

Cleavage of Bis(thiophosphinyl)disulfanes, $R_2P(S)SSP(S)R_2$ ($R = Et, Ph$), by a Low-Valent Palladium Dimer

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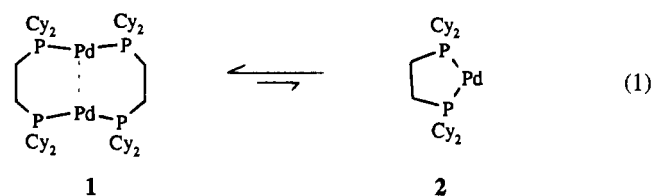
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The reaction of $Pd_2(\mu\text{-dcpe})_2$ (dcpe = 1,2-bis(dicyclohexylphosphino)ethane) with the bis(thiophosphinyl)disulfanes, $R_2P(S)SSP(S)PR_2$ ($R = Et, Ph$), give the ionic complexes $[(\text{dcpe})Pd(\text{SPR}_2\text{S})]^+[\text{SPR}_2\text{S}]^-$ in 60% (**1**; $R = Et$) and 72% (**2**; $R = Ph$) yields. An unusual dimer, $\{(\text{Et}_2\text{PS}_2)Pd\}_2(\mu\text{-Et}_2\text{PS}_2)_2$, is also isolated in low yield for $R = Et$. The X-ray structure of a benzene solvate of **1** ($\text{C}_{50}\text{H}_{68}\text{P}_4\text{S}_4\text{Pd} \cdot 1.5\text{C}_6\text{H}_6$; monoclinic, $a = 14.628(1) \text{ \AA}$, $b = 16.662(3) \text{ \AA}$, $c = 21.612(4) \text{ \AA}$, $\beta = 107.66(1)^\circ$, $P2_1/n$, $Z = 4$, $R = 0.047(F_o)$, $R_w = 0.056(F_o)$) shows a nearly planar spirocyclic palladium atom in the cation and a free SPR_2S^- anion. Variable-temperature ^{31}P NMR spectra of **1** indicate rapid interchange of the coordinated and free SPR_2S^- counterion in solution at room temperature.

Introduction

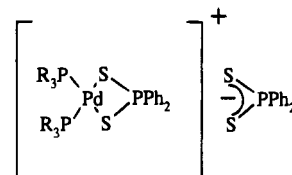
Bis(thiophosphinyl)disulfanes, $R_2P(S)SSP(S)PR_2$, and bis(thiophosphoryl)disulfanes, $(\text{RO})_2P(S)SSP(S)P(\text{OR})_2$, behave as mild oxidizing agents toward metal compounds in low oxidation states to give metal phosphinodithioato, $M-S(S)PR_2$, and phosphorodithioato, $M-S(S)P(\text{OR})_2$, derivatives. Low- or zero-valent complexes can be metal carbonyls,¹ carbonyl metal cyclopentadienyls,² or cyclopentadienyl metal dimers.³ The dithiophosphorus ligands are capable of a variety of bonding modes including mono- and bidentate coordination to one metal center and bridging between two metal centers.

In view of the above behavior, the reactions of bis(thiophosphinyl)disulfanes with zero-valent palladium compounds would be of great interest. Recently, it was shown that the unusual palladium dimer $Pd_2(\mu\text{-dcpe})_2$ (**1**) is in equilibrium with the reactive zero-valent (dcpe)Pd fragment **2** in solution (eq 1).⁴



Consequently, the behavior of **1** and **2** toward bis(thiophosphinyl)disulfanes as a possible entry to interesting phosphinodithioato-palladium complexes was examined.

