The Synthesis of a Novel Molecular Square

Honors Thesis (HONRS 499)

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Abstract

The synthesis and characterization of a novel molecular square [Pd(4,4'-bipyridyl)(P(C_2H_5)$_3$)$_2$(OSO$_2$CF$_3$)$_2$]$_4$ is reported. Beginning with K$_2$PdCl$_4$, successive reactions with P(CH$_2$CH$_3$)$_3$, AgOSO$_2$CF$_3$, and bipyridine were performed to produce this relatively planar molecule in percent yields of 81.9%. Infrared spectra are consistent with the products of each step. This molecular square is a relatively π-electron deficient compound that is earmarked for use in the creation of a unique association called a surface-attached catenane monlayer that has many potential uses as a monolayer and a nanodevice.

Acknowledgements

- I would like to thank my advisor, Dr. Patricia Lang, for showing me the attention to detail that is required in scientific research. I cannot show her enough gratitude for her willingness to help and her patient guidance.

- I would also like to thank the Ball State Chemistry Department for the opportunity to work in the summer research program. It is an exceptional program that has greatly enriched my college experience.

- I have to thank my lab partners, Jessica Juenemann, Ann Nelson, and Abby Tuttle for making research fun, and I owe Jessica special thanks for her assistance with spectra interpretation.

- I would like to thank the Honors College for the chance to further investigate my research work. It allowed me a glimpse into the effort required to publish scientific work.

Preface

This thesis is a summation of work performed by my partners and myself in the Ball State Chemistry Department summer research program on the synthesis of a complex molecular square. Future research groups will use this compound to create a novel association that has many possible uses. As such, the theoretical potential of the molecular square will be discussed along with its place in the current field of study.

Much of the work that is discussed and proposed in this thesis is of a very complex scientific nature. A level of introduction is required even to discuss the topic with chemistry students, and since this thesis is intended for honors college perusal, a few topics will be discussed with an eye toward educating the lay person.

The potential uses of our molecular square center around the field of nanoscience. In today's world of ever-changing technological progress, many scientists have touted nanoscience as the next frontier of which great advancements will be made. Scientists are striving to design compounds that can work like machines on the molecular scale. Futurists imagine nanodevices that can navigate the human blood stream and eliminate cancerous tumors or smaller and faster computers based on molecules rather than silicon chips. While these types of devices are still more fantastical than practical, the groundwork is being laid today for huge advancements on a tiny scale.

In an effort to create useful nanodevices, many investigators have taken the first step in trying to create electrically controlled molecular switches. The basic idea behind this type of work is that you could create a device that is predictably changed when given a certain stimulus. These changes most often involve two molecules that alter their orientation in regards to one another. As an example, imagine a circular molecule A and

a linear molecule B. Now suppose that B passes through the center of A like a string through a bead, and that the circular A sticks to a certain spot on B, called point 1. For these molecules to work as a switch, there would have to be a point 2 along B which A will move to if a controlled change is made. Therefore, the position of the circular A molecule along the linear molecule B is used as the switch. This type of switch is shown in Figure A below. Many other types of switches have been hypothesized, but all possess the common idea that a change in their environment causes a change in the spatial organization of the switch.
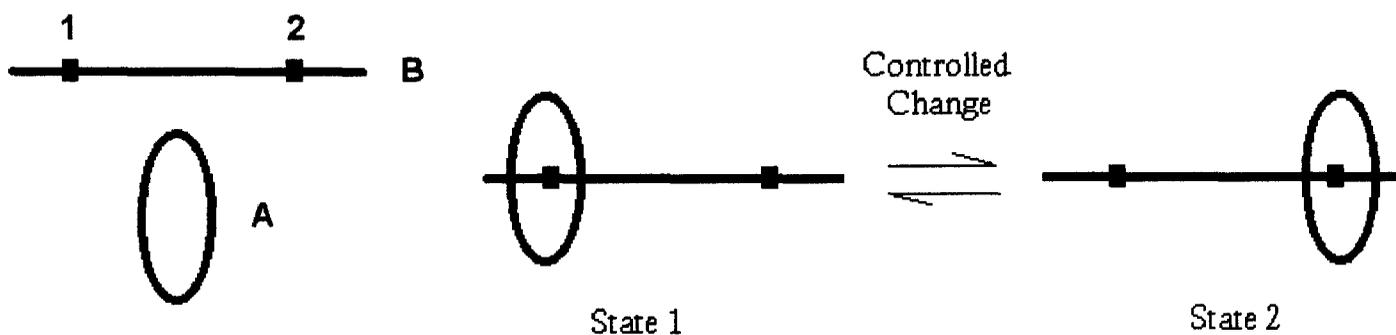
Figure A: This illustration shows a basic model for a molecular switch.

Additionally pertinent to understanding of this thesis are a discussion of monolayers and the use of infrared spectroscopy as an analytical tool. First, just as it sounds, a monolayer is a single layer of molecules that cover a surface. Most monolayers are self-assembling in that the molecules will arrange themselves into organized patterns on the surface of the substrate. Since the monolayer is now what the surrounding environment interacts with, the surface now possesses the properties of the molecules surrounding it. Controlling the properties of surfaces is important in many industrial processes and monolayers are thought to have many potential uses.

Second, IR spectroscopy is a common method of analysis in chemical work, and it is used as part of this synthesis to verify that the correct products have been produced in reactions. The basis for spectroscopy comes from quantum mechanics and the idea that energy transitions occur at certain quantized energy levels. An IR spectrometer shoots the spectrum of IR light through a sample and measures the amount of light that passes through. Since chemical bonds absorb certain wavelengths of light to become vibrationally excited, certain wavelengths of IR light will be absorbed by the sample and not pass through. The IR spectrometer measures what wavelengths of light the sample absorbs, and the resulting pattern is used to verify the identity of the molecule. Tables listing the wavelengths at which certain chemical bonds absorb energy and vibrate are used to help identify the bonds present in the sample based on the absorption spectrum, providing support for the identity of the sample.

The many potential uses of our molecular square discussed in this thesis make it an interesting and important compound to study. However, before it can be studied, this compound must be produced, and as such the synthesis of a molecular square was undertaken and is herein described.

