Qualitative Thermodynamic Study of Linkage Isomerism in Palladium (II) Complexes

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A QUALITATIVE THERMODYNAMIC STUDY OF LINKAGE ISOMERISM IN PALLADIUM(II) COMPLEXES

A thesis presented to the Committee of Graduate Studies and the Department of Chemistry of Union College, Schenectady, New York, in partial fulfillment of the requirements for the degree of Master of Science.

by Walter Michael Gantenbein

By ____________________________

Approved by ____________________________

Approved by ____________________________

Date ____________________________
To my wife, Laura, and my parents, Frances and Walter.
I wish to express my thanks to Professor Charles F. Weick, my Research Advisor, for suggesting this topic and for his guidance, assistance, and encouragement in its completion.

I also wish to thank Professor John G. Lanese and Professor John R. Sowa for their suggestions.
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ABSTRACT

The purpose of this research was to investigate linkage isomerism in dithiocyanatobistriphenylarsinepalladium (II), dithiocyanato-2,2'-bipyridinepalladium (II), and thiocyanatotetraethyl diethylenetriaminemine-palladium (II) thiocyanate.

Studies of linkage isomerism in these compounds were made in the pure solid state using a Differential Scanning Calorimeter. The instrumental data was supplemented with visual observations of the isomerization.

These calorimetric measurements were made possible by the wide range of heating rates available with the Differential Scanning Calorimeter. Thus, by choosing the proper heating rates, thermodynamic changes were detected for the isomerization of the triphenylarsine and tetraethyl diethylenetriamine compounds.
The following abbreviations will be used throughout the text of this paper:

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<tr>
<td>bipy</td>
<td>2,2'-bipyridine</td>
<td><img src="image" alt="bipy" /></td>
</tr>
<tr>
<td>dien</td>
<td>diethylenetriamine</td>
<td>( H_2N(CH_2)_2NH(CH_2)_2NH_2 )</td>
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<tr>
<td>Et₄dien</td>
<td>tetraethylenetriamine</td>
<td>( (C_6H_5)_2N(CH_2)_2\text{NH}(CH_2)_2\text{NH}(C_6H_5)_2 )</td>
</tr>
<tr>
<td>phen</td>
<td>o-phenanthroline</td>
<td><img src="image" alt="phen" /></td>
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<tr>
<td>Ph₃As</td>
<td>triphenylarsine</td>
<td>( (C_6H_5)_3\text{As} )</td>
</tr>
<tr>
<td>Ph₃P</td>
<td>triphenylphosphine</td>
<td>( (C_6H_5)_3\text{P} )</td>
</tr>
<tr>
<td>Ph₃Sb</td>
<td>triphenylstibine</td>
<td>( (C_6H_5)_3\text{Sb} )</td>
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INTRODUCTION

Linkage isomerism was known to Werner in the late nineteenth century when he studied nitro-nitrito complexes of cobalt(III).

During the past five years there has been renewed interest in linkage isomerism. Thiocyanato-isothiocyanato complexes of palladium(II) and platinum(II) were prepared and studied. The nature of the metal-SCN bond, i.e., whether it is S-bonded or N-bonded is dependent on the other ligands coordinated to the metal. Furthermore, it was discovered that with certain ligands such as 2,2'-bipyridine, triphenylarsine, and tetraethyl-diethylenetriamine both the S-bonded and N-bonded isomers could be isolated. This was accomplished by preparing the S-bonded complex at low temperatures and isolating it before it rearranged to the N-bonded complex. The N-bonded complex was obtained by heating the S-bonded complex.

This research investigated the mechanism of the isomerization process through calorimetric measurements of linkage isomerism in the thiocyanato-palladium(II) complexes previously mentioned using the Differential Scanning Calorimeter.

The procedure developed here gave good results with two of the three compounds studied and offers a potential tool for future investigations of linkage isomerism in the solid state.
I. HISTORY

Linkage Isomerism

An ambidentate ligand is one which contains two different donor groups, only one of which can coordinate with a particular metal ion at one time. These ligands give rise to complexes differing in the point of ligand attachment. The resulting complexes are called linkage isomers (1).

Nitro-Nitrito Linkage Isomerism

Werner was the first to recognize that the nitro and nitrito complexes of cobalt(III) having the composition \( (\text{NH}_3)_5\text{CoNO}_2\cdot X_2 \) (where \( X = \text{Cl} \) or \( \frac{1}{2} \text{SO}_4 \)) were examples of a more general phenomenon which he referred to as salt isomerism (2).

Utilizing the rate law for the nitrosation of ammonia and the ammines, \( \text{rate} = k(\text{ammine})(\text{HNO}_2)^2 \), Pearson et al. attempted to explain the rate of formation of nitrito complexes from the aquo complexes \( \text{cis} = \text{[Co en}_2(\text{NO}_2)\text{H}_2\text{O}]^{+2} \) and \( \text{[Co(NH}_3\text{H}_2\text{O}]^{+3} \) (3).

In weakly acidic solution, the nitrosating agent, \( \text{N}_2\text{O}_3^+ \), attacks the unshared pair of electrons on the ammine nitrogen by splitting into \( \text{N}_2^+ \) and \( \text{NO}_2^- \). Similarly, in the nitrosation of hydroxo groups, the attack of the \( \text{N}_2\text{O}_3^{-} \) will be on the oxygen atom of the hydroxo group via the following mechanism (4):

\[
\text{Co-OH} + \text{O} \equiv \text{N} \equiv \text{O} \rightarrow \text{Co} \equiv \text{O} \equiv \text{H} \\
\text{O} \equiv \text{N} \equiv \text{O} \equiv \text{N} \equiv \text{O} \\
\rightarrow \text{Co} \equiv \text{O} \equiv \text{N} \equiv \text{O} + \text{H}^+ + \text{NO}_2^- \\
\]

\( ^{18}_0 \) studies demonstrated that the isomerization of \( \text{RONO} \) to \( \text{RNO}_2 \) was intramolecular in solution. This conclusion was reached on the basis that less than 2% exchange between \( \text{RNO}_2^* \) and \( \text{NO}_2^- \) took
place after 50 hours. As a result, a heptacoordinated activated state was proposed (5) for the isomerization reaction:

\[
\text{R}_5 - \text{Co} - \text{ONO} \xrightarrow{\text{activation}} \text{R}_5 - \text{Co} \xrightarrow{\text{isomerization}} \text{R}_5\text{CoNO}_2
\]

Based on the foregoing considerations the following mechanism for the preparation of the nitritopentamminecobalt(III) complex was recently given as (6):

\[
\begin{align*}
\text{Co(NH}_3\text{)}_5\text{Cl}^+ + \text{H}_2\text{O} &\rightarrow \text{Co(NH}_3\text{)}_5\text{OH}_2^+ + \text{Cl}^- & (1) \\
\text{Co(NH}_3\text{)}_5\text{OH}_2^+ + \text{H}_2\text{O} &\rightarrow \text{Co(NH}_3\text{)}_5\text{OH}^2+ + \text{H}_3\text{O}^+ & (2) \\
2 \text{HNO}_2 &\rightarrow \text{N}_2\text{O}_3 + \text{H}_2\text{O} & (3) \\
\text{(NH}_3\text{)}_5\text{CoOH}^+ + \text{N}_2\text{O}_3 &\rightarrow \text{(NH}_3\text{)}_5\text{Co} - \text{O}----\text{H} & (4) \\
\text{(NH}_3\text{)}_5\text{CoONO}^+ + \text{HNO}_2 &\rightarrow \text{(NH}_3\text{)}_5\text{CoNO}_2^2+ & (5)
\end{align*}
\]

Using a method of synthesis implicit in the above mechanism, the complexes \(\text{(NH}_3\text{)}_5^M\text{ONO}^+\) \(n\) where \(M=\text{Rh(III)}\) and \(\text{Ir(III)}\) were
also prepared (7).

The most important result of the above study was the demonstration that under the conditions of the experiment the low energy path followed in equation (4) of the mechanism given for the synthesis of \( \left( \text{NH}_3 \right)_5 \text{CoONO} \) \( ^+ \), which does not involve the breaking of the metal-0 bond, yields the nitrito product. Thus it is possible to isolate and characterize the kinetically stable nitrito product before it isomerizes to the thermodynamically more stable nitrite linkage isomer (8).