Palladium(II) complexes of phosphinodithioic acids are well-known. The diphenylphosphinodithioate $Pd(\text{S}_2\text{PPh}_2)_2$ was described as a monomeric red-orange complex.^{5,6} This diphenylphosphinodithioate complex reacts with tertiary phosphines to form compounds (adducts) initially described as five- and six-coordinate complexes.⁶ These were later reformulated as tetracoordinate ion-pair compounds of the type.^{7,8}



An X-ray crystal structure determination of $[Pd(\text{S}_2\text{PPh}_2)_2]-(\text{PEt}_3)_2\text{S}_2\text{PPh}_2$ confirmed this type of structure.⁹ Palladium(II) phosphinodithioates with BPh_4^- and PF_6^- counterions are also known as well as neutral compounds of the type $PdX(\text{PR}_3)_2(\text{S}_2\text{PPh}_2)_2$ ($X = \text{halogen}$).¹⁰

Results and Discussion

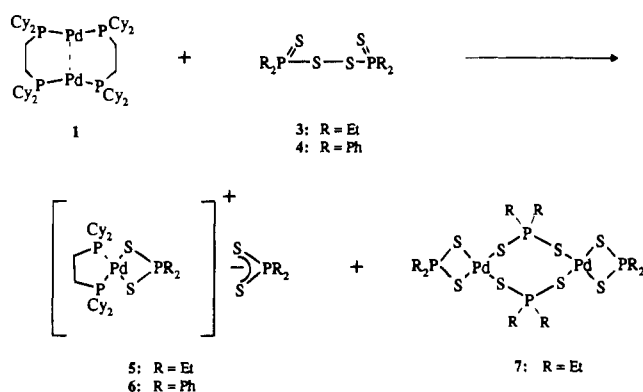
A dark red solution of $Pd_2(\mu\text{-dcpe})_2$ (**1**) was added to a slight excess of the bis(phosphinyl)disulfanes **3** and **4** at 0°C . The major isolated products are the monomeric palladium species **5** and **6**, which are formed in 60% and 77% yields respectively (Scheme 1). For the reaction of **1** with **3**, a small amount (2%)

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Scheme 1



of the unusual dimer **7** could also be isolated. The ionic complex **5** is a colorless solid whereas **6** is an orange solid which gives pink solutions. Both are air-stable compounds soluble in most polar organic solvents. The ionic nature of these complexes is established by their high molar conductivity in nitromethane (**5**; $43.1 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^{-2}$; **6**, $22.0 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^{-2}$), in addition to the crystal structure of **5**.

An X-ray structure of **5** as a benzene solvate was obtained from a crystal grown by the slow evaporation of a benzene solution. Atomic coordinates and selected non-hydrogen bond distances and angles are listed in Tables 1–3, respectively.

An ORTEP drawing of the spirocyclic cation, $(\text{dcpe})\text{Pd}(\text{SPe}_2\text{S})^+$, is shown in Figure 1. The four-membered PdSPS ring is slightly puckered, a dihedral angle of $15.0(3)^\circ$ being formed between the $\text{S}(1)-\text{Pd}-\text{S}(2)$ and $\text{S}(1)-\text{P}3-\text{S}(2)$ planes. The coordination geometry about the Pd atom shows a slight tetrahedral distortion from the ideal square-planar geometry.¹¹ The endocyclic palladium angles $\text{S}(1)-\text{Pd}-\text{S}(2)$, $83.99(7)^\circ$, and $\text{P}(1)-\text{Pd}-\text{P}(2)$, $86.41(7)^\circ$, are somewhat less than the idealized values of 90° due to ring constraints. The $\text{S}-\text{P}-\text{S}$ bond angle in the chelate ring is $107.7(1)^\circ$. The $\text{Pd}-\text{S}$ (2.404(2) and 2.398(2) Å), $\text{Pd}-\text{P}$ (2.259(2) and 2.259(2) Å), and $\text{P}-\text{S}$ (2.015(3) and 2.016(3) Å) bond lengths are within normal values and comparable to those found for $[(\text{Et}_3\text{P})_2\text{Pd}(\text{SPPPh}_2\text{S})^+][\text{SPPPh}_2\text{S}^-]$.⁹

The SPR_2S^- counterion, shown in Figure 2, shows a pseudotetrahedral phosphorus atom with a $\text{S}-\text{P}-\text{S}$ bond angle of $118.3(2)^\circ$ and $\text{P}-\text{S}$ bond lengths of 1.982(3) and 1.977(3) Å. The more obtuse $\text{S}-\text{P}-\text{S}$ angle and shorter $\text{P}-\text{S}$ bond lengths relative to the coordinated SPR_2S moiety are consistent with expected partial multiple bond character in the free ion. There exists no significant intermolecular contact between this anion and the palladium cation, nor are there important contacts between either of the ions and the solvent benzene.¹²