Introduction

The goal of this research project is the synthesis of [Pd(4,4'-bipyridyl)(P(C$_2$H$_5$)$_3$)$_2$(OSO$_2$CF$_3$)$_2$]$_4$, a molecular square shown in Figure 1 below.
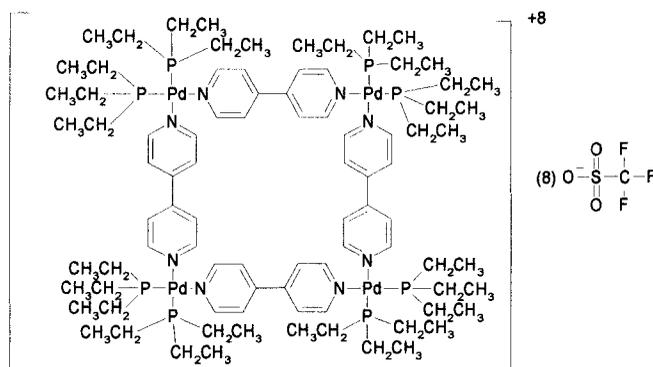

Figure 1

The sides of the square are composed of conjoined six-membered rings containing nitrogen atoms on their terminal ends, commonly known as bipyridinium units. These bipyridiniun units are linked by positively charged metal palladium ions to form a square. The associated (OSO$_2$CF$_3$)$^{-1}$ anions, commonly known as triflate ions, are present as counterions to balance the charge on the square compound.

The molecular square possesses some unique properties. The propensity of the metal chelating corners to form square planar bonds allows for the efficient assembly of the molecule. Since metal ions are used to construct the corners, the bipyridinium square portion of the molecule lies nearly in a single plane.(8) The bipyridinium units that make up the sides of the square are π-deficient components. A π-deficient molecule lacks the full complement of electrons that it can hold in its π orbitals. This fact allows it to interact with molecules rich in π electrons by forming charge transfer complexes.

Charge transfer complexes are associations in which the π electrons in one molecule interact with an empty π orbital in another molecule, causing a complexation of the two molecules. In this type of interaction, the π electrons from a molecule with a

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greater supply move from their highest occupied molecular orbital (HOMO) into the

lowest unoccupied molecular orbital (LUMO) of the molecule that has fewer π electrons.

In this way, electrons seek to occupy a more stable, lower energy state, and this

interaction serves to bind the two molecules together.

For example, the dithiol hydroquinone derivative shown in Figure 2 possesses a π

rich aromatic region that allows it to form a charge transfer complex with our molecular

square. When mixed in solution, spectroscopic studies suggest the formation of an

association between these two compounds where the dithiol threads through the center of

the square, noncovalently linking the two molecules. Spectral data also suggests the

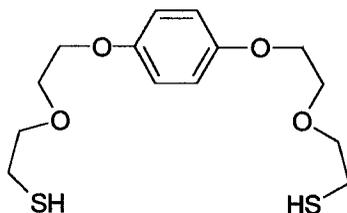association of a second dithiol along the perimeter of the square.

Figure 2

Once a dithiol molecule has been threaded through the center of the molecular

square, the properties of the dithiol can then be taken advantage of to create a unique

association. Sulfur groups on the dithiol form covalent bonds with gold surfaces.(6) If

these covalent bonds are formed while the molecule is threaded through the square, both

components are bound onto the gold surface. The molecular square and dithiol are now

locked together into a complex despite the fact that a covalent bond has not formed

between the two molecules. This type of complex is known as a catenane, and is locked

together by mechanical restraints rather than covalent bonds. Figure 3
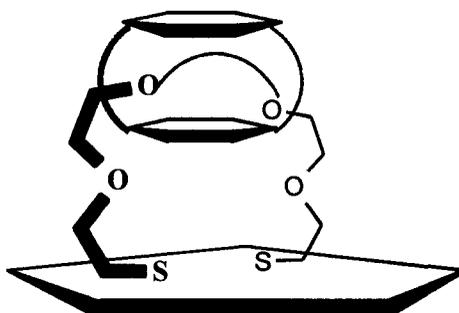
Gold Surface

Figure 3

shows a representation of our catenane, where the dithiol passes through the center of the

square before bonding to the gold surface at each terminus.

The bonding of the dithiol and the molecular square to the gold surface has

another interesting characteristic in that it is laid down as a monolayer on the surface. A

monolayer is a spreading of molecules across a surface to evenly cover it with one layer

of the molecules usually in a very organized, even crystalline structure. Monolayers alter

the properties of the surfaces on which they attach, potentially making them capable of

attracting or repelling different compounds.(11) Occasionally, monolayers are only

loosely associated with the surfaces they cover by noncovelant interactions. However,

our catenane monolayer is attached to the gold surface covalently, making it a very stable

complex. Figure 4 below shows an example of monolayer formation, in this case

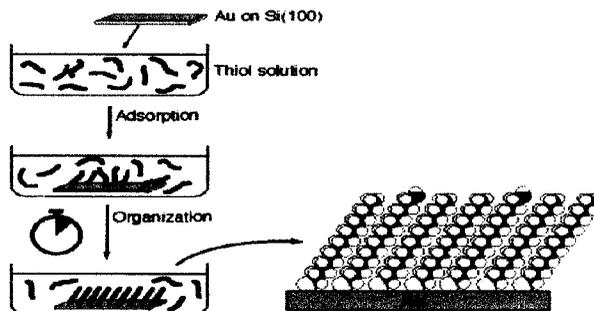alkanethiols arranging themselves on a gold surface.

Figure 4

The subject of monolayers is one of intense study due to the many possible applications of these associations and because of their advantageous properties. These monolayers are formed by molecules that arrange and attach themselves in an orderly fashion to the designated surface, essentially allowing the monolayer to repair any damage to itself if placed in an environment containing a surplus of the molecules.(11) Coating a surface with a monolayer allows for the control of the properties of that surface. This control of properties can be exploited in many ways. Monolayers can potentially be used to prevent rusting or degradation by shielding the surface from the environment. Other possible uses include lining of fuel cells and industrial components to increase efficiency by limiting surface effects and the coating of working components to lessen the mechanical wear and tear on the surfaces of machines.

The coating of a gold surface with our components to form a catenane monolayer could confer many interesting characteristics to the gold surface. One possibility centers on the ability of the positively charged metal corners of our molecular square to bind complex anions. As such, a square attached to a surface could cause the localization of negatively charged ions by drawing them to the surface. This property could be useful in ion detection. When a complex anion is bound to the square, a change in absorbance of light could be detected to signal the presence of the anion. The binding of anions by the catenane monolayer could also be used as a filtration system in which these complex anions could be collected from a solution onto the catenane surface.

