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In Search of Geminites: The Synthesis and Structural Characterization of $[Pd\{(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2\}(SeCN)_2]$ (n = 1,2,3) and $[Pd\{(C_6H_5)_2PCH_2\text{-}o\text{-}C_6H_4\text{-}CH_2P(C_6H_5)_2\}(SeCN)_2]$

CHRISTINE A. GRYGON, WILLIAM C. FULTZ*, ARNOLD L. RHEINGOLD and JOHN L. BURMEISTER**
Department of Chemistry, University of Delaware, Newark, Del. 19716, U.S.A.

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Abstract

Unlike its thiocyanate analogues, which involve the formation of the geminite $[Pd\{(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2\}(SCN)(NCS)]$ and the di-N-bound complex $[Pd\{(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2\}(NCS)_2]$, the corresponding selenocyanate complexes contain only Se-bound groups, as determined by the results of single crystal X-ray diffraction studies. Se-bonding is also maintained in the $[Pd\{(C_6H_5)_2PCH_2\text{-}o\text{-}C_6H_4\text{-}CH_2P(C_6H_5)_2\}(SeCN)_2]$ complex, based on the results of IR studies. Only in the case of the $(C_6H_5)_2PCH_2P(C_6H_5)_2$ palladium(II) complexes, do both pseudohalides exhibit analogous bonding via their chalcogen atoms. The selenocyanate's bonding pattern is thus dominated by the soft/soft interaction afforded by Pd–SeCN bonding, remaining impervious to increasing steric demands of the diphosphine ligands.

Introduction

The coordination chemistry of ambidentate ligands, such as the thiocyanate ion, has produced a veritable cornucopia of interesting questions pertaining to structure and bonding [1, 2]. One of the most intriguing has been generated by the existence of geminites, *i.e.* complexes wherein *both* bonding modes of a given ambidentate ligand are represented, e.g. $[Pd\{(C_6H_5)_2P(CH_2)_3N(CH_3)_2\}(SCN)(NCS)]$ [3]. Put another way, these complexes involve internal linkage isomerism. In particular, the series $[Pd\{(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2\}(\text{thiocyanate})_2]$ (n = 1, di-S-bound; n = 2, mono-S-, mono-N-bound; n = 3, di-N-bound) [4] has spawned much discussion and debate concerning the interplay between the steric and electronic factors that have created the bonding pattern observed [5].

We therefore found the synthesis of the corresponding series of selenocyanate complexes, $[Pd\{(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2\}(\text{selenocyanate})_2]$, to be of compelling interest. This task was made all the more tantalizing by the observation that only one complex, $[Pd\{(C_2H_5)_2N(CH_2)_2NH(CH_2)_2N(C_2H_5)_2\}NCSe][B(C_6H_5)_4]$, has ever been reported [6] wherein the normal M(soft)–SeCN bonding pattern has been reversed by the introduction of another ligand into the coordination sphere. The synthesis of the first member of the series, $[Pd\{(C_6H_5)_2PCH_2P(C_6H_5)_2\}(SeCN)_2]$, which also led serendipitously to the isolation and structural characterization of its structural isomer, $[Pd\{(C_6H_5)_2PCH_2P(Se)(C_6H_5)_2\}(CN)(SeCN)]$, has already been communicated [7]. We now wish to describe the results of our successful attempts to synthesize the two higher members of the series (n = 2, 3), as well as the corresponding complex of α,α'-bis(diphenylphosphino)-*o*-xylene.

Experimental

All chemicals and solvents used were of reagent grade or better. Protective rubber gloves were worn during the handling of all selenium containing compounds.

Preparation of Tetrabutylammonium Selenocyanate, $[(CH_3(CH_2)_3)_4N]SeCN$

This salt was prepared using the method employed by Burmeister and Williams [8]. The product, a white solid, was obtained in 76% yield and characterized by a strong, sharp ionic ν(CN) band in the infrared at 2080 cm^{-1}.