The formation of **5** and **6** likely proceeds via the reaction of equilibrium amounts of $(\text{dcpe})\text{Pd}$ (**2**) with the disulfanes to give intermediate neutral complexes, $(\text{dcpe})\text{Pd}(\text{SPR}_2\text{S})_2$ (**9**; Scheme 2). This initial step is supported by the reaction of **1** with organic disulfides to give palladium disulfides, the result of $\text{S}-\text{S}$ bond cleavage by $(\text{dcpe})\text{Pd}$.¹³ The intermediate complexes, **9**,

Table 1. Positional Parameters and Their Estimated Standard Deviations^a

atom	x	y	z	B(Å ²)
Pd	0.19748(4)	0.03280(3)	0.28673(2)	2.67(1)
S1	0.2885(1)	-0.0598(1)	0.2435(1)	4.42(5)
S2	0.2708(1)	0.1324(1)	0.23714(9)	4.74(5)
S4	-0.0500(2)	-0.1861(1)	0.4732(1)	6.23(6)
S5	-0.0594(2)	-0.3079(2)	0.3453(1)	6.01(6)
P1	0.1197(1)	0.1212(1)	0.33206(8)	2.75(4)
P2	0.1317(1)	-0.0641(1)	0.33269(8)	2.74(4)
P3	0.3510(1)	0.0401(1)	0.22265(9)	4.04(4)
P4	-0.0552(1)	-0.2960(1)	0.43713(9)	3.89(5)
C1	0.0410(5)	0.0668(4)	0.3697(3)	3.0(2)
C2	0.0781(5)	-0.0174(4)	0.3910(3)	3.2(2)
C111	0.1970(5)	0.1829(4)	0.3968(3)	3.1(2)
C112	0.2498(5)	0.2493(4)	0.3728(4)	3.9(2)
C113	0.3126(5)	0.2992(5)	0.4283(4)	4.5(2)
C114	0.3834(6)	0.2464(6)	0.4778(4)	5.4(2)
C115	0.3321(6)	0.1818(5)	0.5023(4)	4.9(2)
C116	0.2681(5)	0.1322(5)	0.4477(3)	3.9(2)
C121	0.0439(5)	0.1919(4)	0.2736(3)	3.2(2)
C122	-0.0141(5)	0.2478(5)	0.3029(4)	4.3(2)
C123	-0.0703(7)	0.3084(5)	0.2526(4)	6.8(3)
C124	-0.1297(7)	0.2680(6)	0.1932(5)	7.7(3)
C125	-0.0727(7)	0.2142(6)	0.1634(4)	6.3(3)
C126	-0.0188(6)	0.1523(5)	0.2132(4)	4.6(2)
C211	0.0359(5)	-0.1238(4)	0.2772(3)	3.4(2)
C212	0.0695(6)	-0.1697(5)	0.2272(4)	4.9(2)
C213	-0.0120(6)	-0.2205(5)	0.1845(4)	5.5(2)
C214	-0.0981(7)	-0.1713(6)	0.1509(4)	6.2(3)
C215	-0.1316(7)	-0.1248(6)	0.2004(5)	6.7(3)
C216	-0.0518(6)	-0.0743(5)	0.2439(4)	5.5(2)
C221	0.2254(5)	-0.1337(4)	0.3784(3)	3.7(2)
C222	0.1902(5)	-0.2016(5)	0.4129(4)	4.5(2)
C223	0.2727(6)	-0.2565(5)	0.4465(5)	6.1(2)
C224	0.3536(6)	-0.2125(6)	0.4932(4)	6.0(2)
C225	0.3893(6)	-0.1455(6)	0.4585(4)	5.7(2)
C226	0.3080(5)	-0.0886(5)	0.4247(4)	4.6(2)
C311	0.3532(6)	0.0380(6)	0.1395(4)	6.2(2)
C312	0.4056(7)	-0.0305(6)	0.1222(4)	8.2(3)
C321	0.4744(6)	0.0467(5)	0.2731(4)	5.5(2)
C322	0.4902(7)	0.0471(7)	0.3449(5)	8.0(3)
C411	-0.1580(6)	-0.3441(5)	0.4486(4)	6.2(2)
C412	-0.1768(7)	-0.4313(6)	0.4230(5)	8.7(3)
C421	0.0466(6)	-0.3523(6)	0.4856(4)	6.2(3)
C422	0.0744(9)	-0.3442(7)	0.5566(5)	8.6(4)
C1s	0.8236(7)	0.0135(7)	0.4071(5)	7.7(3)*
C2s	0.7867(8)	-0.0283(7)	0.3548(5)	8.5(3)*
C3s	0.7404(8)	0.0074(7)	0.2995(5)	8.1(3)*
C4s	0.7312(7)	0.0905(7)	0.2971(5)	7.7(3)*
C5s	0.7710(8)	0.1332(7)	0.3520(5)	8.4(3)*
C6s	0.8176(7)	0.0935(7)	0.4067(5)	8.0(3)*
C7s	0.9645(8)	0.0190(8)	0.0499(6)	9.7(3)*
C8s	1.0516(9)	0.0447(8)	0.0509(6)	10.2(4)*
C9s	1.089(1)	0.0296(9)	-0.0003(7)	11.2(4)*

