H, 3.93; N, 4.40. ^1H NMR (400 MHz, d^6 -DMSO, 25 °C): δ 4.83 (s, 14H, H_1), 7.35 – 7.45 (m, 6H, H_3), 7.79 – 7.85 (m, 3H, H_4), 8.51 – 8.54 (m, 6H, H_2), ^{19}F (376.2 MHz, d^6 -DMSO, 25 °C): δ -77.7 (s, F_1).
 UV-Visible [CH_2Cl_2 λ_{max} (nm) 405.0 (4.0×10^3)].

Synthesis of [Pd₃Tr₂(DMAP)₃](BF₄)₂ (3**)** To a solution of [P-n-Bu₄][Pd₃Tr₂Br₃] (100.4 mg, 0.10 mmol) and DMAP (371.4 mg, 3.04 mmol) in CH₂Cl₂ (30 mL), AgBF₄ (194.4 mg, 0.61 mmol) was added at room temperature with stirring to give a reddish-brown solution and a silver colored precipitate. The solution was filtered and diethyl ether (100 mL) was added, yielding a dark red precipitate. The solution was filtered and the precipitate was washed with diethyl ether (2 x 25 mL) and dried in vacuo. Repeated attempts to crystallize **3** gave crystals of **5b**. Yield: 47.5 mg (65 %). Anal. Calcd. For C₃₅H₄₄B₂F₈N₆Pd₃ : C, 40.36; H, 4.26; N, 8.07. Found: C, 40.90; H, 4.84; N, 7.92. ¹H NMR (400 MHz, d⁶-DMSO, 25 °C): δ 3.00 (s, 18H, H₅), 4.66 (s, 14H, H₁), 6.68 (d, 6H, H₃), 7.95 (bs, 6H, H₂). ¹⁹F (376.2 MHz, d⁶-DMSO, 25 °C): δ -148.3 (s, F₁). UV-Visible [CH₂Cl₂ λ_{max} (nm) 401.0 (13.7 x 10³)].

Alternate Synthesis of [Pd₃Tr₂(DMAP)₃](BF₄)₂ (3) To a solution of [Pd₂(4-MeO-dba)₃].CHCl₃ (100.2 mg, 0.088 mmol) and DMAP (20.3 mg, 0.166 mmol) in CH₂Cl₂ (30 mL), Tr·BF₄ (22.1 mg, 0.124 mmol) was added at room temperature with stirring. The purple colour of the [Pd₂(4-MeO-dba)₃].CHCl₃ changed rapidly to give a reddish-brown solution containing a dark

precipitate. After 18 hours the solution was filtered and the solid precipitate was washed with *tert*-butyl methyl ether (2x20 mL) and dried in vacuo. Yield: 72.3 mg (56 %). Characterization data for the collected brown solid was identical to that of **3** reported above.

Synthesis of $[\text{Pd}_3\text{Tr}_2(\text{DMAB})_3](\text{SO}_3\text{CF}_3)_2$ (4**)** To a solution of $[\text{PPh}_4][\text{Pd}_3\text{Tr}_2\text{Br}_3]$ (72.0 mg, 0.0066 mmol) and DMAB (76.2 mg, 0.521 mmol) in CH_2Cl_2 (50 mL), AgSO_3CF_3 (184.0 mg, 0.716 mmol) was added and the solution was stirred for 16 h. The filtrate was reduced in volume to ~ 30 mL and hexanes (100 mL) were added, yielding a dark red precipitate. The solution was filtered and the red precipitate was washed with hexanes (2 x 25 mL) and dried in vacuo. The product was then crystallized via vapor diffusion of diethyl ether into CH_2Cl_2 . Yield: 59.4 mg (72 %). Anal. Calcd. For $\text{C}_{43}\text{H}_{44}\text{F}_6\text{N}_6\text{O}_6\text{Pd}_3\text{S}_2$: C, 41.71; H, 3.58; N, 6.79. Found: C, 40.71; H, 3.42; N, 6.82. ^1H NMR (400 MHz, d^6 -DMSO, 25 $^\circ\text{C}$): δ 2.98 (s, 18H, H_5), 4.87 (s, 14H, H_1), 6.74 (d, 6H, H_3 , $J_{\text{HH}} = 9$ Hz), 7.52 (d, 6H, H_2 , $J_{\text{HH}} = 9$ Hz). ^{19}F (376.2 MHz, d^6 -DMSO, 25 $^\circ\text{C}$): δ -77.8 (s, F_1). UV-Visible [CH_2Cl_2 λ_{max} (nm) 400.1 (7.9×10^3)].

