Insertion of Alkenyl Sulfides into a Palladium−Aryl Bond. 1. Synthesis and Evolution of a Three-Membered Thiopalladacycle. X-ray Crystal Structure of a New Tetrameric Palladium Derivative with Bridging (Phenylthio)alkyl Ligands

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A three-membered dimeric (phenylthio)alkylpalladacycle (mixture of diastereoisomers) has been synthesized by Pd−C_6F_5 addition to the double bond of phenyl vinyl sulfide. The coordination mode of the organic moiety changes slowly in solution from a chelating σ-κS-yl to a bridging $\mu(\sigma$-κS-yl), and the palladacyclopropane isomerizes to an unusual tetrameric palladium complex; the X-ray crystal structure of this latter derivative has been determined, and it shows that each pair of palladium atoms are linked by either two bridging chlorine atoms or two bridging (phenylthio)alkyl moieties. The tetramer has four chiral carbon atoms and has S_4 symmetry (*meso* form), showing that the crystals are formed stereospecifically from the diastereomeric mixture of dimers. The decomposition pathways of the palladacyclopropane complex have been analyzed. Two main routes have been observed, i.e., (a) 1,2-hydrogen shift and Pd−SR β-elimination, which occurs in refluxing toluene, and (b) hydrolysis of the C−S bond to give an aldehyde and a palladium thiolate, predominant at room temperature in the presence of ligands such as tetrahydrothiophene.

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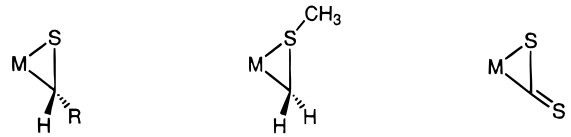
Introduction

Three-membered organometallic metallacycles involving a donor atom bearing a lone pair are not very common in transition metal organometallic chemistry.[1] Among this type of complexes a few examples of sulfur-containing metallacyclopropane structures can be found, such as thioaldehyde metallacycles (A, Chart 1),[2] (methylthio)methyl derivatives (B, Chart 1),[3] and other related (methylthio)metallacyclopropanes.[4] A resonant metallathiocyclopropane structure also contributes to explain the bonding of unsaturated substrates, such as CS_2, to low-valent metal complexes (C, Chart 1).[5a] Three-membered metallacycles are also present in the complexes obtained by coordination of other dithio derivatives, which usually act as bridging ligands in a variety of modes.[5b] In this paper, we describe the preparation of a new three-membered (phenylthio)alkyl palladacycle, synthesized by Pd−aryl addition to the double bond of a vinyl sulfide. Several decomposition routes found for this complex are also analyzed.

Chart 1



A **B** **C**

The (methylthio)methyl moiety has been shown to adopt different coordination modes: monodentate σ-yl; chelating σ-κS-yl (B, Chart 1); or bridging μ-(σ-κS-yl). All these arrangements have been found in palladium chemistry,[3,6−8] and no interconversion between these coordination modes has been reported. Here an unprecedented isomerization of a palladacycle with a chelating σ-κS-yl (phenylthio)alkyl ligand to an oligomer with bridging μ-(σ-κS-yl) ligands is reported.

Results

Synthesis and Characterization of the Palladacycles. The reaction of equimolar amounts of [Pd-

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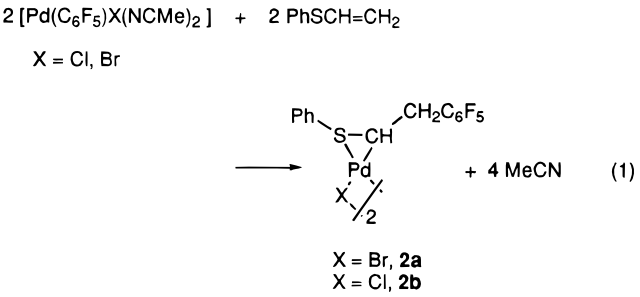
$(C_6F_5)Br(NCMe)_2]$ (**1a**) and phenyl vinyl sulfide in CH_2Cl_2 at room temperature gave complex **2a** (eq 1) as



a yellowish orange solid in high yield (83%). When the reaction was carried out in an NMR tube, in $CDCl_3$, a small amount of the organic derivative, vinylpentafluorobenzene, was also detected (2% based on the integration of the ^{19}F NMR signals of the C_6F_5 group). The reaction was also performed using $[Pd(C_6F_5)Cl(NCMe)_2]$ (**1b**) as starting material, and an analogous complex, **2b**, was obtained (eq 1). **2a**,**b** were identified by ^1H, ^{19}F, ^{13}C NMR and C, H elemental analysis; the corresponding data can be found in the Experimental Section. Since **2a** and **2b** bear the same organometallic ligand and show the same behavior, only the identification and reactions of **2a** will be discussed.

The ^{19}F NMR spectrum of complex **2a** clearly shows that it is a mixture of two isomers in $CDCl_3$ at room temperature (ratio 2.5:1), each showing an ABX system in the ^1H NMR spectrum, which indicates that a $CHCH_2$ moiety is present in both **2a** isomers. Each isomer exhibits two singlets in the aliphatic region of the $^{13}C\{^1H\}$ spectrum that can be assigned to Pf*C*H_2 (δ 27.1 and 24.5 ppm for each isomer) and Pd*C*HS (δ 65.0 and 58.8 ppm for each isomer) in good agreement with the chemical shifts observed for other pentafluorophenyl-substituted alkyl sulfide palladacycles.[9] Thus, after insertion of the double bond into the Pd−C_6F_5 bond, coordination of the S atom gives an unusual three-membered palladacycle. As far as we know, only one other example of this type of palladium complex has been reported.[3a,d,e]

