

## The Conjunctive Response to Steric Hindrance in Dithiocyanato[bis(diphenylphosphino)alkyl or aryl]palladium(II) Complexes: a New Look at a Classic Series

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### Abstract

The molecular structures of eight closely related dithiocyanato[bis(diphenylphosphino)alkyl or aryl]palladium(II) complexes have been determined by single crystal X-ray diffraction studies: *N,S*-dithiocyanato[1,3-bis(diphenylphosphino)propane]palladium(II), two separate crystals, grown from  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{NO}_2$  solutions, of the complex *N,S*-dithiocyanato[1,4-bis(diphenylphosphino)butane]palladium(II), *S,S* and *N,S*-dithiocyanato[*cis*-1,2-bis(diphenylphosphino)ethylene]palladium(II), *S,S*- and *N,S*-dithiocyanato[*o*-bis(diphenylphosphino)benzene]palladium(II) and *N,S*-dithiocyanato[ $\alpha,\alpha'$ -bis(diphenylphosphino)-*o*-xylene]palladium(II). These results, when coupled with those of previously published studies, conclusively show that the generally accepted premise that increasing steric hindrance in *cis*-dithiocyanato complexes tends to exclusively promote the formation of nitrogen-bound thiocyanates is erroneous. The predominate formation of *N,S*-bound geminites in these complexes strongly suggests that there is a *conjunctive response* of the two thiocyanate groups to steric pressure. The *N,S*-dithiocyanato configuration minimizes interaction with bulky substituents on other ligands and with each other. The *S*-bound thiocyanates in these complexes are invariably tilted toward the other thiocyanate group, and often use the angular nature of the Pd–SCN bond to tilt up to  $73^\circ$  out of the coordination plane to further minimize steric interactions.

### Introduction

The exceptional utility of the ambidentate thiocyanate ion as a sensitive and convenient probe of the character of select bonding sites on a metal atom has been well-exploited by chemists for three decades

[1–3]. The electronic characteristics of the sulfur and nitrogen bonding modes of the thiocyanate moiety are significantly different. The mode of thiocyanate coordination, which is readily ascertained by a variety of physical methods [1–3], reveals much about the nature of the coordination site on the central metal atom.

There is considerable interest in those factors [1–3] which influence the mode of thiocyanate coordination to metal atoms, other than the electronic character of the metal and the thiocyanate in and of themselves. While numerous hypotheses have been proposed [1–3] to account for the nature and strength of these influences, few have prompted as much discussion and debate as the 'steric control' model proposed by Palenik *et al.* [4, 5].

Palenik *et al.* used the observed [4, 5] bonding mode pattern in the series  $[\text{Pd}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\text{thiocyanate})_2]$  ( $n = 1$ , di-*S*-bound;  $n = 2$ , *S,N*-bound;  $n = 3$ , di-*N*-bound) as the primary basis for their hypothesis. They argued that, since the electronic effects of the phosphines are essentially constant, the dramatic change in bonding mode exhibited by the thiocyanates must be due solely to the increased steric hindrance of the phenyl groups created by the increasing P–Pd–P bond angle ( $n = 1$ ,  $73.3^\circ$ ;  $n = 2$ ,  $85.1^\circ$ ;  $n = 3$ ,  $89.3^\circ$ ). By inference, they suggested that explanations based on electronic effects that had previously been advanced to explain bonding mode reversals such as that found [6] for the series  $[\text{Pd}(\text{SCN})_4]^{2-}$ , *trans*- $[\text{Pd}(\text{NH}_3)_2(\text{SCN})_2]$ , *trans*- $[\text{Pd}(\text{PPh}_3)_2(\text{NCS})_2]$ , were incorrect. The Palenik model has become a standard example of the operation of steric effects on linkage isomerism in inorganic chemistry textbooks [7, 8].

It should be noted, however, that electronic effects are also operative in these complexes. This is, perhaps, most clearly illustrated by the geminite  $[\text{Pd}\{(\text{H}_3\text{C})_2\text{N}(\text{CH}_2)_3\text{PPh}_2\}(\text{SCN})(\text{NCS})]$ , prepared by Meek *et al.* [9]. Huheey [8, 10] has pointed out that, despite the fact that this geminite and the aforementioned di-*N*-bound  $[\text{Pd}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\text{NCS})_2]$  complex [4, 5] have identical Pd–P bond lengths and

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very similar bond angles (the N–Pd–P angle in the geminite is  $92.4^\circ$  versus  $89.1^\circ$  for the P–Pd–P angle in the bisphosphine), the N-bound thiocyanate in the geminite is *trans*, not *cis*, to the strongly *trans*-directing phosphine group. Furthermore, the Pd–NCS bond lengths are virtually identical in the two complexes.

It has long been assumed that sulfur-bound thiocyanate is the more sterically demanding coordination mode, due to the larger size of the sulfur atom and the smaller angular mode of M–SCN coordination (approaching  $90^\circ$ ) [1–3]. Basolo and his co-workers [11] were the first to predict and experimentally verify that the increased steric hindrance created by other ligands in the coordination sphere favored N-bound thiocyanate ( $[\text{Pd}(\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2)\text{SCN}]^+$  versus  $[\text{Pd}\{(\text{C}_2\text{H}_5)_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{N}(\text{C}_2\text{H}_5)_2\}\text{NCS}]^+$ ). The analogous complexes containing the selenocyanate ion,  $\text{SeCN}^-$ , have been found to behave in the same manner [12].

As a consequence of the foregoing, it has generally been assumed that increased steric hindrance in the vicinity of the coordinated thiocyanate will *always* tend to favor N-bonding. It is this assumption that is challenged in this paper.

## Experimental

The phosphine ligands were purchased from Strem Chemicals, Inc., Newburyport, MA. All chemicals and solvents were of reagent grade or better, and were used as received. The compounds  $\text{K}_2[\text{Pd}(\text{SCN})_4]$  [13] and  $[\text{Pd}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\text{NCS})(\text{SCN})]$  [14] were prepared by methods given in the literature.

### *N,S*-Dithiocyanato[1,4-bis(diphenylphosphino)-butane]palladium(II), $[\text{Pd}(\text{dpb})(\text{NCS})(\text{SCN})]$

$\text{K}_2[\text{Pd}(\text{SCN})_4]$  (0.2314 g, 0.5550 mmol) was dissolved in 35 ml of ethanol, and the resulting solution was filtered. The ligand, 1,4-bis(diphenylphosphino)-butane (0.2339 g, 0.5484 mmol), was completely dissolved in 15 ml of  $\text{CH}_2\text{Cl}_2$ , and added to the metal-containing solution at the rate of one drop/second. A bright yellow solid formed 30 s after all of the ligand solution had been added. Two well-defined peaks in the  $\nu_{\text{CN}}$  region, 2121 (s, sp) and 2091 (vs, br)  $\text{cm}^{-1}$  indicated that the compound was the *N,S*-dithiocyanato isomer. This product was recovered in 83% yield, based on the metal. This yellow complex turned to a red solid at  $230^\circ\text{C}$ , and melted at  $245^\circ\text{C}$ . Elemental analysis gave the following results (found (calc.)): C, 55.06 (55.52); H, 4.44 (4.35); N, 4.30 (4.32)%. Two different crystals, grown from  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{NO}_2$ , were analyzed by X-ray diffraction. Both proved to be the *N,S*-dithiocyanato geminite.

### *S,S*- and *N,S*-Dithiocyanato[*cis*-1,2-bis(diphenylphosphino)ethylene]palladium(II), $[\text{Pd}(\text{dpv})(\text{SCN})_2]$ and $[\text{Pd}(\text{dpv})(\text{NCS})(\text{SCN})]$

Two methods were employed to synthesize this complex. Both involved initial formation of the Magnus salt,  $[\text{Pd}(\text{Ph}_2\text{PCH}=\text{CHPPh}_2)_2][\text{Pd}(\text{SCN})_4]$ , followed by solvation and recrystallization to give the desired non-ionic form.

$\text{K}_2[\text{Pd}(\text{SCN})_4]$ , (0.3035 g, 0.7279 mmol), was completely dissolved in 35 ml of ethanol, and the resulting solution was filtered. *cis*-1,2-Bis(diphenylphosphino)ethylene (0.3181 g, 0.8025 mmol) was completely dissolved in 35 ml of  $\text{CH}_2\text{Cl}_2$ , and added to the filtered metal-containing solution at the rate of one drop/second. Upon addition of approximately one-half of the ligand solution, the pink Magnus salt formed. Infrared analysis of this salt gave  $\nu_{\text{CN}}$  peaks at 2113 (s, sp), 2106 (vs, sp), 2068 (m, sp), 2056 (vs, sp), and 2053 (m, sh)  $\text{cm}^{-1}$ . The two peaks below 2060  $\text{cm}^{-1}$  probably indicate the presence of ionic thiocyanate in the form  $[\text{Pd}(\text{Ph}_2\text{PCH}=\text{CHPPh}_2)_2][\text{SCN}]_2^*$ . The pink Magnus salt was also obtained using the method of Chow and McAuliffe [16]. This solid gave  $\nu_{\text{CN}}$  peaks at 2115 (w, sp), 2109 (w, sp), 2072 (m, sp), 2059 (s, sp) and 2054 (s, sh)  $\text{cm}^{-1}$ . This has been incorrectly identified as [17]  $[\text{Pd}(\text{dvp})(\text{SCN})_2]$  in the solid state.

Partial dissolution of approximately 0.2 g of the Magnus salt in 250 ml of ethanol at  $60^\circ\text{C}$  gave a yellow supernatant solution. The remaining Magnus salt was filtered out, and the filtrate evaporated to 30 ml at  $60^\circ\text{C}$ . The remainder of the solvent was evaporated at room temperature, leaving approximately 0.02 g of yellow–orange solid. Two peaks were observed in the  $\nu_{\text{CN}}$  region: 2114 (s, sp) and 2076 (s, br)  $\text{cm}^{-1}$ . A crystal obtained by this method was analyzed by X-ray diffraction, and shown to contain both the *N,S*-dithiocyanato and *S,S*-dithiocyanato isomers.

The alternative preparation is similar to that reported by Levason and McAuliffe [18]. Approximately 0.3 g of the Magnus salt,  $[\text{Pd}(\text{Ph}_2\text{PCH}=\text{CHPPh}_2)_2][\text{Pd}(\text{SCN})_4]$ , was completely dissolved in 50 ml of boiling *N,N*-dimethylformamide. The solution was orange–yellow for one minute, and then turned bright yellow. After cooling the solution to room temperature, 45 ml of distilled water was added to one portion. The beige–yellow solid which immediately formed was collected by filtration, and washed with distilled water, ethanol, and diethyl ether. The product was recovered in approximately 80% yield, based on the metal. This complex decomposed at  $268^\circ\text{C}$ . Infrared  $\nu_{\text{CN}}$  peaks of equal

\*Compare with the  $\nu_{\text{CN}}$  peaks at 2114, 2106, and 2101  $\text{cm}^{-1}$  for the Magnus salt of the analogous ethane derivative and 2052  $\text{cm}^{-1}$  for ionic thiocyanate in  $[\text{Pd}(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)_2](\text{SCN})_2$  [15].

intensity at 2115 (s, sp), and 2078 (s, br)  $\text{cm}^{-1}$  clearly indicated a mixture of the *S,S*-dithiocyanato and *N,S*-dithiocyanato isomers. The samples used for a subsequent solvent screen, the results of which will be reported in a separate paper [19], were prepared in this manner.

