# Insertion of Alkenyl Sulfides into a Palladium−Aryl Bond. 2. Stabilization of σ-yl-κS Chelates and Decomposition Reactions through C−S Cleavage

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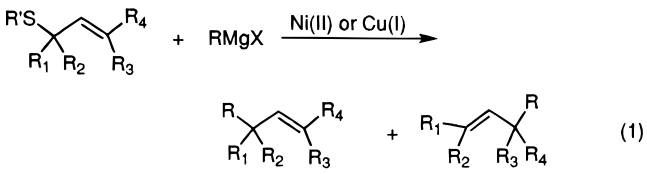
The reaction of $[Pd(C_6F_5)Br(NCMe)_2]$ with the allylic sulfides $R^1SCH_2CH{=}CH_2$ ($R^1 = -CH_2CH{=}CH_2$, Me), *n*-BuSCHMeCH=$CH_2$, and *n*-$BuSCH_2CH{=}CHMe$ results in insertion of the double bond into the Pd−$C_6F_5$ bond and β-SR elimination (C−S cleavage) to give the corresponding (pentafluorophenyl)alkenes and a palladium thiolate. With alkenyl sulfides of longer carbon chains $RS(CH_2)_nCH{=}CH_2$ (R = *n*-Bu, Ph; *n* = 2, 3) five-membered (*n* = 2, **13**, **14**) or six-membered (*n* = 3, **16**, **17**) σ-yl-κS-palladacycles were obtained. The six-membered derivatives isomerize to the corresponding five-membered palladacycles (**18**, **19**) by one-step Pd-migration (Pd−H elimination−readdition). Inversion of the coordinated sulfur is observed in these derivatives, and the dynamic process has been studied for the monomeric complexes [(σ-κS-(Rthio)alkyl)Pd(acac)] (**13b**, **14b**, **18b**, **19b**). $\Delta G^{\ddagger}_{Tc}$ values show that the S-inversion is easier for the Ph-substituted than for the *n*-Bu-substituted complexes. The decomposition of the σ-yl-κS palladacycles occurs through Pd-migration and, when Pd and S are placed three bonds apart in the chain, β-SR elimination; this is the same process observed in the reaction of $[Pd(C_6F_5)Br(NCMe)_2]$ with allylic sulfides. Double bond isomerization of the (pentaflurophenyl)alkene products formed in the decomposition reactions is observed, catalyzed by "Pd−H" intermediates. Double pentafluorophenyl arylation is also observed in some cases.

## Introduction

Alkenyl sulfides have been used as substrates in Heck-type reactions to give substituted unsaturated derivatives.[1−6] C−S bond cleavage has been observed in the reaction of vinyl and allylic sulfides with Grignard or organomercuric reagents catalyzed by Ni(II),[1,4,6] Pd(II),[1,5] and Cu(I)[2,3] compounds. In some cases, both the terminal olefin and the C−S bond of allylic sulfides have been directly attacked by alkyl or aryl groups from the Grignard reagents, and a mixture of organic compounds were obtained (eq 1).[1−3] However, the selective attack to either the terminal double bond[3] or C−S bond[3,4−6] in allyl and vinyl sulfides has also been reported.




(1)

On the other hand, alkenyl sulfides are potential chelating ligands toward palladium. Five and a half-membered palladacycles with $\eta^2$-ene-κS butenyl sulfides as ligands have been prepared.[7−10] Three-membered[11−13] or five-membered[14−18] σ-yl-κS (alkylthio)alkylpalladium derivatives are also known. Thus, alkenyl sulfides are suitable substrates to study the Heck reaction in detail, and since S is a good donor atom for Pd, after insertion of the double bond into the Pd−R bond the stabilization of intermediates through S-coordination may be possible.