Both the S atom and the C atom in the palladacycle are chiral. This should give rise in the dimeric complex to up to eight diastereoisomers (with their corresponding enantiomers). Besides, the palladacycles can adopt either a trans or a cis arrangement in the dimer, which doubles the number of possible isomers. However, only two distinct diastereoisomers are observed by ^{19}F NMR as two separate sets of signals. The two $^{19}F_{para}$ resonances that appear for **2a** in toluene at room temperature (internal capillary with DMSO-d_6 as lock solvent) convert into one at 70 °C. The ^{19}F NMR of **2a** in CD_3CN at room temperature shows only one isomer. The inversion of the coordinated sulfur atom was found to be fast in the other three-membered palladacycle described, as this inversion process occurs without cleavage of the Pd−S bond.[3e] Thus, if the S-atom racemizes in the NMR time scale, it seems that the two diastereoisomers observed are due to the dimeric nature of the complex. Either the chirality of the carbon or the cis or trans arrangement of the palladacycles in the dimer could produce the two isomers observed. The chemical shift difference between the ^{19}F signals of both isomers (around 0.5 ppm) favors the second possibility, which provides a more different chemical environment for the pentafluorophenyl groups in both isomers. The presence of CD_3CN easily promotes a bridge-splitting process and interconverts the diastereoisomers. The interconversion is more difficult in the poorly coordinating toluene. It seems, then, that the lone pair of the S-atom exhibits little activity as a bridge-splitting promoter. For steric reasons, it is unlikely that the S-atom can act as the promoter of cleavage of the halo bridges of a second dimer unless it decoordinates first. Thus, this "intermolecular" bridge-splitting is associated to a comparatively high energy S-decoordination of the chelate and must be slow (see below, rearrangement to a tetramer).

A yellow solid can be obtained when **2a** is reacted with 2 mol of PPh_3 in CH_2Cl_2 solution (Scheme 1). Its ^{19}F and ^1H NMR spectra indicate that the solid is a mixture of two monomeric isomers, **3a** and **3b**, in a 7.7:1 ratio, which could not be separated. The ^1H NMR spectrum of the mixture shows two ABX systems with a pattern similar to that found for **2a**, and its assignment was made by comparison with the ^1H NMR spectrum of **2a**. The major isomer **3a** was assigned a cis P−Pd−C arrangement on the basis of the small value $^2J_{PC}$ found ($^2J_{PC}$ = 5.6 Hz).[10]

Bromination of 2a. Bromination of **2a** was carried out by adding bromine to a CH_2Cl_2 solution of **2a** at room temperature (Scheme 1). A brown precipitate formed immediately. After 4 h, the brown solid, $PdBr_2$ mixed with a small amount of $[PhSPdBr]_n$ and Pd(0), was separated from a colorless filtrate. After evaporation of the solvent, the oily residue was analyzed by ^1H, ^{19}F NMR, and GC−MS. A mixture of organic derivatives was found: phenyl 1-bromo-2-(pentafluorophenyl)-ethyl sulfide (**4**, 79%), 2-(pentafluorophenyl)acetaldehyde (**5**, 12%), (*E*)-phenyl 2-(pentafluorophenyl)vinyl sulfide (**6**, 7%), and (*Z*)-phenyl 2-(pentafluorophenyl)-vinyl sulfide (**7**, 2%). The ratios in parentheses are based on integration of the ^{19}F NMR signals of the C_6F_5 group. The structure of **4** was confirmed by a $^1H\{^{19}F\}$ decoupling experiment. The ^1H NMR spectrum of **4** shows an ABX pattern, and each signal of the AB system is further split into triplets with a small coupling constant, corresponding to $^4J_{HF}$ involving the F_{ortho} of the C_6F_5 group; this coupling disappears in the $^1H\{^{19}F\}$-decoupled spectrum. The reaction of **2a** with Br_2 to form **4** gives support to the structure of **2a** as a three-membered palladacycle arising from coordination of a sulfur atom and a σ-bonded C to palladium. Attempts at separation of the mixture by preparative TLC (silica sheet) eluting with *n*-hexane gave four pure compounds corresponding to **6** (R_f = 0.60), **7** (R_f = 0.45), **5** (R_f = 0), and a new derivative, 1,1-bis(phenylthio)-2-(pentafluorophenyl)ethane (**8**, R_f = 0.30). No **4** was found. **8** was identified by ^1H, ^{19}F NMR and GC−MS, and its appearance can be attributed to decomposition of **4** to form **8** in the course of operation.

Decomposition Reactions of 2a. Complex **2a** is fairly stable both in the solid state and in chloroform solution. However, decomposition occurs in refluxing toluene. After 16 h, a mixture of organic compounds