*S,S*- and *N,S*-Dithiocyanato[*ortho*-bis(diphenylphosphino)benzene]palladium(II),  $[\text{Pd}(\text{dpbz})(\text{SCN})_2]$  and  $[\text{Pd}(\text{dpbz})(\text{NCS})(\text{SCN})]$

The *N,S*-dithiocyanato isomer of this complex was previously prepared by Levason and McAuliffe [18] by refluxing the reactants in boiling *N,N*-dimethylformamide to give the desired non-ionic product.

The *N,S*-dithiocyanato isomer used in this study was prepared by a procedure similar to that outlined by Palenik *et al.* [4] to keep the synthetic procedures as constant as possible throughout the entire series.  $\text{K}_2[\text{Pd}(\text{SCN})_4]$  (0.2207 g, 0.5293 mmol) was completely dissolved in 40 ml of ethanol, and the resulting solution was filtered. The ligand, *ortho*-bis(diphenylphosphino)benzene (0.2381 g, 0.5333 mmol), was completely dissolved in 15 ml of  $\text{CH}_2\text{Cl}_2$ , and added to the metal-containing solution at a rate of one drop/second. While adding the ligand solution, the metal-containing solution turned from its original deep red color to an orange–yellow color. No precipitate had formed after addition of all of the ligand solution. The solution was placed in an ice-bath, and a beige–yellow solid formed after 5 min. Stirring was continued for another 40 min. This solid complex was collected on a filter, and washed with distilled water, ethanol and diethyl ether. The complex was then recrystallized from  $\text{CH}_2\text{Cl}_2$  and hexanes. Two distinct  $\nu_{\text{CN}}$  peaks at 2119 (s, sp) and 2082 (vs, br)  $\text{cm}^{-1}$  indicated the presence of the *N,S*-dithiocyanato isomer. The yield after recrystallization was 68%, based on the metal. Elemental analysis gave the following results (found (calc.)): C, 49.90 (56.78); H, 3.55 (3.57); N, 3.65 (4.14)%. The molecular structure of this complex, as determined by X-ray diffraction analysis, revealed that a molecule of  $\text{CH}_2\text{Cl}_2$  is trapped in the solid-state lattice. If one assumes that the sample sent for elemental analysis (which was recrystallized from  $\text{CH}_2\text{Cl}_2$ ) contained one molecule of  $\text{CH}_2\text{Cl}_2$  in its lattice, the results of the elemental analysis are more reasonable. Incorporating one molecule of  $\text{CH}_2\text{Cl}_2$  into the calculations gives (found (calc.)): C, 49.90 (52.57); H, 3.55 (3.48); N, 3.65 (3.71). The  $[\text{Pd}(\text{dpbz})(\text{NCS})(\text{SCN})]$  crystal was prepared by dissolving approximately 5 mg of the complex in 15 ml of  $\text{CH}_2\text{Cl}_2$ , followed by evaporation of the solvent at room temperature. The *S,S*-dithiocyanato crystal was prepared by complete dissolution of approximately 5 mg of the *N,S*-dithiocyanato isomer in 20 ml of methanol, followed by evaporation of the solvent at room temperature.

*N,S*-Dithiocyanato[ $\alpha, \alpha'$ -bis(diphenylphosphino)-*o*-xylene]palladium(II),  $[\text{Pd}(\text{dpx})(\text{NCS})(\text{SCN})]$

**Note:** The ligand,  $\alpha, \alpha'$ -bis(diphenylphosphino)-*o*-xylene, is air-sensitive. All manipulations were done under  $\text{N}_2$ , except for the addition of the ligand solution to the metal-containing solution. Limited air exposure (time < 15 min) appeared to have no effect on the product formed or its yield.

$\text{K}_2[\text{Pd}(\text{SCN})_4]$  (0.3511 g, 0.8421 mmol) was completely dissolved in 80 ml of ethanol at room temperature, and the resulting solution was filtered. The ligand,  $\alpha, \alpha'$ -bis(diphenylphosphino)-*o*-xylene (0.4500 g, 0.9483 mmol), was added to 10 ml of deaerated  $\text{CH}_2\text{Cl}_2$ , and added in one portion to the metal-containing solution. A bright yellow solid immediately formed, then redissolved within 15 s. The solution was stirred for 2 h, and a yellow solid formed. This second precipitate was collected by filtration, and washed with distilled water, ethanol and diethyl ether. Infrared analysis of the  $\nu_{\text{CN}}$  region revealed two peaks of equal intensity and shape at 2117 (s, sp) and 2112 (s, sp)  $\text{cm}^{-1}$  as well as another at 2069 (vs, br)  $\text{cm}^{-1}$  indicating the *N,S*-dithiocyanato isomer. The yield was 75%, based on the metal. This complex decomposed at 277 °C. Elemental analysis of  $[\text{Pd}(\text{dpx})(\text{NCS})(\text{SCN})]$  gave the following results (found (calc.)): C, 57.86 (55.58); H, 3.82 (4.05); N, 4.09 (4.02)%.

This reaction was repeated, except that the ligand solution was added in 0.5 ml portions over 15 min, rather than in one portion. Addition of the ligand was stopped after the initial formation of a yellow–orange solid, which may correspond with the first solid formed in the first synthesis. This solid was collected on a filter, and washed with distilled water, ethanol and diethyl ether. Infrared analysis of this solid gave  $\nu_{\text{CN}}$  peaks at 2116 (s, sp) and 2112 (s, sp)  $\text{cm}^{-1}$ , as well as a peak at 2080 (s, br)  $\text{cm}^{-1}$ , indicating the *N,S*-dithiocyanato isomer. The filtrate from this solid was also yellow. One hundred ml of distilled water was added to this filtrate. The solution was stirred for ten days at room temperature, after which the volume of the solution had been reduced to 20 ml. A considerable amount of bright yellow solid formed. This was collected on a filter, and washed with distilled water. Ethanol was not used because it readily dissolved the product. Infrared analysis of the  $\nu_{\text{CN}}$  region gave peaks at 2159 (s, sp), 2126 (m, sp), 2120 (m, sh), 2098 (m, sp) and 2083 (m, sp)  $\text{cm}^{-1}$ , indicating the presence of some dinuclear bridging through thiocyanate.

### Infrared Spectroscopy

Infrared spectra were recorded on a Perkin-Elmer 180 spectrometer. A normal scan over the  $\nu_{\text{CN}}$  region, 2300–2000  $\text{cm}^{-1}$ , and a ten-fold abscissa expansion scan over the region 2200–2000  $\text{cm}^{-1}$  were recorded for each complex. General peak shapes and intensities

TABLE 1. Ligands and their Abbreviations

| Ligand                                                     | Abbreviation |
|------------------------------------------------------------|--------------|
| Bis(diphenylphosphino)methane                              | dpm          |
| 1,2-Bis(diphenylphosphino)ethane                           | dpe          |
| 1,3-Bis(diphenylphosphino)propane                          | dpp          |
| 1,4-Bis(diphenylphosphino)butane                           | dpb          |
| <i>cis</i> -1,2-Bis(diphenylphosphino)ethylene             | dpv          |
| <i>o</i> -Bis(diphenylphosphino)benzene                    | dpbz         |
| $\alpha,\alpha'$ -Bis(diphenylphosphino)- <i>o</i> -xylene | dpx          |
| 1-Diphenylphosphino-3-dimethylaminopropane                 | dppn         |
| 1,3-Bis(diphenylphosphino)-2-trifluoromethylpropene        | tfmp         |

are abbreviated as sp (sharp), br (broad), sh (shoulder), s (strong), m (medium), w (weak), and may be prefixed with v (very). Samples were analyzed as Nujol mulls between KBr or NaCl plates, and the spectrophotometer was calibrated daily to polystyrene.

#### Melting Points

A Thomas Hoover melting point apparatus was used to determine the melting or decomposition point of each complex. The reported values are uncorrected.

#### Elemental Analyses

Elemental analyses were performed by the Micro-analytical Laboratory of the Chemistry Department, University of Illinois at Urbana.

#### X-ray Crystallography

All crystals were attached to a glass fiber with epoxy cement. Intensity measurements were collected on a Nicolet R3 diffractometer using graphite monochromatized Mo K $\alpha$  radiation.

Molecular structures were solved and refined using the Nicolet SHELXTL (version 4.0) programs. An empirical absorption correction was applied to the data using  $\psi$ -scan data from close-to-axial reflections. Absorption-corrected data were refined by a six-parameter procedure to define a pseudoellipsoid used to calculate the corrections. A profile-fitting procedure was applied to the data to improve the precision of the measurement of weak reflections. No correction for decay was required for any of the crystals.

In all cases, the direct-methods technique (SOLV) yielded the position of the palladium atom. All other non-hydrogen atoms were located by difference-Fourier techniques. All non-hydrogen atoms were refined anisotropically using blocked-cascade, least-squares refinement methods. The hydrogen atom positions were calculated in idealized positions using  $d$  (C–H) = 0.96 Å, and thermal parameters equal to 1.2 times the isotropic equivalent value for the atom to which the hydrogen atom was attached.

#### Results

A list of the ligands used and/or discussed in this paper is shown in Table 1. Table 1 also includes a list of the corresponding abbreviations utilized for these ligands.

The molecular structures of the following eight complexes were determined by single crystal X-ray diffraction studies: *N,S*-dithiocyanato[1,3-bis(diphenylphosphino)propane]palladium(II), two separate crystals, grown from CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>NO<sub>2</sub> solutions, of the complex *N,S*-dithiocyanato[1,4-bis(diphenylphosphino)butane]palladium(II), *S,S*- and *N,S*-dithiocyanato[*cis*-1,2-bis(diphenylphosphino)ethylene]palladium(II), *S,S*- and *N,S*-dithiocyanato[*o*-bis(diphenylphosphino)benzene]palladium(II), and *N,S*-dithiocyanato[ $\alpha,\alpha'$ -bis(diphenylphosphino)-*o*-xylene]palladium(II). A view of each of these complexes, approximately normal to the coordination plane, is shown in Figs. 1 through 7. Summaries of crystal and intensity data and compilations of important bond angles and bond lengths are provided in Tables 2 through 22.

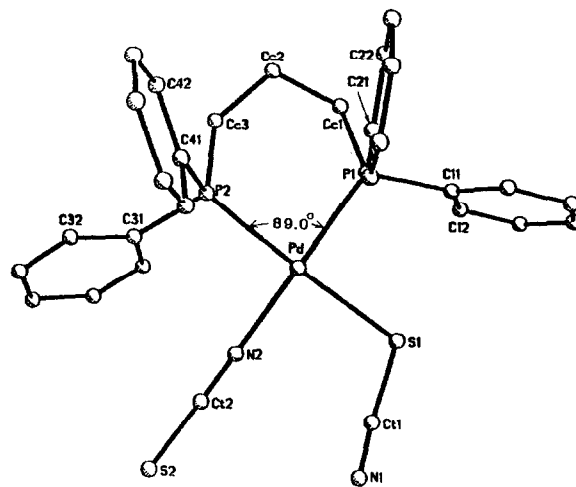


Fig. 1. Molecular structure of [Pd(dpp)(NCS)(SCN)].