Another possible characteristic conferred on the gold surface by the presence of our molecular square could arise from its relative lack of π electrons. Due to this π electron deficient nature, the molecular square component of the catenane could attract

molecules rich in π electrons. This type of association is used to complex the square with the dithiol, but spectral data indicates a second dithiol molecule concurrently associates with the side of the square. This would seem to indicate that the potential of the molecular square to form interactions of this type is not exhausted by the formation of a charge transfer complex to produce the catenane. The association of a π rich target molecule with the catenane would cause an observable change in charge transfer wavelength that could be used as an indicator of its presence. Another possible means of detection could result if a π rich target could associate with multiple catenanes on multiple free-floating particles in solution. These multiple associations could cause an aggregation and the formation of precipitate. This precipitate could be used as either an indicator or a device for sequestering of the target molecule. A theoretical example of the interaction between a free-floating version of our catenane and a target molecule is shown in Figure 5 below.
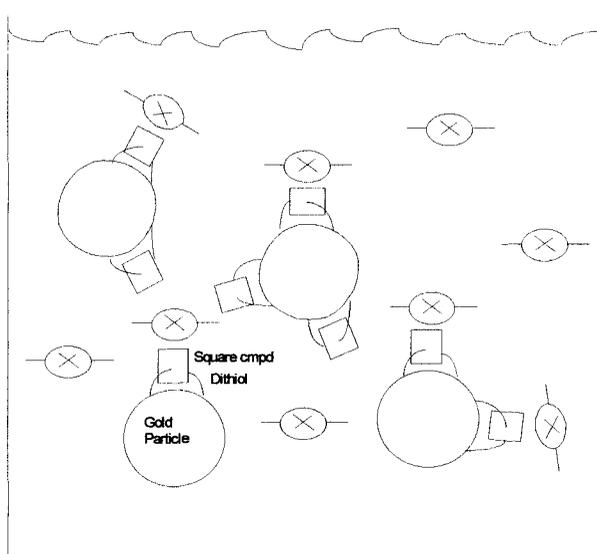
Our Catenane in Solution with a Target Molecule

—⊗— = a target molecule

Figure 5

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Another possible use for our catenane arises from the way in which the components interact. Since the molecular square and dithiol are mechanically bonded together, the components of our catenane monolayer often have the potential to change their positions relative to each other. It is possible that adding or removing electrons in the environment could cause a change in the relationship between the molecular square and the dithiol through the rotation or shifting of one component in relation to the other. If this change could be used as a triggering device or a kind of "molecular switch," the catenane could theoretically be used to send or receive signals. The possibility of a catenane that could predictably alter its orientation based on its environment is an area of special interest to those working to develop nanodevices.

One of the foremost researchers in the area of nanodevices is Dr. J. Fraser Stoddart. Stoddart and his colleagues have worked to create self-assembling complexes that have the potential to be used as molecular switches. Their work is centered around three possible types of molecular switches, pseudorotaxanes, rotaxanes, and catenanes.

In a pseudorotaxane, charge transfer complexes usually link a ring structure over a linear structure in solution so that the linear molecule threads through the center of the ring, much like the initial interaction between our dithiol and molecular square. The ring structure is free to move on and off of the linear molecule depending on the surrounding environment. The idea behind this type of switch would be that in certain environments the ring would be found associated with the linear molecule, while in others situations it would be floating freely or associated with another molecule. The position of the ring molecule could then hypothetically be used to indicate the change in its surroundings and perhaps be used in some way to pass on a signal.

Rotaxanes resemble pseudorotaxanes in that a ring molecule is usually associated with a linear molecule through charge transfer interactions. However, in rotaxanes, the ring molecule is not free to move off of the linear molecule. Instead, large chemical groups are added to the ends of the linear molecule to make it difficult for the ring to escape. The linear component of a rotaxane usually possesses two sites at which the ring structure can bind. These two possible binding locales are engineered so that one is a more suitable site for the ring to interact with until the other site is reduced or oxidized, at which time the second site becomes the more favorable piece with which the ring can interact. In this way, the position of the ring along the linear molecule is used as the hypothetical switch.

As stated above, catenanes are molecular associations created by a mechanical bond between two components rather than a covalent bond. Most of Stoddart's work with catenanes involves two interlocked rings. One of the rings will possess multiple binding sites around which the other ring will orient itself based on the surrounding environment. The position of the two rings in relation to each other is then used as the indicator or switch. Stoddart and his associates have had some success with producing associations that change with the voltage of the system, an exciting step toward the production of nanodevices.(3)

A step further in the direction of our research was taken by Dr. George Gokel. Dr. Gokel and his colleagues have attached a linear component to a surface rather than using two rings to mechanically lock the components together.(6) This step forms a catenane and localizes it onto a surface. In his study, Dr. Gokel used a component from one of Dr. Stoddart's catenanes, called a paraquat square, and an associated alkane thiol

to attach the two molecules to a gold surface and form a catenane. A representation of

Dr. Gokel's catenane is shown in Figure 6 below. In most of Dr. Stoddart's work, the

created complexes were absorbed onto a surface through specialized techniques.

However, Dr. Gokel's use of covalent bonds to attach the catenane to the surface forms a

stronger interaction and a more stable association between the surface and the molecules.

This type of association holds promise in that a strongly fixed position of the molecules is

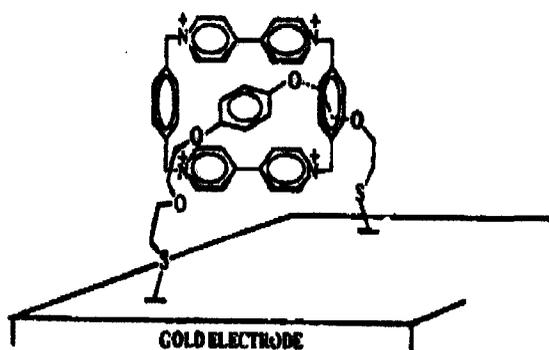desirable when determining possible properties and uses of these molecules.


Figure 6

Molecules like Dr. Gokel's catenane are intriguing associations that warrant

further study. However, the paraquat square that Gokel uses to form his catenane is

difficult to synthesize and is produced in fairly low yields. Dr. Stoddart and his

associates have tried multiple procedures to synthesize the square and obtained a yield of

only 32% at best.(1) To aid in the study of surface attached catenanes it would be

desirable to find components more readily and efficiently synthesized. The answer

comes in the form of Pd(II) and Pt(II) macrocyclic squares studied by Dr. Peter J. Stang.

Dr. Stang and his colleagues specialize in creating large compounds using

transition metals and coordination chemistry(7) to aid in assembly of the desired product.