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Scheme 1

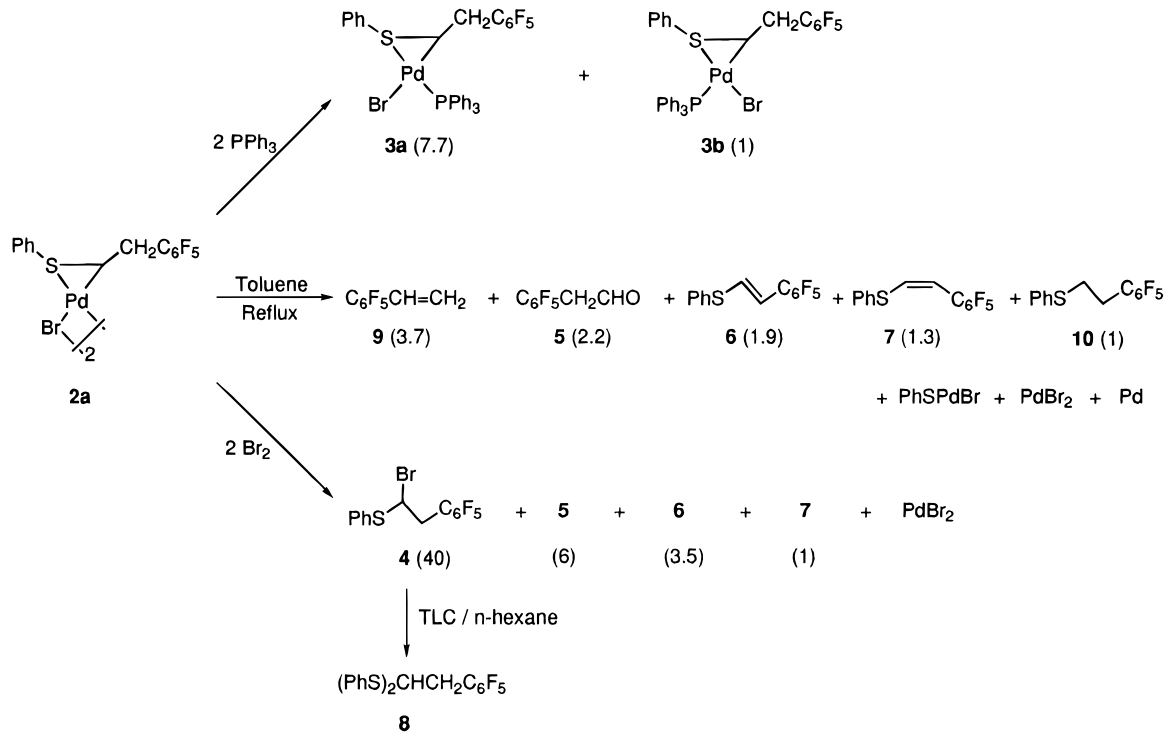

Table 1. Decomposition of 2a in the Presence of tht

entry	additive	time (days)	organic products (ratio)[a]	amount decomposed[a] (%)
1		1	**5**	28
		7	**5** (31), **6** (1)	89
2	$HClO_4-H_2O$[b]	1	**5** (6), **6** (1), **10** (3.5)	87
		7	**5** (7.4), **6** (1), **10** (4.5)	91
3	$KOH-H_2O$[b]	1	**5** (2.7), **6** (1)	11
		7	**5** (3.1), **6** (1)	18

[a] The ratios are based on the integration of ^{19}F NMR signals. [b] One drop of 70% aqueous $HClO_4$ or 1 M aqueous KOH was added in entries 2 and 3, respectively.

had formed: **9**, **5**, **6**, **7**, and phenyl 2-(pentafluorophenyl)ethyl sulfide (**10**), plus a dark brown solid containing $[PhSPdBr]_n$, $PdBr_2$, and Pd metal (Scheme 1). The molar ratios of these organic compounds are 3.7:2.2:1.9:1.3:1 on the basis of integration of ^{19}F NMR signals in toluene (acetone-d_6 was used as external lock solvent). **9** was identified by comparison with a commercial sample. The other C_6F_5-substituted compounds were identified by analyses of ^1H and ^{19}F NMR spectra and GC−MS after evaporation of the toluene.

With the aim of understanding the mechanism of formation of aldehyde **5** from **2a** and how the cleavage of the C−S bond occurs, the decomposition of **2a** in $CDCl_3$ was carried out in the presence of different additives. The addition of a 4-fold amount of tetrahydrothiophene (tht) accelerates the decomposition moderately. Only one isomer is observed on addition of this ligand as a result of cleavage of the bromine bridges by tht. The decomposition reaction was also monitored by ^{19}F NMR spectroscopy in the presence of acid or base at room temperature. The results are given in Table 1.

The addition of acid produces a dramatic acceleration in the decomposition of **2a** (Table 1, entry 2). The major complex is the aldehyde **5**; the products of Pd-H elimination (**6**) and acid attack on the starting complex (**10**) are also found. The addition of base slows down the decomposition process (Table 1, entry 3). Thus, acid attack must play an important role in the hydrolysis (see Discussion).

Characterization of [Pd(μ-Cl){μ-(σ-κ-PhSCHCH$_2$-C$_6$F$_5$)}]$_4$ (11). Careful crystallizations of complexes **2** and **3** were attempted in order to obtain suitable crystals for structural determination by X-ray diffraction analysis. The crystallization was successful only for the chloro-bridged complex **2b**. After 2 months in a mixture of CH_2Cl_2/Et_2O at −20 °C, orange crystals were obtained that correspond to the tetrameric complex [Pd(μ-Cl){μ-(σ-κ-PhSCHCH$_2$C$_6$F$_5$)}]$_4$ (**11**).

The ^{19}F NMR spectrum of **11** in $CDCl_3$ at room temperature shows the presence of only one type of C_6F_5 group, and the ^1H NMR spectrum shows one ABX pattern (δ: $H^1 = 4.62$, $H^2 = 3.30$, and $H^{2'} = 2.19$), which must be the result of the molecular symmetry.

An X-ray diffraction study of **11** was undertaken. Figure 1 shows the molecular structure of the tetrameric complex. Selected bond lengths and bond angles along with their estimated standard derivations are given in Table 2. The complex is tetranuclear with exact crystallographic S_4 symmetry. The four palladium atoms are located at the corners of a tetrahedron. The environment of each palladium atom is square planar with the palladium coordinated by two chlorine, sulfur, and C(1) atoms. The remarkable feature of the molecular structure is that each of the four (phenylthio)methyl groups acts as a bidentate ligand bridging two $Pd_2(\mu\text{-Cl})_2$ units. The S_4 molecular symmetry explains the equivalence observed for the chiral moieties in the tetramer (while they produce diastereoisomers in the dimer), since the molecule is a *meso* form.

The Pd−C bond length in the present complex (2.036 Å) is similar to the distances found for other related structures: [PdCl(σ-κ-CH$_2$SCH$_3$)(PPh$_3$)],[3d] [PdCl(σ-CH$_2$-SCH$_3$)(PPh$_3$)$_2$],[6] [Pd{μ-(σ-κ-CH$_2$SCH$_3$)}$_2$]$_4$,[7] and [Pd$_3$(μ-