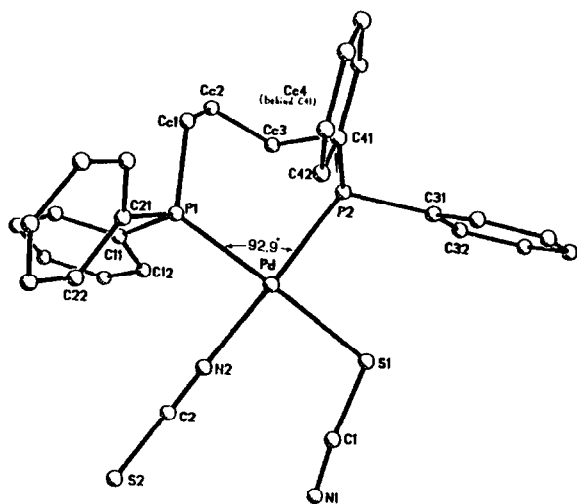


Fig. 2. Molecular structure of  $[\text{Pd}(\text{dpb})(\text{NCS})(\text{SCN})]$  (from  $\text{CH}_2\text{Cl}_2$ ).

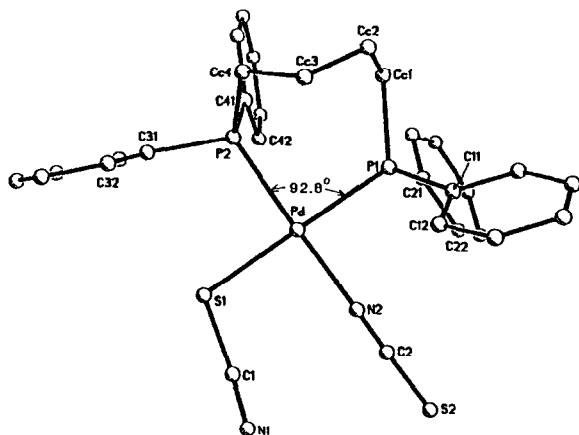


Fig. 3. Molecular structure of  $[\text{Pd}(\text{dpb})(\text{NCS})(\text{SCN})]$  (from nitromethane).

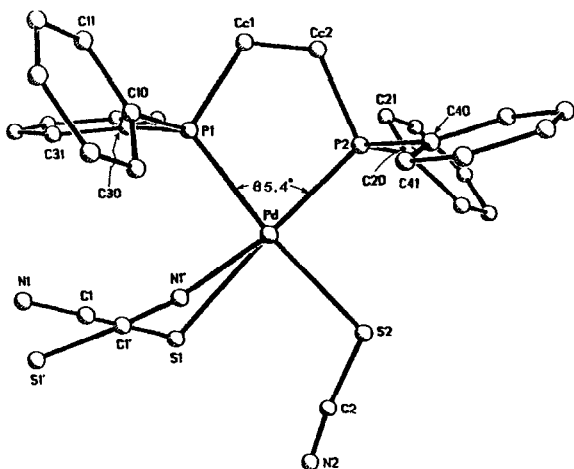


Fig. 4. Molecular structure of  $[\text{Pd}(\text{dpv})(\text{SCN})_2]$  and  $[\text{Pd}(\text{dpv})(\text{NCS})(\text{SCN})]$ . Note: both structures are shown in this figure. There is approximately 50% occupancy of one coordination site by S1 and approximately 50% occupancy of the same site by N1'.

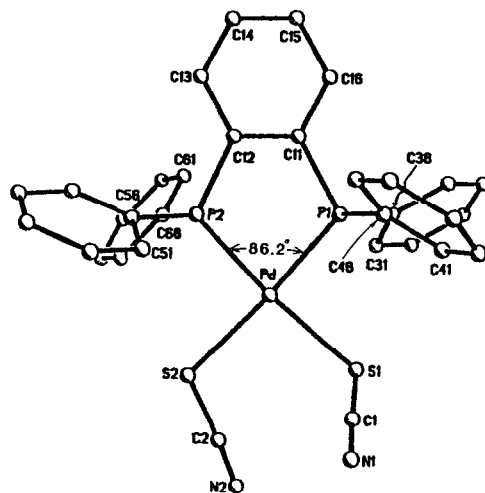


Fig. 5. Molecular structure of  $[\text{Pd}(\text{dpbz})(\text{SCN})_2]$ .

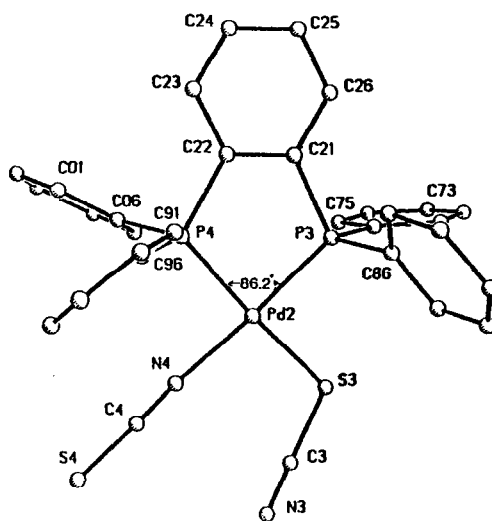


Fig. 6. Molecular structure of  $[\text{Pd}(\text{dpbz})(\text{NCS})(\text{SCN})]$ .

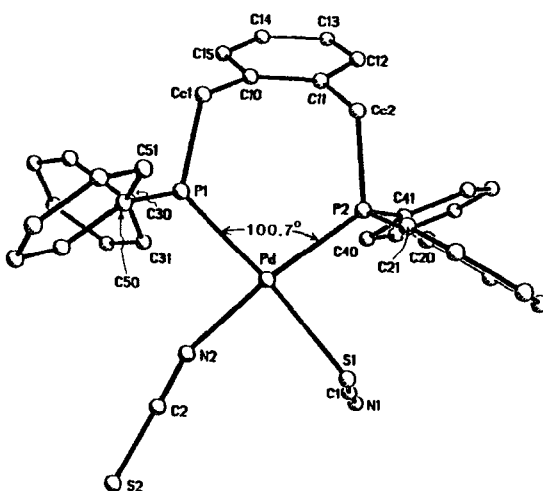


Fig. 7. Molecular structure of  $[\text{Pd}(\text{dpx})(\text{NCS})(\text{SCN})]$ .

TABLE 2. Crystal and Intensity Data Collection Summary, [Pd(dpp)(NCS)(SCN)]

|                                                           |                                                                                |
|-----------------------------------------------------------|--------------------------------------------------------------------------------|
| Molecular formula                                         | PdC <sub>29</sub> H <sub>26</sub> N <sub>2</sub> P <sub>2</sub> S <sub>2</sub> |
| Solvent of crystallization                                | CH <sub>2</sub> Cl <sub>2</sub>                                                |
| Formula weight (g/form)                                   | 635.03                                                                         |
| Molecular weight (g/mol)                                  | 635.03                                                                         |
| <i>a</i> (Å)                                              | 13.324(4)                                                                      |
| <i>b</i> (Å)                                              | 10.466(1)                                                                      |
| <i>c</i> (Å)                                              | 28.815(6)                                                                      |
| β (°)                                                     | 90.79(2)                                                                       |
| Volume (Å <sup>3</sup> )                                  | 3181.07(1.36)                                                                  |
| Crystal system                                            | monoclinic                                                                     |
| Space group                                               | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                             |
| ρ (calc.) (g/cm <sup>3</sup> )                            | 1.34                                                                           |
| <i>Z</i>                                                  | 4                                                                              |
| Crystal dimensions (mm)                                   | 0.40 × 0.21 × 0.21                                                             |
| Crystal color                                             | yellow                                                                         |
| Radiation                                                 | Mo Kα                                                                          |
| Absorption coefficient, μ(Mo Kα) (cm <sup>-1</sup> )      | 9.90                                                                           |
| Temperature (°C)                                          | 26 ± 2                                                                         |
| Scan speed (° min <sup>-1</sup> )                         | 3.00/15.00                                                                     |
| Scan type                                                 | θ – 2θ                                                                         |
| Scan range                                                | 1.8 + Δ(α <sub>1</sub> – α <sub>2</sub> )                                      |
| Standards monitored                                       | 3/200                                                                          |
| 2θ Limits (°)                                             | 4.0 ≤ 2θ ≤ 45.0                                                                |
| Reflections collected                                     | ± <i>h</i> , <i>k</i> , <i>l</i>                                               |
| No. reflections collected                                 | 6228                                                                           |
| Unique reflections                                        | 5533                                                                           |
| Unique reflections used                                   | 4779 ( <i>n</i> = 2.0)                                                         |
| Weighting factor, <i>g</i> <sup>a</sup>                   | 0.00110                                                                        |
| <i>R</i> <sup>b</sup>                                     | 0.0517                                                                         |
| <i>R</i> (Fw) <sup>c</sup>                                | 0.0653                                                                         |
| GOF                                                       | 1.331                                                                          |
| Highest peak on final difference map (e Å <sup>-3</sup> ) | 0.77                                                                           |

$$^a \text{Weight} = 1/[\sigma^2(F) + |g|(F^2)], \quad ^b R = \sum(|F_o| - |F_c|)/\sum|F_o|, \quad ^c R_w = [\sum w^{1/2}(|F_o| - |F_c|)]/\sum w^{1/2}(F_o).$$

TABLE 3. Important Bond Lengths, [Pd(dpp)(NCS)(SCN)]

| Atoms   | Bond length (Å) |
|---------|-----------------|
| Pd–S1   | 2.370(2)        |
| Pd–P2   | 2.283(2)        |
| Pd–P1   | 2.257(2)        |
| Pd–N2   | 2.036(6)        |
| S1–Ct1  | 1.650(8)        |
| P1–Cc1  | 1.820(8)        |
| N1–Ct1  | 1.137(11)       |
| Cc1–Cc2 | 1.547(10)       |
| S2–Ct2  | 1.619(7)        |
| P2–Cc3  | 1.836(7)        |
| N2–Ct2  | 1.146(9)        |
| Cc2–Cc3 | 1.551(10)       |

There are two sets of crystal data for the complex [Pd(dpb)(NCS)(SCN)] (see Figs. 2 and 3, Tables 5 through 10). Two separate crystals of this complex were grown from two different solvents (CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>NO<sub>2</sub>), and independently analyzed by X-ray diffraction techniques.