Preparation of Tetrabutylammonium Tetraselenocyanatopalladate(II), $[(CH_3(CH_2)_3)_4N]_2[Pd(SeCN)_4]$

This compound was synthesized from $[CH_3(CH_2)_3)_4N]SeCN$ and $PdCl_2$, according to the procedure of Burmeister and Williams [8]. The red–

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*Current address: J. M. Huber Corporation, P.O. Box 310, Havre de Grace, Md. 21078, U.S.A.

**Author to whom correspondence should be addressed.

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orange product was obtained in 28% yield. The characteristic ν(CN) band appeared at 2100 cm^{-1} in its infrared spectrum.

Preparation of Diselenocyanato(bis(diphenylphosphino)-alkane and -o-xylene) Palladium(II) Complexes

These complexes were synthesized at 25 °C by a procedure similar to that reported by Meek *et al.* [9] for the analogous thiocyanate complexes. Modifications of the Meek preparative method included the use of methanol as the reaction solvent (in place of absolute ethanol) and acetone as the recrystallization solvent. A summary of colors, melting point data, infrared information, yields, and microanalytical data is presented in Table I. The abbreviations used for the ligands are defined in a footnote to Table I. In the case of $[Pd(dpx)(SeCN)_2]$, exposure to air was minimized, as the ligand itself is air sensitive. The complexed product, however, is air stable. When the dpm ligand is used in this procedure, formation of the monophosphine selenide, [Pd(dpmSe)(CN)(SeCN)], results [7]. The synthesis of the $[Pd(dpm)(SeCN)_2]$ complex itself required the use of an alternate procedure [7].

Infrared Measurements

Infrared spectra from 4000 to 400 cm^{-1} were recorded on a Perkin-Elmer 180 Grating Infrared Spectrophotometer. Ten-fold abscissa scans were measured on the same instrument. Nujol mulls between KBr plates were used for all solid samples. Polystyrene film was used for daily calibration.

Elemental Analyses

Elemental microanalyses were carried out by Schwarzkopf Microanalytical Laboratory in Woodside, New York.

Melting Points

Melting point determinations were made on a Thomas Hoover Capillary Melting Point Apparatus.

X-ray Crystallography

Crystals of $[Pd(dpe)(SeCN)_2]$ and $[Pd(dpp)(SeCN)_2]$ suitable for X-ray diffraction were obtained by slow evaporation of acetone solutions. The yellow crystals were attached to glass fibers with epoxy cement. Data were collected on a Nicolet R3 diffractometer using graphite-monochromated Mo Kα radiation. Pertinent crystallographic parameters are summarized in Tables II and III.

The crystal structures were solved and refined using the SHELXTL (Version 4.0) Program Library (Nicolet Corp., Madison, Wis.). 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 either crystal.

The palladium atom positions were obtained by direct methods. All other nonhydrogen atoms were located by difference-Fourier techniques. All nonhydrogen atoms were refined anisotropically using blocked-cascade, least-squares refinement methods. The hydrogen atom positions were calculated in idealized positions on the basis of 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.

Drawings of the structures of the $[Pd(dpe)(SeCN)_2]$ and $[Pd(dpp)(SeCN)_2]$ complexes are shown in Figs. 1 and 2. Atomic coordinates are given in Tables III and IV. Important bond distances and angles are shown in Table V.

Discussion

By employing an identical series of ligands, it was hoped that the electronic environment surrounding the palladium center would be relatively constant in both the thiocyanate and selenocyanate complexes. By varying the carbon backbone within these ligands, steric influences on the selenocyanate bonding mode resulting from varying degrees of crowding by the phenyl rings could then be monitored. The most

TABLE I. Experimental Data for Diselenocyanato(bis(diphenylphosphino)-alkane and -o-xylene) Palladium(II) Complexes

Complex[a]	Color	Melting point (°C)	Yield (%)	Analysis (calc./found) C	H	N	ν(CN) (cm^{-1})
$[Pd(dpm)(SeCN)_2]$ [b]	dark yellow	180	73	(46.28/44.12)	(3.16/2.93)	(4.00/3.75)	2130, 2121
$[Pd(dpe)(SeCN)_2]$	yellow	177	45	(47.05/47.29)	(3.38/3.38)	(3.92/3.86)	2130
$[Pd(dpp)(SeCN)_2]$	gold	160	50	(47.79/46.97)	(3.60/3.75)	(3.84/3.84)	2110
$[Pd(dpx)(SeCN)_2]$	yellow	201	57	(51.63/51.45)	(3.58/3.41)	(3.54/3.55)	2136, 2130

[a] Abbreviations: dpm = bis(diphenylphosphino)methane, dpe = 1,2-bis(diphenylphosphino)ethane, dpp = 1,3-bis(diphenylphosphino)propane, dpx = α,α'-bis(diphenylphosphino)-o-xylene. [b] Prepared [7] via an alternate route, starting with $Pd(C_2H_3O_2)_2$.

