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Syntheses of Palladium(II) Chalcogenide Complexes. Solid State Structure of $[(CH_3)_2NCS_2]Pd(PEt_3)SCH_3$

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Introduction

Monomeric late metal thiolates and alkoxides have been receiving increasing attention.[1,2] Current interest in late metal thiolates stems from their proposed intermediacy in the desulfurization of organosulfur compounds[1b,c] and in many catalytic organic reactions.[1d] They also serve as potential precursors to transition metal sulfides.[1e] Similarly, late metal alkoxides have been implicated in many important catalytic reactions.[2]

Our interest in late metal chalcogenides resulted from the preparation of a series of unusually stable palladium(II) alkyls of the form $[(CH_3)_2NCS_2]Pd(PEt_3)(alkyl)$ (alkyl = methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl).[3] In an effort to explore this system further, we were interested in whether stable thiolates or alkoxide complexes, especially those containing β-hydrogen atoms, could also be prepared. We report herein the synthesis and characterization of several palladium(II) chalcogenides. A crystal structure of $[(CH_3)_2NCS_2]Pd(PEt_3)SCH_3$ is also presented.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere either with standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. ^1H, ^{13}C, and ^{31}P NMR chemical shifts are reported in ppm versus TMS, TMS, and H_3PO_4, respectively. The triethylphosphine proton resonances are seen as two multiplets having relative intensities of 1:4:6:4:1 (doublet of quartets centered near 1.7−1.6 ppm for the methylene groups) and 1:2:2:2:1 (doublet of triplets centered near 1.2−1.0 ppm for the methyl groups). $(Me_2NCS_2)Pd(PEt_3)Cl$ was prepared according to a literature method.[3b] $NaSCH_3$ and $HSC_6H_4CH_3$ were purchased from Aldrich and used as received. $NaOC_6H_5$ was prepared by reaction of phenol with NaH in THF. Elemental analyses were performed by Robertson Microlit Laboratories, Inc.

Table 1. Crystallographic Data for the Structural Analysis

formula	$C_{10}H_{24}PdNPS_3$	V, Å^3	1672.8
mol wt	391.88	Z	4
cryst system	monoclinic	radiation (λ, Å)	Mo K (0.710 73)
space group	$P2_1/n$	temp, °C	23
a, Å	8.862(2)	ϱ_{calcd}, g cm^{-3}	1.56
b, Å	11.892(2)	μ, cm^{-1}	15.3
c, Å	15.874(2)	R_F[a]	0.034
β, deg	90.49(2)	R_{wF}[b]	0.049

[a] $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ [b] $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F)$.

$(Me_2NCS_2)Pd(PEt_3)OC_6H_5$. A solid mixture of $(Me_2NCS_2)Pd(PEt_3)Cl$ (0.15 g; 0.39 mmol) and $NaOC_6H_5$ (0.060 g; 0.80 mmol) was dissolved in toluene (7 mL), and the resulting mixture was allowed to stir at room temperature for 2 h. The reaction mixture was filtered and the filtrate concentrated before being treated with an equal volume of hexanes (ca. 2 mL). Orange crystals were obtained by cooling overnight at −20 °C (0.16 g; 0.37 mmol; 93%); mp = 100−101 °C. ^1H NMR ($CDCl_3$), δ: 7.03, 6.46 (m, m; 4, 1; C_6H_5); 3.26, 3.25 (s, s; 3, 3; $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6), δ: 209.8 (s; NCS_2); 170.3, 129.2, 121.0, 114.3 (s, s, s, s; C_6H_5); 37.7, 37.1 (s, s; $N(CH_3)_2$); 14.6 (d; J_{CP} = 26 Hz; $P(CH_2CH_3)_3$); 8.0 (d; J_{CP} = 2 Hz; $P(CH_2CH_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 25.9. Anal. Calcd for $C_{15}H_{26}NOPPdS_2$: C, 41.14; H, 5.98; N, 3.20. Found: C, 41.13; H, 5.98; N, 3.20.