In this work, the stable arylating reagent $[Pd(C_6F_5)Br(NCMe)_2]$ is reacted with $RS(CH_2)_nCH{=}CH_2$ (R = *n*-Bu, Ph, $-CH_2CH{=}CH_2$; *n* = 1−3). As already described, the simplicity of the $^{19}F$ NMR spectral pattern of the pentafluorophenyl group makes of this technique a convenient tool to investigate the fate of the intermediates formed after insertion of the double bond

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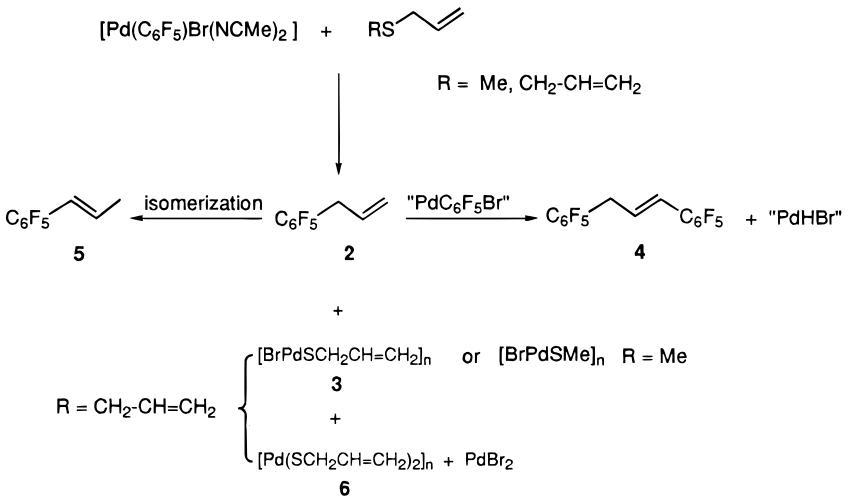
**Table 1. Reactions of [Pd($C_6F_5$)Br($NCMe)_2$] with Allylic Sulfides**

| entry | sulfide | Pd($C_6F_5$)Br/sulfide | organic products (molar ratio) | palladium products |
|---|---|---|---|---|
| 1 | diallyl sulfide | 1/1 | **2** (33), **4** (9), **5** (1) | **3**, **6**, $PdBr_2$, PdS, Pd |
| 2 | diallyl sulfide | 2/1 | **2** (9), **4** (7.5), **5** (1) | $PdBr_2$, PdS, Pd |
| 3 | allyl methylsulfide | 1/1 | **2** (2.5), **4** (2.6), **5** (1) | $[MeSPdBr]_n$, $PdBr_2$, PdS, Pd |

**Scheme 1**



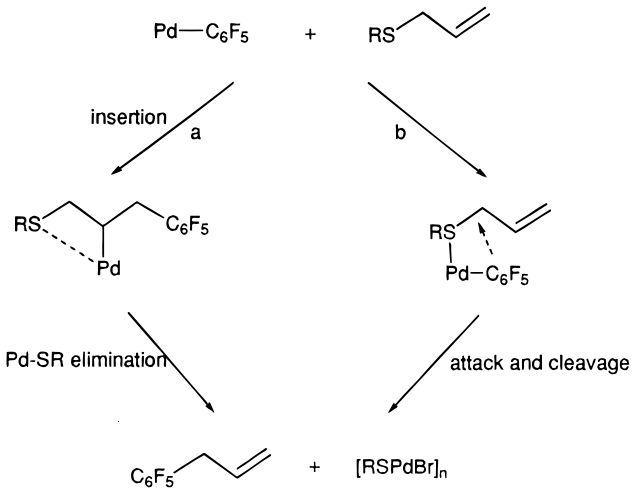

into the Pd−$C_6F_5$ bond.[19] Six- and five-membered $\sigma$-yl-$\kappa S$ chelating complexes are detected or isolated and their isomerization and final decomposition is analyzed, thus gaining insight into the mechanism of C−S bond cleavage.

## Results

**Reactions with Allyl Sulfides.** The reactions of diallyl sulfide or allyl methyl sulfide with [Pd($C_6F_5$)Br($NCMe)_2$] give products resulting from C-S bond cleavage (Scheme 1). The reactions proceed through coordination of the unsaturated substrate to Pd(II) followed by insertion of the double bond into the Pd$C_6F_5$ moiety and then $\beta$-elimination of a Pd thiolate. The experiments were carried out with different reactant ratios, and the results are given in Table 1. The organic products were identified by $^{19}F$ and $^1H$ NMR and GC−MS and also, when solids, by elemental analysis. All these data are given in the Experimental Section.