Their studies include many types of cyclic nanostructures, including well-characterized

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macrocyclic squares formed by linking bipyridinium units into a square structure using transition metal corners. This type of molecule is a stable assembly that efficiently forms into a square planar organization.(10) Our molecular square is this type of molecule, and possesses many properties discussed above that allow it to form a similar catenane to that produced by the paraquat square but possesses the added advantage of theoretically being produced more efficiently and in greater yields. Therefore, the synthesis and study of [Pd(4,4'-bipyridyl)(P(C$_2$H$_5$)$_3$)$_2$(OSO$_2$CF$_3$)$_2$]$_4$, (our molecular square) is undertaken to allow for the study of its association with a dithiol to form a surface attached catenane monolayer in correlation with other research being done in the field of nanodevices and with an eye toward other potential uses.

Experimental

The production of the palladium molecular square can be achieved through a three step process using components readily available for purchase.

PEt$_3$
triethylphosphine
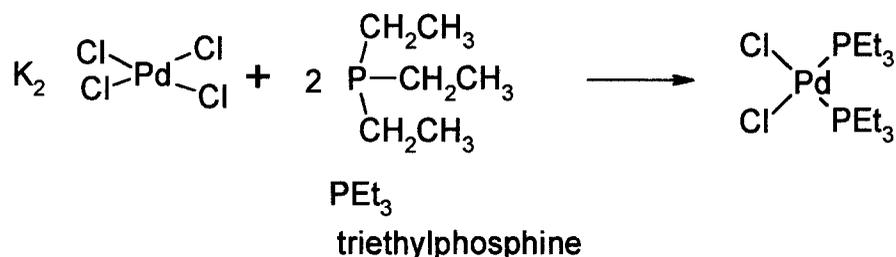
Step 1

Preparation of cis-dichloro-bis(triethylphosphine)palladium(II). Two grams of K$_2$PdCl$_4$ purchased from Aldrich were placed in a 250 ml flask equipped with a stir bar and a sidearm attached to a supply of argon gas to maintain an inert atmosphere. Water was deoxygenated by bubbling argon through it for an hour, and 10 ml of this was added to the flask to dissolve the K$_2$PdCl$_4$, producing a dark brown color. Eleven ml of 1M (C$_2$H$_5$)$_3$P was added to this mixture to attain the 55:100 molar ratio of K$_2$PdCl$_4$ to

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triethylphosphine indicated by literature. The triethylphosphine is a highly reactive

compound, and to keep it viable it was transferred by syringe through septum on the

stock solution and the reaction flask. The mixture of K_2PdCl_4, $(C_2H_5)_3P$, and

deoxygenated H_2O was allowed to stir for an hour at room temperature, producing a

yellow color. After stirring, the flask was heated on a steam bath for an hour, and the

resulting solid was filtered using a Buchner funnel and washed with the previously

produced deoxygenated H_2O. This filtered solid was then ground using a mortar and

pestle and dried under vacuum for an hour.

To obtain the correct molecular geometry, the product was placed in a sealed 250

ml flask equipped with a stir bar, and 15 ml deoxygenated pentane was added. Eleven

drops of triethylphosphine were added to the reaction flask by syringe, and the reaction

was allowed to stir for 10 minutes, causing a color change from brown to olive green.

The resulting solid was filtered using a Buchner funnel and washed with deoxygenated

pentane. The solid obtained from the funneling was allowed to dry for an hour under

vacuum. The sample evinced a light brown color after drying, and was then placed in a

100 ml beaker for recrystallization using acetonitrile. The recrystallization produced

long, yellow crystals of solid $PdCl_2(P(C_2H_5)_3)_2$. The dried crystals weighed 2.11 g, an

83.3 % yield. An infrared spectrum was taken to verify production of the desired

compound.

Step 2

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Preparation of cis-Pd(P(C$_2$H$_5$)$_3$)$_2$(OSO$_2$CF$_3$)$_2$ In this addition of triflate ions to

the palladium metal center, a very large concern was the moisture and light-sensitive

nature of the silver triflate used in the reaction. As such, all flasks used were dried in an

oven overnight and maintained in an argon atmosphere with the exclusion of light while

the reaction was proceeding. A mass of .2043 g PdCl$_2$(P(C$_2$H$_5$)$_3$)$_2$ was placed in a 125 ml

Schlenk flask along with .3177 g of Ag(OSO$_2$CF$_3$) and 20 ml CH$_2$Cl$_2$. These compounds

were allowed to stir for 3 hours at room temperature, changing from an orange color to a

yellow nature. A unique filtering system shown in the attached Figure 7 was used to

separate the desired aqueous layer from the solid layer. The liquid collected was a yellow

color, while the solid left behind was white. After the liquid layer is collected, low H$_2$O

diethyl ether was added with swirling and cooling to precipitate the desired product out of

the CH$_2$Cl$_2$ solvent. The sample was then dried under vacuum to obtain a light yellow-

white powder weighing .310 g, a 98.1% yield. The infrared spectrum of the product was

taken to verify its identity.

Step 3
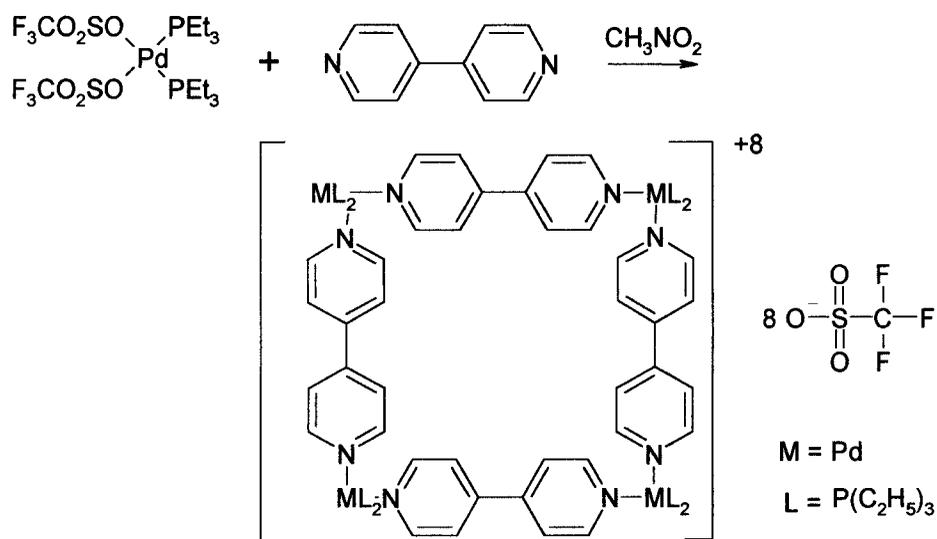
Preparation of [Pd(4,4'-bipyridyl)(P(C₂H₅)₃)₂(OSO₂CF₃)₂]₄ To a Schlenk

flask maintained in an argon atmosphere, 25 ml CH_3NO_2, .035 g bipyridine, and .107 cis-