$(Me_2NCS_2)Pd(PEt_3)SCH_3$. A solid mixture of $(Me_2NCS_2)Pd(PEt_3)Cl$ (0.15 g; 0.39 mmol) and $NaSCH_3$ (0.030 g; 0.40 mmol) was dissolved in THF (7 mL), and the solution was allowed to stir for 12 h at room temperature. The THF was removed under vacuum and the resulting solid mixture extracted with toluene (3 mL). After cannula filtration, the bright orange toluene extract was treated with an equal volume of hexane and the mixture cooled overnight at −20 °C to yield strawlike orange crystals (0.15 g; 0.38 mmol; 97%); mp = 101−102 °C. ^1H NMR (C_6D_6), δ: 2.68 (s; 3; SCH_3); 2.52, 2.50 (s, s; 3, 3; $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6), δ: 37.9, 37.6 (s, s; $N(CH_3)_2$); 15.8 (d; J_{CP} = 27 Hz; $P(CH_2CH_3)_3$); 14.8 (d; J_{CP} = 5 Hz; SCH_3); 8.23 (d; J_{CP} = 2 Hz; $P(CH_2CH_3)_3$). The NCS_2 carbon atom was not observed. $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 25.0. Anal. Calcd for $C_{10}H_{24}NPPdS_3$: C, 30.65; H, 6.17; N, 3.57. Found: C, 30.81; H, 6.09; N, 3.40.

$(Me_2NCS_2)Pd(PEt_3)SC_6H_4CH_3$. A solid mixture of $(Me_2NCS_2)Pd(PEt_3)Cl$ (0.15 g; 0.39 mmol) and $HSC_6H_4CH_3$ (0.05 g; 0.4 mmol) was dissolved in THF (7 mL). Gaseous ammonia was bubbled into the reaction mixture for several minutes. Immediately, the bright yellow solution turned orange-red and NH_4Cl precipitated. The mixture was allowed to stir for 2 h at room temperature before removing the THF under vacuo. The solid mixture was extracted with toluene (2 mL) and cannula filtered. The filtrate was treated with an equal volume of hexane and cooled overnight at −20 °C. Bright orange crystals resulted (0.13 g; 0.28 mmol; 72%); mp = 110−111 °C. ^1H NMR (C_6D_6), δ: 8.03, 6.99 (d, d; 2, 2; J_{HH} = 8 Hz; C_6H_4); 2.40, 2.25 (s, s; 3, 3; $N(CH_3)_2$); 2.09 (s; 3; $SC_6H_4CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6), δ: 210.7 (s; NCS_2); 142.3, 135.6, 133.0, 129.0 (d, s, s, s; J_{CP} = 4 Hz; $SC_6H_4CH_3$); 38.0, 37.5 (s, s; $N(CH_3)_2$); 21.3 (s; $SC_6H_4CH_3$); 15.9 (d; J_{CP} = 27 Hz; $P(CH_2CH_3)_3$); 8.5 (s; $P(CH_2CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 24.4. Anal. Calcd for $C_{16}H_{28}NPPdS_3$: C, 41.07; H, 6.03; N, 2.99. Found: C, 40.99; H, 5.56; N, 2.96.

Crystallographic Analysis of $(Me_2NCS_2)Pd(PEt_3)SCH_3$. Yellow crystals of $(Me_2NCS_2)Pd(PEt_3)SCH_3$ were grown by slow diffusion of hexanes into a saturated toluene solution. A crystal was mounted in a thin wall capillary tube on a CAD-4 diffractometer. The unit cell dimensions were determined and refined from 25 general reflections. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. Data were collected in the $\omega/2\theta$ scan mode with a 0.8° + (0.35 tan θ)° scan range. The structure was solved by the heavy atom method and refined by using MolEN.[4] All hydrogen atoms were included in the structure factor calculations but were not refined. Full-matrix least-squares refinements were carried out for reflections with $I > 3\sigma(I)$ where $\sigma(I)$ was derived from counting statistics. Absorption corrections were performed by the method of Walker and Stuart using a Fourier function.[5] Atomic positions are shown in Table 2.