When equimolar amounts of [Pd($C_6F_5$)Br($NCMe)_2$] (**1**) and allyl sulfide are mixed in $CH_2Cl_2$ (Scheme 1), allyl pentafluorobenzene (**2**) and $[BrPdSCH_2CH{=}CH_2]_n$ (**3**) are formed as major compounds. Part of **2** undergoes further arylation by "Pd($C_6F_5$)Br" to give 1,3-bis(pentafluorophenyl)-1-propene (**4**), which was isolated as a white solid. A small amount of *trans*-1-(pentafluorophenyl)-1-propene (**5**) was found. It was formed by isomerization of **2** catalyzed by Pd−H generated under the reaction conditions (the final step in the formation of the bisaryl derivative **4** is Pd−H elimination). Bis(allenethiolato)palladium (**6**) was obtained as orange crystals, and its formation can be explained by exchange between molecules of compound **3** to give **6** and $PdBr_2$. As shown in Table 1, when the Pd:allyl-moiety ratio increases the amount of compound **4** formed clearly rises (**4** amounts to 43% of organic products in entry 2 and 43% in entry 3 versus 21% in entry 1). Moreover, the allyl-containing palladium complexes **3** and **6** disappear as a result of total reaction with "Pd($C_6F_5$)Br". Compounds **3** and $[MeSPdBr]_n$ are very insoluble, and it was not possible to separate them from PdS, $PdBr_2$, and Pd also formed in the reactions; their $^1H$ NMR spectra were recorded in DMSO-$d_6$ as solvent, where they are soluble.

**Scheme 2**




The observed C−S bond cleavage could occur either by Pd$C_6F_5$ addition to the double bond and subsequent $\beta$-elimination of Pd−S or by direct attack of the $C_6F_5$ group to the C−S bond (Scheme 2). In order to clarify the mechanism of this process, the reactions with *n*-butyl 1-buten-3-yl sulfide and *n*-butyl but-2-enyl sulfide were studied since the final products obtained will depend on the reaction mechanism. The reactions of these organic sulfides with equimolar amounts of [Pd($C_6F_5$)Br($NCMe)_2$] were carried out in $CDCl_3$ in NMR tubes.

With *n*-butyl 1-buten-3-yl sulfide (Scheme 3) 50% conversion was observed after 3 h, and the elimination products (*E*)-1-(pentafluorophenyl)-2-butene (**7**) and (*Z*)-1-(pentafluorophenyl)-2-butene (**8**) were found in a ratio **7**:**8** = 4:1 by $^{19}F$ NMR analyses. After 1 day the reaction