Single crystal X-ray diffraction

Single crystal X-ray diffraction data were collected on either Nonius KappaCCD (**1**) or Bruker SMART (**2**, **4** & **5b**) diffractometers. The EvalCCD³⁴ and SMART/SAINT³⁵ software packages were used for data processing; structures were solved with SIR92³⁶ or SHELXS³⁷ and refined using SHELXL³⁷. In all cases hydrogen atoms were placed geometrically, with C–H distances in the range 0.95–0.99 Å (according to hybridization) and refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ($U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl hydrogen atoms).

In the structure of **2** one of the tetrafluoroborate counterions (the atoms B1 to F4) was refined using a whole-molecule, two-part disorder model with a refined major:minor occupancy ratio of 66:44 %. Restraints were used on this disordered counterion to keep the displacement parameters and bond distances similar to the ordered counterion.

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Supporting information available.

CCDC 1428954-1428956 and 1429150 contains the supplementary crystallographic data for **1b**, **2**, **4** and **5b**. These data can be obtained free of charge via <https://summary.ccdc.cam.ac.uk/structure-summary-form>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. The supplementary data for the above complexes and **5** can also be found, in the online version, at <http://dx.doi.org/>

Scheme, Figure and Table Captions

- Scheme 1: Synthesis pathways for complexes **1** - **4**.
- Figure 1. UV-visible spectra of complexes **1a**, **1b**, **3**, **4** and [PBU₄][Pd₃Tr₂Br₃] in dichloromethane. Absorption normalized to 1.0 at 400 nm for comparison purposes.
- Figure 2. UV-visible spectra of **3** in dichloromethane, methanol and acetonitrile. Absorption normalized to 1.0 at 400 nm for comparison purposes.
- Figure 3. Plot of **1b** at 50% probability level with hydrogen atoms and counterions omitted.
- Figure 4. Plot of **2** at 30% probability level with anions omitted.
- Figure 5. Plot of **4** at 50% probability level with solvent molecule and counterions omitted.
- Figure 6. Plot of **5** at 50% probability level with hydrogen atoms omitted.
- Table 1. Crystal data for compounds **1b**, **2**, **4** and **5**.
- Table 2. Selected bond lengths (Å) and angles (°) for compounds **1b**, **2**, **4** and **5**.

Scheme 1: Synthesis pathways for complexes 1 - 4.

Figure 1. UV-visible spectra of complexes **1a**, **1b**, **3**, **4** and [PBu₄][Pd₃Tr₂Br₃] in dichloromethane. Absorption normalized to 1.0 at 400 nm for comparison purposes.

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Figure 3. Plot of **1b** at 50% probability level with hydrogen atoms and counterions omitted.

Figure 4. Plot of **2** at 30% probability level with anions omitted.

Figure 5. Plot of **4** at 50% probability level with solvent molecule and counterions omitted.

Figure 6. Plot of **5a** at 50% probability level with hydrogen atoms and counterions omitted.

Table 1. Crystal data for compounds **1b**, **2**, **4** and **5a**.^a

	1b	2	4	5a
Moiety Formula	C ₂₉ H ₂₉ N ₃ Pd ₃ ²⁺ · 2CF ₃ O ₃ S ₂ ⁻ ·	C ₂₀ H ₂₃ N ₃ Pd ₃ ²⁺ · 2BF ₄ ⁻	C ₄₁ H ₄₄ N ₆ Pd ₃ ²⁺ · 2CF ₃ O ₃ S ₂ ⁻ · ·CH ₂ Cl ₂	C ₁₄ H ₂₀ Ag ⁺ · 2BF ₄ ⁻
Total Formula	C ₃₁ H ₂₉ F ₆ N ₃ O ₆ P d ₃ S ₂	C ₂₀ H ₂₃ B ₂ F ₈ N ₃ P d ₃	C ₄₄ H ₄₆ Cl ₂ F ₆ N ₆ O ₆ Pd ₃ S ₂	C ₁₄ H ₂₀ AgBF ₄ N ₄
Formula weight	1036.89	798.23	1323.09	439.02
Radiation type	MoKα, 0.71073 Å	MoKα, 0.71073 Å	MoKα, 0.71073 Å	MoKα, 0.71073 Å
Space group	Monoclinic, <i>C2/c</i>	Monoclinic, <i>P21/n</i>	Triclinic, <i>P-1</i>	Monoclinic, <i>C2/c</i>
<i>a</i> , Å	11.676(3)	12.8290(15)	12.714(3)	17.589(3)
<i>b</i> , Å	17.369(4)	10.6833(12)	13.882(3)	11.3015(16)
<i>c</i> , Å	16.657(5)	18.159(2)	16.122(4)	33.974
α, deg	90	90	110.029(3)	90
β, deg	94.991(17)	96.773(2)	94.841(3)	102.938(2)
γ, deg	90	90	110.899(3)	90
<i>V</i> , Å ³	3365.3(14)	2471.5(5)	2427.3(10)	6582.2(16)
<i>Z</i>	4	4	2	16
ρ _{calc.} , g cm ⁻³	2.047	2.145	1.810	1.772
μ, mm ⁻¹	1.793	2.235	1.372	1.270
<i>T</i> , K	150(2)	220(2)	120(2)	100(2)
Reflections collected	23919	18517	15134	45267
Independent reflections	3854	4850	8011	8209
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0348, wR2 = 0.0529	R1 = 0.0358, wR2 = 0.0700	R1 = 0.0570, wR2 = 0.1181	R1 = 0.0375, wR2 = 0.0780
^a Programs used. Data collection and reduction: SMART, SAINT and APEX2. ³⁸ Absorption correction: SADABS. ³⁹ Structure solution and refinement: SHELXTL and OLEX2. ^{40,41} Molecular graphics: DIAMOND. ⁴²				