TABLE II. Crystal and Intensity Data Collection Summary for [Pd(dpe)(SeCN)$_2$] and [Pd(dpp)(SeCN)$_2$]

Molecular formula	$PdSe_2P_2C_{28}H_{24}N_2$	$PdSe_2P_2C_{29}H_{26}N_2$
Molecular weight	714.75	728.78
a (Å)	11.304(4)	9.822(1)
b (Å)	16.351(4)	11.721(2)
c (Å)	15.270(6)	12.960(2)
α (°)	90	89.52(1)
β (°)	100.00(3)	74.68(1)
γ (°)	90	87.41(1)
V (Å^3)	2779(2)	1437.2(4)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
ρ (calc.) (g/cm^3)	1.71	1.68
Z	4	2
Diffractometer	Nicolet R3m/u	Nicolet R3M/u
Radiation	Mo Kα(graphite-monochromated)	Mo Kα(graphite-monochromated)
Absorption coefficient μ(Mo Kα), (cm^{-1})	35.99	32.75
Temperature (°C)	26 ± 2	24 ± 2
Scan speed (°/min)	3.5–15.0	4.0–20.0
Scan type	$\theta-2\theta$	$\theta-2\theta$
Scan range	$1.8 + (\alpha_1 - \alpha_2)$	$2.0 + (\alpha_1 - \alpha_2)$
Standards monitored	$3^{\mathrm{std}}/200^{\mathrm{rflns}}$	$3^{\mathrm{std}}/150^{\mathrm{rflns}}$
2θ Limits (°)	3.0–50.0	3.0–47.0
Reflections collected	$\pm h, k, +l$	$\pm h, k, \pm l$
Reflections collected	5423	4611
Unique reflections	4247	4255
Unique reflections observed	3620 with $F_{\mathrm{obs}} > 2.0\sigma(F_{\mathrm{obs}})$	3486 with $F_{\mathrm{obs}} > 2.0\sigma(F_{\mathrm{obs}})$
Weighting factor (g)[a]	0.0012	0.00037
R (F) [b]	0.060	0.048
R (F_w) [c]	0.066	0.045
GOF	1.245	1.233
Highest peak on final difference map (e/Å^3)	1.35[d]	1.04[e]

[a] $w^{-1} = \sigma^2(F_o) + gF_o^2$. [b] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [c] $R_w = [\Sigma w^{1/2}(|F_o| - |F_c|)]/\Sigma w^{1/2}(F_o)$. [d] Peak is 0.94 Å from Pd(1). [e] Peak is 0.93 Å from Se(1).

TABLE III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for [Pd(dpe)(SeCN)$_2$]