$Pd(P(C_2H_5)_3)_2(OSO_2CF_3)_2$ were added and allowed to stir for 2 hours at room

temperature. The solution was then reduced to 25% of its original volume by rotary

evaporation, and 15 ml diethyl ether was added to cause a precipitation. This solution

was then vacuum dried, producing an off-white color solid. After recrystallization using

nitromethane and diethyl ether to precipitate the desired product, .109 g of the palladium

square was obtained, an 81.9% yield. An infrared spectrum was taken of the product to

support the assumption of a successful synthesis.

Accessory Step

Our lab group was able to obtain some excess solid $PdCl_2$ from another research

group. This compound can be converted to the K_2PdCl_4 required for Step 1 in the

synthesis through a fairly simple procedure. The K_2PdCl_4 can be purchased for use in the

reactions, but the production of it from an available source was appealing due to the cost

associated with purchasing the compound. In a 125 ml beaker, 1.296 g of $PdCl_2$ (one

mole) was combined with 1.096 g KCl (two moles) in amount of methanol required to

dissolve both compounds. After stirring overnight, the precipitate was obtained via

vacuum filtration using a Buchner funnel and dried under vacuum, resulting in 2.22 g of

K_2PdCl_4, a yield of 93.1%.

Data/Results

The infrared spectrum was taken for each of the reaction products to support the

identity of the compound. The tables below list the frequencies of light at which the

molecules absorb, the type of molecular vibration this absorption is indicative of, and the

reference used to determine what each peak in absorption represented.

ν_A: asymmetric stretching mode
ν_S: symmetric stretching mode
δ: bending mode

Table 1: This table lists the IR assignments for the attached graph labeled Spectrum 1.

This sample is the product of Step 1 of the synthesis. The peaks observed

Between 2600 and 2400 cm^{-1} are omitted because they are indicative of CO_2 molecules

present in the chamber of the IR spectrometer.

Frequency of Vibration (cm^{-1})	Band Assignment	Reference/Justification
2963.29	$\nu_A CH_3$	Reference 4 p.223, Reference 5
2929.61	$\nu_A CH_2$	Ref. 4 p.223, Ref. 5
2909.40	$\nu_S CH_3$	Ref. 4 p.223, Ref. 5
2875.72	$\nu_S CH_2$	Ref. 4 p.223, Ref. 5
1452.70	$\delta_A CH_3$ (deformation)	Ref. 4 p.226, Ref. 5
1409.06	$\delta R-CH_2 P$	Ref. 4 p.228, Ref. 5
1375.48	$\delta_S CH_3$ (deformation)	Ref. 4 p.226, Ref. 5
1264.68	CH_2 wag	Ref. 4 p.229
1029.65	CH_2 twist	Ref. 4 p.229
764.39	CH_3 rock	Ref. 4 p.229
730.82	CH_2 symmetric rock	Ref. 4 p.231

Table 2: The following table corresponds to Spectrum 2, the product from Step 2 of the

synthesis.

Frequency of Vibration (cm^{-1})	Band Assignment	Reference/Justification
2957.22	$\nu_A CH_3$	Reference 4 p.223, Reference 5
2923.51	$\nu_A CH_2$	Ref. 4 p.223, Ref. 5
2869.58	$\nu_S CH_3, \nu_S CH_2$	Ref. 4 p.223, Ref. 5
1451.52	$\delta_A CH_3$ (deformation)	Ref. 4 p.226, Ref. 5
1411.14	$\delta R-CH_2 P$	Ref. 4 p.228, Ref. 5
1374.12	$\delta_S CH_3$ (deformation)	Ref. 4 p.226, Ref. 5
1256.35	νCF_3	Ref. 4 p.360
1172.23	$\nu_A SO_3$	Ref. 4 p.355
1034.27	$\nu_S SO_3$	Ref. 4 p.355
765.07	δCF_3	Ref. 4 p.360
728.06	CH_2 symmetric rock	Ref. 4 p. 231

Table 3: This table shows the IR analysis of what should be the final product, our molecular square. Again, the 2600 to 2400 cm^{-1} are omitted as CO_2 gas molecules in the spectrometer chamber.

Frequency of Vibration (cm^{-1})	Band Assignment	Reference/Justification
3007.66 – 3148.73	CH stretching on bipyridine ring	Reference 5
2953.92	$\nu_A CH_3$	Ref. 4 p.223, Ref. 5
2920.33	$\nu_A CH_2$	Ref. 4 p.223, Ref. 5
2846.43	$\nu_S CH_2, \nu_S CH_3$	Ref. 4 p.223, Ref. 5
1611.83	bipyridine ring vibration	Ref. 4 p.273

1591.76	bipyridine ring vibration	Ref. 4 p.273
1454.56	$\delta_A CH_3$	Ref. 4 p.226, Ref. 5
1411.06	$\delta R\text{-}CH_2P$ (deformation)	Ref. 4 p.228, Ref. 5
1380.95	$\delta_S CH_3$	Ref. 4 p.226, Ref. 5
1257.14	νCF_3 (triflate counterion)	Ref. 4 p.360, Ref. 8
1153.40	$\nu_A SO_3$ (triflate counterion)	Ref. 4 p.355, Ref. 8
1029.59	$\nu_S SO_3$ (triflate counterion)	Ref. 4 p.355, Ref. 8
758.55	δCF_3 (triflate counterion)	Ref. 4 p.360, Ref. 5

The results obtained from IR spectroscopy indicate that the intended products were obtained in all three reactions, with no significant data to suggest otherwise. All three steps in the synthesis can be deemed successful and efficient means of synthesizing our molecular square based on the spectroscopic data and the percent yields of the reactions.

Summary

Supporting the work of Stang, this synthesis shows that when care is taken in the reactions and experimental setups, the palladium molecular square can be produced in high yields. The production of this compound was run on a fairly small scale due to the costly nature of the materials used, but one would assume that scaled up reactions could be made to produce similar results. Infrared spectra of the products of each step in the synthesis seem to confirm that the desired reactions are taking place and that the protocols used have been successful.