Results and Discussion

The reaction of $(Me_2NCS_2)Pd(PEt_3)Cl$ with $NaSCH_3$ or NaOPh in THF or aromatic solvents affords the substitution

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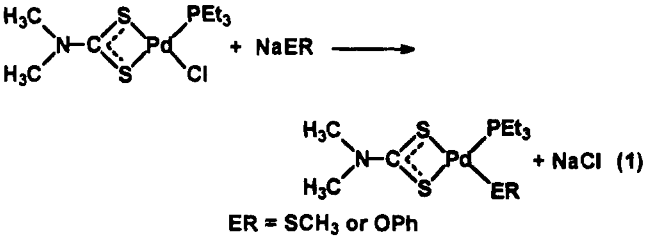
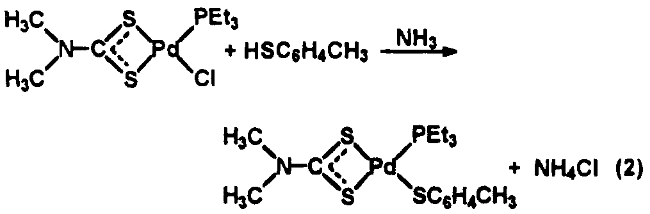
Table 2. Positional Parameters and Their Estimated Standard Deviations for $[(CH_3)_2NCS_2]Pd(PEt_3)SCH_3$

atom	x	y	z	B_{eq},[a] Å^2
Pd	0.10770(4)	0.16329(3)	0.34305(2)	3.444(7)
S1	0.0946(2)	0.1723(1)	0.49051(8)	4.88(3)
S2	0.2476(2)	0.0096(1)	0.39128(8)	4.81(3)
S3	−0.0377(2)	0.3180(1)	0.31152(9)	5.42(3)
P	0.1476(2)	0.1304(1)	0.20450(8)	3.96(3)
N	0.2477(5)	0.0002(4)	0.5597(2)	5.1(1)
C1	−0.0845(9)	0.3852(6)	0.4098(4)	7.7(2)
C2	0.2031(5)	0.0537(4)	0.4913(3)	4.2(1)
C3	0.3302(8)	−0.1052(6)	0.5569(4)	7.3(2)
C4	0.2107(8)	0.0410(6)	0.6432(3)	7.4(2)
C5	0.0158(7)	0.1875(5)	0.1288(3)	5.6(1)
C6	0.1562(7)	−0.0186(5)	0.1826(3)	5.7(1)
C7	0.3235(7)	0.1904(6)	0.1675(4)	6.2(2)
C8	−0.1491(8)	0.1376(7)	0.1386(4)	7.2(2)
C9	0.1605(9)	−0.0540(6)	0.0913(4)	8.6(2)
C10	0.4559(8)	0.1684(7)	0.2222(5)	8.1(2)

[a] $B_{eq} = ((8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j a_i a_j)$.

products in high yields as shown in eq 1. A *p*-methylbenzenethiolate complex is obtained by reaction of (Me_2NCS_2)-$Pd(PEt_3)Cl$ with *p*-$HSC_6H_4CH_3$ in the presence of NH_3 (eq 2).





All three compounds are soluble in aromatic solvents and are moderately air stable as solids. As with the alkyl complexes of this system,[3] the methanethiolate complex (which also possesses a ligand capable of β-hydrogen elimination) is quite thermally robust. Warming this complex to 80 °C in an NMR tube resulted in little to no decomposition. Stable amide and phosphide complexes could not be prepared by similar procedures.