Atom	x	y	z	U[a]
Pd(1)	6532(1)	3211(1)	1728(1)	33(1)
Se(1)	8164(1)	3801(1)	1033(1)	55(1)
Se(2)	7395(1)	3820(1)	3184(1)	55(1)
P(1)	5033(2)	2762(1)	2427(1)	37(1)
P(2)	5553(2)	2506(1)	531(1)	34(1)
N(1)	7850(7)	3317(5)	−873(5)	70(3)
N(2)	9082(11)	5099(7)	2804(8)	76(5)
C(1)	7952(8)	3486(5)	−138(6)	57(3)
Cc(1)	4291(7)	1901(4)	1805(5)	40(3)
C(2)	8424(7)	4605(5)	2930(6)	54(3)
Cc(2)	4132(7)	2136(5)	811(5)	40(3)
C(11)	5429(7)	2440(5)	3582(5)	44(3)
C(12)	5883(8)	1663(6)	3774(6)	59(3)
C(13)	6200(9)	1407(7)	4630(7)	75(4)
C(14)	6080(9)	1914(8)	5302(7)	84(5)
C(15)	5654(8)	2711(7)	5138(6)	71(4)
C(16)	5308(8)	2960(6)	4255(6)	57(3)
C(21)	6368(7)	1602(4)	276(5)	34(2)
C(22)	7560(7)	1505(5)	610(5)	45(3)
C(23)	8181(8)	808(5)	434(6)	56(3)
C(24)	7614(8)	205(5)	−94(5)	54(3)
C(25)	6410(8)	293(5)	−454(5)	53(3)
C(26)	5779(8)	980(4)	−269(5)	44(3)
C(31)	3870(7)	3532(5)	2384(5)	40(3)
C(32)	2784(7)	3359(5)	2654(5)	43(3)
C(33)	1868(8)	3947(6)	2553(6)	59(3)
C(34)	2042(8)	4679(5)	2177(6)	63(4)
C(35)	3122(9)	4861(6)	1909(7)	73(4)
C(36)	4028(9)	4289(5)	2024(6)	58(3)
C(41)	5029(7)	3060(4)	−499(5)	39(3)
C(42)	5127(8)	2763(5)	−1319(5)	53(3)
C(43)	4610(10)	3193(6)	−2082(6)	69(4)
C(44)	4046(9)	3911(6)	−2005(7)	70(4)
C(45)	3954(9)	4223(6)	−1207(7)	67(4)
C(46)	4457(8)	3804(5)	−439(6)	58(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

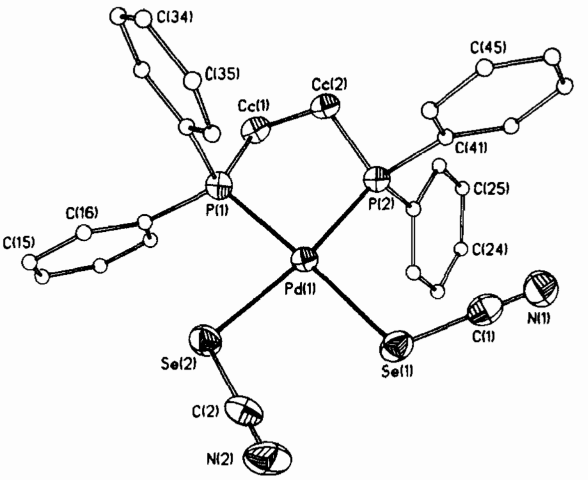

Fig. 1. Molecular structure and labeling scheme for [Pd(dpe)-$(SeCN)_2$]. Hydrogen atoms have been deleted. Thermal ellipsoids are shown at the 50% probability level.

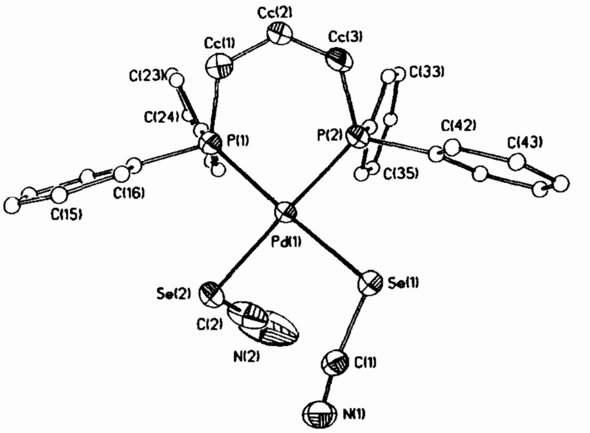

Fig. 2. Molecular structure and labeling scheme for [Pd(dpp)-$(SeCN)_2$]. Hydrogen atoms have been deleted. Thermal ellipsoids are shown at the 50% probability level.

severe steric restrictions were provided by the dpx ligand, since its backbone structure must remain planar due to its aromatic nature. However, the ligand does not remain in the plane of the remainder of the molecule upon coordination to palladium. Although the crystal structure of [Pd(dpx)$(SeCN)_2$] has not yet been determined, the analogous thiocyanate complex can be used for comparison. In this case, the P–Pd–P bond angle, 100.7(1)°, is the largest of the series [10]. In contrast, the ligands dpe and dpp contain an alkyl backbone which allows for puckering within the chain upon coordination. Theoretically, greater steric interactions should be expected to promote the nearly linear and less sterically demanding N-bound isomer, as has already been observed [4] for the thiocyanate series.