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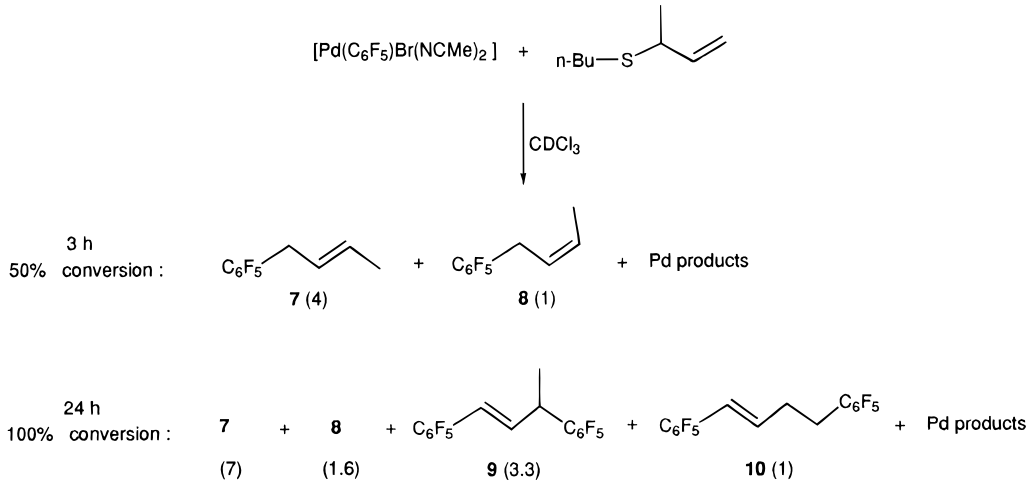
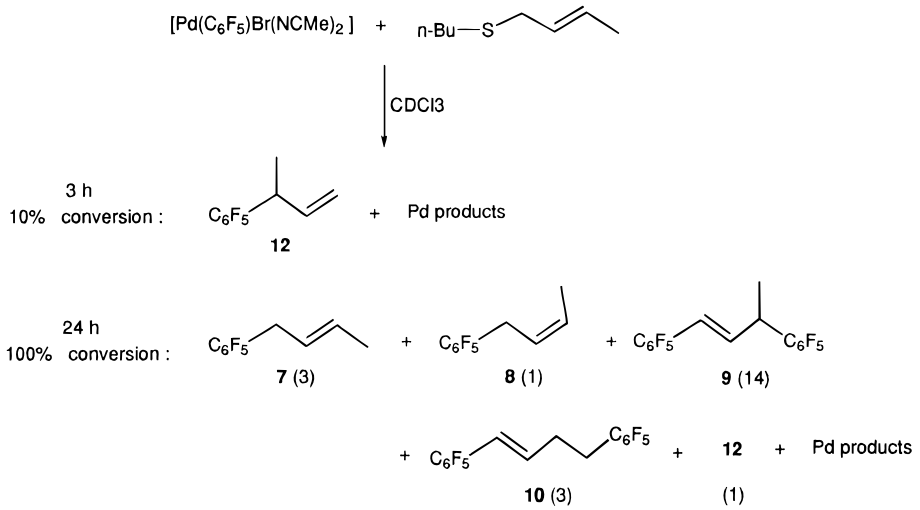
**Scheme 3**




**Scheme 4**




was complete, and a mixture of organic compounds **7**, **8**, (*E*)-3-methyl-1,3-bis(pentafluorophenyl)-1-propene (**9**), and (*E*)-1,4-bis(pentafluorophenyl)-1-butene (**10**) was obtained (ratio: 7:1.6:3.3:1). The formation of bis(pentafluorophenyl) compounds is due to reaction of **7** or the putative 4-(pentafluorophenyl)-1-butene (**11**, formed from isomerization of **7**) with "Pd($C_6F_5$)Br" synthons.

The reaction of *n*-butyl but-2-enyl sulfide with [Pd($C_6F_5$)Br($NCMe)_2$] (Scheme 4) showed 10% conversion after 3 h and gave only 3-methyl-3-(pentafluorophenyl)-1-propene (**12**), derived from olefin insertion into the Pd−$C_6F_5$ bond and subsequent $\beta$-SR elimination. After 24 h, compounds **7**, **8**, **9**, **10**, and **12** had been formed (ratio: 3:1:14:3:1). Since the reaction is slow and there is a large amount of unreacted "Pd($C_6F_5$)Br" synthons, most of **12** was easily pentafluoroarylated to afford **9**. The final step in this reaction, Pd−H elimination to give the alkene, generates significant amounts of "PdHBr" species, which probably react with the starting *n*-Bu$SCH_2CH{=}CHCH_3$ and add to the double bond with subsequent cleavage of the C−S bond to generate $CH_3$-$CH_2CH{=}CH_2$; this product can react with "Pd($C_6F_5$)-Br" species and lead to the formation of **7**, **8**, and **10**. The reaction is slower than the corresponding of *n*-butyl 1-buten-3-yl sulfide, probably due to the higher substitution of the double bond, and secondary reactions such as the Pd−H addition described become important.