The reaction of $(Me_2NCS_2)Pd(PEt_3)Cl$ with excess $NaOCH_3$ does not yield a similar product. On the basis of NMR spectroscopic data, the product appears to be $(Me_2NCS_2)Pd$-$(O{=}PEt_3)OCH_3$ (a singlet at 52.9 ppm in the ^{31}P NMR spectrum as well as a 52 Hz carbon−phosphorus coupling constant is consistent with the presence of a phosphine oxide ligand[6]). Unfortunately, definitive characterization of this compound was not obtained.

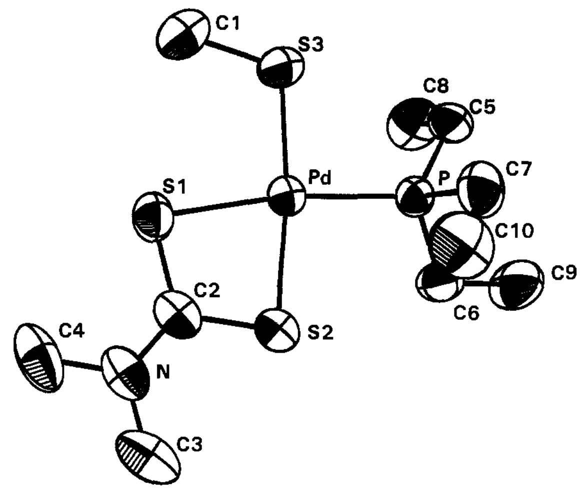
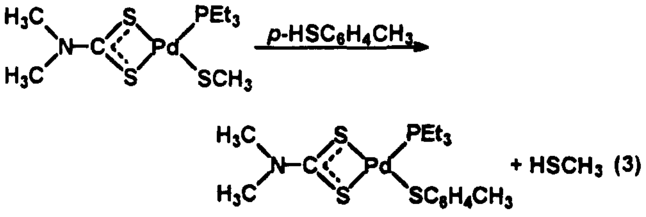


Figure 1. ORTEP diagram for $[(CH_3)_2NCS_2]Pd(PEt_3)SCH_3$.

Table 3. Selected Bond Distances and Angles for $(Me_2NCS_2)Pd(PEt_3)SCH_3$

	Bond Distances (Å)		
Pd−S1	2.347(1)	Pd−P	2.264(1)
Pd−S2	2.333(2)	S3-C1	1.805(7)
Pd−S3	2.299(2)		
	Bond Angles (deg)		
S1−Pd−S2	74.88(5)	S2−Pd−P	95.55(5)
S1−Pd−S3	98.52(5)	S3−Pd−P	91.05(5)
S1−Pd−P	170.39(5)	Pd−S3-C1	107.4(2)
S2−Pd−S3	173.37(5)		

The thiolate ligand in $(Me_2NCS_2)Pd(PEt_3)SCH_3$ is quantitatively exchanged when reacted with excess *p*-methylbenzenethiol (eq 3). As discussed previously,[7] this exchange reaction likely takes place via an I_a mechanism in which the incoming thiol coordinates to palladium and undergoes exchange by a hydrogen-bonded intermediate.



The solid state structure of $(Me_2NCS_2)Pd(PEt_3)SCH_3$ has been determined by X-ray crystallography. An ORTEP diagram is provided in Figure 1 and important bond distances and angles are reported in Table 3. The overall coordination geometry about the palladium atom is essentially square planar (sum of four angles about palladium is 360°). The S1−Pd−S2 angle is restricted by the chelate ring to 74.88(5)°. The S1−Pd−S3 bond angle compensates to the greatest extent for the low angle by opening to 98.52(5)° with the S2−Pd−P angle at 95.55(5)°. For comparison, the analogous S2−Pd−P angle in $((CH_2)_4$-$NCS_2)Pd(PEt_3)(\eta^1$- $CH(CH_3)_2)$[3b] opens to 100.71(4)° whereas the S1−Pd−C angle (analogous to the S1−Pd−S3 angle in the structure reported here) is only 95.3(1)°.