The general technique developed for the preparation and study of nitro-nitrito linkage isomers formed the basis for the preparation and study of other linkage isomer systems. By carefully controlling the reaction conditions, the kinetically stable but thermodynamically unstable product can be isolated prior to its isomerization to the thermodynamically stable product.

**Other Linkage Isomer Systems**

In 1963, the preparation of linkage isomers of the thiocyanatopalladium(II) complexes were reported. Utilizing the proper reaction conditions, later described in the experimental section of this paper, the S-bonded isomers dithiocyanato-2,2'-bipyridinepalladium(II) and dithiocyanatobistriphenylarsinepalladium(II) were prepared. These were later converted to the thermodynamically more stable N-bonded isothiocyanato isomers by heating (9).

In 1966 the isolation of the thiocyanate and hexafluorophosphate salts of the S-bonded thiocyanatotetraethylidiethylenetriamine-
palladate(II) ion was reported. The hexafluorophosphate salt was later converted to the thermodynamically more stable isothiocyanato-complex by heating in solution. The thiocyanate salt reportedly underwent isomerization, as indicated by a color change, at room temperature in the solid state (10).

In the same year, evidence based on infrared studies for the three possible linkage isomers of the complexes of tri-(2-pyridyl)amine, abbreviated tripyam, with copper(II) thiocyanate was reported. The complexes Cu(tripyam)(SCN)$_2$, Cu(tripyam)(SCN)(NCS), and Cu(tripyam)(NCS)$_2$ were reported to have been isolated (11).

The synthesis of linkage isomers of the selenocyanate ion was reported in 1967 by Burmeister et al. Linkage isomers of $\text{Pd X (Et}_4\text{dien)} B(C_6H_5)_4$ where $X = \text{SeCN}$ and $\text{NCSSe}$ were isolated. Support for the structure was found in microanalytical results, molar conductivity in dimethylformamide and infrared spectra (12).

Many other linkage isomer systems have been reported in the literature. N-bonded and S-bonded isomers of derivatives of the simple metal carbonyl, Mn(CO)$_5$SCN were synthesized. The derivatives cis-Mn(CO)$_2$bipyNCS and trans-Mn(CO)$_3$(Ph$_2$P)$_2$NCS are N-bonded as opposed to cis-Mn(CO)$_3$(Ph$_2$Sb)$_2$SCN which is S-bonded (13). Bridged polynuclear complexes exhibiting linkage isomerism have been reported. The selenocyanate complex of cadmium, $\left[(\text{C}_4\text{H}_9\text{N})_2\text{Cd(CNSe)}_6\right]^-$ contains the dimeric anion (14).
The bridged compound, di-u-thiocyanatobis [chlorotripropylphosphine-platinum(II)] contains a pair of linkage isomers which exist in $\alpha$ and $\beta$ forms (15):

$$\begin{align*}
\text{(yellow)} \\
\text{greenish-yellow}
\end{align*}$$

**THEORETICAL EXPLANATIONS OF LINKAGE ISOMERISM**

**Steric Factors**

Basolo et. al. prepared thiocyanatodiethylenetriaminepalladate (II) nitrate, $[\text{Pd(dien)SCN}] \text{NO}_3^-$, and the analogous N-bonded complex, $N,N',N''$-tetraethyldiethylenetriaminepalladate(II) nitrate, $[\text{Pd(Et}_4\text{dien})\text{NCS}] \text{NO}_3^-$. Based on the fact that the steric
requirements for the angular $M$-SCN bond are greater than those for the linear $M$-NCS bond, they concluded that due to the presence of the four ethyl groups, the $Et_4$ dien complex was $N$-bonded whereas the dien complex, with no ethyl groups, was $S$-bonded. Furthermore, since $Et_4$ dien does not $\mathcal{W}$-bond, steric factors are probably the controlling factor in this complex (16).

Electronic Factors

Introductory Explanation of Class (a) and (b) Metals

Ahrland, Chatt and Davies proposed that despite the lack of a uniform pattern of relative coordinating affinities of all ligand atoms for all acceptor molecules and ions there are some distinct features with regard to these affinities. First of all, the coordinating affinities of the first atom in each of the three ligand groups in the Periodic Table differ greatly from those of the second atom, i.e., there is a difference between $N$ and $P$, $O$ and $S$, and $F$ and $Cl$. Secondly, there are two classes of acceptors. Class (a) acceptors are those which form their most stable complexes with the first atom in the ligand groups, i.e., $N$, $O$, and $F$. Class (b) acceptors form their most stable complexes with the second and subsequent atoms in the ligand groups (17).

Class (a) acceptors include most metals in their common valency states and the hydrogen ion. Affinities of ligands for class (a) metals parallel the basicities of the ligands. Class (b) acceptors include the metals which form stable olefin complexes. Class (b) behavior is associated with the availability of $d$-electrons from the
metal for dative $\pi$-bonding. The metals exhibiting class (b) behavior are Cu(I), Pd(II), Ag(I), Au(I), Pt(II), and Hg(II) (18). They occupy a triangular area in the Periodic Table as shown below (19).

```
    Fe   Co   Ni   Cu(I)   Zn   Ga
   /\   /\   /\   /\   /\   /\   /\   /\  
   Ru  Rh  Pd(II)  Ag  Cd  In
  /\  /\  /\  /\  /\  /\  /\  /\  /\  /\  
Os  Ir  Pt(II)  Au  Hg  Tl
```

Due to the fact that the different oxidation states of borderline elements such as Mn, Fe, Co, Ru, Os, Mo, and W to the left of the class (b) group, and Tl, Pb, and Bi to the right of the class (b) group have different characteristics, the boundary between class (a) and class (b) acceptors is somewhat diffuse. In the group to the left of the class (b) metals multiple valency is common. Many of these elements exhibit class (a) or class (b) behavior according to their oxidation states, with the higher valencies having class (a) characteristics and the lower valencies having class (b) characteristics due to the fact that the d-electrons are more available for dative $\pi$-bonding in the lower oxidation state (20).

Pearson proposed additional criteria. Class (a) metals or "hard" acids prefer to bind to "hard" or non-polarizable bases whereas class (b) metals or "soft" acids prefer to bind to "soft" or polarizable bases (21).
The following sequence of complex ion stability for atoms in the ligand groups of the Periodic Table was given by Pearson (22):

class (a): $N > P > As > Sb > Bi$

class (b): $N < P > As > Sb > Bi$

class (a): $O > S > Se > Te$

class (b): $O < S < Se < Te$

class (a): $F > Cl > Br > I$

class (b): $F < Cl < Br < I$

Utilizing the class (a)-class(b) and hard-soft acids and bases concepts, three explanations of the influence of electronic effects have been offered to account for linkage isomers.

Inorganic Symbiosis

As was stated in the previous discussion of class (a) and class (b) acceptors, some metals are borderline cases, exhibiting class (a) or class (b) behavior depending on their oxidation states.

A metal such as cobalt would, according to Chatt et al., exhibit class (a) behavior in its $+3$ oxidation state and class (b) behavior in its $+2$ oxidation state.

It has been proposed that the covalent bonding between a class (b) ligand or "soft" base and a borderline metal, such as cobalt, in its higher oxidation state is so strong that the charge on the metal atom is partially reduced thereby promoting class (b) behavior. Thus, the more class (b) ligands that are associated with a metal, the greater will be the tendency of the metal to exhibit class (b) behavior. For halopentamminecobalt(III) ions, the fluoro complex
is the most stable and the iodo complex is the least stable whereas for the halopentacyanocobalt(III) ions, the iodo complex is the most stable (23). In the cyanide ligand, coordination is through the carbon atom which results in a predominantly covalent bond, leading to an accumulation of negative charge on the cobalt (24) and resulting in greater stability for the iodo complex.

The stable form of the selenocyanatopentacyanocobalt(III) ion is, however, the N-bonded isomer and not the Se-bonded isomer as would be expected on the basis of the above considerations. This theory is, therefore, limited in its applications (25).