Special considerations do have to be taken in the production of the molecular square. In all chemical reactions it is important to limit outside contaminants, but in this synthesis that goal becomes especially difficult in Step 2 of the reaction when light and moisture in the air become significant possible contaminants. To overcome this difficulty, some novel protocols were used to ensure the isolation of the reactants in an inert atmosphere as shown in the attached Figure 7. The refinement of experimental setups requires some trial and error, and problems with less successful trials allowed for the generation of better procedures to ensure the viability of the products and reactants.
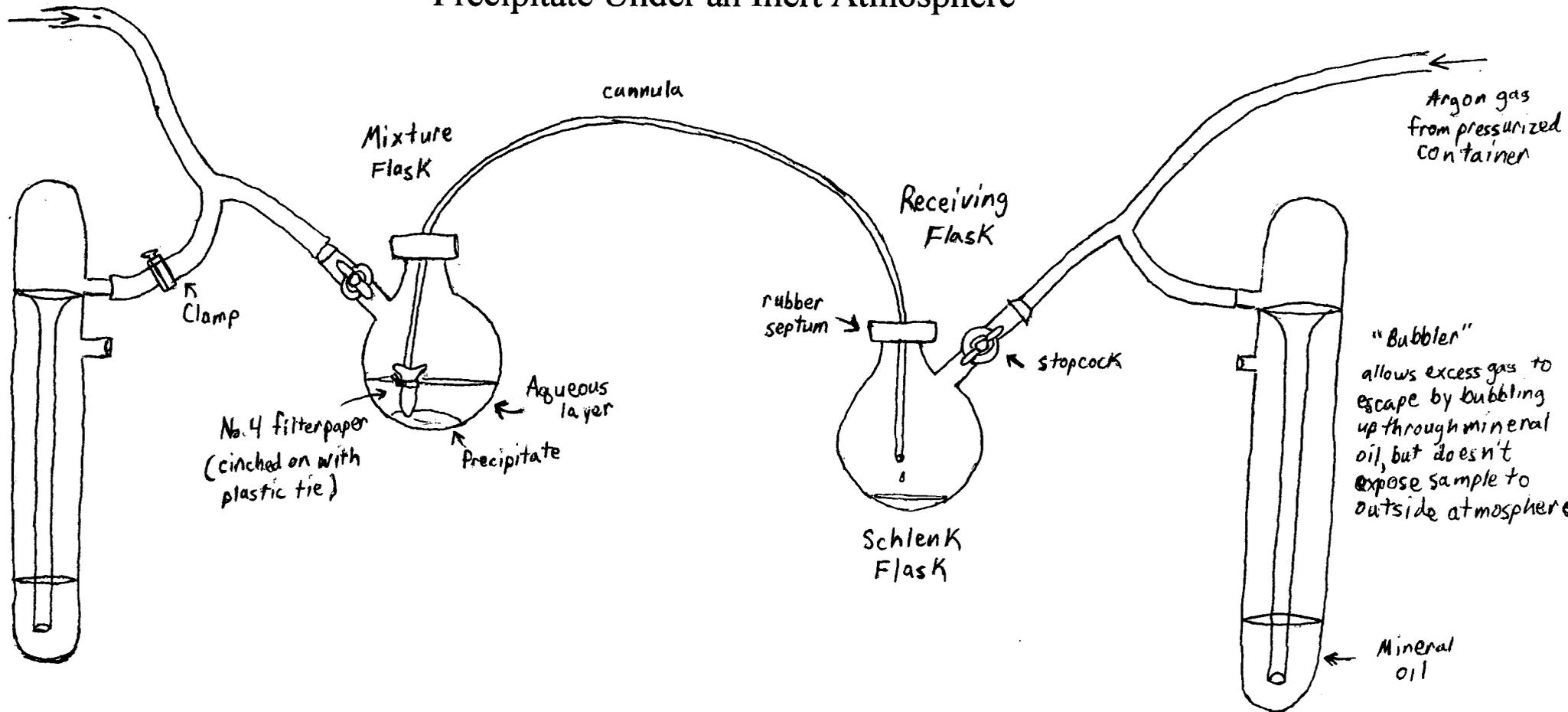
Bearing some resemblance to the paraquat square used by Gokel and associates but exhibiting better yields in synthesis, our palladium square seems an excellent candidate for use in production of a catenane monolayer by associating it with the dithiol compound in Figure 2 and a gold surface. Further studies are required to determine the exact uses and properties of this kind of association, but all indications point to this group of compounds forming a feasible and useful complex.

It remains to be seen if a catenane formed using the palladium square will prove useful as a nanodevice. If detectable changes do occur in the catenane orientation, the daunting task of harnessing this molecular switch for use as a molecular machine still looms as it does over all current work in this field. Still, the devices of the future have to be built a piece at a time, and the first step is the production of the base machinery. The more likely immediate uses for our catenane arise from its properties as a monolayer on a surface. It is entirely within the realm of modern technology to exploit the ability of the molecular square to sequester complex anions or π electron rich compounds for use as a kind of filter. The catenane monolayer could also function like other monolayers in

lessening degradation or controlling the properties of a surface. A full exploration of the properties of this catenane monolayer will have to be undertaken before its best uses can be determined. However, the formation of a catenane monolayer using a palladium square, dithiol, and gold surface is a novel idea and warrants study almost regardless of possible uses.