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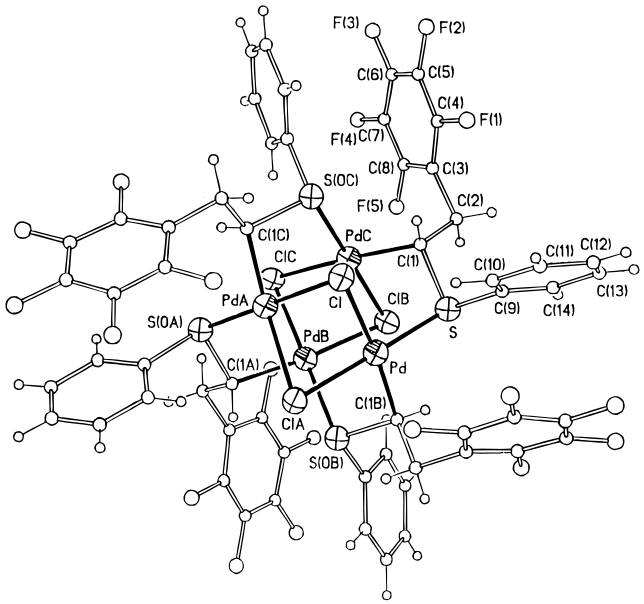

Figure 1. ORTEP plot of complex $[Pd(\mu\text{-}Cl)\{\mu\text{-}(\sigma\text{-}\kappa\text{-}PhSCHCH_2C_6F_5)\}]_4$ (**11**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 11[a]

Pd−C(1B)	2.036(8)	Pd−S	2.308(2)
Pd−Cl(A)	2.392(2)	Pd−Cl	2.469(2)
Cl−Pd(A)	2.392(2)	S−C(1)	1.849(9)
C(1)−Pd(C)	2.036(8)	Pd−Pd(A)	2.917(2)
C(1B)−Pd−S	88.0(3)	C(1B)−Pd−Cl(A)	90.2(3)
S−Pd−Cl(A)	175.17(8)	C(1B)−Pd−Cl	173.1(3)
Pd−S−Cl	98.66(8)	Cl(A)−Pd−Cl	83.28(10)
C(1B)−Pd−Pd(A)	125.2(2)	S−Pd−Pd(A)	123.62(7)
Cl(A)−Pd−Pd(A)	54.36(6)	Cl−Pd−Pd(A)	51.92(6)
Pd(A)−Cl−Pd	73.73(7)	C(1)−S−Pd	103.9(3)
S−C(1)−Pd(C)	106.4(4)		

[a] Symmetry transformations used to generate equivalent atoms: (A) $-x+1+1, -y+1/2, z+1-1$; (B) $y+3/4, -x+5/4, -z+1/4$; (C) $-y+5/4, x-3/4, -z+1/4$.

$O_2CMe)_3\{\mu\text{-}(\sigma\text{-}\kappa\text{-}MeSCHR)\}_3]$,[8] and it is consistent with the expected Pd(II)−C(sp^3) single bond length[11] and that reported for alkylpalladium(II) complexes (2.083 Å).[12] The Pd−S distance found for **11** (2.308 Å) is slightly shorter than those found for the three-membered ring palladacycle present in $[PdCl(\sigma\text{-}\kappa\text{-}CH_2SCH_3)(PPh_3)]$ or for tetrameric complex $[Pd\{\mu\text{-}(\sigma\text{-}\kappa\text{-}CH_2SCH_3)\}_2]_4$, probably due to the lower *trans* influence of the Cl atom compared to PPh_3 or CH_2SPh groups, but it is similar to the Pd−S bond lengths in $[Pd_3(\mu\text{-}O_2CMe)_3\{\mu\text{-}(\sigma\text{-}\kappa\text{-}MeSCHR)\}_3]$ and dialkyl thioethers (2.283 Å).[12] The S−C(1) bond length (1.849 Å) corresponds to the estimated single bond value of the S−C(sp^3) link (1.82 Å) and is similar to that found in the complex $[Pd\{\mu\text{-}(\sigma\text{-}\kappa\text{-}CH_2SCH_3)\}_2]_4$; however, it is longer than the corresponding distance in $[PdCl(\sigma\text{-}\kappa\text{-}CH_2SCH_3)(PPh_3)]$ and $[Pd_3(\mu\text{-}O_2CMe)_3\{\mu\text{-}(\sigma\text{-}\kappa\text{-}MeSCHR)\}_3]$. The S−Pd−C angle in complex **11** is in the normal value range found for a palladium square-planar structure. The existence of two distinct Pd−Cl bond lengths can be attributed to the different *trans* influence of the ligands, the longer (2.469 Å) being found for the Cl *trans* to the σ-bonded carbon and the shorter (2.392 Å) corresponding to the Cl *trans* to coordinated sulfur atom. The distance between each pair of palladium atoms in $Pd_2(\mu\text{-}Cl)_2$ units is 2.917 Å, which is shorter than twice the covalent radius of Pd (*viz.* 2.98 Å),[13] but longer than that found in elemental palladium (2.751 Å).[14] Thus, direct interaction between the palladium atoms is unlikely. Similar Pd−Pd distances (2.864−2.946 Å) have been observed in multinuclear palladium complexes containing bridging acetate groups.[15] The shorter Pd−Pd distance in complex **11** is a result of considerable folding of the $Pd_2(\mu\text{-}Cl)_2$ rings; that is, the chlorine bridge is bent, which is a reflection of ligand interactions and steric requirements.

Discussion

Addition of Pd−C_6F_5 to the double bond of phenyl vinyl sulfide produces a three-membered thiometallacycle of high stability, **2**. A resonance hybrid C═S ↔ C−S has been suggested to play a role in stabilizing this type of three-membered ring palladium complexes.[16] We could not determine the value of the S−C distance in our palladacycles, but a S−C bond length (1.756 Å) slightly shorter than the estimated S−C single bond length (1.82 Å) has been found in the structural determination of the other palladium thiometallacyclopropane complex reported in the literature, thus supporting the above-mentioned proposal.[3a,d]

The μ-(σ-κ) coordination mode for the alkylthio moiety, less strained, seems to give complexes thermodynamically more stable than those bearing the chelating form of the ligand as shown by the slow interconversion of complex **2b** to the tetranuclear complex **11**. The inversion of the coordinated S atom is known to be fast and does not need decoordination. This leaves the carbon atom as the only chiral center to be considered. Its chirality, however, is enough to allow us to recognize two different mechanisms in the rearrangement of complex **2b**, which are shown in Scheme 2.