Effective Charge On The Metal Atom

Experiments with manganese carbonyl systems suggest that the effective charge on the metal atom may be significant in determining the nature of the linkage isomers obtained. Thus the complex Mn(CO)$_5$SCN is S-bonded presumably because of the electron withdrawing effects of the carbonyl groups. Replacement of a carbonyl group with a basic ligand would tend to increase electron density on the manganese. It has been found that complexes containing bases weaker than triphenylphosphine are S-bonded whereas complexes containing stronger bases such as pyridine, bipyridine, and triphenylphosphine are N-bonded with reference to the SCN ligand (26).

This theory is confusing and apparently incorrect in that it implies that a withdrawal of electron density from the metal favors class (b) behavior while an increase in negative charge on the metal, through σ-bonding with strong bases, enhances class (a) behavior (27).
The exact opposite of this is the hard-soft concept as proposed by Pearson, previously mentioned in this paper. Groups which transfer negative charge to the metal atom effectively reduce the oxidation state of the metal atom thereby promoting a decrease in class (a) behavior.

Pi-Bonding

The class (b) metals described by Ahrland, Chatt, and Davies, have filled d-orbitals immediately under their valency shells and are therefore able to undergo dative $\pi$-bonding with ligands having vacant d-orbitals in their valency shell (28).

The double bond binding a ligand to a central class (b) metal may be thought of as having a $\sigma$-component and a $\pi$-component. The $\sigma$-component is the bond formed by the donation of a lone pair of electrons from the donor atom or group to the central metal atom. Overlap of a filled d- or dp-hybrid orbital of the metal with a vacant p-, d-, or dp- hybrid orbital of the ligand results in the formation of a dative $\pi$-bond and accounts for the $\pi$-component (29). A typical $\pi$-bonded structure is represented in Figure 1.

Besides ligands with available empty d-orbitals on the central donor atom such as P, As, Sb, and I, unsaturated ligands such as carbonyl and isonitrile would also be able to accept metal d-electrons through the use of empty but not too unstable molecular orbitals (30).

Turco and Pecile, in considering thiocyanate complexes, advanced the theory that antibonding $\pi$-orbitals and empty d-orbitals of the sulfur atom confer acceptor properties on the sulfur end of the
Figure 1. Schematic representation of the $\text{R}_2\text{P}-\text{Pt}$ bond
thiocyanate group. The additional stability of the metal-S bond results from the interaction of the empty sulfur orbitals with d-electrons in the filled non-bonding d-orbitals of the metal. The availability of the metal d-electrons and their relative energy as compared with that of the orbitals of the thiocyanate determine the extent of the additional stability of the metal-S bond. Strong π-electron acceptors, such as triphenylphosphine, could reduce the availability of the metal d-electrons and bring about a change from a metal-S bonded complex to a metal-N bonded one (31).

Pyridine has the ability to withdraw d-electron density from the metal atom. Thus, bonding in pyridine-palladium(II) complexes is Pd-NCS. Alkyl substitution, however, opposes the withdrawal of metal d-electrons, relative to pyridine, by donating electron density into the pyridine ring. Thus bonding in the analogous π-picoline and 4-n-amylpyridine palladium(II) complexes is Pd-SCN. Also, alkyl pyridines, being more basic, may undergo greater σ-bonding and thereby increase the electron density on the palladium atom, further promoting Pd-SCN bonding (32).

Thus, π-bonding ligands have a tendency to reduce electron density on the metal atom thereby changing class (b) metal behavior to class (a) metal behavior with the accompanying change from the metal-S bond to the metal-N bond (33).

Electronic and/or steric factors may account for the differences in bonding of triphenylphosphinepalladium(II) complexes and triphenylstibinepalladium(II) complexes. Ph₃P is a better π-bonder
than $\text{Ph}_3\text{Sb}$. Furthermore, the smaller phosphorous atom would place the bulky phenyl groups closer to the metal atom. Thus the better electron withdrawing properties and greater steric hindrance of $\text{Ph}_3\text{P}$ results in palladium (II) complexes that have the Pd-NCS bond as opposed to the Pd-SCN bond in $\text{Ph}_3\text{Sb}$ complexes. Triphenylarsine, $\text{Ph}_3\text{As}$, is a borderline ligand between $\text{Ph}_3\text{P}$ and $\text{Ph}_3\text{Sb}$ (34).
Preparation of potassium tetra thiocyanatopalladate(II)

Potassium tetra thiocyanatopalladate(II) was prepared by allowing palladous chloride to react with a slight excess of potassium thiocyanate in an alcoholic medium (35). The reaction is as follows:

\[ \text{PdCl}_2 + 4\text{KSCN} \rightarrow \text{K}_2\left[\text{Pd(SCN)}_4\right] + 2\text{KCl} \]

4.58 grams of potassium thiocyanate was dissolved in 70 ml of 95% ethanol in a 100 ml round bottom flask by heating on an electric hot plate. After solution of the KSCN, 2.00 gms of palladous chloride was added to the flask. The PdCl₂ did not completely dissolve. The reaction mixture was refluxed for 1 hour, cooled and filtered. A ruby red filtrate was obtained and a light-brown precipitate remained on the filter. Upon evaporation of the alcohol, a dark red solid was isolated. This solid, presumed to be impure \( \text{K}_2\left[\text{Pd(SCN)}_4\right] \), was recrystallized from water, dried by washing with 20% ethanol in ethyl ether, and stored in a vacuum desiccator over \( \text{P}_2\text{O}_5 \) for 48 hours. A yield of 3.55 grams or 75% of \( \text{K}_2\left[\text{Pd(SCN)}_4\right] \) was obtained.

The purity of the compound was determined by infrared spectrophotometry and analysis for palladium. A Nujol mull of the material was run on a Perkin-Elmer Model 21 IR spectrophotometer. A strong band was observed at 2080 cm⁻¹; two shoulders were observed at 709 cm⁻¹ and 698 cm⁻¹; a weak band was observed at 705 cm⁻¹. The material was also analyzed on a Beckman IR-10 infrared spectrophotometer.
which resolved the band at 2080 cm\(^{-1}\) into two strong bands at 2120 cm\(^{-1}\) and 2095 cm\(^{-1}\). The results were in good agreement with the literature values (36) and are summarized in Table I.

**TABLE I**

<table>
<thead>
<tr>
<th>INFRARED ABSORPTION FREQUENCIES FOR (\text{K}_2\left[\text{Pd(SCN)}_4\right])</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Literature values (cm(^{-1}))</strong></td>
<td><strong>Observed values (cm(^{-1}))</strong></td>
</tr>
<tr>
<td>2118, 2086 bd</td>
<td>2120 s, 2095 s</td>
</tr>
<tr>
<td>700 sh, 690 sh</td>
<td>709 sh, 698 sh</td>
</tr>
<tr>
<td>703</td>
<td>705 w</td>
</tr>
</tbody>
</table>

Other literature values (37) reported for infrared stretching frequencies of \(\text{K}_2\left[\text{Pd(SCN)}_4\right]\) are 2122 cm\(^{-1}\) and 2093 cm\(^{-1}\) for C-N stretch and 709 cm\(^{-1}\) and 703 cm\(^{-1}\) for C-S stretch.

The method selected for the analysis of palladium was the precipitation of the metal as the iodide (38, 39). Three 0.1 gram samples of \(\text{K}_2\left[\text{Pd(SCN)}_4\right]\) were converted to \(\text{PdCl}_2\) by boiling with aqua regia and evaporating cautiously to dryness over a bunsen burner in a 50 ml beaker covered with a ribbed watch glass. The residue was dissolved in approximately 20 ml of 20% HCl. Any residue that spattered onto the watchglass was washed into the beaker with a few ml of 20% HCl. Precipitation was done at room temperature by the dropwise addition of 10% KI solution. The precipitated \(\text{PdI}_2\) was flocculated by heating the solution to near-boiling and then filtered.
into a previously tared Gooch crucible with an asbestos pad. After washing with several portions of warm water, the precipitate was dried by washing with ethanol, ether, and storing in a desiccator over CaCl$_2$ until constant weight was achieved. PdI$_2$ cannot be dried in an oven since it evolves iodine at 100 °C. The results of the analysis are summarized in Table 2.