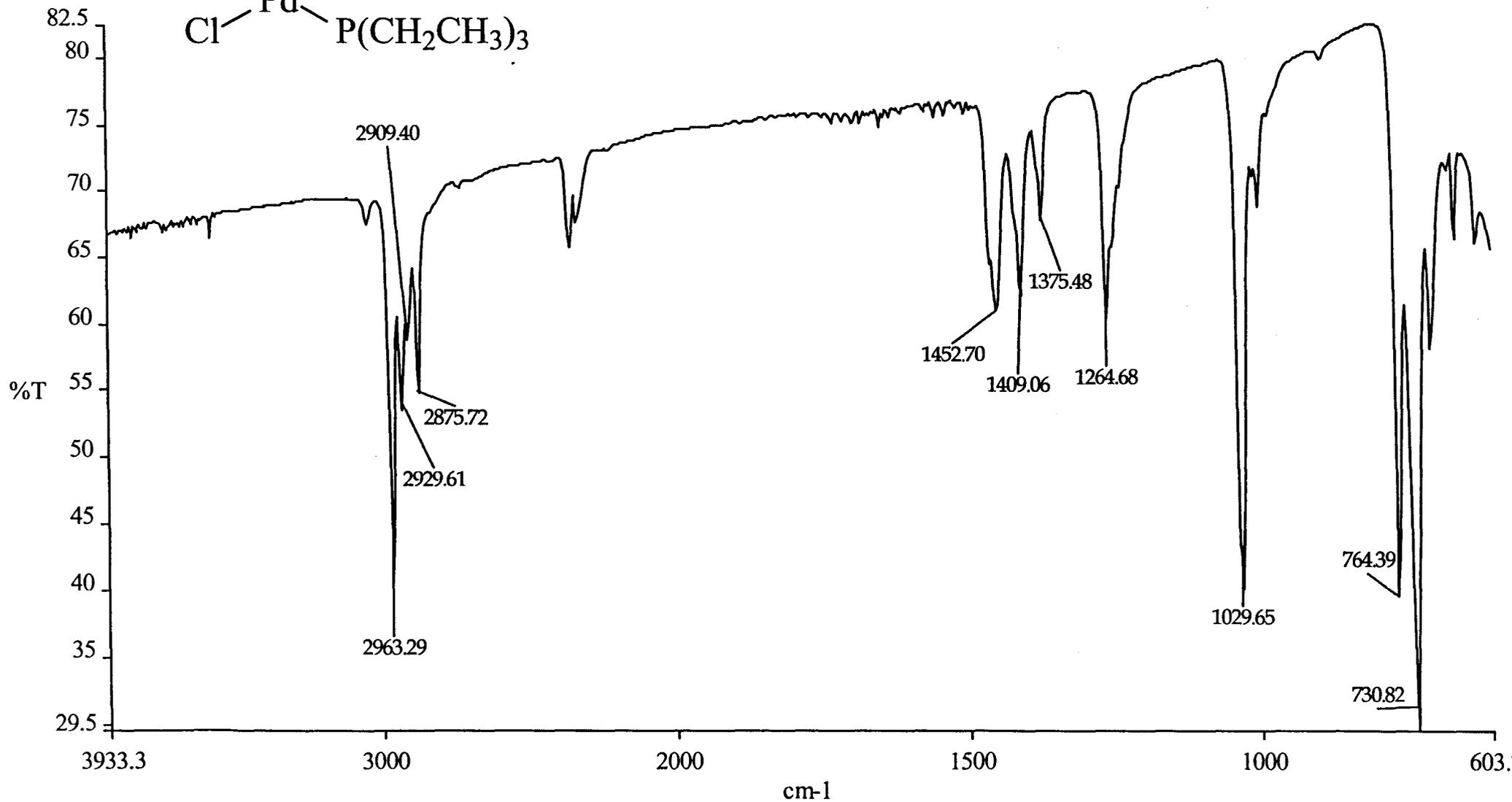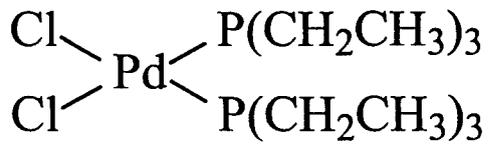**Figure 7:** Separation of Aqueous Layer from Precipitate Under an Inert Atmosphere

Argon gas from pressurized container

cannula

Mixture Flask

Receiving Flask

Argon gas from pressurized container

Clamp

rubber septum

stopcock

"Bubbler" allows excess gas to escape by bubbling up through mineral oil, but doesn't expose sample to outside atmosphere

No. 4 filterpaper (cinched on with plastic tie)

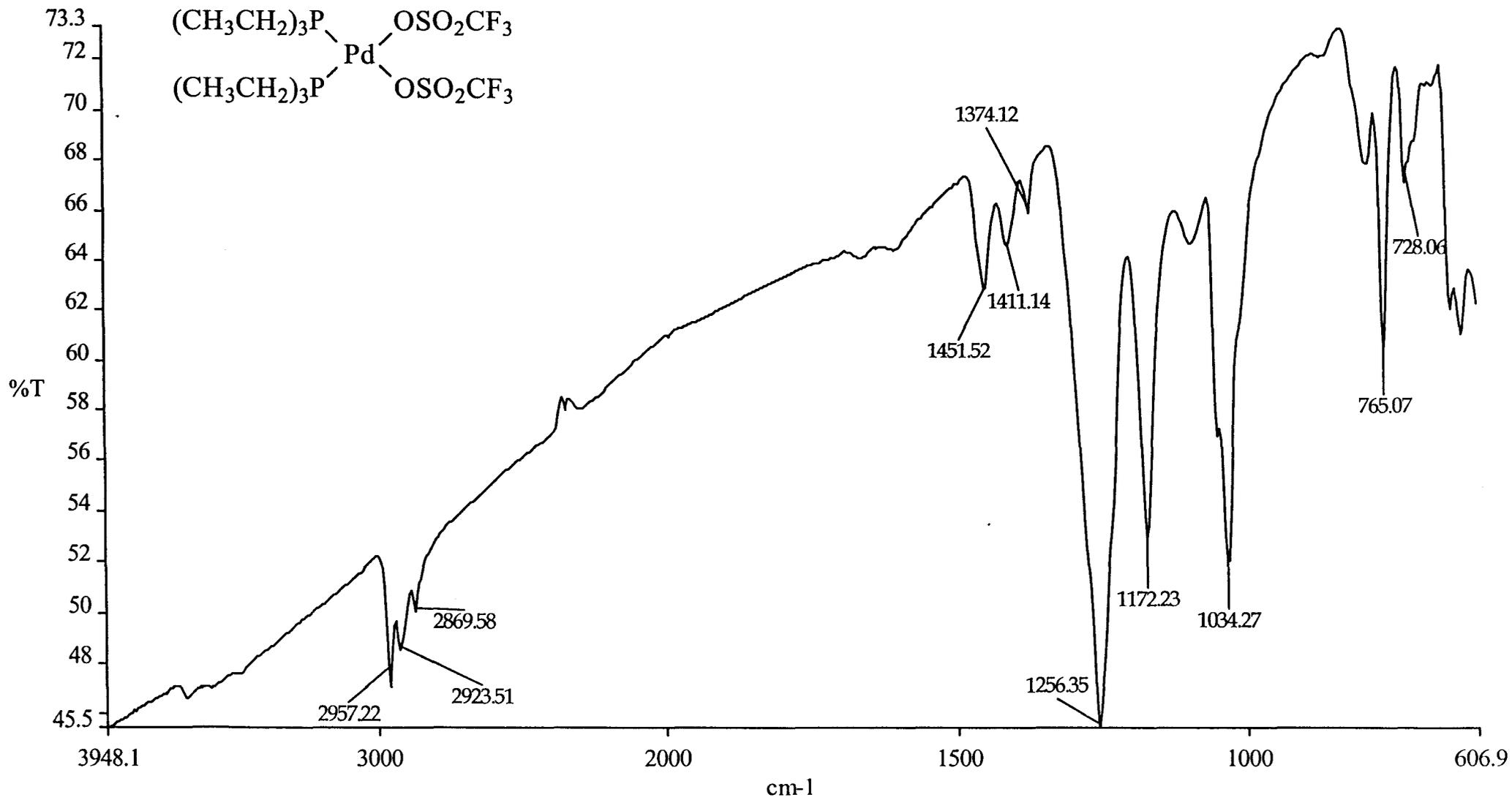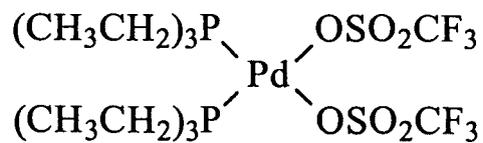Aqueous layer