TABLE 4. Important Bond Angles, [Pd(dpp)(NCS)(SCN)]

| Atoms       | Angle (°) |
|-------------|-----------|
| P1–Pd–P2    | 89.0(1)   |
| S1–Pd–P1    | 88.4(1)   |
| P1–Pd–N2    | 176.0(2)  |
| S1–Pd–P2    | 177.1(1)  |
| S1–Pd–N2    | 92.5(2)   |
| P2–Pd–N2    | 90.1(2)   |
| Pd–S1–Ct1   | 107.3(3)  |
| Pd–P1–Cc1   | 114.9(2)  |
| Pd–P2–Cc3   | 115.7(2)  |
| Pd–N2–Ct2   | 171.2(6)  |
| S1–Ct1–N1   | 173.1(9)  |
| S2–Ct2–N2   | 179.0(6)  |
| P1–Cc1–Cc2  | 115.2(5)  |
| Cc1–Cc2–Cc3 | 112.8(6)  |
| P2–Cc3–Cc2  | 115.0(5)  |

In contrast, the two isomers [Pd(dpv)(SCN)<sub>2</sub>] and [Pd(dpv)(NCS)(SCN)] are both in the same crystal (see Tables 11–13). One of the thiocyanate coor-

TABLE 5. Crystal and Intensity Data Collection Summary, [Pd(dpb)(NCS)(SCN)] (from CH<sub>2</sub>Cl<sub>2</sub>)

|                                                                    |                                                                                |
|--------------------------------------------------------------------|--------------------------------------------------------------------------------|
| Molecular formula                                                  | PdC <sub>30</sub> H <sub>28</sub> N <sub>2</sub> P <sub>2</sub> S <sub>2</sub> |
| Solvent of crystallization                                         | CH <sub>2</sub> Cl <sub>2</sub>                                                |
| Formula weight (g/form)                                            | 649.06                                                                         |
| Molecular weight (g/mol)                                           | 649.06                                                                         |
| <i>a</i> (Å)                                                       | 10.472(3)                                                                      |
| <i>b</i> (Å)                                                       | 18.931(4)                                                                      |
| <i>c</i> (Å)                                                       | 16.841(4)                                                                      |
| $\beta$ (°)                                                        | 104.97(2)                                                                      |
| Volume (Å <sup>3</sup> )                                           | 3225.23(1.24)                                                                  |
| Crystal system                                                     | monoclinic                                                                     |
| Space group                                                        | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                             |
| $\rho$ (calc.) (g/cm <sup>3</sup> )                                | 1.338                                                                          |
| <i>Z</i>                                                           | 4                                                                              |
| Crystal dimensions (mm)                                            | 0.20 × 0.20 × 0.32                                                             |
| Crystal color                                                      | yellow                                                                         |
| Radiation                                                          | Mo K $\alpha$                                                                  |
| Absorption coefficient, $\mu$ (Mo K $\alpha$ ) (cm <sup>−1</sup> ) | 8.09                                                                           |
| Temperature (°C)                                                   | 24 ± 2                                                                         |
| Scan speed (° min <sup>−1</sup> )                                  | 4.0/20.0                                                                       |
| Scan type                                                          | $\theta$ – $2\theta$                                                           |
| Scan range                                                         | 0.9 + $\Delta(\alpha_1 - \alpha_2)$                                            |
| Standards monitored                                                | 3/200                                                                          |
| 2 $\theta$ Limits (°)                                              | 3.0 ≤ 2 $\theta$ ≤ 50.0                                                        |
| Reflections collected                                              | ± <i>h</i> , <i>k</i> , <i>l</i>                                               |
| Unique reflections                                                 | 5720                                                                           |
| Unique reflections used                                            | 4714 ( <i>n</i> = 2.0)                                                         |
| Weighting factor, <i>g</i> <sup>a</sup>                            | 0.00134                                                                        |
| <i>R</i> (F) <sup>b</sup>                                          | 0.0572                                                                         |
| <i>R</i> (Fw) <sup>c</sup>                                         | 0.0694                                                                         |
| <i>GOF</i>                                                         | 1.197                                                                          |
| Highest peak on final difference map (e Å <sup>−3</sup> )          | 0.51                                                                           |

<sup>a</sup>,<sup>b</sup>,<sup>c</sup>See Table 2 for footnotes.TABLE 6. Important Bond Lengths, [Pd(dpb)(NCS)(SCN)] (from CH<sub>2</sub>Cl<sub>2</sub>)

| Atoms   | Bond length (Å) |
|---------|-----------------|
| Pd–P1   | 2.291(2)        |
| Pd–P2   | 2.265(2)        |
| Pd–S1   | 2.365(2)        |
| Pd–N2   | 2.045(5)        |
| P1–Cc1  | 1.824(7)        |
| P2–Cc4  | 1.834(8)        |
| S1–C1   | 1.661(7)        |
| S2–C2   | 1.621(7)        |
| N1–C1   | 1.143(9)        |
| N2–C2   | 1.138(9)        |
| Cc1–Cc2 | 1.527(11)       |
| Cc2–Cc3 | 1.534(10)       |
| Cc3–Cc4 | 1.518(9)        |

dination sites in this crystal is occupied, approximately 50% of the time, by a sulfur-bound thiocyanate (S1–C1–N1 in Fig. 4) and 50% of the time by a nitrogen-bound thiocyanate (N1'–C1'–S1' in Fig. 4). The other coordination site is fully occupied by a

TABLE 7. Important Bond Angles, [Pd(dpb)(NCS)(SCN)] (from CH<sub>2</sub>Cl<sub>2</sub>)

| Atoms       | Angle (°) |
|-------------|-----------|
| P1–Pd–P2    | 92.9(1)   |
| P1–Pd–S1    | 177.4(1)  |
| P2–Pd–S1    | 88.6(1)   |
| P1–Pd–N2    | 85.8(2)   |
| P2–Pd–N2    | 176.7(2)  |
| S1–Pd–N2    | 92.6(2)   |
| Pd–P1–Cc1   | 118.6(2)  |
| Pd–P2–Cc4   | 115.3(2)  |
| Pd–S1–C1    | 104.0(3)  |
| Pd–N2–C2    | 163.6(6)  |
| S1–C1–N1    | 175.1(7)  |
| S2–C2–N2    | 178.5(7)  |
| P1–Cc1–Cc2  | 114.6(4)  |
| Cc1–Cc2–Cc3 | 115.4(6)  |
| Cc2–Cc3–Cc4 | 115.7(5)  |
| P2–Cc4–Cc3  | 116.7(5)  |

sulfur-bound thiocyanate (S2–C2–N2). Bond lengths and bond angles for the remainder of the molecule were calculated as averages for these two isomers;

TABLE 8. Crystal and Intensity Data Collection Summary, [Pd(dpb)(NCS)(SCN)] (from nitromethane)

|                                                                    |                                                                                |
|--------------------------------------------------------------------|--------------------------------------------------------------------------------|
| Molecular formula                                                  | PdC <sub>30</sub> H <sub>28</sub> N <sub>2</sub> P <sub>2</sub> S <sub>2</sub> |
| Solvent of crystallization                                         | CH <sub>3</sub> NO <sub>2</sub>                                                |
| Formula weight (g/form)                                            | 649.06                                                                         |
| Molecular weight (g/mol)                                           | 649.06                                                                         |
| <i>a</i> (Å)                                                       | 10.455(4)                                                                      |
| <i>b</i> (Å)                                                       | 19.141(5)                                                                      |
| <i>c</i> (Å)                                                       | 16.872(7)                                                                      |
| $\beta$ (°)                                                        | 109.52(3)                                                                      |
| Volume (Å <sup>3</sup> )                                           | 3269(2)                                                                        |
| Crystal system                                                     | monoclinic                                                                     |
| Space group                                                        | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                             |
| $\rho$ (calc.) (g/cm <sup>3</sup> )                                | 1.22                                                                           |
| <i>Z</i>                                                           | 4                                                                              |
| Crystal color                                                      | yellow                                                                         |
| Radiation                                                          | Mo K $\alpha$                                                                  |
| Absorption coefficient, $\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> ) | 8.05                                                                           |
| Temperature (°C)                                                   | 24 $\pm$ 2                                                                     |
| Scan speed (° min <sup>-1</sup> )                                  | 3.0/15.0                                                                       |
| Scan type                                                          | $\omega$ -2 $\theta$                                                           |
| Scan range                                                         | 1.9 + $\Delta(\alpha_1 - \alpha_2)$                                            |
| Standards monitored                                                | 3/200                                                                          |
| 2 $\theta$ Limits (°)                                              | 4.0 $\leq$ 2 $\theta$ $\leq$ 47.0                                              |
| Reflections collected                                              | $\pm h, k, l$                                                                  |
| No. reflections collected                                          | 5193                                                                           |
| Unique reflections                                                 | 4495                                                                           |
| Unique reflections used                                            | 3901 ( <i>n</i> = 2.5)                                                         |
| Weighting factor, <i>g</i> <sup>a</sup>                            | 0.00033                                                                        |
| <i>R</i> (F) <sup>b</sup>                                          | 0.0475                                                                         |
| <i>R</i> (Fw) <sup>c</sup>                                         | 0.0512                                                                         |
| <i>GOF</i>                                                         | 1.520                                                                          |
| Highest peak on final difference map (e Å <sup>-3</sup> )          | 0.78                                                                           |

<sup>a,b,c</sup>See Table 2 for footnotes.

TABLE 9. Important Bond Lengths, [Pd(dpb)(NCS)(SCN)] (from nitromethane)

| Atoms   | Bond length (Å) |
|---------|-----------------|
| Pd–P1   | 2.296(1)        |
| Pd–P2   | 2.269(1)        |
| Pd–S1   | 2.368(2)        |
| Pd–N2   | 2.045(5)        |
| P1–Cc1  | 1.821(6)        |
| P2–Cc4  | 1.835(6)        |
| S1–C1   | 1.673(6)        |
| S2–C2   | 1.623(6)        |
| N1–C1   | 1.135(9)        |
| N2–C2   | 1.146(8)        |
| Cc1–Cc2 | 1.536(9)        |
| Cc2–Cc3 | 1.514(8)        |
| Cc3–Cc4 | 1.511(7)        |

hence, the molecular structure shows the *S,S*- and *N,S*-dithiocyanato isomers in one picture, for comparative purposes.

The complex [Pd(dpbz)(NCS)(SCN)] (see Fig. 6, Tables 17–19) has a disorder problem in one thio-

TABLE 10. Important Bond Angles, [Pd(dpb)(NCS)(SCN)] (from nitromethane)

| Atoms       | Angle (°) |
|-------------|-----------|
| P1–Pd–P2    | 92.8(1)   |
| P2–Pd–S1    | 88.5(1)   |
| P1–Pd–S1    | 177.5(1)  |
| P1–Pd–N2    | 85.5(1)   |
| S1–Pd–N2    | 93.1(1)   |
| Pd–P2–Cc1   | 119.0(2)  |
| Pd–P2–Cc4   | 114.9(2)  |
| Pd–S1–C1    | 104.1(2)  |
| Pd–N2–C2    | 163.8(4)  |
| S1–C1–N1    | 176.0(6)  |
| S2–C2–N2    | 178.1(6)  |
| P1–Cc1–Cc2  | 114.5(4)  |
| Cc1–Cc2–Cc3 | 115.9(5)  |
| Cc2–Cc3–Cc4 | 115.8(4)  |
| P2–Cc4–Cc3  | 117.7(4)  |

cyanate group (*R* = 10%). There are two complete molecules per asymmetric unit. One of these is a 'well-behaved' *N,S*-dithiocyanato molecule. The other molecule in the unit cell, along with the associated