### Table 2

**Analysis of K$_2$[Pd(SCN)$_4$] for Palladium**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight K$_2$[Pd(SCN)$_4$] (grams)</th>
<th>PdI$_2$ calc. (grams)</th>
<th>PdI$_2$ found (grams)</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.1141</td>
<td>0.0986</td>
<td>0.0996</td>
<td>101.00</td>
</tr>
<tr>
<td>II</td>
<td>0.1125</td>
<td>0.0972</td>
<td>0.0973</td>
<td>100.00</td>
</tr>
<tr>
<td>III</td>
<td>0.1270</td>
<td>0.1097</td>
<td>0.1105</td>
<td>100.70</td>
</tr>
</tbody>
</table>

The above results indicated that pure K$_2$[Pd(SCN)$_4$] was obtained.

A final test of purity was the Differential Scanning Calorimeter (DSC) scan of the compound. K$_2$[Pd(SCN)$_4$] melts at 241-242 °C (514-515 °K) as shown in Figure 2. This indicates that the K$_2$[Pd(SCN)$_4$] was pure.

The scan was made on a Perkin-Elmer DSC-1B Differential Scanning Calorimeter. The following operating conditions were used:

Average = 200
Figure 2. DSG curve of $K_2\left[Pd(SCN)_4\right]$
Differential = 4.90
Slope = 345
Range = 16
Scan speed = 20 °C/minute
Recorder chart speed = 1.0 in./minute
Recorder sensitivity = 0.1 volt FSD

TRIPHENYLARSINE DERIVATIVES

Preparation and study of dithiocyanatobistriphenylarsinepalladium(II)

1.03 grams of $K_2\left[\text{Pd(SCN)}_4\right]$ dissolved in 25 ml of absolute ethanol and 5 drops of water, and 1.52 grams of $\text{Ph}_3\text{As}$, dissolved in 25 ml of absolute ethanol and 5 drops of ethyl ether, were cooled to 0 °C then mixed in a vessel surrounded by an ice bath. After stirring for 1 minute, the yellow-orange S-bonded product was precipitated by the addition of 50 ml of ice water, isolated, washed first with ice-cold ethanol followed by ice-cold ethyl ether, and dried in a vacuum desiccator over $\text{P}_2\text{O}_5$. A yield of 1.70 grams or 82.5% was obtained.

The reaction is as follows (40, 41):

\[
\text{NCS}_{\text{Pd}} + 2(\text{C}_6\text{H}_5)_{\text{As}} \xrightarrow{0 \text{ °C}} \text{C}_6\text{H}_5\text{H}_2 \xrightarrow{\text{CSN}_{\text{Pd}}} \text{C}_6\text{H}_5\text{As}(\text{C}_6\text{H}_5)_3
\]

yellow-orange

The criteria of purity used for $\text{Pd(SCN)}_2(\text{Ph}_3\text{As})_2$ were the melting point, as determined by visual observation and DSC scan, and the infrared spectrum.

A small amount of $\text{Pd(SCN)}_2(\text{Ph}_3\text{As})_2$ was placed in a capillary
melting point tube. This was placed in a Mel-Temp melting point apparatus and the temperature was increased at the rate of 18 °C/minute. At 165 °C, the compound changed from a yellow-orange solid to a dark red, amorphous semi-solid. The mass remained amorphous and became lighter in color until 195 °C when it melted, turning to a red liquid.

The material was next studied calorimetrically using the Perkin-Elmer DSC-1B. The following operating conditions were used:

- Average = 160
- Differential = 490
- Slope = 400
- Scan rate = 20 °C/minute
- Range = 8
- Starting temperature = 325 °K
- Chart speed = 5 in./minute
- Recorder sensitivity = 0.01 volt FSD

Prior to scanning each sample, a tin standard was run to check the calibration of the instrument. A typical DSC curve obtained for a 1.7 mg tin standard is shown in Figure 3.

3.3 mg of Pd(SCN)$_2$(Ph$_3$As)$_2$ was weighed into the aluminum sample pan and scanned using the instrument parameters listed above. The DSC curve exhibited an endotherm with a maximum at 168 °C (441 °K) followed by an exotherm with a minimum at 172 °C (445 °K) and a melting point endotherm occurred at 195.7 °C (468.7 °K).

During the course of analyzing the S-bonded Ph$_3$As compound on the
Figure 3. DSC curve for tin standard
DSC, several different temperature scan rates were tried. At the higher rates available, 40 °C/minute and 80 °C/minute, inaccurate melting points were obtained. The curves were also distorted due to the rapid sloping of the baseline. At the lower scan rates tried, the endotherm at 168 °C was successively diminished as the scan speed was reduced and at the rate of 5 °C/minute it was barely visible with respect to the exotherm. At 1.25 °C/minute, both the endotherm and exotherm disappeared. It was concluded that holding the S-bonded isomer at elevated temperatures for the prolonged time periods associated with slow scan rates was analogous to heating the material in an oven at 150 °C for 30 minutes, i.e., the crystal change and subsequent linkage isomerism were so gradual and extended that the sensing elements of the DSC were incapable of detecting any change. Upon this basis, the scan rate selected which provided accurate results with a minimum of exposure time was 20 °C/minute. The DSC curve for Pd(SCN)$_2$(Ph$_3$As)$_2$ is shown in Figure 4.

A KBr pellet of Pd(SCN)$_2$(Ph$_3$As)$_2$ was prepared using a Wilks minipress. The infrared spectrum of the compound was then obtained using a Beckman IR-10 spectrophotometer. This spectrum exhibited a sharp peak for the C-N stretch at 2110 cm$^{-1}$.

Both the infrared and melting point data were in good agreement with the literature values (41) reported for Pd(SCN)$_2$(Ph$_3$As)$_2$ and confirmed that the compound under examination was Pd(SCN)$_2$(Ph$_3$As)$_2$. The results are shown in Table 3.
TABLE 3

A COMPARISON OF LITERATURE AND OBSERVED VALUES FOR Pd(SCN)$_2$(Ph$_3$As)$_2$

<table>
<thead>
<tr>
<th></th>
<th>melting point</th>
<th>C-N stretch</th>
<th>C-S stretch</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Literature</td>
<td>195.0</td>
<td>2119</td>
<td></td>
<td>yellow-orange</td>
</tr>
</tbody>
</table>

| Observed | 195.0 (visual) | 2110        |             | yellow-orange |
|          | 195.7 (DSC)    |             |             |             |

Preparation and study of diisothiocyanatobistriphenylarsinepalladium(II)

100 mg of Pd(SCN)$_2$(Ph$_3$As)$_2$ was heated at 156 °C for 30 minutes (40, 41). At the end of the heating period, the bright yellow N-bonded isomer was obtained. The reaction is as follows:

\[
\begin{align*}
\text{Ph}_3\text{As} & \quad \text{SCN} \\
\text{Pd} & \quad \text{Ph}_3\text{As} \\
\text{NCS} & \quad \text{AsPh}_3
\end{align*}
\]

\[
\begin{align*}
\text{Pd} & \quad 156 \degree \text{C, 30 minutes} \\
\text{NC} & \quad \text{Sc} \\
\text{Ph}_3\text{As} & \quad \text{Ph}_3\text{As} \\
\text{AsPh}_3 & \quad \text{AsPh}_3
\end{align*}
\]

A small amount of the material was placed in a capillary melting point tube and heated at the rate of 18 °C/minute in a Mel-Temp melting point apparatus. No change in crystal structure was observed at 165 °C. The compound remained bright yellow and solid until 195 °C when it melted to a red liquid.
The DSC curve for the N-bonded isomer, obtained under the same conditions as the DSC curve for the S-bonded isomer, exhibited no endotherm at 165 °C or exotherm at 172 °C. A melting point endotherm was observed at 195.7 °C (468.7 °K). The DSC curve is shown in Figure 5.

The infrared spectrum of the N-bonded isomer was obtained with a KBr pellet of the compound. There was a broad C-N stretch at 2070 cm⁻¹ and a C=S stretch at 840 cm⁻¹.

Both the melting point data and infrared data were in good agreement with the literature values (41) and confirmed that the compound under investigation was Pd(NCS)₂(Ph₃As)₂. The results are shown in Table 4.