^a Atoms with asterisks were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as follows: $(\frac{1}{3})[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

may subsequently undergo a facile chelate-driven intramolecular displacement of a SPR_2S^- ligand to form the ultimate ionic products.

Specific evidence for the interconversion of $(\text{dcpe})\text{Pd}(\text{SPe}_2\text{S})_2$ and **5** is seen from the variable-temperature NMR behavior of **5** (Figure 3). At room temperature, complex **5** shows only a single sharp ^{31}P resonance at $\delta = 95.9$ ppm with two broad and almost indiscernible peaks at $\delta = 73.2$ and 117.9 ppm. As the solution temperature is lowered, these initially broad peaks begin to sharpen and a limiting spectrum is reached at 233K with a peak ratio of 1:2:1. On the basis of this integration, the resonance at 95.9 ppm is assigned as the phosphorus atoms of the dcpe, and the resonances at 73.2 and

(11) Positional deviations from the least-squares coordination plane (in Å): Pd, 0.0085(5); P(1), -0.053(2); P(2), 0.001(2); S(1), -0.061(2); S(2), 0.002(2).

(12) The shortest cation-anion contact is 2.87 Å between S(4), an anion sulfur, and H(422a), a cyclohexyl hydrogen on the backside of the dcpe ligand of the cation. The shortest non $\text{H}\cdots\text{H}$ contact is 2.81 Å, between an anion sulfur, S(5), and a hydrogen, H(4s), of a solvent benzene.

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Table 2. Important Bond Distances (Å)

distance ^a		distance ^a	
Pd-S1	2.404(2)	S4-P4	1.982(3)
Pd-S2	2.398(2)	S5-P4	1.977(3)
Pd-P1	2.259(2)	P3-C311	1.808(9)
Pd-P2	2.259(2)	P3-C321	1.81(1)
S1-P3	2.015(3)	P4-C411	1.786(9)
S2-P3	2.016(3)	P4-C421	1.80(1)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3. Selected Bond Angles (deg)

angle ^a		angle ^a	
S1-Pd-S2	83.99(7)	S2-P3-C311	110.9(4)
S1-Pd-P1	176.74(9)	S2-P3-C321	112.5(3)
S1-Pd-P2	94.12(7)	C311-P3-C321	106.5(4)
S2-Pd-P1	95.46(7)	S4-P4-S5	118.3(2)
S2-Pd-P2	178.08(8)	S4-P4-C411	107.0(3)
P1-Pd-P2	86.41(7)	S4-P4-C421	109.0(4)
Pd-S1-P3	84.21(9)	S5-P4-C411	108.9(4)
Pd-S2-P3	84.35(9)	S5-P4-C421	107.5(3)
S1-P3-S2	105.7(1)	C411-P4-C421	105.5(5)
S1-P3-C311	110.7(3)	C122-C121-C126	111.1(6)
S1-P3-C321	110.7(3)	C121-C122-C123	110.8(7)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