TABLE 11. Crystal and Intensity Data Collection Summary, [Pd(dpv)(SCN)<sub>2</sub>] and [Pd(dpv)(NCS)(SCN)]

|                                                                    |                                                                                |
|--------------------------------------------------------------------|--------------------------------------------------------------------------------|
| Molecular formula                                                  | PdC <sub>28</sub> H <sub>22</sub> N <sub>2</sub> P <sub>2</sub> S <sub>2</sub> |
| Solvent of crystallization                                         | ethanol (60 °C)                                                                |
| Formula weight (g/form)                                            | 618.98                                                                         |
| Molecular weight (g/mol)                                           | 618.98                                                                         |
| <i>a</i> (Å)                                                       | 10.047(4)                                                                      |
| <i>b</i> (Å)                                                       | 15.648(4)                                                                      |
| <i>c</i> (Å)                                                       | 17.375(6)                                                                      |
| $\beta$ (°)                                                        | 100.98(3)                                                                      |
| Volume (Å <sup>3</sup> )                                           | 2681(1)                                                                        |
| Crystal system                                                     | monoclinic                                                                     |
| Space group                                                        | <i>P</i> 2 <sub>1</sub> / <i>n</i>                                             |
| $\rho$ (calc.) (g/cm <sup>3</sup> )                                | 1.53                                                                           |
| <i>Z</i>                                                           | 4                                                                              |
| Crystal color                                                      | yellow                                                                         |
| Radiation                                                          | Mo K $\alpha$                                                                  |
| Absorption coefficient, $\mu$ (Mo K $\alpha$ ) (cm <sup>−1</sup> ) | 9.60                                                                           |
| Temperature (°C)                                                   | 24 ± 2                                                                         |
| Scan speed (° min <sup>−1</sup> )                                  | 4.00/20.0                                                                      |
| Scan type                                                          | $\theta - 2\theta$                                                             |
| Scan range                                                         | 1.8 + $\Delta(\alpha_1 - \alpha_2)$                                            |
| Standards monitored                                                | 3/200                                                                          |
| 2 $\theta$ Limits (°)                                              | 4.0 ≤ 2 $\theta$ ≤ 50.0                                                        |
| Reflections collected                                              | ± <i>h</i> , <i>k</i> , <i>l</i>                                               |
| No. reflections collected                                          | 4812                                                                           |
| Unique reflections                                                 | 4371                                                                           |
| Unique reflections used                                            | 3238 ( <i>n</i> = 2.5)                                                         |
| Weighting factor, <i>g</i> <sup>a</sup>                            | 0.00002                                                                        |
| <i>R</i> ( <i>F</i> ) <sup>b</sup>                                 | 0.0588                                                                         |
| <i>R</i> ( <i>F</i> <sub>w</sub> ) <sup>c</sup>                    | 0.0412                                                                         |
| <i>GOF</i>                                                         | 1.395                                                                          |
| Highest peak on final difference map (e Å <sup>−3</sup> )          | 0.51                                                                           |

<sup>a,b,c</sup>See Table 2 for footnotes.TABLE 12. Important Bond Lengths, [Pd(dpv)(SCN)<sub>2</sub>] and [Pd(dpv)(NCS)(SCN)]

| Atoms   | Bond length (Å) |
|---------|-----------------|
| Pd–P1   | 2.256(2)        |
| Pd–P2   | 2.246(2)        |
| Pd–S1   | 2.448(8)        |
| Pd–S2   | 2.369(2)        |
| Pd–N1'  | 1.913(12)       |
| P1–Cc1  | 1.812(6)        |
| P2–Cc2  | 1.803(6)        |
| S1–C1   | 1.638(16)       |
| S2–C2   | 1.642(7)        |
| N1–C1   | 1.130(21)       |
| N2–C2   | 1.131(10)       |
| Cc1–Cc2 | 1.308(9)        |
| S1'–C1' | 1.641(23)       |
| C1'–N1' | 1.130(25)       |

CH<sub>2</sub>Cl<sub>2</sub> molecule, suffers from disorder in one thiocyanate group and in the solvent molecule. However, this does not influence the 'well-behaved' molecule in the unit cell. See also 'Supplementary Material'.

Table 23 lists the P–Pd–P bond angle and corresponding mode of dithiocyanate coordination for

TABLE 13. Important Bond Angles, [Pd(dpv)(SCN)<sub>2</sub>] and [Pd(dpv)(NCS)(SCN)]

| Atoms       | Angle (°) |
|-------------|-----------|
| P1–Pd–P2    | 85.4(1)   |
| P2–Pd–S1    | 175.0(1)  |
| P2–Pd–S2    | 88.3(1)   |
| P1–Pd–N1'   | 86.0(4)   |
| P1–Pd–S1    | 98.8(2)   |
| P1–Pd–S2    | 172.0(1)  |
| S1–Pd–S2    | 87.8(2)   |
| P2–Pd–N1'   | 171.1(4)  |
| S2–Pd–N1'   | 100.5(4)  |
| Pd–P1–Cc1   | 108.4(2)  |
| Pd–S1–C1    | 117.0(10) |
| Pd–S2–C2    | 107.6(3)  |
| P1–Cc1–Cc2  | 118.1(5)  |
| P2–Cc2–Cc1  | 119.7(5)  |
| S1–C1–N1    | 177.4(25) |
| S2–C2–N2    | 174.1(7)  |
| S1'–C1'–N1' | 175.9(18) |
| Pd–N1'–C1'  | 167.5(14) |

those dithiocyanato[bis(diphenylphosphino)alkyl or aryl]palladium(II) complexes that have been structurally characterized for the first time in this paper,

TABLE 14. Crystal and Intensity Data Collection Summary, [Pd(dpbz)(SCN)<sub>2</sub>]

|                                                           |                                                                                |
|-----------------------------------------------------------|--------------------------------------------------------------------------------|
| Molecular formula                                         | PdC <sub>32</sub> H <sub>24</sub> N <sub>2</sub> P <sub>2</sub> S <sub>2</sub> |
| Solvent of crystallization                                | methanol                                                                       |
| Formula weight (g/form)                                   | 669.04                                                                         |
| Molecular weight (g/mol)                                  | 669.04                                                                         |
| <i>a</i> (Å)                                              | 10.749(4)                                                                      |
| <i>b</i> (Å)                                              | 19.191(5)                                                                      |
| <i>c</i> (Å)                                              | 15.421(6)                                                                      |
| β (°)                                                     | 108.95(3)                                                                      |
| Volume (Å <sup>3</sup> )                                  | 3008(2)                                                                        |
| Crystal system                                            | monoclinic                                                                     |
| Space group                                               | <i>P</i> 2 <sub>1</sub> / <i>n</i>                                             |
| ρ (calc.) (g/cm <sup>3</sup> )                            | 1.49                                                                           |
| <i>Z</i>                                                  | 4                                                                              |
| Crystal color                                             | yellow                                                                         |
| Radiation                                                 | Mo Kα                                                                          |
| Absorption coefficient, μ(Mo Kα) (cm <sup>-1</sup> )      | 8.80                                                                           |
| Temperature (°C)                                          | 24 ± 2                                                                         |
| Scan speed (° min <sup>-1</sup> )                         | 3.00/15.00                                                                     |
| Scan type                                                 | θ – 2θ                                                                         |
| Scan range                                                | 1.4 + Δ(α <sub>1</sub> – α <sub>2</sub> )                                      |
| Standards monitored                                       | 3/200                                                                          |
| 2θ Limits (°)                                             | 4.0 ≤ 2θ ≤ 45.0                                                                |
| Reflections collected                                     | ± <i>h</i> , <i>k</i> , <i>l</i>                                               |
| No. reflections collected                                 | 4363                                                                           |
| Unique reflections                                        | 3967                                                                           |
| Unique reflections used                                   | 3098 ( <i>n</i> = 2.0)                                                         |
| Weighting factor, <i>g</i> <sup>a</sup>                   | 0.00047                                                                        |
| <i>R</i> (F) <sup>b</sup>                                 | 0.0526                                                                         |
| <i>R</i> (Fw) <sup>c</sup>                                | 0.0491                                                                         |
| <i>GOF</i>                                                | 1.156                                                                          |
| Highest peak on final difference map (e Å <sup>-3</sup> ) | 0.54                                                                           |

a,b,cSec Table 2 for footnotes.

TABLE 15. Important Bond Lengths, [Pd(dpbz)(SCN)<sub>2</sub>]

| Atoms   | Bond length (Å) |
|---------|-----------------|
| Pd–S1   | 2.402(2)        |
| Pd–P1   | 2.238(2)        |
| Pd–S2   | 2.379(2)        |
| Pd–P2   | 2.267(2)        |
| S1–C1   | 1.623(8)        |
| S2–C2   | 1.652(8)        |
| P1–C11  | 1.813(8)        |
| P2–C12  | 1.817(7)        |
| N1–C1   | 1.165(11)       |
| N2–C2   | 1.155(10)       |
| C11–C12 | 1.382(9)        |

TABLE 16. Important Bond Angles, [Pd(dpbz)(SCN)<sub>2</sub>]

| Atoms      | Angle (°) |
|------------|-----------|
| P1–Pd–P2   | 86.2(1)   |
| S1–Pd–S2   | 98.0(1)   |
| S1–Pd–P1   | 87.2(1)   |
| S2–Pd–P2   | 89.8(1)   |
| S1–Pd–P2   | 169.0(1)  |
| Pd–S1–C1   | 102.6(3)  |
| Pd–S2–C2   | 106.2(3)  |
| Pd–P1–C11  | 108.9(2)  |
| Pd–P2–C12  | 109.1(2)  |
| S1–C1–N1   | 176.9(7)  |
| S2–C2–N2   | 176.1(7)  |
| P1–C11–C12 | 119.1(5)  |
| P2–C12–C11 | 116.6(5)  |

as well as the complexes [Pd(dpm)(SCN)<sub>2</sub>], [Pd-(dpe)(NCS)(SCN)] and [Pd(dpp)(NCS)<sub>2</sub>] (from Palenik’s series [4, 5]) and [Pd(tfmp)(SCN)<sub>2</sub>] [21].

In each case, the donor ligands are arranged in an approximately square planar configuration, with only minor deviations from the least-squares planes. The deviation of the non-coordinated end of the thio-

cyanate moiety from the coordination plane was used to calculate the tilt of the coordinated thiocyanate out of the coordination plane, a factor of importance in the steric arguments presented in this paper. These tilt angles are shown in Table 24.

TABLE 17. Crystal and Intensity Data Collection Summary, [Pd(dpbz)(NCS)(SCN)]<sup>a</sup>

|                                                                    |                                                                                |
|--------------------------------------------------------------------|--------------------------------------------------------------------------------|
| Molecular formula                                                  | PdC <sub>32</sub> H <sub>24</sub> N <sub>2</sub> P <sub>2</sub> S <sub>2</sub> |
| Solvent of crystallization                                         | CH <sub>2</sub> Cl <sub>2</sub>                                                |
| Formula weight (g/form)                                            | 669.04                                                                         |
| Molecular weight (g/mol)                                           | 669.04                                                                         |
| <i>a</i> (Å)                                                       | 22.017(18)                                                                     |
| <i>b</i> (Å)                                                       | 15.108(4)                                                                      |
| <i>c</i> (Å)                                                       | 22.798(16)                                                                     |
| $\beta$ (°)                                                        | 118.05(5)                                                                      |
| Volume (Å <sup>3</sup> )                                           | 6693(6)                                                                        |
| Crystal system                                                     | monoclinic                                                                     |
| Space group                                                        | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                             |
| <i>Z</i>                                                           | 4                                                                              |
| Crystal dimensions (mm)                                            | 0.4 × 0.35 × 0.35                                                              |
| Crystal color                                                      | yellow                                                                         |
| Radiation                                                          | Mo K $\alpha$                                                                  |
| Absorption coefficient, $\mu$ (Mo K $\alpha$ ) (cm <sup>−1</sup> ) | 8.65                                                                           |
| Temperature (°C)                                                   | 25 ± 2                                                                         |
| Scan speed (° min <sup>−1</sup> )                                  | 3.00/10.00                                                                     |
| Scan type                                                          | $\theta$ – $2\theta$                                                           |
| Scan range                                                         | 0.8 + $\Delta(\alpha_1 - \alpha_2)$                                            |
| Standards monitored                                                | 3/200                                                                          |
| $2\theta$ Limits (°)                                               | 3.0 ≤ $2\theta$ ≤ 45.0                                                         |
| Reflections collected                                              | ± <i>h</i> , <i>k</i> , <i>l</i>                                               |
| No. reflections collected                                          | 10000                                                                          |
| Unique reflections                                                 | 8603                                                                           |
| Unique reflections used                                            | 6173 ( <i>n</i> = 3.0)                                                         |

<sup>a</sup>Refined to only *R* = 10%, due to disorder problem (see text).TABLE 18. Important Bond Lengths, [Pd(dpbz)(NCS)(SCN)]<sup>a</sup>

| Atoms   | Bond length (Å) |
|---------|-----------------|
| Pd2–N4  | 2.020(15)       |
| Pd2–S3  | 2.386(6)        |
| Pd2–P3  | 2.229(6)        |
| Pd2–P4  | 2.239(6)        |
| P3–C21  | 1.796(16)       |
| P4–C22  | 1.816(31)       |
| C21–C22 | 1.417(28)       |
| S3–C3   | 1.681(21)       |
| C3–N3   | 1.107(29)       |
| N4–C4   | 1.144(22)       |
| C4–S4   | 1.640(20)       |

<sup>a</sup>Refined to only *R* = 10%, due to disorder problem (see text).