<table>
<thead>
<tr>
<th>TABLE 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>A COMPARISON OF LITERATURE AND OBSERVED VALUES FOR Pd(NCS)₂(Ph₃As)₂</td>
</tr>
<tr>
<td>Melting point</td>
</tr>
<tr>
<td>oC</td>
</tr>
<tr>
<td>Literature</td>
</tr>
<tr>
<td>Observed</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
Figure 5. DSC curve of Pd(NGS)_2(Ph_3As)_2

Degrees Kelvin

Scale Depreciation
2,2'-Bipyridine Derivatives

Preparation and Study of Dithiocyanato-2,2'-bipyridinepalladium(II)

1.03 grams of $K_2\left[Pd(SCN)_4\right]$ dissolved in 10 ml of 95% ethanol and 5 drops of $H_2O$, and 0.4 grams of 2,2'-bipyridine dissolved in 10 ml of 95% ethanol and 5 drops of ethyl ether, were cooled to $-78\,^\circ C$ in a dry ice-acetone bath, then mixed in a vessel also surrounded by a dry ice-acetone bath. The solution was removed from the bath and after 10 minutes had become opaque. An orange solid was filtered off and immediately upon filtration a light yellow-orange solid separated in the filtrate. This material was isolated, washed with $-78\,^\circ C$ ethanol and ethyl ether and dried in a vacuum desiccator over $P_2O_5$. A yield of 0.76 grams or 81.5% was obtained. The reaction is as follows (40):

$$\begin{align*}
\text{NCS} & \quad \text{SCN} & -2 \\
Pd \quad + \quad \text{bipy} & \quad \text{at} \quad -78\,^\circ C \\
\text{C}_2\text{H}_5\text{OH} & \\
\text{light yellow-orange}
\end{align*}$$

The reaction was run twice. Absolute ethanol was used first. This produced a dark orange solid which did not isomerize when heated. Upon running the reaction a second time with 95% ethanol, the desired product was obtained.

The purity of the reaction product, presumed to be $Pd(SCN)_2(\text{bipy})$, was determined by visual observations of the melting point, DSC scan,
and infrared spectrophotometry.

A small amount of the material was placed in a capillary melting point tube and heated at the rate of 27 °C/minute in a Mel-Temp melting point apparatus. The material changed from a light orange-yellow solid to a light yellow solid from 155 °C to 165 °C (428 °K-438 °K) without undergoing any visible change in crystal structure, i.e., no amorphous state was formed as in the triphenylarsine derivative. The Pd(SCN)$_2$(bipy) remained solid until 270 °C (543 °K), when it melted to a brown liquid which subsequently decomposed.

The calibration of the DSC was checked with a tin standard. 3.2 mg of Pd(SCN)$_2$(bipy) was weighed into an aluminum sample pan and scanned on the DSC using the following operating parameters:

- Average = 160
- Differential = 490
- Slope = 400
- Scan speed = 20 °C/minute
- Range = 8
- Starting temperature = 325 °K
- Chart speed = 5 inches/minute
- Recorder sensitivity = 0.01 volt FSD

No change was detected in the region where the color change was observed during the visual examination of the melting process, 155 °C-165 °C (428 °K-438 °K). A melting point endotherm with a maximum at 269.8 °C (542.8 °K) was observed. This was in good agreement with the visually observed melting point. The DSC curve is shown in Figure 6.
Figure 6 and Figure 7. Typical DSC curves for Pd(SCN)$_2$(bipy) and Pd(NCS)$_2$(bipy)
A small amount of the Pd(SCN)$_2$(bipy) was mixed with dry KBr, compressed in a Wilks mini-press, and analyzed using a Beckman IR-10 spectrophotometer. A sharp peak was noticed at 2108 cm$^{-1}$, the C-N stretching frequency. This was in good agreement with the literature value (41).

Both the melting point data and the infrared spectrum confirmed that the material under analysis was Pd(SCN)$_2$(bipy). This data is summarized in Table 5.

### TABLE 5

A COMPARISON OF LITERATURE AND OBSERVED VALUES FOR Pd(SCN)$_2$(bipy)

<table>
<thead>
<tr>
<th></th>
<th>Melting point</th>
<th>C-N stretch</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Literature</td>
<td>270.0°C</td>
<td>2108 s, sp</td>
<td>yellow-orange</td>
</tr>
<tr>
<td>Observed</td>
<td>270.0°C (visual)</td>
<td>2108 s, sp</td>
<td>yellow-orange</td>
</tr>
<tr>
<td></td>
<td>269.8°C (DSC)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Preparation and study of diisothiocyanato-2,2'-bipyridinepalladium(II)

Approximately 100 mg of Pd(SCN)$_2$(bipy) was heated in an oven at 156 °C for 30 minutes. At the end of this time a light yellow solid was obtained. The reaction is as follows (40, 41):
The N-bonded isomer was analyzed by visual observation of the melting point, DSC scan, and infrared spectrophotometry.

A small amount of the material was placed in a capillary melting point tube and heated at the rate of 27 °C/minute in a Mel-Temp melting point apparatus. The light yellow compound remained solid until 270 °C when it melted to a dark brown liquid which subsequently decomposed.

3.6 mg of Pd(NCS)₂(bipy) was weighed into an aluminum sample pan and scanned on the DSC under the same conditions as the S-bonded isomer. The material exhibited a melting point endotherm at 544.2 °K (271.2 °C). This is in good agreement with the visually observed melting point. The DSC curve for the N-bonded isomer is represented in Figure 7.

A small amount of the Pd(NCS)₂(bipy) was mixed with dry KBr, compressed in a Wilks mini-press, and analyzed using a Beckman IR-10 infrared spectrophotometer. A strong broad peak at 2100 cm⁻¹ and a sharp medium peak at 840 cm⁻¹ were observed. These were in good agreement with the literature values for Pd(NCS)₂(bipy) infrared stretching frequencies (41).

Both the melting point data and infrared spectrum verified that the compound under analysis was Pd(NCS)₂(bipy). The results are summarized in Table 6.
TABLE 6
A COMPARISON OF LITERATURE AND OBSERVED VALUES FOR Pd(NCS)$_2$(bipy)

<table>
<thead>
<tr>
<th></th>
<th>Melting point</th>
<th>C-N stretch</th>
<th>C-S stretch</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Literature</td>
<td>270.0 °C</td>
<td>2100 s, br</td>
<td>842 m</td>
<td>light yellow</td>
</tr>
<tr>
<td>Observed</td>
<td>270.0 °C (visual)</td>
<td>2100 s, br</td>
<td>840 m, sp</td>
<td>light yellow</td>
</tr>
<tr>
<td></td>
<td>271.2 °C (DSC)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TETRAETHYLDIETHYLENEDIAMINE DERIVATIVES

Preparation and study of thiocyanatotetraethylidiethylenetriamine-palladium(II) thiocyanate

2 ml of Et$_4$dien, pre-cooled to -10 °C in a salt-ice bath was added to a solution of 0.95 grams of K$_2$[Pd(SCN)$_4$] in 10 ml of acetone, also at -10 °C. The reaction mixture became light yellow in color. Removal of the solvent was accomplished by evaporation in a 25 ml suction flask surrounded by a salt-ice bath using a small funnel to direct the flow of air onto the surface of the solvent. When the solvent volume reached approximately 3 ml, yellow crystals separated. These were collected on a filter, washed successively with small amounts of ice-cold water, alcohol, and ether, air dried and stored at 0 °C. A yield of approximately 0.150 grams was obtained.

The purity of the material, presumed to be [Pd(SCN)(Et$_4$dien)] SCN,
was determined by analysis for palladium content, visual and DSC melting point determination, and the infrared spectrum.

Weighed amounts of the material were analyzed for palladium by ignition. The results, as shown in Table 7, indicate that the compound under examination was \([\text{Pd(SCN)(Et}_4\text{dien)}] \text{SCN}\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample weight</th>
<th>% Pd calculated</th>
<th>% Pd observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>0.0288</td>
<td>24.3</td>
<td>26.0</td>
</tr>
<tr>
<td>II.</td>
<td>0.0329</td>
<td>&quot;</td>
<td>25.5</td>
</tr>
<tr>
<td>III.</td>
<td>0.0381</td>
<td>&quot;</td>
<td>25.4</td>
</tr>
</tbody>
</table>

As a further check, the palladium residue was dissolved in aqua regia, converted to \(\text{PdCl}_2\), and precipitated as the iodide by the method previously described in this paper. The results, shown in Table 8, verify the results found in the analysis for palladium content by ignition.
TABLE 8

CONVERSION OF PALLADIUM RESIDUE TO PdI₂

<table>
<thead>
<tr>
<th>Weight of Pd metal from ignition (mg)</th>
<th>PdI₂ calculated mg</th>
<th>PdI₂ found mg</th>
<th>Yield-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>23.6</td>
<td>24.1</td>
<td>101.9</td>
</tr>
<tr>
<td>8.0</td>
<td>26.1</td>
<td>24.2</td>
<td>92.7</td>
</tr>
<tr>
<td>9.2</td>
<td>31.3</td>
<td>29.3</td>
<td>93.5</td>
</tr>
</tbody>
</table>

The slight inaccuracies were attributed to the fact that small amounts of material were taken for analysis.