An explanation of this relatively larger S1−Pd−S3 angle is found in the orientation of the SCH_3 group. The methyl substituent bound to the sulfide is oriented away from the phosphine ligand and is oriented nearly in the square plane defined by the palladium coordination sphere. The C1S3−PdP torsion angle is −174.4°. This value contrasts with our earlier

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results for the structures of $((CH_2)_4NCS_2)Pd(PEt_3)(\eta^1\text{-}CH(CH_3)_2)$[3b] and $((CH_2)_4NCS_2)Pd(PEt_3)(\eta^1\text{-}CH(CH_3)CN)$,[3c] where the groups bonded to the α-carbon atom of the alkyl ligand are also oriented away from the phosphine ligand but straddle the square plane of the donor atoms. In the structure of the isopropyl complex CC−PdP torsion angles are −67.4 and 55.4° and in the cyanide complex 61 and −62°. The opening of the S1−Pd−S3 angle relieves C1•••S1 nonbonding interactions.

The coplanar arrangement observed in $(Me_2NCS_2)Pd(PEt_3)SCH_3$ also appears rather uncommon among other reported monomeric palladium thiolates. Clegg and González-Duarte report canting above and below the mean square plane defined about palladium for the two 4-mercapto-1-methylpiperidine ligands in $Pd(SC_5H_9NMe)_2(dppe)$ with torsion angles of 45.1 and 40.3°.[8a] In addition, Yamamoto states that the phenyl plane of the thiolate ligand in $PdEt(SPh)(PMe_3)_2$ is nearly perpendicular to the coordination plane about palladium.[8b] Even though the SCH_3 group is coplanar with the square plane defined by the palladium coordination sphere, the Pd−S3-C1 angle is normal at 107.4(2)°. For comparison, analogous angles are 104.2(1) and 106.1(1)° in $Pd(SC_5H_9NMe)_2(dppe)$[8a] and 109.2(3)° in $PdEt(SPh)(PMe_3)_2$.[8b]

The Pd−S3 bond distance of 2.299(2) Å is 0.05 Å shorter than expected from the sum of the covalent radii[9] and 0.04 Å shorter than the average Pd−S distances for the dithiocarbamate ligand. In addition, this bond is at least 0.04 Å shorter than any terminal palladium(II) thiolate bond previously reported.[8] The orientation of the thiolate ligand in $(Me_2NCS_2)Pd(PEt_3)SCH_3$ and the short $Pd-SCH_3$ bond length can be explained by electron π-donation of a lone pair on the thiolate sulfur atom to a π-acceptor orbital on the palladium atom.

This strong $Pd-SCH_3$ bonding is also evident in the nearly equivalent Pd−S1 and Pd−S2 bond distances, suggesting similar *trans* influences exerted by the SCH_3 and phosphine ligands. The *trans* influence exerted by phosphines is known to be high.[11] For example, in the structures of three square planar $Rh[P(CH_3)_3]_3SC_6H_4\text{-}p\text{-}X$ complexes the Rh−P bond distances *trans* to the thiolate ligand average 0.06 Å shorter than the *cis* Rh−P bond distances.[12] In all of these structures, the phenyl group is rotated out of the square plane of the donor atoms. Thus in $(Me_2NCS_2)Pd(PEt_3)SCH_3$, the SCH_3 ligand exerts a *trans* influence that is about equal to that of the phosphine ligand, an unusually strong influence for a thiolate ligand.

We have noted previously[3] that the $(Me_2NCS_2)Pd(PEt_3)X$ system has unusually low interligand steric effects. We propose that these low steric effects allow the thiolate ligand to be coplanar with the square plane of the donor atoms, the orientation that is best for π-donation to the palladium from the sulfur atom.

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Supplementary Material Available: Tables of complete data collection information, bond distances, bond angles, anisotropic thermal parameters, and positional parameters of H atoms (8 pages). Ordering information is given on any current masthead page.

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(9) This distance was calculated from the Pd−C bond distance in $((CH_2)_4NCS_2)Pd(PEt_3)(\eta^1\text{-}CH(CH_3)_2)$[3b] and the covalent radii of carbon and sulfur.[10]

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