The relation of the axis of coordinated thiocyanate to the coordination plane is easily seen in views directly parallel to the coordination plane. These views are shown in Fig. 8.

### Discussion

A perusal of the observed bonding modes, shown in Table 23 in order of increasing P–Pd–P bond angle

TABLE 19. Important Bond Angles, [Pd(dpbz)(NCS)(SCN)]<sup>a</sup>

| Atoms      | Angle (°)  |
|------------|------------|
| P3–Pd2–P4  | 86.0(2)    |
| P3–Pd2–S3  | 90.5(2)    |
| N4–Pd2–S3  | 95.6(4)    |
| P4–Pd2–N4  | 88.4(4)    |
| P4–Pd2–S3  | 172.7(3)   |
| P3–Pd2–N4  | 173.0(5)   |
| Pd2–N4–C4  | 162.1(2.2) |
| Pd2–S3–C3  | 103.2(7)   |
| Pd2–P3–C21 | 109.4(6)   |
| Pd2–P4–C22 | 109.7(8)   |
| S3–C3–N3   | 179.4(2.8) |
| N4–C4–S4   | 176.0(2.0) |
| P3–C21–C22 | 117.3(1.5) |
| P4–C22–C21 | 115.8(1.9) |

<sup>a</sup>Refined to only *R* = 10%, due to disorder problem (see text).

of the bisphosphine ligands, reveals that the P–Pd–P bond angle and the incidence of thiocyanate coordination through the nitrogen atom are clearly *not* directly proportional. According to Palenik's 'steric control' model [4, 5], the P–Pd–P bond angle is considered to be an indicator of the degree of steric

TABLE 20. Crystal and Intensity Data Collection Summary, [Pd(dpx)(NCS)(SCN)]

|                                                                    |                                                                                |
|--------------------------------------------------------------------|--------------------------------------------------------------------------------|
| Molecular formula                                                  | PdC <sub>34</sub> H <sub>28</sub> N <sub>2</sub> P <sub>2</sub> S <sub>2</sub> |
| Solvent of crystallization                                         | acetonitrile                                                                   |
| Formula weight (g/form)                                            | 697.10                                                                         |
| Molecular weight (g/mol)                                           | 697.10                                                                         |
| <i>a</i> (Å)                                                       | 12.756(4)                                                                      |
| <i>b</i> (Å)                                                       | 15.564(4)                                                                      |
| <i>c</i> (Å)                                                       | 16.957(6)                                                                      |
| $\beta$ (°)                                                        | 112.05(3)                                                                      |
| Volume (Å <sup>3</sup> )                                           | 3120(2)                                                                        |
| Crystal system                                                     | monoclinic                                                                     |
| Space group                                                        | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                             |
| $\rho$ (calc.) (g/cm <sup>3</sup> )                                | 1.48                                                                           |
| <i>Z</i>                                                           | 4                                                                              |
| Crystal color                                                      | yellow                                                                         |
| Radiation                                                          | Mo K $\alpha$                                                                  |
| Absorption coefficient, $\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> ) | 8.4                                                                            |
| Temperature (°C)                                                   | 24 $\pm$ 2                                                                     |
| Scan speed (° min <sup>-1</sup> )                                  | 3.50/20.0                                                                      |
| Scan type                                                          | $\theta - 2\theta$                                                             |
| Scan range                                                         | 1.8 + $\Delta(\alpha_1 - \alpha_2)$                                            |
| Standards monitored                                                | 3/200                                                                          |
| 2 $\theta$ Limits (°)                                              | 4.0 $\leq$ 2 $\theta$ $\leq$ 45.0                                              |
| Reflections collected                                              | $\pm h, k, l$                                                                  |
| No. reflections collected                                          | 4530                                                                           |
| Unique reflections                                                 | 4090                                                                           |
| Unique reflections used                                            | 3486 ( <i>n</i> = 2)                                                           |
| Weighting factor, $g^a$                                            | 0.00051                                                                        |
| <i>R</i> (F) <sup>b</sup>                                          | 0.0501                                                                         |
| <i>R</i> (Fw) <sup>c</sup>                                         | 0.0467                                                                         |
| <i>GOF</i>                                                         | 1.276                                                                          |
| Highest peak on final difference map (e Å <sup>-3</sup> )          | 0.57                                                                           |

<sup>a,b,c</sup>See Table 2 for footnotes.

TABLE 21. Important Bond Lengths, [Pd(dpx)(NCS)(SCN)]

| Atoms   | Bond length (Å) |
|---------|-----------------|
| Pd–P1   | 2.295(2)        |
| Pd–S1   | 2.380(2)        |
| Pd–P2   | 2.262(2)        |
| Pd–N2   | 2.061(5)        |
| P1–Cc1  | 1.833(6)        |
| P2–Cc2  | 1.830(7)        |
| S1–C1   | 1.594(11)       |
| N1–C1   | 1.151(14)       |
| S2–C2   | 1.629(8)        |
| N2–C2   | 1.144(9)        |
| Cc1–C10 | 1.507(11)       |
| Cc2–C11 | 1.495(9)        |
| C10–C11 | 1.397(8)        |

interaction of the phenyl rings with the thiocyanate coordination sites. In fact, geminite formation (N,S-coordination) predominates *throughout* the series.

In attempting to explain these results, it is instructive to first consider steric effects on thiocyanate

TABLE 22. Important Bond Angles, [Pd(dpx)(NCS)(SCN)]

| Atoms       | Angle (°) |
|-------------|-----------|
| P1–Pd–P2    | 100.7(1)  |
| P2–Pd–S1    | 84.2(1)   |
| P2–Pd–N2    | 172.5(2)  |
| P1–Pd–S1    | 173.6(1)  |
| P1–Pd–N2    | 86.5(2)   |
| S1–Pd–N2    | 88.4(2)   |
| Pd–P1–Cc1   | 121.2(2)  |
| Pd–P2–Cc2   | 120.7(2)  |
| Pd–S1–C1    | 101.3(3)  |
| Pd–N2–C2    | 155.7(6)  |
| S1–C1–N1    | 173.7(8)  |
| S2–C2–N2    | 178.5(8)  |
| P1–Cc1–C10  | 114.1(5)  |
| P2–Cc2–C11  | 112.1(5)  |
| Cc1–C10–C11 | 120.6(6)  |
| Cc2–C11–C10 | 122.3(6)  |

bonding in monothiocyanate and *trans*-dithiocyanate complexes. In these cases, the results are much easier to understand, since changes in electronic *trans*-

TABLE 23. Summary of P-Pd-P Bond Angles and Thiocyanate Coordination Modes

| Complex                          | $\angle \text{P-Pd-P}$ | Bonding modes | Reference |
|----------------------------------|------------------------|---------------|-----------|
| [Pd(dpm)(SCN) <sub>2</sub> ]     | 73.3(1)                | S,S           | 4, 5      |
| [Pd(dpe)(NCS)(SCN)]              | 85.1(1)                | N,S           | 4, 5      |
| [Pd(dpv)(SCN) <sub>2</sub> ]     | 85.4(1)                | S,S           | this work |
| [Pd(dpv)(NCS)(SCN)]              | 85.4(1)                | N,S           | this work |
| [Pd(dpbz)(NCS)(SCN)]             | 86.0(1)                | N,S           | this work |
| [Pd(dpbz)(SCN) <sub>2</sub> ]    | 86.2(1)                | S,S           | this work |
| [Pd(dpp)(NCS)(SCN)]              | 89.0(1)                | N,S           | this work |
| [Pd(dpp)(NCS) <sub>2</sub> ]     | 89.3(1)                | N,N           | 4, 5      |
| [Pd(tfmp)(SCN) <sub>2</sub> ]    | 90.6(2)                | S,S           | 21        |
| [Pd(dpb)(NCS)(SCN)] <sup>a</sup> | 92.8(1)                | N,S           | this work |
| [Pd(dpb)(NCS)(SCN)] <sup>b</sup> | 92.9(1)                | N,S           | this work |
| [Pd(dpx)(NCS)(SCN)]              | 100.7(1)               | N,S           | this work |

<sup>a</sup>Crystal grown from CH<sub>3</sub>NO<sub>2</sub>.<sup>b</sup>Crystal grown from CH<sub>2</sub>Cl<sub>2</sub>.

influences are either minimized or non-existent, and steric encroachment occurs symmetrically from *both* sides of a given thiocyanate.

An unequivocal example of steric control of monothiocyanate bonding in a Pd(II) complex (diethylenetriamine *versus* 1,1,7,7-tetraethyldiethylenetriamine [11]) has already been described in the 'Introduction'. Compelling examples of steric control of *trans*-dithiocyanato bonding modes have also been reported.

Hill *et al.* [22] synthesized and characterized four complexes of the type [Pd(Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>)(NCS)<sub>2</sub>] (*n* = 6, 8, 10 and 12). The bidentate ligand was reported to chelate in each of these complexes in a *trans* manner. (These complexes, incidentally, were polynuclear in some cases.) Infrared peaks confirmed thiocyanate coordination exclusively through the nitrogen atom ( $\nu_{\text{CN}}$  range: 2081 to 2076 cm<sup>-1</sup>). They proposed that steric interactions with the bulky phenyl groups of the phosphine ligand were apparently minimized by the linear Pd-NCS configuration.

Likewise, a significant steric effect was isolated in the series *trans*-[Pd(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(NCS)<sub>2</sub>] (stable), *trans*-[Pd(As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(SCN)<sub>2</sub>] (unstable), *trans*-[Pd(As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(NCS)<sub>2</sub>] (stable) and *trans*-[Pd(Sb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(SCN)<sub>2</sub>] (stable), by Burmeister and Basolo [23]. Although there may be minor electronic differences of one coordinated thiocyanate on another via a *trans*-influence, the observed mode of thiocyanate coordination in all four cases can be rationalized solely on the basis of steric considerations. In *trans*-[Pd(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(NCS)<sub>2</sub>], the relatively short Pd-P bond length (approximately 2.3 Å) pulls the phenyl groups into close proximity to both thiocyanate coordination sites, leading to significant crowding. The relatively long Pd-Sb bond length (approximately 2.6 Å), in contrast, keeps the bulky phenyl groups away from the thiocyanate sites, permitting coordination to the palladium(II) atom via the electronically-favored sulfur atom (a soft-soft

interaction). There have been no reports of the *N,S*-dithiocyanato isomer in *trans*-dithiocyanato complexes.

When steric influences were first invoked to explain thiocyanate coordination trends in *cis*-dithiocyanato palladium(II) or platinum(II) complexes, the assumption that steric crowding necessarily created an environment 'favoring' linear M-NCS coordination was unquestioned. The two situations, however, are *not* completely analogous, and therein lies the error in Palenik's steric control model.