In the infrared spectrum of the material, taken in a KBr pellet, the C-N stretching frequencies were observed at 2090 cm⁻¹ and 2030 cm⁻¹. There was a slight shoulder at 825 cm⁻¹.

The melting process of $\left[\text{Pd}(\text{SCN})(\text{Et₄dien})\right]\text{SCN}$ was observed next. A small amount of the material was placed in a capillary melting point tube and heated at the rate of approximately 18 °C/minute in a Mel-Temp melting point apparatus. The material became slightly amorphous over the range 90 °C to 115 °C. From 115 °C to 120 °C there was an abrupt color change from yellow to pale yellow. At 186 °C, the compound melted to a dark red liquid.

14.1 mg of $\left[\text{Pd}(\text{SCN})(\text{Et₄dien})\right]\text{SCN}$ was weighed into an aluminum sample pan and heated on the DSC under the following conditions:

Average = 160

Differential = 490
Slope = 400
Scan speed = 40 °C/minute
Range = 8
Starting temperature = 325 °K
Recorder chart speed = 5 inches/minute
Recorder sensitivity = 0.01 volt FSD

An exotherm with a minimum at 131 °C (404 °K) followed by a melting point endotherm at 201.8 °C (474.8 °K) was observed for \[ \text{Pd(SCN)(Et}_4\text{dien)} \] SCN. The discrepancy in the melting point obtained by visual observation and the DSC was attributed to the rapid scan rate of 40 °C/minute. The DSC curve for \[ \text{Pd(SCN)(Et}_4\text{dien)} \] SCN is shown in Figure 8.

The scan rate of 40 °C/minute was selected after several trial runs at slower scan rates revealed a diminution of the exotherm at 404 °K. Even at the scan rate of 20 °C/minute, which proved satisfactory for the triphenylarsine derivative, the exotherm was barely visible. Apparently, the longer exposure to elevated temperatures resulted in a more gradual transition. Therefore, a certain measure of accuracy was sacrificed in order that the exotherm might be readily seen. It was also necessary, under the conditions of the experiment, to adjust the Range setting to 64 after the exotherm had been passed in order that the melting point endotherm might be seen. Without this correction, the sensitivity of the instrument, which proved adequate for the transition exotherm, was excessive with respect to the melting point endotherm. This resulted in an off-scale deflection for the melting point.
Figure 8. DSC curve of \[ \text{Pd(SeN)} \text{Et}_4 \text{dien} \] in SCN. Degrees Kelvin vs. Scale detection.

Range setting adjusted to 64.
Preparation and study of isothiocyanatotetraethyldiethylene-triamminepalladium(II)-thiocyanate

The preparation of \[ \text{Pd(NCS)(Et}_4\text{dien)} \text{SCN} \] by heating the S-bonded isomer was not given in the literature. It was mentioned (42) that the yellow S-bonded compound changed to a pale yellow solid after standing at room temperature for approximately 3 days. The bright yellow S-bonded isomer was converted to the pale yellow N-bonded isomer, \[ \text{Pd(NCS)(Et}_4\text{dien)} \text{SCN} \], by heating the former at 125 °C for 45 minutes. The reaction is as follows:

\[
\text{Pd(NCS)(Et}_4\text{dien)} + \overset{125 \text{ °C, 45 minutes}}{\rightarrow} \text{Pd(NCS)(Et}_4\text{dien)} \]

A small amount of the N-bonded isomer was placed in a capillary melting point tube and heated at the rate of 18 °C/minute in a Mel-Temp melting point apparatus. The material remained pale yellow and solid until 186 °C when it melted to a dark red liquid.

14.1 mg of \[ \text{Pd(NCS)(Et}_4\text{dien)} \text{SCN} \] was weighed into an aluminum sample pan and analyzed on the DSC under the same conditions as the S-bonded isomer. The DSC curve exhibited a melting point endotherm at 201.7 °C (474.7 °K). There was no exotherm at 404 °K. The DSC curve for the N-bonded isomer is shown in Figure 9.

The infrared spectrum of \[ \text{Pd(NCS)(Et}_4\text{dien)} \text{SCN} \] exhibited SCN stretching frequencies at 2090 cm⁻¹ and 2020 cm⁻¹. There was a medium C-S stretching peak at 825 cm⁻¹ for the N-bonded isomer.
Figure 9. DSC curve of [Pa(NGS)(Et₄dien)] SCN

Degrees Kelvin

Range setting adjusted to 64
Quantitation of DSC results

Enthalpies for the observed changes in the DSC curves of the compounds tested were calculated by constructing suitable baselines for the appropriate curves for tin (figure 10), Pd(SCN)$_2$(Ph$_2$As)$_2$ (Figure 11), and [Pd(SCN)(Et$_4$diem)] SCN (Figure 12), cutting out and weighing tracings of the peaks made on good quality typewriter paper, and substituting the weights into the following formula (43):

$$\Delta H = \frac{[\Delta H_{\text{t.m.}}][\text{weight of sample peak}][\text{chart speed}][\text{range setting}]}{[\text{tin fusion}][\text{chart speed}][\text{range setting}] - \text{peak weight}[\text{range setting}][\text{for tin}][\text{for sample}]}$$

The value for the enthalpy calculated in formula (1) was expressed on the basis of sample weight as follows:

$$\Delta H (\text{cal/gm}) = \frac{\Delta H}{\text{sample weight in grams}}$$

Finally, the enthalpy calculated in (2) was expressed on a molar basis as follows:

$$\Delta H (\text{cal/mole SCN}^-) = \Delta H (\text{cal/gm}) \times 58.08 \text{ grams/mole SCN}^-$$

The quantitative results of the above calculations are summarized in Table 9.
Figure 10. Baseline interpolation for tin fusion peak

Figure 11. Baseline interpolation for transition peaks of Pd(SCN)$_2$(Ph$_3$As)$_2$
Figure 12. Baseline interpolation for transition peak of $\left[ \text{Pd(Se)}(\text{Et}_4\text{dien}) \right] \text{SCN}$
TABLE 9

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heating rate</th>
<th>H-endothrm cal/mole SCN⁻</th>
<th>H-exotherm cal/mole SCN⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(SCN)_2(Ph_3As)_2</td>
<td>10</td>
<td>319</td>
<td>-465</td>
</tr>
<tr>
<td>&quot;</td>
<td>10</td>
<td>328</td>
<td>-503</td>
</tr>
<tr>
<td>&quot;</td>
<td>20</td>
<td>705</td>
<td>-479</td>
</tr>
<tr>
<td>Pd(SCN)_2(bipy)</td>
<td>20</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[Pd(SCN)(Et_4dien)]^+</td>
<td>40</td>
<td>—</td>
<td>-106</td>
</tr>
<tr>
<td>&quot;</td>
<td>40</td>
<td>—</td>
<td>-114</td>
</tr>
</tbody>
</table>

Triphenylarsine compounds

A comparison of the visual observations of the melting process with DSC results indicates there is good agreement between the two sets of data. Furthermore, it can be concluded that the endotherm at 168 °C is representative of the crystal change visually observed in the S-bonded isomer at 165 °C.

From inspection of the visual and DSC melting point data, it is apparent that the endotherm followed by an exotherm at 168 °C-172 °C is characteristic of the S-bonded isomer. Furthermore, it can be concluded that the exotherm represents the enthalpy due to isomerization from the less stable S-bonded isomer to the more stable N-bonded isomer and that this isomerization is preceded by a crystal change in the S-bonded compound.
Steric factors and electronic factors based on the differing atomic size and η-acceptor abilities of P, As, and Sb have been suggested as explanations for the bonding in Ph₃P, Ph₃As, and Ph₃Sb thiocyanatopalladium(II) compounds.