These results support mechanism a in Scheme 2 for the cleavage of the carbon−sulfur bond in the reaction of allylic sulfides with "Pd($C_6F_5$)Br" synthons: insertion of the olefin double bond into the Pd−$C_6F_5$ bond to give an unstable alkyl palladium complex followed by elimination of the Pd−SR group at the $\beta$-position. The insertion−SR elimination mechanism has been found in the reaction of allylic aryl sulfides with $RhH(PPh_3)_4$.[20] The $\beta$-SR elimination promoted by nickel has also been reported.[21]

**Reactions with But-3-enyl Sulfides.** Complexes **13a** and **14a** are easily prepared in good yields by reaction of [Pd($C_6F_5$)Br($NCMe)_2$] with the corresponding butenyl sulfides, as shown in Scheme 5.

To clarify some features of the NMR spectra of these two derivatives (see below), their corresponding monomeric acetylacetonato complexes **13b** and **14b** were obtained by treatment of the dimers with Tl(acac).

Tables 2 and 3 collect the $^{19}F$ and $^1H$ NMR data of complexes **13a**, **13b**, **14a**, **14b**, and other derivatives prepared from other alkenyl sulfides, which will be discussed in the following sections. The $^1H$ NMR spectra were assigned with the help of homonuclear $^1H$ COSY and decoupling experiments when necessary.

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**Scheme 5**

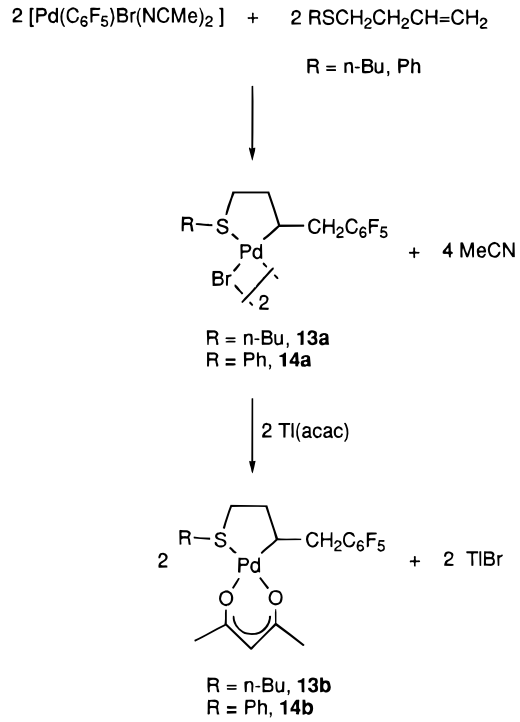


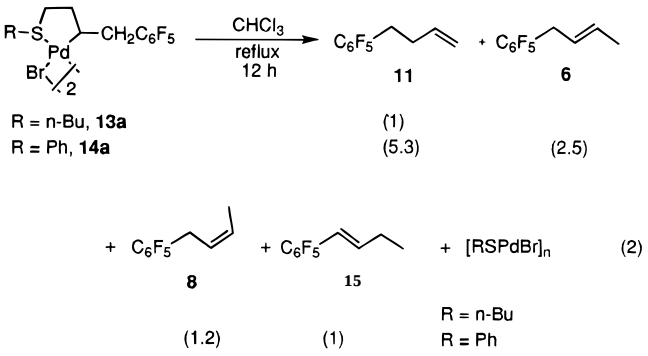

**Table 2. $^{19}$F NMR Data for Palladium Complexes[a]**

| complex | $F_{meta}$ | $F_{para}$[b] | $F_{ortho}$ |
|---|---|---|---|
| **13a** | −163.2 (b) | −158.3 (b) | −143.2 (b) |
| **13b** | −164.0 (b) | −159.7 (b) | −143.9 (b) |
| **14a** | −163.1 (b) | −158.1 (b) | −143.0 (b) |
| **14b** | −163.9 (m) | −159.5 (t) | −143.8 (m) |
| **16** | −163.8 (b) | −159.0 (b) | −142.6 (b) |
| **17**[c] | −163.5 (b) | −158.7 (b) | −142.4 (b) |
| **18a** | −163.6 (b) | −158.9 (b) | −144.7 (b) |
| **18b**[d] | −164.3/−164.3 (b) | −159.7/−160.0 (b) | −144.4/−144.8 (b) |
| **19a** | −163.5 (b) | −158.8 (b) | −144.6 (b) |
| **19b** | −164.1 (m) | −159.6 (t) | −144.7 (b) |

[a] $\delta$, measured on a Bruker AC-300 spectrometer at 293 K using $CDCl_3$ as solvent (except when otherwise noted), downfield from $CFCl_3$ as reference. [b] $^3J_{F-F}$ = 20−21 Hz. [c] 273 K. [d] Isomers are observed as two broad signals in a ratio of 1.4:1 for **18b**.