The first one concerns the interconversion of the dimers, which are formed in a nonstereoselective fashion and give rise to diastereoisomers. For their interconversion bridge splitting to give monomers is enough. This splitting is a very fast process when it is assisted by coordinating solvents (such as CD_3CN) and much slower when the solvent is only poorly coordinating (toluene, $CDCl_3$). Whether the process becomes dissociative in the latter has not been investigated.

The second process, formation of the tetramer from the dimers, occurs, and only the meso form is obtained stereoselectively; the process is extremely slow. This process involves necessarily the following steps: (i) S-decoordination, since the C−S chelating ligand has to change to C−S bridging (we believe that the low rate of the process is associated to the high activation energy of this step) and (ii) splitting of the chloro bridges, since a direct dimerization of the dimers should produce diastereomeric tetramers and this is not observed.

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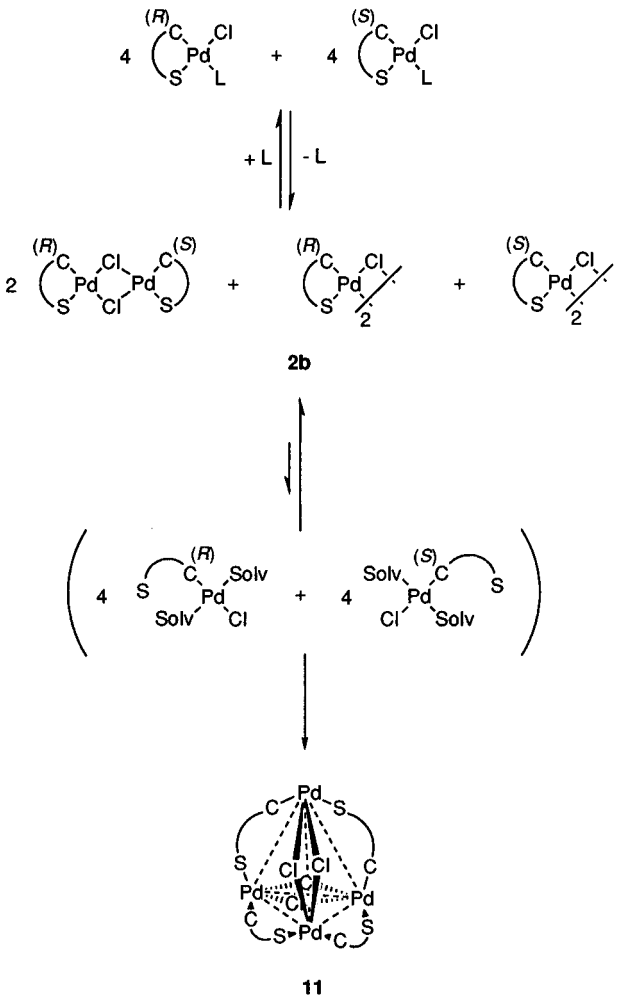
Scheme 2

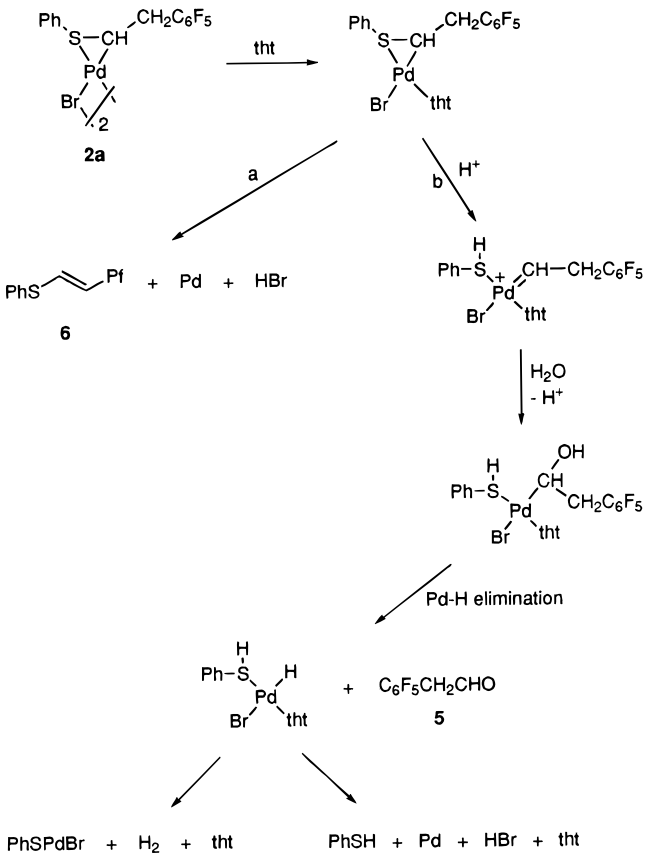


In order to stress the need for both processes, and for the sake of conciseness, monomeric bridge-split and S-decoordinated species are drawn in Scheme 2. Obviously they are statistically and thermodymamically very unlikely. It seems more reasonable that dimeric species with chloro bridges and only one decoordinated S atom use this atom to attack a second dimeric species and promote its bridge splitting and so on.

The extreme slowness of the process makes the stereoselection possible, in spite of the fact that the difference in energy between the meso form and other possible tetramers is likely to be small. Probably for steric reasons, the meso form is the thermodynamic product of the reaction.