η-bonding ligands, in a trans position to the SCN group, tend to make dη-electrons on palladium less available for dative η-bonding to empty d-orbitals and antibonding η-orbitals on the sulfur atom. Thus, the Pd-S bond will be weakened in proportion to the η-bonding ability of the Ph₃P, Ph₃As, and Ph₃Sb ligands. Infrared studies using other complex systems, however, indicate that the η-acceptor properties of P, As, and Sb do not differ sufficiently to account for linkage isomerism.

Ligands such as nitrite ion can undergo η-bonding with a metal through back donation of electron density from dη metal orbitals (non-bonding dₓᵧ, dₓz, and dᵧz orbitals in complexes containing no other η-bonding ligands) to vacant antibonding η-orbitals on the nitrogen atom. This has the effect of stabilizing the dη metal orbitals. The presence of the dη electrons in the antibonding η-orbitals of the nitrogen results in a lowering of the formal N-O bond order. Therefore, as the amount of back donation of dη electron density increases, the asymmetric and symmetric N-O stretching frequencies should decrease. In a series of complexes $[ML₂(NO₂)₂]$, where the metal ion is kept the same, the values of the asymmetric and symmetric stretching frequencies will vary with the η-bonding ability of the L ligands (44). Table 10 summarizes the nitrite
stretching frequencies for some palladium and platinum complexes.

TABLE 10
NITRITE INFRARED FREQUENCIES FOR THE \([ML_2(\text{NO}_2)_2]\) COMPLEXES
\((\pm 1 \text{ cm}^{-1})\)

<table>
<thead>
<tr>
<th>Ligand or compound</th>
<th>Asymmetric N-O stretch</th>
<th>Symmetric N-O stretch</th>
</tr>
</thead>
<tbody>
<tr>
<td>M = Pd(II)</td>
<td>Pd(II)</td>
<td>Pt(II)</td>
</tr>
<tr>
<td>P((\text{C}_6\text{H}_5)_3)</td>
<td>1414 s</td>
<td>1417 s</td>
</tr>
<tr>
<td>As((\text{C}_6\text{H}_5)_3)</td>
<td>1412 s</td>
<td>1411 s</td>
</tr>
<tr>
<td>Sb((\text{C}_6\text{H}_5)_3)</td>
<td>1408 s</td>
<td>1399 s</td>
</tr>
<tr>
<td></td>
<td>1324 s</td>
<td>1336 s</td>
</tr>
<tr>
<td></td>
<td>1327 s*</td>
<td>1334 s</td>
</tr>
<tr>
<td></td>
<td>1320 s</td>
<td>1328 s</td>
</tr>
</tbody>
</table>

* anomalous behavior

In general, there is an increase in the N-O stretching frequencies as the \(\pi\)-bonding ability of the L ligand increases in the order Ph$\text{Sb}$$\preceq$Ph$\text{As}$$\preceq$Ph$\text{P}$. This difference in \(\pi\)-bonding ability of P, As, and Sb could be explained on the basis of differences in d-orbital overlap. The empty 3d orbitals of the smaller phosphorous will overlap with the filled d-orbitals on palladium more effectively than the 4d and 5d orbitals of arsenic and antimony respectively.

The N-O stretching frequencies increase because as the \(\pi\)-bonding ability of the ligand increases, back donation of metal d\(_\pi\) electron
density to empty antibonding $\pi$-orbitals on the nitrogen atom decreases, and thus the N-O bond order increases. However, as can be seen from Table 10, there are only slight changes in the frequencies indicating that there is very little difference in the $\pi$-bonding abilities of the three ligands.

Central ligand atoms, such as P, As, and Sb, donate a pair of unshared electrons to the metal atom through the formation of metal-ligand $\sigma$ bonds. Thus the electron density donated to the metal atom through metal-ligand $\sigma$-bonding tends to oppose the effects of electron density withdrawal through metal-ligand $\pi$-bonding. The extent to which a ligand can increase electron density on the metal atom through $\sigma$-bonding is determined by the ligands' basicity. Since the three ligands being considered here are relatively weak bases ($pK_a$ in $H_2O$ for $\text{Ph}_3\text{P} = 2.73$) and since their basicities can be expected to follow the order $\text{Ph}_3\text{Sb} < \text{Ph}_3\text{As} < \text{Ph}_3\text{P}$, which would tend to oppose the previously discussed $\pi$-bonding effects, it is reasonable to assume that any shift seen in the N-O stretching frequency is primarily due to $\pi$-bonding effects.

It may be assumed, therefore, that the controlling factor in the isomerism of the thiocyanato $\text{Ph}_3\text{P}$, $\text{Ph}_3\text{As}$, and $\text{Ph}_3\text{Sb}$ palladium(II) complexes is steric hindrance. This can be seen on the basis of the following considerations.

Using bond distances determined by infrared studies of isotopic species of NCS$^-$, Jones (47) was able to calculate the contributions by the resonance structures of NCS$^-$ based on $N-C$, the bond distance is
1.17 Å and for C-S, the bond distance is 1.61 Å. From these values, the following resonance contributions were obtained using Paulings formula:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>N≡C–S⁻</td>
<td>71%</td>
</tr>
<tr>
<td>II</td>
<td>N≡C≡S</td>
<td>12%</td>
</tr>
<tr>
<td>III</td>
<td>N²⁺≡C≡S</td>
<td>17%</td>
</tr>
</tbody>
</table>

Lewis et. al. state that on the basis of X-ray studies the important forms for the bonded thiocyanate are as follows (48):

Free ion  Metal-N bonding  →  Metal-S bonding

(a) N≡C–S⁻  (d) M⁺≡C–S⁻  (g) M–S
(c) N²⁺≡C≡S  (f) N–N

For sulfur bonding (g) will be important whereas for nitrogen bonding forms (d) and (f) will be important. Form (f) probably results from electron drift toward the nitrogen atom upon coordination of form (c) with the metal atom. Based on Jones' data, it can be inferred that form (f), because of the minor resonance contribution of (c), is not as important as form (d). Thus sulfur bonded M–S–C bonds are angular and therefore have greater steric requirements than the linear M–N–C bonds.

The size of the donor atom of the coordinating ligand also determines the degree of steric hindrance. Specifically, for Ph₃P,
Ph₃As, and Ph₃Sb, the size of the phosphorous, arsenic, and antimony atoms will determine the amount of steric effect that the bulky phenyl groups have on the thiocyanate groups' bonding. Phosphorous, with a covalent radius of 1.06 Å (49), allows the phenyl groups to approach closer to the thiocyanate than antimony, which has a covalent radius of 1.38 Å (50). Thus, with Ph₃P the linear Pd-N-C-S configuration, with smaller steric requirements, is favored while for Ph₃Sb, the phenyl groups are sufficiently removed from the palladium to permit sulfur bonding. Arsenic, with a covalent radius of 1.19 Å (51), is intermediate between phosphorous and antimony. At lower temperatures the Ph₃As derivative is S-bonded whereas upon heating it isomerizes to the N-bonded complex.

The visual observations of the melting process, together with all the thermodynamic data obtained on the DSC, suggest that the isomerization of Pd(SCN)₂(Ph₃As)₂ is due to steric factors and offer some evidence for the mechanism of the isomerization process. At sufficiently low temperatures, the Ph₃As derivatives is S-bonded because this isomer is easier to form. The intermediate size of the arsenic atom maintains the phenyl groups at sufficient distance from the palladium to permit stable Pd-S bonding. The Pd(SCN)₂(Ph₃As)₂ prepared for this study has been kept for 6 months at room temperature without any change as evidenced by its color and IR spectrum. Upon heating, the S-bonded isomer absorbs enough energy to undergo a crystal change which is followed by isomerization to the N-bonded isomer. The process could be accounted for by the formation of an
unstable hexacoordinated intermediate, shown in Figure 13, or a polymer-type complex, either of which rearrange to the N-bonded complex. The DSC curve, which exhibits an endotherm followed by an exotherm, supports the formation of an intermediate prior to isomerization. Interestingly, at the two heating rates used, a larger enthalpy was noted for the endotherm at the more rapid heating rate while the enthalpy for the exotherm remained constant at 482 ± 19 calories per mole of SCN⁻. This suggests that the rearrangement to the intermediate is a gradual process and that at the faster heating rate a greater number of molecules are brought to the activated state in a shorter time period resulting in a greater endotherm.