In square planar palladium(II) or platinum(II) complexes involving tridentate, *trans*-bidentate, or two monodentate, mutually-*trans* ligands with bulky side groups, the thiocyanate moieties are contacted on *both* sides by these bulky substituents. Because of restricted rotation about the angular Pd-SCN bond, sulfur-bound thiocyanate cannot assume a configuration which minimizes interaction with the bulky substituents of the non-thiocyanate ligand(s).

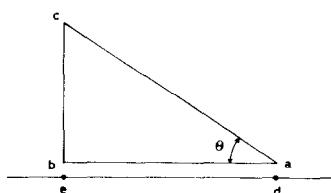
In contrast, in square planar, *cis*-dithiocyanato palladium(II) and platinum(II) complexes, each thiocyanate moiety interacts sterically with only *one* set of bulky substituents on the other ligand(s). On the other side of each thiocyanate is another relatively small thiocyanate group. Examples of these cases include the *cis*-chelating bidentate diphosphine ligands which are the focus of Palenik's series and its more than three-fold expansion in this study. In each of the molecular structure views normal to the coordination plane, shown in Figs. 1 through 7, one sees that the sulfur-bound thiocyanate is invariably angled away from the large phenyl rings, toward the other coordinated thiocyanate group. Palenik's dpm and dpe complexes [4, 5], Meek's dppn complex [9], and Simpson's *S,S*-dithiocyanato trifluoromethylpropene derivative, [Pd(tfmp)(SCN)<sub>2</sub>] [21], show this as well.

Sulfur-bound thiocyanate has considerably greater freedom in *cis*-dithiocyanato palladium(II) complexes to assume a sterically-favored configuration. Views of

TABLE 24. Tilt of Coordinated Thiocyanate Out of the Coordination Plane<sup>a,b</sup>

| Complex                          | Atoms      | Distance from Plane | $\theta$ (°) | Reference |
|----------------------------------|------------|---------------------|--------------|-----------|
| [Pd(dpm)(SCN) <sub>2</sub> ]     | –S1C1N1    | 0.9760              | 20.7         | 5         |
|                                  | –S2C2N2    | 0.3055              | 6.20         |           |
| [Pd(dpe)(NCS)(SCN)]              | –N2C2S2    | –0.6715             | –15.1        | 5         |
|                                  | –S1C1N1    | –0.9203             | –18.4        |           |
| [Pd(dpv)(SCN) <sub>2</sub> ]     | –S1C1N1    | 0.5090              | 11.9         | this work |
|                                  | –S2C2N2    | –1.0330             | –23.7        |           |
| [Pd(dpv)(NCS)(SCN)]              | –S2C2N2    | –1.0330             | –23.7        | this work |
|                                  | –N1'C1'S1' | 0.3323              | 7.1          |           |
| [Pd(dpbz)(SCN) <sub>2</sub> ]    | –S1C1N1    | 2.1200              | 54.7         | this work |
|                                  | –S2C2N2    | –0.8712             | –21.4        |           |
| [Pd(dpbz)(NCS)(SCN)]             | e          | e                   | e            | this work |
| [Pd(dpp)(NCS)(SCN)]              | –N2Ct2S2   | 0.5438              | 11.3         | this work |
|                                  | –S1Ct1N1   | –0.4416             | –9.1         |           |
| [Pd(dpp)(NCS) <sub>2</sub> ]     | –N+C1+S+   | –0.4429             | –7.4         | 5         |
|                                  | –NC1S      | 0.4429              | 7.4          |           |
| [Pd(dppn)(NCS)(SCN)]             | –N2C2S2    | –0.1140             | –1.3         | 20        |
|                                  | –S1C1N3    | 0.5206              | 9.7          |           |
| [Pd(dpb)(NCS)(SCN)] <sup>c</sup> | –N2C2S2    | 0.8735              | 17.9         | this work |
|                                  | –S1C1N1    | –0.0223             | –0.5         |           |
| [Pd(dpb)(NCS)(SCN)] <sup>d</sup> | –N2C2S2    | 0.8791              | 18.6         | this work |
|                                  | –S1C1N1    | –0.0421             | –0.9         |           |
| [Pd(dpx)(NCS)(SCN)]              | –N2C2S2    | –0.8014             | –17.1        | this work |
|                                  | –S1C1N1    | 2.5979              | 73.5         |           |

<sup>a</sup>Negative and positive angles are relative numbers to indicate positions above and below the coordination plane. <sup>b</sup>Calculation of tilt out of coordination plane was done by the following method. The thiocyanate moiety was assumed to be linear (actual range: 173.0° to 179.4°). The tilt of the coordinated thiocyanate moiety out of the coordination plane can be represented as a triangle, as shown below. The coordination plane is  $\overline{de}$ ,  $\overline{ad}$  is the deviation of the coordinated atom of the thiocyanate moiety



from the computer-generated least-squares plane, the thiocyanate moiety itself is  $\overline{ac}$ , and  $\overline{bc}$  is the deviation of the non-coordinated atom of the thiocyanate moiety from the least squares plane minus the length  $\overline{ad}$ . Length  $\overline{ac}$  was determined by adding the S–C and C–N bond lengths. The tilt  $\theta$  of thiocyanate from the coordination plane, then, is:  $\theta = \sin^{-1} [\overline{bc}/\overline{ac}]$ . <sup>c</sup>Crystal grown from nitromethane. <sup>d</sup>Crystal grown from methylene chloride. <sup>e</sup>Insufficient refinement.

these complexes directly parallel to the coordination plane, presented in Fig. 8, show that sulfur-bound thiocyanate can tilt as much as 73° out of the coordination plane. The tilt of the thiocyanate moiety out of the coordination plane for all of the complexes in the extended series of dithiocyanato[bis(diphenylphosphino)alkyl or aryl]palladium(II) complexes is summarized in Table 24. The angular Pd–SCN bond enables one coordinated thiocyanate to bend away (often out of the coordination plane) from the large

substituents of the other ligands, and minimize unfavorable interaction.

Why, then, in complexes with large steric hindrance, such as [Pd(dpb)(NCS)(SCN)] and [Pd(dpx)(NCS)(SCN)], do we observe the *N,S*-dithiocyanato isomer rather than the *S,S*-dithiocyanato isomer? The evidence suggests that the mode of coordination of two thiocyanate moieties in a *cis* manner cannot be considered as two independent events; rather, there is a *conjunctive response* of the two thiocyanate groups

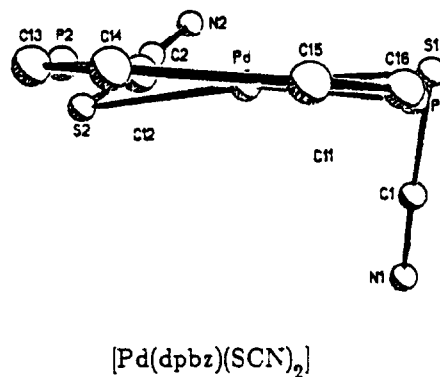
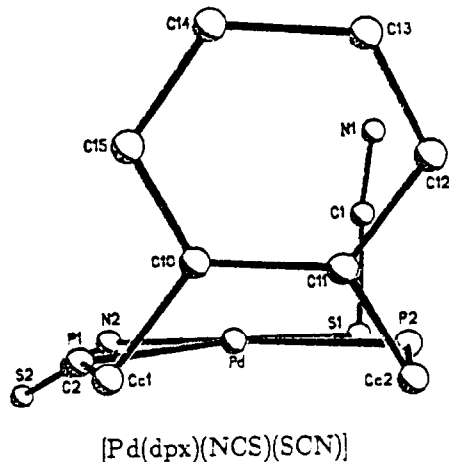
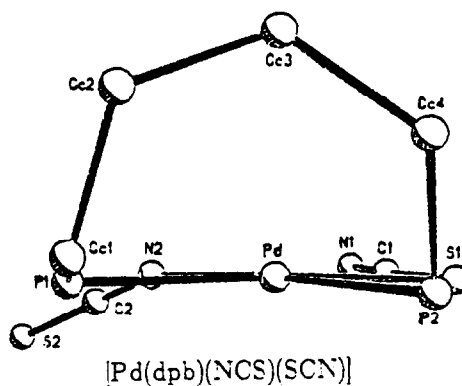
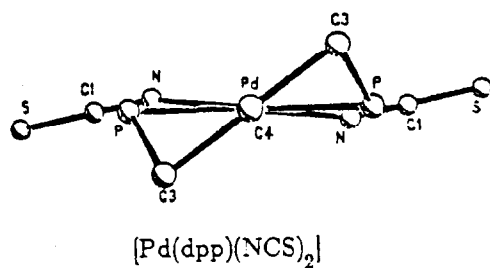
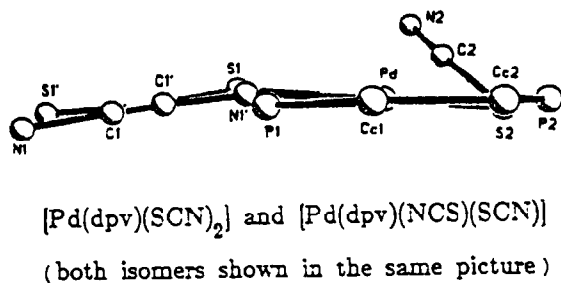
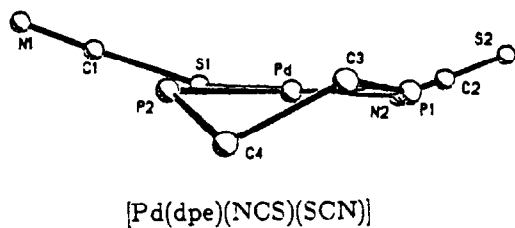
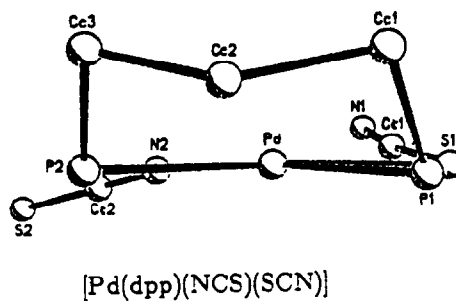
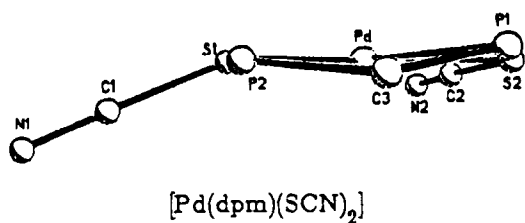


Fig. 8. View across the coordination plane.

to steric pressure. The *N,S*-dithiocyanato configuration minimizes interaction with bulky substituents on other ligands and with each other.

In summary, monothiocyanato or *trans*-dithiocyanato palladium(II) complexes will show exclusive coordination through the nitrogen atom when

bounded on both sides by ligands exerting sufficiently strong steric effects on the thiocyanate sites. They will exhibit exclusive coordination through the sulfur atom when these steric effects are minimal, because of the favorable soft–soft interaction between the palladium(II) cation and the sulfur atom of the thiocyanate ion.

In *cis*-dithiocyanato complexes, the assumption that one will observe thiocyanate coordination at sterically-hindered sites solely through the nitrogen atom is invalid. Generally, coordination through the sulfur atom at one site is sterically favored because the angular Pd–SCN bond permits configurations which minimize interaction with both the large substituents on other ligands and the other coordinated thiocyanate moiety. Five apparent exceptions to the new theory appear in Table 23. They merit special mention here as to how they fit into this new scheme of response to steric pressure.