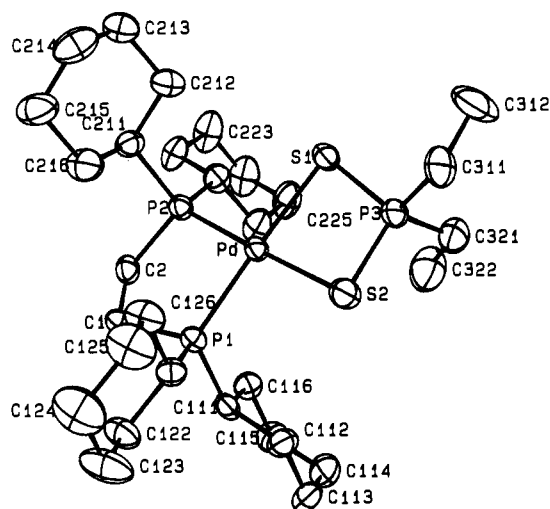


Figure 1. ORTEP drawing of $(dcpe)Pd(SPEt_2S)_2^+$. Thermal ellipsoids are shown at the 30% probability level.

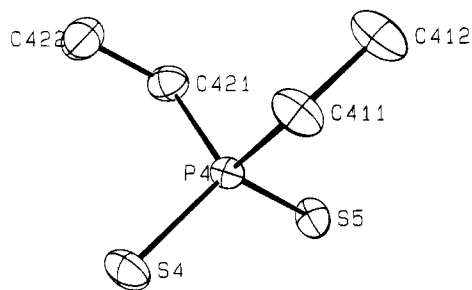


Figure 2. ORTEP drawing of the counterion, $SPEt_2S^-$. Thermal ellipsoids are shown at the 30% probability level.

117.9 ppm are assigned to free and coordinated SPR_2S^- moieties, respectively.¹⁴ Attempts to warm a sample of **5** above room temperature resulted in further broadening of these resonances into the baseline. However, coalescence could not be observed due to decomposition of the complex above 328 K.

The dinuclear palladium compound **7** is isolated as bright red platelike crystals. The dimeric nature of these complexes

is revealed by the FAB-MS, which show a prominent $M^+ + 1$ ion at 825 amu. Two distinct phosphorus resonances at 107.9 and 119.8 ppm are observed as well as two different ethyl environments in the ^{13}C NMR. The compound is essentially nonconducting ($9.7 \Omega^{-1} mol^{-1} cm^{-2}$), consistent with a covalent structure with both bridging and chelating dithiophosphane groups. Attempts to grow X-ray-quality crystals of this compound have been unsuccessful to date.

Experimental Section

General Procedures. All experiments were performed under an inert atmosphere of dry nitrogen or argon employing standard Schlenk techniques. Photolyses were performed using a Rayonet photochemical reactor containing 16 low-pressure mercury (254 nm) lamps.

Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl under a blanket of nitrogen. Toluene, hexane, and acetonitrile were distilled from calcium hydride under a blanket of nitrogen. Dichloromethane and acetone were purchased from EM science and used as received. 1,2-bis(dicyclohexylphosphino)ethane was purchased from Strem and used as received. Silver oxalate was prepared from $AgNO_3$ and $K_2C_2O_4$ in water.¹⁵ $(dcpe)PdCl_2$ was prepared from $Pd(PhCN)_2Cl_2$ and 1,2-bis(dicyclohexylphosphino)ethane.¹⁶ $Et_2P(S)SSP(S)PEt_2$ and $Ph_2P(S)SSP(S)PPh_2$ were prepared by literature methods.¹⁷