Although complex **2a** is quite stable, its decomposition occurs when refluxed in toluene or slowly at room temperature in the presence of ligands such as tht. The main decomposition pathway for this complex in refluxing toluene gives vinylpentafluorobenzene (**9**) by a one-step Pd-migration to the C_6F_5-substituted carbon and β-SR elimination.[17] However, at room temperature in the presence of tht the main decomposition pathway is different and, although it also involves cleavage of C−S bond in the three-membered palladium complex, gives aldehyde **5** as the main product (Scheme 3). Interestingly, **5** is not a product of the Wacker oxidation of **9**

Scheme 3



since terminal olefins give ketones as the only product.[18] In the presence of tht the decomposition of **2a** to aldehyde is dramatically accelerated by acid, which suggests that the protonation of the sulfur atom occurs in the first step.[19] The hydrolytic mechanism is outlined in Scheme 3 and it is consistent with our results. Protonation of the S-atom and opening of the three-membered ring through C−S bond cleavage generates an intermediate palladium alkylidene that undergoes nucleophilic attack by OH^-.[4,19−21] Pd−H elimination at this point produces the aldehyde. At the same time, Pd−H elimination in complex **2a** with no C−S cleavage also occurs to generate C_6F_5-substituted alkenyl sulfide **6** as a minor product (path a, Scheme 3). Another possible and perhaps competitive decomposition pathway of the intermediate Pd alkylidene is the direct oxidation by oxygen, which is a process known for other transition metal carbene complexes.[22] In fact, the reaction slows down noticeably in the absence of oxygen but still occurs. The addition of tht promotes the aldehyde formation, but its role is unclear. Coordination of this ligand to the metal by bridge cleavage could reduce the amount of donation of the (phenylthio)alkyl sulfur to the metal; this would make the sulfur atom more prone to acid attack, which would trigger the

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process. Attempts at producing the aldehyde catalytically by reaction of the Pd hydride formed with phenyl vinyl sulfide have proved unsuccessful up to now.

Experimental Section

General Comments. ^{19}F, ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AC-300 and ARX-300 instruments. Chemical shifts are reported in δ units (parts per million, ppm) downfield from Me_4Si for ^{1}H and ^{13}C, $CFCl_3$ for ^{19}F, and H_3PO_4 (85% in aqueous solution, external reference) for ^{31}P. Carbon and hydrogen analyses were carried out on a Perkin-Elmer 2400 CHN elemental analyzer.

All solvents were dried and distilled before use by standard methods. Phenyl vinyl sulfide was purchased from Aldrich. $[Pd(C_6F_5)Br(NCMe)_2]$ was prepared as previously reported.[23]

Preparation of $[Pd(C_6F_5)Cl(NCMe)_2]$ (1b). Freshly prepared, wet AgCl (1 g, 6.9 mmol) was added to a solution of **1a** (1 g, 2.3 mmol) in acetonitrile (10 mL). The suspension was stirred for 72 h in the dark. The yellow precipitate that had formed was filtered through Celite, and the yellow-orange solution was evaporated to dryness. The residue was dissolved in CH_2Cl_2 and filtered through $MgSO_4$. MeCN (0.5 mL) was added to the filtrate, and the solution was evaporated to ca. 2 mL; Et_2O (5 mL) was added, and a yellow solid was obtained that was filtered, washed with Et_2O, and air dried (0.54 g, 60% yield). A second batch can be obtained by adding Et_2O (2 mL) to the mother liquors and cooling (0.1 g, 11% yield).

1b: ^{19}F (CD_3CN, δ, 282 MHz) -161.1 (m, F_{meta}), -157.2 (t, $J = 19.5$ Hz, F_{para}), -117.5 (m, F_{ortho}); ^{1}H NMR (CD_3CN, δ, 300 MHz) 2.15 (s); IR (Nujol mull, cm^{-1}) 2336 (w, ν CN), 2323 (s, ν CN), 2309 (w, ν CN), 2296 (s, ν CN), 344 (s, ν PdCl). Anal. Calcd for $C_{10}H_6ClF_5N_2Pd$: C, 30.71; H, 1.53; N, 7.16. Found: C, 30.90; H, 1.50; N, 6.92.

Preparation of 2a. Phenyl vinyl sulfide (0.060 mL, 0.459 mmol) was added to a solution of $[Pd(C_6F_5)Br(NCMe)_2]$ (0.200 g, 0.459 mmol) in CH_2Cl_2 (5 mL). After 2 h of stirring, activated carbon was added to the dark yellow solution, and the solution was filtered. The filtrate was concentrated to 2 mL, and *n*-hexane (1 mL) was added. A yellowish orange solid **2a** was isolated (0.186 g, 83% yield).

2a: ^{19}F ($CDCl_3$, δ, 282 MHz) $-162.0/-162.7$* (b, F_{meta}), $-156.0/-156.5$* (b, F_{para}), $-142.7/-142.4$* (b, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 300 MHz) 8.0−7.4 (m, 5H, Ph), 4.1 (b, 1H, CH), 3.21/2.69* (b, 1H, $J = 14.7$ Hz, CH_2Pf), 2.99/2.38* (b, 1H, $J = 14.7$ Hz, CH_2Pf); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ, 75.4 MHz), 144.7 (bd, $^{1}J_{CF} = 244$ Hz, C_6F_5), 140.0 (bd, $^{1}J_{CF} = 240$ Hz, C_6F_5), 137.2 (db, $^{1}J_{CF} = 252$ Hz, C_6F_5), 132.4 (Ph), 131.2 (C^1-Ph), 130.4 (Ph), 129.7 (Ph), 112.0 (b, C_6F_5), 65.0/58.8* (C^1), 27.1/24.3* (C^2). Anal. Calcd for $C_{28}H_{16}Br_2F_{10}Pd_2S_2$: C, 34.35; H, 1.65. Found: C, 34.06; H, 1.69.

2b was prepared in a similar way but using the chloro derivative **1b** as starting material.

2b: ^{19}F ($CDCl_3$, δ, 282 MHz), $-162.1/-162.7$* (b, F_{meta}), $-156.0/-156.5$* (b, F_{para}), $-142.7/-142.5$* (b, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 300 MHz) 8.0/7.8* (m, 2H, Ph), 7.5/7.4* (m, 3H, Ph), 4.03 (b, 1H, CH), 3.12/2.60* (b, 1H, CH_2Pf), 2.95/2.30* (b, 1H, CH_2Pf). Anal. Calcd for $C_{28}H_{16}Cl_2F_{10}Pd_2S_2$: C, 37.77; H, 1.81. Found: C, 37.33; H, 1.80.

*: value for the minor diastereoisomer.