Fluxional behavior was observed for **13b** and **14b**, and the process was studied by $^{19}$F NMR at variable temperature. At low temperature (243 K), each complex shows two sets of $^{19}$F resonances corresponding to two diastereoisomers resulting from the fact that the two coordinated atoms in the palladacycle are chiral. The effect is clearly observed in the $F_{para}$ region for **13b** (two triplets in 1:1.3 ratio) and the $F_{ortho}$ resonances of **14b** (two signals in 1:1.3 ratio). Upon heating the spectra of **13b** and **14b** coalesce to one set of signals ($T_c$ = 293 K for **13b** and $T_c$ = 268 K for **14b** at 282 MHz). This effect is attributed to inversion at the coordinated sulfur atom of the ligand, which interconverts both distereoisomers. The activation free energy $\Delta G^{\ddagger}$, at the coalescence temperature, for the inversion process is $\Delta G^{\ddagger}_{293K}$ = 61.37 ± 0.19 kJ/mol for **13b** and $\Delta G^{\ddagger}_{268K}$ = 53.99 ± 0.18 kJ/mol for **14b**. These values are consistent with the values reported for the inversion of thioethers coordinated to Pd.[22]

Complexes **13a** and **14a** are stable as solids. In $CDCl_3$ solution **13a** is fairly stable too. However, compound **14a** slowly decomposes. The stability of **13a** and **14a** was studied looking at the evolution of their $^{19}$F and $^1$H NMR spectra at room temperature. In 1 week, 12% of complex **14a** had decomposed to the organic compounds **7**, **8**, **11**, and 1-(pentafluorophenyl)-1-butene (**15**); in addition, a dark brown solid, $[PhSPdBr]_n$, was obtained. However, only 2% of **13a** had decomposed to **11** after 1 week. When solutions of either complex in $CHCl_3$ were refluxed for 12 h, 87% of **14a** or 13% of **13a** decomposed. The resulting organic products and their ratios (in parentheses) are summarized in eq 2. Thus, the *n*-butyl substituted sulfide derivative is




clearly more stable than the corresponding phenyl one. This is consistent with the results found for similar palladium complexes with $\sigma$-yl-$\kappa S$ chelating ligands.[14]

4-(Pentafluorophenyl)-1-butene (**11**) is the only organic compound observed in the decomposition of **13a**, but a large number of isomeric (pentafluorophenyl)-butenes are formed when **14a** decomposes. However it seems that, in this latter case, **11** is again the product immediately formed when **14a** decomposes, and the other olefins come from the isomerization of **11** promoted by the starting Pd complex **14a**. To test this hypothesis, a 2-fold molar amount of allyl pentafluorobenzene (**2**) was added to **13a** in $CDCl_3$ solution. The $^{19}$F and $^1$H NMR spectra showed that 50% of **2** isomerized to **5** after 1 week, yet the decomposition of **13a** was not accelerated.

**Reactions with Pent-4-enyl Sulfides.** Complexes **16** and **17** are formed via reaction between $[Pd(C_6F_5)Br(NCMe)_2]$ and the corresponding pent-4-enyl sulfide at 293 K for 0.5 h, or at 273 K for 1 h, as shown in Scheme 6. Purification of these complexes was unsuccessful since they isomerize by one-step Pd migration to the more stable five-membered palladacyclic complexes **18a** and **19a**. The processes were followed by $^{19}$F NMR at room temperature, and after 1 h 70% of **17** had isomerized to **19a**, but only 10% of **16** had converted into **18a**. The isomerization rate was studied for complex **17**. The process is first order on the Pd complex with a rate constant $k = (2.31 \pm 0.08) \times 10^{-4}\ s^{-1}$. From the Eyring equation the activation free energy for isomerization of **17** is $\Delta G^{\ddagger}_{293K}$ = 92.1 ± 0.2 kJ mol$^{-1}$. Thus, it seems that the attainment of an adequate ring size, and so a more stable situation, promotes the isomerization of these and other palladium complexes, such as the derivatives with $\eta^2$-ene-$\kappa S$ ligands $PdCl_2[MeSCH_2C(Me)_2CH_2CH{=}CH_2]$ and $PdCl_2[MeS(CH_2)_3CH{=}CH_2]$.[7,8]

