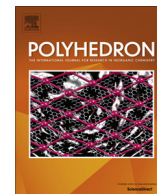




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## Tripalladium(0) sandwich complexes with nitrogen based ligands

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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.

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### 1. 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 ( $\text{C}_7\text{H}_7^+$ ). 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

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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.

## 2. Results and discussion

### 2.1. Synthesis

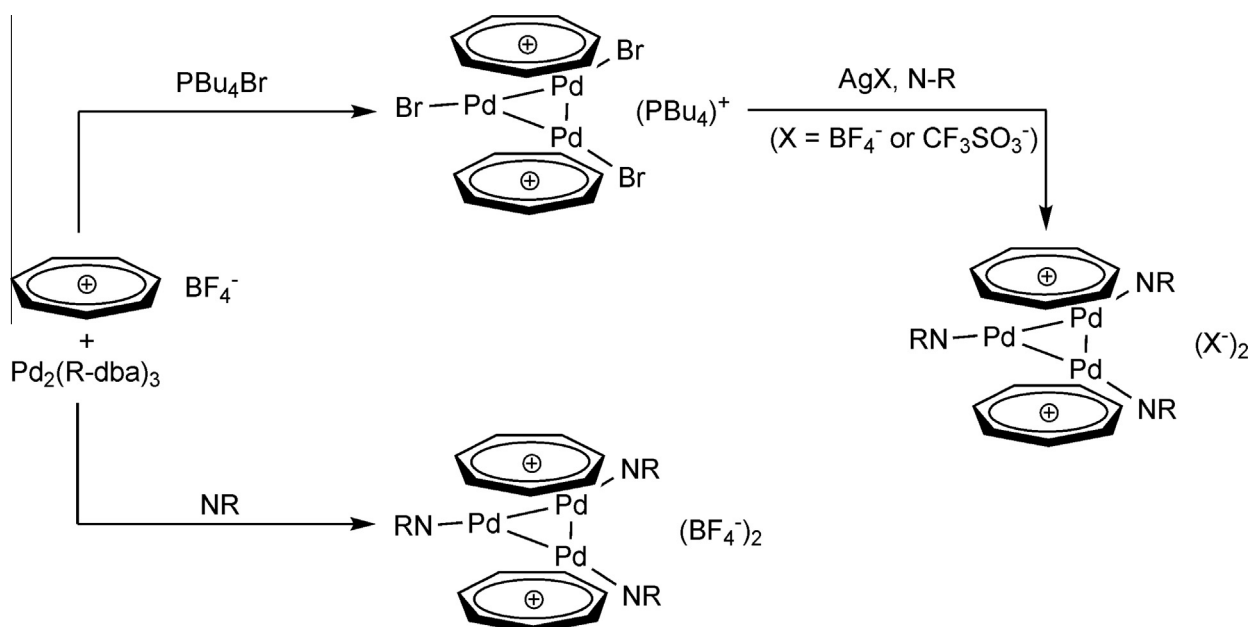
Our group has previously reported the synthesis of a series of pnictogen complexes  $[\text{Pd}_3\text{Tr}_2(\text{XPh}_3)_3][(\text{BF}_4)_2]$  ( $\text{X} = \text{N}, \text{P}$  or  $\text{Sb}$ ) via the reaction of  $[\text{P}-n\text{-Bu}_4][\text{Pd}_3\text{Tr}_2\text{Br}_3]$  with  $\text{AgBF}_4$  and an excess of  $\text{XPh}_3$  in dichloromethane [12]. In certain reactions, use of silver tetrafluoroborate ( $\text{AgBF}_4$ ) or silver triflate ( $\text{AgSO}_3\text{CF}_3$ ) 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  $\text{AgBF}_4$  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).  $^1\text{H}$  NMR in  $d_6$ -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  $^1\text{H}$  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 ( $\sim 2.48$  ppm) and water ( $\sim 3.30$  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 ( $\sim 9.2$  ppm) were observed. The formation of the expected product was also confirmed by the absence of any signal in the  $^{31}\text{P}$  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  $^{19}\text{F}$  NMR. Replacement of  $\text{AgBF}_4$  with  $\text{AgSO}_3\text{CF}_3$  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  $[\text{Pd}_3\text{Tr}_2(\text{Py})_3][(\text{BF}_4)_2]$  ( $\text{Py} = \text{pyridine}$ ) (**1a**) and  $[\text{Pd}_3\text{Tr}_2(\text{Py})_3][(\text{SO}_3\text{CF}_3)_2]$  (**1b**) respectively.

The  $^1\text{H}$  NMR spectrum between 6 and 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  $^1\text{H}$  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.  $^1\text{H}$  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  $\text{BF}_4^-$  and  $\text{CF}_3\text{SO}_3^-$  to bind to the  $[\text{Pd}_3\text{Tr}_2]^{2+}$  unit [12,20].

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  $\text{AgBF}_4$  and 4-dimethylaminopyridine in dichloromethane gave the new complex  $[\text{Pd}_3\text{Tr}_2(\text{DMAP})_3]$



Scheme 1. Synthesis pathways for complexes 1–4.

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