The amorphous appearance of the intermediate suggests that the intermediate is polymeric in structure. A possible bridge-type structure for this polymer is represented in Figure 14.

The formation of such a polymer would take place by an intermolecular mechanism whereas the hexacoordinated intermediate would be formed via an intramolecular mechanism. Burmeister et al. noted that the rate of isomerization of Pd(SCN)₂(Ph₂As)₂ was slower in a KBr pellet than in the pure solid state (52). If the bromide ions are assumed to occupy trans positions above and below the plane of the molecule, their presence would inhibit the formation of either intermediate.

The polymeric intermediate is probably easier to form because it has less stringent steric requirements than the hexacoordinated intermediate. The hexacoordinated intermediate would also require
Figure 13. Suggested hexacoordinated intermediate for the isomerization of $\text{Pd}({\text{SCN}})_2(\text{Ph}_3\text{As})_2$ to $\text{Pd}({\text{NCS}})_2(\text{Ph}_3\text{As})_2$. 
Figure 14. Suggested bridged polymer intermediate for the isomerization of $\text{Pd(}\text{SCN})_2(\text{Ph}_3\text{As})_2$ to $\text{Pd(NCS})_2(\text{Ph}_3\text{As})_2$.
a strained octahedral structure which is energetically more difficult to attain than a conventional octahedral structure. These considerations indicate that the polymeric structure is probably the intermediate of choice.

2,2'-Bipyridine Compounds

The experimental results were inconclusive for dithiocyanato-2,2'-bipyridinepalladium(II). Although a definite color change was observed in the heating of the S-bonded bipyridine derivative, no crystal change was observed. Furthermore, the DSC curve revealed no thermal change at all. Some explanations as to the cause of isomerism in this complex might help to account for the experimental data.

At \(-78^\circ\text{C}\), the S-bonded bipyridine complex can be isolated while at room temperature only the N-bonded isomer is obtained. Substituting o-phenanthroline for bipyridine yields the S-bonded isomer at room temperature.

Burmeister et. al. could not account for the fact that bipyridine and o-phenanthroline produce different bonding except to state that small differences in the ligands are sufficient to cause a change in bond type (53).

Both bipyridine and o-phenanthroline form dative \(\pi\)-bonds with palladium. This is accomplished by overlap of the \(d\sigma\) orbitals of palladium with the empty antibonding \(\pi\)-orbitals of the ligand. Thus \(d\sigma\) electron density is withdrawn from the palladium. If this withdrawal is extensive enough, \(d\sigma\) electron density for dative \(\pi\)-bonding
to the antibonding $\pi$-orbitals and empty d-orbitals of the thiocyanate sulfur could be reduced to a point where the Pd-S bond is weakened.

It has been shown that the C-C bond distance between the two pyridine rings in bipyridine is 1.50 Å, which is a bond order slightly less than 1 (54). In the square planar dithiocyanato-2,2'-bipyridine palladium(II) complex, the C-C bond between the two pyridine rings, having an order of approximately 1, could be bent or distorted slightly allowing the pyridine rings to move closer to the palladium. With o-phenanthroline, however, the rigidity introduced by the third aromatic ring would prevent any bending. Thus the empty antibonding $\pi$-orbitals of the bipyridine could overlap to a greater extent than those of o-phenanthroline, with the d$\pi$ orbitals of palladium. In other words, bipyridine is a better $\pi$-bonding ligand than o-phenanthroline. This would account for N-bonding in the 2,2'-bipyridine derivatives and S-bonding in the o-phenanthroline derivatives. It has also been suggested (55) that greater $\pi$-electron delocalization in the three-ring o-phenanthroline molecule results in smaller antibonding $\pi$-orbitals which means less overlap with d$\pi$ orbitals of palladium and hence less d$\pi$ electron withdrawal from the palladium.

Infrared studies of the O-N=O stretching frequencies in the complex $[\text{ML'}(\text{NO}_2)_2]$ confirm that 2,2'-bipyridine is a better $\pi$-bonding ligand than o-phenanthroline. The reasons for this have already been discussed (see pp. 42-44) in the discourse on $\text{Ph}_3\text{P}$, $\text{Ph}_3\text{As}$, and $\text{Ph}_3\text{Sb}$ ligands in the $[\text{ML}_2(\text{NO}_2)_2]$ complex. There is, however, evidence from these infrared O-N=O stretching frequencies that the difference in
\( \pi \)-bonding ability between bipyridine and o-phenanthroline is slightly greater than the difference between the \( \pi \)-bonding abilities of the three ligands mentioned previously. This is apparent from the greater difference in the N-O stretching frequencies as summarized in Table 11 (56).

<table>
<thead>
<tr>
<th>TABLE 11</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>INFRARED STRETCHING FREQUENCIES FOR NITRITE IN</strong> ( [ML'(NO_2)_2] ) <strong>COMPLEXES</strong> (( \text{cm}^{-1} ))</td>
</tr>
<tr>
<td>Ligand ((L'))</td>
</tr>
<tr>
<td>M =</td>
</tr>
<tr>
<td>bipy</td>
</tr>
<tr>
<td>phen</td>
</tr>
</tbody>
</table>

It is apparent that the isomerization and high thermodynamic instability of \( \text{Pd(SCN)}_2(\text{bipy}) \) can be attributed to a weakening of the Pd-S bond due to electronic factors. This high instability could account for the lack of any discernible change in the DSC curve.

**Tetraethylhexammine Compounds**

It has been previously shown in this paper (see pp. 5-6) that the controlling factor in the linkage isomerism of \( \text{Et}_{44 \text{dien}} \) compounds is steric hindrance.
From inspection of the DSC curves, it can be concluded that the exotherm at 404 °K is characteristic of the S-bonded isomer and represents the change in enthalpy due to isomerization to the N-bonded isomer. The exotherm minimum at 404 °K (131 °C) was in fairly good agreement with the observed color change at 115 °C-120 °C, keeping in mind that in the DSC scan a much more rapid rate of heating was used. Unlike the Ph₃As compound, the Et₄dien complex did not exhibit any marked change in crystal structure and, as would be expected, the DSC curve showed no endotherm.

Basolo et al. reported that at room temperature in the solid state there was complete isomerization of $[\text{Pd(SCN)}(\text{Et₄dien})]$ SCN in three days while under the same conditions no isomerization of $[\text{Pd(SCN)}(\text{Et₄dien})]$ PF₆ was observed (57). This would suggest that the isomerization of the Et₄dien complexes in the solid state proceeds by an intramolecular process involving the SCN⁻ ion.
SUMMARY

It has been demonstrated that the Differential Scanning Calorimeter is a valuable instrument for investigating linkage isomerism in palladium(II) complexes.

For the dithiocyanatobistriphenylarsinepalladium(II) complex it was possible to propose a mechanism for the isomerization process based on the visually observed change in crystal state and the DSC data. The endotherm in the DSC curve of this complex supports the existence of an intermediate for which two structures were proposed. In the dithiocyanatotetraethylendiamminepalladium(II) complex, only an exotherm was noted in the DSC scan which was in agreement with the visually observed process where no crystal change was apparent. For both the triphenylarsine and tetraethylendiammine complexes the DSC data provided additional evidence for the support of linkage isomerism. In the case of the dithiocyanato-2,2′-bipyridinepalladium(II) complex the experimental data was inconclusive.

Although this research was mainly qualitative in nature, preliminary thermodynamic measurements indicate that the Differential Scanning Calorimeter can be used for quantitative measurements of the isomerization process.
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(7) Ibid., pp. 1-5.

(8) Ibid., pp. 1-5.


(14) Frazer, pp. 303-304.

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(28) Leden and Chatt, p. 2938.


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(42) Basolo, Baddley, and Wiedenbaum, pp. 1576-1577.


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(50) Ibid., Side 2.

(51) Ibid., Side 2.

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(53) Ibid., p. 1591.


(55) Private communication.


(57) Basolo, Baddley, and Wiedenbaum, p. 1578.