The comparisons between the dpe and dpp thiocyanate and selenocyanate complexes shown in Table VI indicate that the hoped for similarities in electronic and steric environments provided by the dpe and dpp ligands in both series were realized, in point of fact. The P–Pd–P bond angles adopted by the dpe and dpp ligands are influenced to a negligible degree by the identity of the coordinated pseudohalide. Even the Pd–P bond distances exhibit only minor variations as a function of the pseudohalide atom *trans* to them. By way of contrast, the bonding modes adopted by the pseudohalides exhibit remarkable variations. The dpe ligand produced the aforementioned thiocyanate geminite [4] and the dpp ligand yields a di-N-bound thiocyanate complex [4], whereas all of the coordinated selenocyanates, including those in the dpx complex, are Se-bound.

TABLE IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for [Pd(dpp)$(SeCN)_2$]

Atom	*x*	*y*	*z*	U^a
Pd(1)	3720(1)	3427(1)	11360(1)	34(1)
Se(1)	5247(1)	3302(1)	9521(1)	52(1)
Se(2)	5681(1)	3863(1)	12156(1)	53(1)
P(1)	2158(2)	3748(1)	12990(1)	43(1)
P(2)	2008(2)	2650(1)	10726(1)	37(1)
N(1)	6096(6)	4073(5)	9479(4)	63(3)
N(2)	6905(8)	1463(7)	12004(10)	161(6)
C(1)	6981(7)	3773(5)	8573(4)	46(2)
C(2)	6421(8)	2399(8)	12041(7)	63(4)
Cc(1)	389(6)	4241(6)	12918(5)	53(2)
Cc(2)	–365(8)	3425(7)	12362(6)	33(3)
Cc(3)	258(6)	3346(5)	11147(5)	47(2)
C(11)	2620(7)	4924(6)	13726(5)	36(2)
C(12)	2944(6)	4771(6)	14696(5)	55(3)
C(13)	3321(7)	5686(7)	15200(5)	61(3)
C(14)	3417(7)	6747(7)	14760(5)	67(3)
C(15)	3130(8)	6895(6)	13791(6)	76(3)
C(16)	2717(8)	5992(7)	13273(6)	64(3)
C(21)	1923(6)	2547(6)	13893(4)	51(3)
C(22)	700(7)	2444(7)	14720(5)	60(3)
C(23)	571(11)	1506(9)	15393(7)	103(3)
C(24)	1615(13)	680(8)	15274(7)	104(5)
C(25)	2317(11)	773(7)	14472(6)	93(4)
C(26)	2958(8)	1702(6)	13777(3)	72(3)
C(31)	1348(5)	1132(5)	11162(4)	39(2)
C(32)	617(7)	613(6)	11296(3)	59(3)
C(33)	574(6)	–534(7)	11564(6)	72(3)
C(34)	1752(9)	–1109(7)	11713(6)	73(4)
C(35)	2982(6)	–564(6)	11524(6)	72(3)
C(36)	3046(7)	575(5)	11323(5)	57(3)
C(41)	2343(6)	2547(3)	9274(4)	40(3)
C(42)	3143(7)	3496(6)	8694(5)	38(3)
C(43)	3425(6)	3439(6)	7591(5)	66(3)
C(44)	3943(7)	2437(6)	7060(5)	63(3)
C(45)	3182(7)	1432(6)	7629(5)	57(3)
C(46)	3886(8)	1533(5)	8741(5)	48(3)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE V. Selected Bond Lengths and Angles for $[Pd(dpe)(SeCN)_2]$ and $[Pd(dpp)(SeCN)_2]$