Precipitate

Schlenk Flask

Mineral oil

Procedure

Push argon into receiving flask to purge, then stop argon flow. Open argon flow and stopcock to mixture flask. Close clamp to bubbler on mixture flask side and make sure that stopcock on receiving flask side is open. As pressure builds in mixture flask, the liquid aqueous phase is pushed through the cannula into the receiving flask. Excess pressure on the receiving flask side is relieved by the attached bubbler without exposing the sample to outside air.

Spectrum 1: Dichloro-bis(triethylphosphine)Palladium(II) IR

Spectrum 2: Palladium Triflate IR

$(CH_3CH_2)_3P$ OSO_2CF_3

Pd

$(CH_3CH_2)_3P$ OSO_2CF_3

%T

cm-1

73.3, 72, 70, 68, 66, 64, 62, 60, 58, 56, 54, 52, 50, 48, 45.5

3948.1, 3000, 2000, 1500, 1000, 606.9

1374.12
1411.14
1451.52
2869.58
2923.51
2957.22
1256.35
1172.23
1034.27
765.07
728.06

Spectrum 3: Palladium Square IR

IR spectrum with axes labeled %T (vertical, from 67.9 to 81.2) and cm-1 (horizontal, from 3948.1 to 618.0). Labeled peaks: 2953.92, 2920.33, 2846.43, 1611.83, 1591.76, 1454.56, 1411.06, 1380.95, 1257.14, 1153.40, 1029.59, 758.55, 728.43, 634.74.
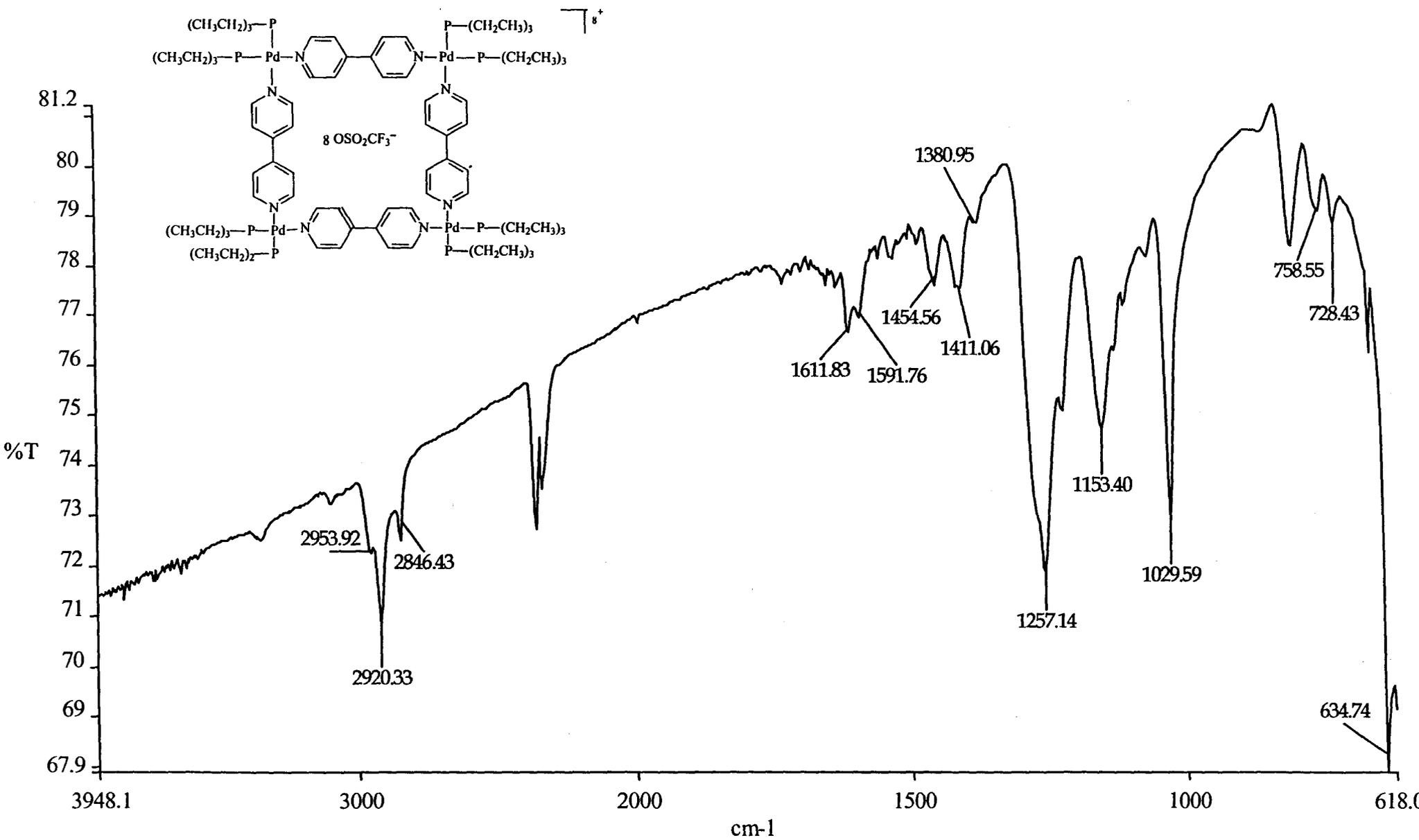
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