Preparation of 3. Complex **2a** (0.300 g, 0.306 mmol) dissolved in CH_2Cl_2 (10 mL) was mixed with PPh_3 (0.161 g, 0.612 mmol). After 30 min the yellow solution was evaporated to 0.5 mL, and ether (5 mL) was added. A yellow solid formed (0.419 g, 91% yield). Analysis of ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra indicated that the yellow solid was a mixture of two isomers **3a** and **3b** in a ratio of 7.7 to 1.

3a and **3b.** Anal. Calcd for $C_{32}H_{23}BrF_5PPdS$: C, 51.12; H, 3.08. Found: C, 50.74; H, 3.08.

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3a: ^{19}F ($CDCl_3$, δ, 282 MHz) -161.6 (m, F_{meta}), -155.9 (t, F_{para}), -142.9 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 300 MHz),7.7−7.3 (m, 20H, Ph), 3.96 (dd, 1H, $J = 11.6$, 3.3 Hz, CH), 2.68 (dd, 1H, $J = 14.5$, 11.6 Hz, CH_2Pf), 2.17 (bd, 1H, $J = 14.5$ Hz, CH_2Pf); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ, 75.4 MHz) 144.3 (bd, $^{1}J_{CF} = 246$ Hz, C_6F_5), 140 (bd, $^{1}J_{CF} = 242$ Hz, C_6F_5), 137.3 (bd, $^{1}J_{CF} = 253$ Hz, C_6F_5), 128−134 (4Ph), 113.7 (t, $^{2}J_{CF} = 18.8$ Hz, C_6F_5), 71.1 (d, $^{2}J_{PC} = 5.6$ Hz, C^1), 25.8 (d, $^{3}J_{PC} = 4.0$ Hz, C^2); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ, 121.4 MHz), 31.9 (s).

3b: ^{19}F ($CDCl_3$, δ, 282 MHz) -162.7 (m, F_{meta}), -156.6 (t, F_{para}), -142.1 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 300 MHz) 7.7−7.3 (m, 20H, Ph), 4.17 (bd, 1H, CH), 2.50 (bt, 1H, CH_2Pf), 1.99 (bd, 1H, CH_2Pf); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ, 121.4 MHz) 30.7 (s).

Decomposition of 2a. A solution of **2a** (0.060 g, 0.061 mmol) in toluene (15 mL) was refluxed for 16 h. Analysis of the ^{1}H and ^{19}F NMR spectra and GC−MS showed that the decomposition took place to generate a mixture of organic compounds **9**, **5**, **6**, **7**, and **10** in a ratio of 3.7:2.2:1.9:1.3:1 plus a red brown solid, mainly $[PhSPdBr]_n$.

5: ^{19}F NMR ($CDCl_3$, δ, 282 MHz) -162.3 (m, F_{meta}), -154.9 (t, F_{para}), -142.4 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 300 MHz) 9.77 (b, 1H, C*H*O), 3.88 (b, 2H, PfCH_2); MS (El) *m*/*z* (relative intensity) 210 (M^+, 31), 181 (100), 161 (24), 132 (19), 93 (17).

6: ^{19}F NMR ($CDCl_3$, δ, 282 MHz) -163.3 (m, F_{meta}), -157.5 (t, F_{para}), -144.2 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 300 MHz) 7.3−7.5 (m, 5H, Ph), 7.35 (d, $J = 15.9$ Hz, 1H, PfCH=C*H*), 6.42 (d, $J = 15.9$ Hz, 1H, Pf*CH*=CH); MS (El) *m*/*z* (relative intensity) 302 (M^+, 79), 301 (31), 181 (41), 135 (47), 123 (30), 110 (32), 109 (36), 91 (44), 77 (77), 69 (42), 65 (43), 51 (100), 50 (39).

7: ^{19}F NMR ($CDCl_3$, δ, 282 MHz) -163.0 (m, F_{meta}), -155.7 (t, F_{para}), -138.6 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 300 MHz) 7.3−7.55 (m, 5H, Ph), 6.87 (d, $J = 9.0$ Hz, 1H, PfCH=C*H*), 6.35 (bd, $J = 9.0$ Hz, 1H, Pf*CH*=CH); MS (El) *m*/*z* (relative intensity) 302 (M^+, 72), 301 (29), 181 (34), 135 (49), 123 (33), 110 (34), 91 (48), 77 (72), 69 (45), 65 (47), 51 (100), 50 (37).

10: ^{19}F NMR ($CDCl_3$, δ, 282 MHz) -162.9 (m, F_{meta}), -157.0 (t, F_{para}), -143.8 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 300 MHz) 7.3−7.5 (m, 5H, Ph), 3.13 (m, $J = 7.3$ Hz, 2H, PfCH_2CH_2), 3.01 (t, $J = 7.3$ Hz, 2H, PfCH_2CH_2); MS (El) *m*/*z* (relative intensity) 304 (M^+, 40), 181 (13), 123 (100), 109 (14), 77 (20), 69 (14), 65 (18), 51 (21), 45 (23).

Decomposition of 2a in the Presence of tht and Other Additives. Three NMR tubes were charged with **2a** (0.020 g, 0.0204 mmol), tht (0.0072 mL, 0.0816 mmol), and $CDCl_3$ (0.6 mL). $HClO_4$ (1 drop 70% aqueous solution) and KOH (1 drop, 1 M aqueous solution) were added to the second and third tubes, respectively. The reactions were monitored by ^{19}F NMR for 2 weeks.

Reaction of 2a with Br_2. To a solution of **2a** (0.040 g, 0.0408 mmol) in CH_2Cl_2 (5 mL) was added Br_2 (0.0042 mL, 0.0816 mmol). A brown precipitate formed immediately ($PdBr_2$). One h later the suspension was filtered and the filtrate was evaporated to dryness. A light yellow oily residue was obtained, which was a mixture of **4** (79%), **5** (12%), **6** (7%), and **7** (2%) by analysis of ^{1}H and ^{19}F NMR spectra and GC−MS. The rates in parentheses are based on the integration of ^{19}F NMR signals. Separation of these compounds by silica gel preparative TLC was performed using *n*-hexane as eluent; four batches corresponding to compounds **6** ($R_f = 0.60$), **7** ($R_f = 0.45$), **5** ($R_f = 0$), and a new derivative **8** ($R_f = 0.30$) were obtained. **4** was not found after the chromatographic separation.