Table 2. Selected bond lengths (Å) and angles (°) for compounds **1b**, **2**, **4** and **5**.

1b		2	
Pd(1)-Pd(1A)	2.7374(8)	Pd(1)-Pd(2)	2.7692(6)
Pd(1)-Pd(2)	2.7858(6)	Pd(2)-Pd(3)	2.7404(6)
Pd(2)-Pd(1A)	2.7857(6)	Pd(3)-Pd(1)	2.7526(6)
Pd(1)-N(1)	2.202(3)	Pd(1)-N(1)	2.186(5)
Pd(2)-N(2)	2.208(4)	Pd(2)-N(2)	2.145(5)
		Pd(3)-N(3)	2.155(5)
Pd(1A)-Pd(1)-Pd(2)	60.571(10)	Pd(2)-Pd(1)-Pd(3)	59.507(16)
Pd(1)-Pd(2)-Pd(1A)	58.86(2)	Pd(1)-Pd(2)-Pd(3)	59.945(16)
		Pd(2)-Pd(3)-Pd(1)	60.548(16)
4		5	
Pd(1)-Pd(2)	2.7678(13)	Ag(1)-N(1)	2.112(3)
Pd(2)-Pd(3)	2.7626(11)	Ag(1)-N(3)	2.117(3)
Pd(3)-Pd(1)	2.7534(12)	Ag(2)-N(5)	2.101(3)
Pd(1)-N(1)	2.180(9)	Ag(2)-N(7)	2.104(3)
Pd(2)-N(2)	2.149(9)	Ag(2)-Ag(2i)	3.0344(8)
Pd(3)-N(3)	2.150(9)	Ag(1)-Ag(2)	11.295
Pd(1)-Pd(2)-Pd(3)	59.72(3)		
Pd(2)-Pd(1)-Pd(3)	60.05(3)	N(1)-Ag(1)-N(2)	169.38(11)
Pd(2)-Pd(3)-Pd(1)	60.24(3)	N(3)-Ag(2)-N(4)	170.79(10)

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Tripalladium(0) Sandwich Complexes with Nitrogen Based Ligands

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Synopsis: The synthesis and characterization of a series of complexes based upon a central tripalladium ditropylium (Tr) unit $[\text{Pd}_3\text{Tr}_2]^{2+}$ containing different nitrogen-based ligands is reported. The complexes were synthesized in good yield and characterized by multi-nuclei NMR spectroscopy, elemental microanalysis and single-crystal X-ray crystallography. Variation in the equatorial ligand strongly influences Pd-N bond distances, but has only a minor effect on Pd-Pd distances.

Graphic Abstract:

For review purposes only.

Complex Number	Complex Formula
1a	$[\text{Pd}_3\text{Tr}_2(\text{Pyridine})_3][(\text{BF}_4)_2]$
1b	$[\text{Pd}_3\text{Tr}_2(\text{Pyridine})_3][(\text{SO}_3\text{CF}_3)_2]$
2	$[\text{Pd}_3\text{Tr}_2(\text{MeCN})_3][(\text{BF}_4)_2]$
3	$[\text{Pd}_3\text{Tr}_2(\text{DMAP})_3][(\text{BF}_4)_2]$
4	$[\text{Pd}_3\text{Tr}_2(\text{DMAB})_3][(\text{SO}_3\text{CF}_3)_2]$
5	$[\text{Ag}(\text{DMAP})_2][(\text{BF}_4)]$

Graphical Abstract