	$[Pd(dpe)(SeCN)_2]$	$[Pd(dpp)(SeCN)_2]$
(a) Bond lengths (Å)		
Pd(1)–Se(1)	2.478(1)	2.458(1)
Pd(1)–Se(2)	2.476(1)	2.488(1)
Pd(1)–P(1)	2.275(2)	2.281(1)
Pd(1)–P(2)	2.279(2)	2.286(2)
Se(1)–C(1)	1.837(10)	1.834(7)
Se(2)–C(2)	1.820(9)	1.821(9)
P(1)–Cc(1)	1.819(7)	1.829(6)
P(2)–Cc(2)	1.835(8)	
P(2)–Cc(3)		1.814(6)
N(1)–C(1)	1.142(12)	1.143(9)
N(2)–C(2)	1.136(15)	1.148(12)
Cc(1)–Cc(2)	1.547(11)	1.540(11)
Cc(2)–Cc(3)		1.533(9)
(b) Bond angles (°)		
Se(1)–Pd(1)–Se(2)	91.2(0)	94.1(0)
Se(1)–Pd(1)–P(1)	175.5(1)	172.4(1)
Se(1)–Pd(1)–P(2)	98.5(1)	87.3(1)
Se(2)–Pd(1)–P(1)	85.3(1)	89.1(1)
Se(2)–Pd(1)–P(2)	169.8(1)	168.2(1)
P(1)–Pd(1)–P(2)	85.1(1)	90.9(1)
Pd(1)–Se(1)–C(1)	109.1(3)	106.6(2)
Pd(1)–Se(2)–C(2)	105.0(3)	94.2(3)
Se(1)–C(1)–N(1)	177.1(9)	172.1(5)
Se(2)–C(2)–N(2)	177.5(9)	177.3(10)
Pd(1)–P(1)–Cc(1)	108.5(3)	113.8(2)
Pd(1)–P(2)–Cc(2)	107.6(3)	
Pd(1)–P(2)–Cc(3)		116.2(2)
P(1)–Cc(1)–Cc(2)	106.5(5)	115.3(5)
P(2)–Cc(2)–Cc(1)	110.7(5)	
P(2)–Cc(3)–Cc(2)		114.5(5)
Cc(1)–Cc(2)–Cc(3)		113.4(6)

The results of this work suggest that the palladium–selenium bond distances (see Table VI) are long enough to prevent unfavorable interactions between the bulky phenyl rings and the pseudohalides themselves. The bent arrangement resulting from coordination of the selenium atom to the metal may, indeed, be more sterically viable as the selenocyanate is allowed to maneuver away from the larger aromatic substituents. It is important to note that the more sterically crowded selenocyanate and thiocyanate [10] diphosphine complexes adopt configurations wherein one pseudohalide is positioned out of the plane of the molecule. For example, the angle between the coordination plane and one of the selenocyanates in $[Pd(dpp)(SeCN)_2]$ has been calculated to be approximately 73° (see Fig. 2). This suggests that the arrangement of the $SeCN^-$ moiety is significantly influenced by placement of the neighboring pseudohalide. In the selenocyanate cases, the 'soft–soft' palladium–selenium interaction is so strong that the system prefers to adjust to the steric crowding while maintaining this favorable association, rather than alleviate spatial restrictions through isomerization.

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TABLE VI. Comparisons Between Bond Angles and Bond Lengths

Comparison	$[Pd(dpe)(SCN)(NCS)]$ [a]	$[Pd(dpe)(SeCN)_2]$ [b]	$[Pd(dpp)(NCS)_2]$ [a]	$[Pd(dpp)(SeCN)_2]$ [b]
P–Pd–P angle	85.1(1)°	85.1(1)°	89.32(3)°	90.9(1)°
Pd–P distances (Å)	2.243(3)[c] 2.258(3)[d]	2.275(2)	2.241(1)	2.281(1)
Pseudohalide–Pd–pseudohalide angle	84.4(3)°	91.2°	91.4(1)°	94.1°
Pd–pseudohalide distance (Å)	2.062(10)[e] 2.364(4)[f]	2.478(1)	2.055(3)	2.458(1) 2.488(1)

[a] Data taken from ref. 4. [b] This work. [c] *trans* to –NCS. [d] *trans* to –SCN. [e] Pd–NCS. [f] Pd–SCN.