1H and ^{31}P spectra were recorded on IBM/Bruker AF-200 or GE NMR-400 spectrometer, respectively. 1H NMR shifts are referenced relative to TMS and ^{31}P NMR shifts relative to 85% H_3PO_4 . IR spectra were recorded on a Mattson FT-IR Cygnus 100. UV spectra were recorded on a Hewlett Packard 8452A Diode Array spectrophotometer. Mass spectra were obtained on a Kratos Concept-1H mass spectrometer in the electron impact mode at an ionization potential of 70 eV, and in the positive ion FAB mode using nitrobenzoic acid (NBA) as the matrix material. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

$\{(dcpe)Pd\}_2$ (1). A solution containing 62 mg (0.1 mmol) of $(dcpe)Pd(C_2O_4)$ dissolved in 20 mL of CH_3CN was irradiated at room temperature for 40 min. The red precipitate was separated from the mixture upon cooling to 0 °C. The supernatant was removed, and the red precipitate was washed with CH_3CN and dried under vacuum (yield 45 mg, 85%). 1H NMR (C_6D_6): δ 1.06–2.22 (featureless resonance). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 23.43 (s).

$(dcpe)PdP_2S_4C_8H_{20}$ (5). A saturated solution containing 61 mg (0.22 mmol) of $Et_2P(S)SSP(S)Et_2$ was cooled to 0 °C. Over a 5 min period, 50 mg (0.05 mmol) of $\{(dcpe)Pd\}_2$ in toluene was added dropwise. The solution was concentrated under vacuum and cooled to -10 °C, which produced colorless crystals (yield 48 mg, 60%). 1H NMR (C_6D_6): δ 3.0 (2H); 2.1–0.5 (br m, 51H). $^{31}P\{^1H\}$ NMR: δ 96 (s). MS (FAB, MNBA matrix) m/z 681.5 (MH, 100). IR (KBr): 2926, 2850 (s); 1444.7 (m); 1267 (m); 1114 (m); 1047 (m); 1006 cm^{-1} (m).

$(dcpe)PdP_2S_4C_{24}H_{20}$ (6). A solution consisting of 20 mg (0.30 mmol) of $Ph_2P(S)SSP(S)Ph_2$ in 2 mL of toluene was cooled to 0 °C. A toluene solution containing 30 mg of $\{(dcpe)Pd\}_2$ was added dropwise to the chilled solution. The resulting dark red-orange solution was concentrated under vacuum and cooled to -10 °C. An orange-red solid was isolated (yield 10.4 mg, 72%). 1H NMR (C_6D_6): δ 8.2–7.2 (m, 10H); 2.4–1.2 (featureless resonance, 48H). $^{31}P\{^1H\}$ NMR: δ 84.50 (s); 96.0 (s); 52.2 (s). MS (FAB, MNBA matrix) m/z 777.3 (MH^+ , 6.2).

$\{(Et_2PS_2)Pd\}_2(\mu-Et_2PS_2)$ (7). The mother liquor after isolation of $(dcpe)PdP_2S_4C_8H_{20}$ was concentrated and allowed to stand. After 5 days, red crystals formed and were dissolved in C_6H_6 . Slow evaporation of the solvent produced a large red crystal which turned opaque immediately after the solvent was removed. 1H NMR (C_6D_6): δ 1.3 (dq, 4H); 1.0 (dt, 6H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 119.8 (s); 107.9 (s).

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Scheme 2

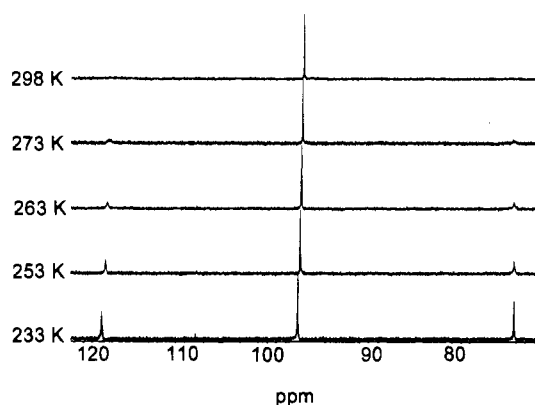
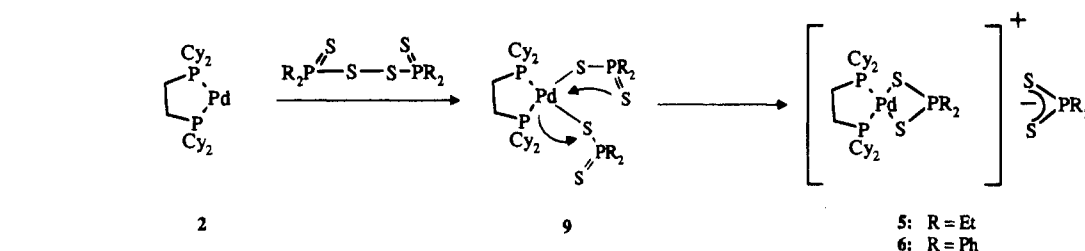