4: ^{19}F NMR ($CDCl_3$, δ, 282 MHz) -162.2 (m, F_{meta}), -155.0 (t, F_{para}), -142.0 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 300 MHz) 7.5 (m, 2H, Ph), 7.4 (m, 3H, Ph), 5.45 (dd, $J = 8.9$, 6.4 Hz, 1H, PfCH_2CH), 3.60 (dd, $J = 14.6$, 6.4 Hz, 1H, PfC*H*H′CH), 3.56 (dd, $J = 14.6$, 8.9 Hz, 1H, PfCH*H*′CH); MS (El) *m*/*z* (relative intensity) 382 [$M^+(Br^{81}) - 2$, 12], 380 [$M^+(Br^{79}) - 2$, 12], 301 (7), 237 (10), 192 (47), 142 (18), 122 (22), 109 (87), 77 (85), 69 (44), 65 (63), 51 (100).

8: ^{19}F NMR ($CDCl_3$, δ, 282 MHz) -162.9 (m, F_{meta}), -156.1 (t, F_{para}), -142.2 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 300 MHz) 7.4

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(m, 4H, Ph), 7.3 (m, 6H, Ph), 4.64 (t, J = 7.8 Hz, 1H, PfCH$_2$C*H*), 3.25 (bd, J = 7.8 Hz, 2H, PfC*H*$_2$CH); MS (El) m/z (relative intensity) 412 (M^+, 2), 303 (20), 181 (10), 135 (39), 109 (100), 77 (11), 69 (10), 65 (27), 51 (12).

Crystal Structure Determination of 11. Crystals of **11** suitable for X-ray diffraction analysis were obtained by maintaining a solution of **2b** in a mixture of CH_2Cl_2 and Et_2O (1/2) at low temperature for 2 months. The appropriate crystal of **11** was glued at the end of a glass fiber with epoxy adhesive. All diffraction measurements were made at room temperature on a Siemens R3m diffractometer using graphite-monochromated Mo Kα X-radiation. Unit cell dimensions were determined from 28 centered reflections in the range $15.0 < 2\theta < 30.0°$. Diffracted intensities were measured in a unique octant of reciprocal space for $3.0 < 2\theta < 50.0°$ by ω Wyckoff scans. Three check reflections (8 3 1, −3 8 −1, and 2 4 10) remeasured after every 100 ordinary data showed no decomposition of the crystal and a variation of *ca.* ±2% over the period of data collection. Of the 3052 intensity data (other than checks) collected, 2674 unique observations remained after averaging of duplicate and equivalent measurements and deletion of systematic absences (R_{int} 0.036); of these, 1705 had $I > 2\sigma(I)$. An absorption correction was applied based on 272 azimuthal scan data (maximum and minimum transmission coefficients were 0.264 and 0.229). Lorentz and polarization corrections were applied.

The structure was solved by Patterson and Fourier methods and refined using the SHELXL-93 program.[24] All non-hydrogen atoms were assigned anisotropic displacement parameters. All hydrogen atoms were constrained to idealized geometries and their positions refined riding on their parent carbon atoms with a common thermal isotropic parameter. Full-matrix least-squares refinement on F^2 of this model (200 parameters) converged to final residual indices $R_1 = 0.061$, $wR_2 = 0.114$, [for the reflections $I > 4s(F)$], $S = 1.52$ [$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]^{1/2}$; $S = [\sum w(F_o^2 - F_c^2)^2/(\text{no. ref} - \text{no. par.})]^{1/2}$]. Weights, w, were set equal to $[\sigma_c^2(F_o^2) + (gP)^2]^{-1}$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$ and g = 0.03. Final difference electron density maps showed no features outside the range +0.98 to −0.93 e Å^{-3}, the biggest being close to the Pd atom (<1 Å). Crystal data and structure refinement for **11** are collected in Table 3.

11: ^{19}F NMR ($CDCl_3$, δ, 282 MHz) −162.0 (m, F_{meta}), −155.5 (t, F_{para}), −142.4 (b, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 300 MHz) 7.4−7.7 (m, 5H, Ph), 4.62 (dd, J = 11.5, 3.8 Hz, 1H, SCH), 3.31 (dd, J = 13.9, 11.5 Hz, 1H, PfC*H*H′), 2.20 (dd, J = 13.9, 3.8 Hz, 1H, PfCH*H*′).

(24) SHELXTL version 5.03, Siemens Analytical Xray, Madison, WI, 1994.

Table 3. Crystal Data and Structure Refinement for 11

emp formula	$C_{56}H_{32}Cl_4F_{20}Pd_4S_4$
formula wt	1780.46
T (K)	293
wavelength (Å)	0.71073
cryst syst	tetragonal
space grp	$I4_1/a$
unit cell dimens	a = 16.849(3) Å, α = 90° b = 16.849(3) Å, β = 90° c = 21.400(3) Å, γ = 90°
volume (Å^3)	6068(2)
Z	8
density (calcd) (Mg/m^3)	1.949
absorp coeff (mm^{-1})	1.580
F(000)	3456
cryst size (mm)	0.30 × 0.15 × 0.15 mm
θ range for data collectn (deg)	1.54−24.98
index ranges	$0 \le h \le 20$, $0 \le k \le 20$, $0 \le l \le 25$
reflns collected	2874
indept reflns	2674 [R(int) = 0.0355]
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	2673/0/200
goodness-of-fit on F^2	1.517
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0612, wR_2 = 0.1142 (1705 data)
largest diff peak and hole (e Å^{-3})	0.985 and −0.929

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Supporting Information Available: Tables of atomic coordinates and isotropic displacement parameters, complete bond lengths and angles, and anisotropic displacement parameters (5 pages). Ordering information is given on any current masthead page.

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