For [Pd(dpm)(SCN)<sub>2</sub>], the existence and stability of the *S,S*-dithiocyanato isomer may be rationalized using the same argument as that offered by Palenik fifteen years ago [4, 5]. The small methylene backbone in the bidentate diphosphine ligand greatly decreases the proximity of the phenyl groups to the thiocyanate sites, as manifested by the very small (73.3°) P–Pd–P bond angle. There is so little steric interaction that the electronically-advantageous coordination of the ‘soft’ sulfur end of thiocyanate to the ‘soft’ palladium(II) cation is observed at both sites, with the entire thiocyanate moiety nearly coplanar with the square planar portion of the molecule (see Fig. 8).

It is important to note that both the *N,N*- [4, 5] and *N,S*- [14] dithiocyanato isomers for [Pd(dpp)-(thiocyanate)<sub>2</sub>] have been structurally characterized at room temperature. The complex [Pd(dpp)(NCS)<sub>2</sub>] may well be the exception, rather than the rule, and may exist at room temperature only because of its higher symmetry. Hunt and Balch have noted [24] that the *N,S*-dithiocyanato isomer is the dominant isomer in solution (CH<sub>2</sub>Cl<sub>2</sub>, DMF and acetone). An investigation of which isomeric form, [Pd(dpp)(NCS)(SCN)] or [Pd(dpp)(NCS)<sub>2</sub>], is the thermodynamically stable isomer would be an important step forward in the solution of this problem.

The existence of the three stable complexes [Pd(dpv)(SCN)<sub>2</sub>], [Pd(dpbz)(SCN)<sub>2</sub>] and [Pd(tfmp)(SCN)<sub>2</sub>] [21], can be explained by the advantage gained by the soft–soft palladium–sulfur interaction, coupled with the large tilt of both sulfur-bound thiocyanate groups out of the coordination plane to accommodate the steric influence of the bulky phenyl rings of the bidentate diphosphine ligands. Table 24 shows that the thiocyanate moieties in [Pd(dpbz)(SCN)<sub>2</sub>] are positioned such that one coordinated thiocyanate is tilted 55° above on side of the coordination plane, and the other is tilted 21° below

the coordination plane. Simpson and co-workers reported [21] that one sulfur-bound thiocyanate in [Pd(tfmp)(SCN)<sub>2</sub>] is tilted 48° out of the coordination plane. The out-of-plane configuration of sulfur-bound thiocyanate in these three complexes sufficiently relieves the steric pressure such that the favorable palladium–sulfur soft–soft interaction is possible.

That both the *S,S*- and *N,S*-dithiocyanato isomers of [Pd(dpbz)(thiocyanate)<sub>2</sub>] are observed may reflect the fact that both isomers are thermodynamically very close in stability. It is important to note that the [Pd(dpbz)(SCN)<sub>2</sub>] crystal was grown by the recrystallization of [Pd(dpbz)(NCS)(SCN)] from methanol. In the solvent study which will be published subsequently [19], it will be shown that methanol promotes thiocyanate coordination through the sulfur atom in [Pd(dpbz)(thiocyanate)<sub>2</sub>] complexes, due to hydrogen-bonding with the uncoordinated N end. This result is in accord with the results of earlier studies of solvent effects on thiocyanate bonding modes [25].

It is probably more than mere coincidence that the dpv, dpbz, and tfmp ligands, all of which yield di-*S*-bound isomers (solely, or in part), all contain a C=C bond in the chelate ring. This suggests the possibility of a concurrent electronic effect which tends to stabilize the Pd–SCN bond. However, it must also be pointed out that the dpv ligand, which also contains a C=C bond in its chelate ring, produces only the *N,S*-bound geminite.

The mixed mode of thiocyanate coordination in [Pd(dppn)(NCS)(SCN)] [9] is, historically, closely intertwined with the larger question of the operation and extent of electronic *trans*-influences on the coordination of thiocyanate in dithiocyanato[bis(diphenylphosphino)alkyl or aryl]palladium(II) complexes. Arguments for the operation of an electronic *trans*-influence in this complex have been presented by Huheey and Grim [10]. That the sulfur-bound thiocyanate is coordinated *cis* to the bulky diphenylphosphine end rather than to the smaller dimethylamine end was cited as evidence that the steric effect was not of primary importance in determining the mode of thiocyanate coordination in this complex. However, in light of the new model of thiocyanate response to steric pressure in *cis*-dithiocyanato complexes presented in this work, one should note that the sulfur-bound thiocyanate is tilted 10° out of the coordination plane and towards the nitrogen-bound thiocyanate. Sulfur-bound thiocyanate is, in fact, the sterically-favored mode of coordination at this crowded site.

There is, however, one piece of evidence that points to the operation of a *trans*-influence in [Pd(dppn)(NCS)(SCN)]. Since steric crowding of the two thiocyanate sites requires *N,S*-dithiocyanato coordination in this complex, two structures are logical

candidates: one in which the sulfur-bound thiocyanate is *cis* to the bulky phenyl groups on the phosphine end of the bidentate ligand, the other in which sulfur-bound thiocyanate is *trans* to the phenyl rings on the phosphorus atom. That the former structure is actually observed may be due to electronic stabilization by the *trans*-influence. Thus, this complex accommodates steric requirements as well as electronic effects.

The model for the *trans*-influence operating in this system of dithiocyanato[bis(diphenylphosphino)alkyl or aryl]palladium(II) complexes essentially postulates that nitrogen-bound thiocyanate is preferred at sites *trans* to the phosphine ligand [2]. One would anticipate that the *trans*-influence for a bidentate diphosphine ligand would be maximized at a P-Pd-P bond angle of  $90^\circ$ , since there would be maximum possible interaction of the diphosphine ligand d orbitals with those of the palladium(II) cation at this angle. Complexes with P-Pd-P bond angles of approximately  $90^\circ$  would be expected to show the *N,N*-dithiocyanato isomer exclusively, if the *trans*-influence was the primary determinant of the mode of thiocyanate coordination in these complexes. In fact, as shown in Table 23, only one of four diphenylphosphine complexes of interest to this problem with P-Pd-P bond angles of  $90 \pm 3^\circ$  is the *N,N*-dithiocyanato isomer. The *trans*-influence, if operating in these complexes, is of secondary importance.

The two isomers [Pd(dpv)(SCN)<sub>2</sub>] and [Pd(dpv)(NCS)(SCN)] merit further discussion as well. Levason and McAuliffe [26] first mentioned this important complex in 1972. This preliminary report indicated that their pink solid (melting point:  $260^\circ\text{C}$ ) was the *N,S*-dithiocyanato isomer. Shortly thereafter, Chow and McAuliffe [16] studied this complex in greater detail. The pink solid was then characterized as the *S,S*-dithiocyanato isomer, based on visible and infrared spectroscopic data. Identification of this compound as the neutral form, rather than the Magnus salt, was on the basis of its non-conductivity in nitromethane solution. Yet, when Hunt and Balch prepared this complex for a study of linkage isomer distribution in solution, they reported that [Pd(dpv)(NCS)(SCN)] is a yellow solid [24].

This dichotomy is now resolved. Although this complex has been pivotal in models concerning the bonding in palladium(II) diphenylphosphine complexes, the initial reports of this complex [26, 16] misidentified the Magnus salt, [Pd(Ph<sub>2</sub>PCH=CHPh<sub>2</sub>)<sub>2</sub>][Pd(SCN)<sub>4</sub>], as *S,S*-dithiocyanato[*cis*-1,2-bis(diphenylphosphino)ethylene]palladium(II). When a sample of the pink solid made by the method of Chow and McAuliffe is placed in ethanol or nitromethane, the supernatant solution becomes yellow, although the pink solid itself is largely insoluble. Evidently, the small percentage of the dithiocyanato[bis(diphenylphosphino)ethylene]palladium(II) monomer

present in the pink solid is soluble in these solvents; the pink solid is not. Another possibility is that the  $K_{\text{eq}}$  for the reaction Magnus salt  $\rightarrow$  [Pd(dpv)(thiocyanate)<sub>2</sub>] is very small. The non-conductivity measurement [16] in nitromethane solution was indeed that of the desired monomeric complex; the isolated pink solid was, on the other hand, the Magnus salt. As a point of confirmation, the  $\nu_{\text{CN}}$  peak at  $2105\text{ (s) cm}^{-1}$  recorded by Chow and McAuliffe [16] for the pink solid is characteristic of the Magnus salt [27].

In 1977, Sanger [28] characterized the dichloride analogs of [Pd(dpv)(thiocyanate)<sub>2</sub>] and [Pd(dpb)(NCS)(SCN)] in solution by <sup>31</sup>P NMR, infrared and Raman spectroscopic methods. These dichloride derivatives were reported [28] as being binuclear and trinuclear, respectively, with *cis* internuclear bridging via the bidentate diphosphine ligands. On this basis, he postulated [28] that "bridging by a diphosphine ligand occurs when the angle PMP which would be subtended by a chelating ligand exceeds  $90^\circ$ ". We have observed only monomeric species in the solid state for our series, which includes four complexes with P-Pd-P bond angles exceeding  $90^\circ$ . The  $100.7^\circ$  P-Pd-P bond angle for the [Pd(dpx)(NCS)(SCN)] monomer conclusively refutes Sanger's postulate for complexes of this series in the solid state.

Sanger [28] correctly predicted that the P-Pd-P bond angle for the vinyl backbone would be larger than that of its ethane analogue. Although the C-C bond length (1.54 Å) for the ethane ligand (dpe) is significantly longer than the C=C bond length (1.33 Å) for the ethylene ligand (dpv), the dpv ligand gives rise to a larger P-Pd-P bond angle than the dpe ligand ( $85.4^\circ$  versus  $85.1^\circ$ ), in accord with Sanger's prediction. The dpv ligand, however, does not give rise to a P-Pd-P bond angle exceeding  $90^\circ$  with a concomitant change to a binuclear species in the dithiocyanato case. The reason for this is that the sp<sup>3</sup>-hybridized orbitals for the saturated backbone of the dpe ligand allows it to "pucker", while the sp<sup>2</sup>-hybridized orbitals of the ethylene backbone remain rigidly coplanar with the coordination sphere. This negates the application of this complex by Palenik and co-workers [4, 5] in support of the 'strictly steric' model, as well as those criticisms of this model levelled by Chow and his co-workers [17] on the basis of the [Pd(dpv)(thiocyanate)<sub>2</sub>] complex having a presumed smaller P-Pd-P bond angle than the analogous ethane complex.

Throughout this argument, the P-Pd-P bond angle has been considered to be directly proportional to the steric influence of the phenyl groups of the bidentate diphosphine ligand. One must keep in mind that this is an approximate relationship, as the orientation of the phenyl groups (the actual effectors of steric hindrance) to the coordination plane and thiocyanate sites plays a significant role as well. In this connection, recent work [29] in our laboratory

involving the selenocyanate analogs of the dpm, dpe, dpp and dpx complexes has yielded results which, to say the least, are food for thought. All three complexes exhibit *only* Pd–SeCN bonding, despite having P–Pd–P bond angles which are very similar to those of the thiocyanates, e.g., [Pd(dpe)(SeCN)<sub>2</sub>], 85.1°; [Pd(dpp)(SeCN)<sub>2</sub>], 90.9°.

### Supplementary Material

A complete listing of atomic positional coordinates, temperature factors, bond lengths, bond angles and anisotropic temperature factors are given in separate appendices for each of these eight novel molecular structures and are available, on request, from the senior author.

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