Figure 3. Low-temperature ^{31}P NMR spectrum (121.7 MHz) of **5** in toluene- d_8 .

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , INEPT): δ 34.8 (CH_2); 33.9 (CH_2); 5.5 (CH_3); 1.2 (CH_3). MS (FAB, MNBA matrix) m/z 825.2 (MH^+ , 8.0).

Low-Temperature NMR. ^{31}P NMR were acquired every 10 °C as the sample was cooled to -70 °C. Spectra were also taken as the sample was slowly warmed to room temperature to prove that this process was indeed reversible and not a quantitative chemical change.

X-ray Crystallography. A colorless, lozenge-shaped crystal of the complex, obtained from the slow evaporation of a benzene solution, was coated with a thin layer of epoxy cement and affixed to the end of a thin glass fiber. General procedures for crystal orientation, unit cell determination, and data collection on the CAD-4 diffractometer have been published.¹⁸ Details specific to the present determination are presented in Table 4. The initial monoclinic cell chosen by the CAD-4 software¹⁹ was confirmed by the observation of $2/m$ diffraction symmetry, and the space group was uniquely determined by the systematic absences observed in the final data set.²⁰ The data were additionally corrected for a 10.5% anisotropic decay in the intensity monitors and for absorption using Ψ scans on four reflections with χ near 90°. The position of the palladium atom was obtained from an origin-removed Patterson map, and the remainder of the structure

(18) Mague, J. T.; Lloyd, C. L. *Organometallics* **1988**, 7, 983.

(19) Enraf-Nonius CAD-4 Software, Version 5.0. Enraf-Nonius, Delft, The Netherlands, 1989.

(20) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol IV, Table 2.2B. (b) Cromer, D. T. *Ibid.* Table 3.2.1.

Table 4. Summary of Crystallographic Data for **5**

formula	$\text{C}_{40}\text{H}_{47}\text{P}_4\text{S}_4\text{Pd} \cdot 1.5\text{C}_6\text{H}_6$
fw	913.59
space group	$P2_1/n$
a , Å	14.628(1)
b , Å	16.662(3)
c , Å	21.612(4)
β , deg	107.66(1)
V , Å ³	5019(3)
Z	4
ρ_{calc} , g cm ⁻³	1.21
μ , cm ⁻¹	6.74
range trans factors	0.8880–0.9982
temp, K	293
$R(F_o)$	0.047
$R_w(F_o)$	0.056

developed by successive cycles of full-matrix, least-squares refinement followed by the calculation of $\Delta\rho$ maps. The neutral atom scattering factors used include corrections for the real and imaginary components of the effects of anomalous dispersion.²¹ One molecule of solvent benzene at full occupancy and one at half-occupancy and disordered about a center of symmetry were located toward the end of the refinement as were a fair number of hydrogen atoms. The latter were included as fixed contributions ($\text{C}-\text{H} = 0.95$ Å) with isotropic thermal displacement parameters 20% larger than those of the attached carbon atoms and updated periodically. The refinement converged without difficulty. All calculations were performed on a VAXstation 3100 computer with the MolEN²² suite of programs. Final refined atomic coordinates are presented in Table 1 while additional crystallographic data are included as supporting information.

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Supporting Information Available: Tables of positional and general displacement parameters, calculated hydrogen positions, and bond lengths and angles (15 pages). Ordering information is available on any current masthead page.

IC950751F

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