Complexes **18a** and **19a** react with Tl(acac) to give monomeric acetylacetonato derivatives **18b** and **19b**, respectively. The structures of **18a** and **19a** can be further supported by the analyses of the $^1$H NMR spectra of **18b** and **19b**. The spectral data of all these complexes are given in Tables 2 and 3.

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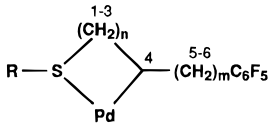
**Table 3. $^1$H NMR Data for the Palladium Complexes[a,b]**

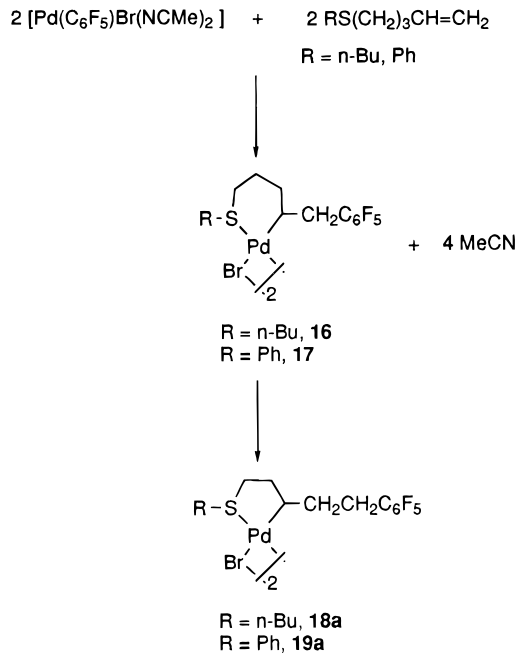



**13a, b**: R = n-Bu; n = 2; m = 1
**14a, b**: R = Ph; n = 2; m = 1
**16**: R = n-Bu; n = 3; m = 1
**17**: R = Ph; n = 3; m = 1
**18a, b**: R = n-Bu; n = m = 2
**19a, b**: R = Ph; n = m = 2

| compd | H$^1$ | H$^2$ | H$^3$ | H$^4$ | H$^5$ | H$^6$ | R | other |
|---|---|---|---|---|---|---|---|---|
| **13a** | 2.98 b (2H) | 1.80 b (1H)<br>0.96 b (1H) | | 3.33 b (1H) | | 3.33 b (1H)<br>2.74 b (1H) | 2.74 b (2H), 1.80 b (2H),<br>1.46 m (2H), 0.96 b (3H) | |
| **13b** | 2.92 b (2H) | 1.48 b (2H) | | 3.38 b m (1H) | | 2.92 b (1H)<br>2.73 b (1H) | 2.73 b (2H), 1.78 m (2H),<br>1.48 m (2H), 0.95 t (7.4, 3H) | 5.26 s (1H), 1.94 s (3H), 1.88 s (3H) |
| **14a** | 3.04 b (2H) | 1.86 b (1H)<br>0.90 b (1H) | | 3.43 b (1H) | | 3.43 b (1H)<br>2.79 b (1H) | 8.0 b (2H), 7.4 b (3H) | |
| **14b** | 3.10 b (1H)<br>2.89 b (1H) | 1.44 b (1H)<br>1.20 b (1H) | | 3.37 b (1H) | | 2.89 b (1H)<br>2.78 b (1H) | 7.9 m (2H), 7.4 m (3H) | 5.30 s (1H), 1.98 s (3H), 1.87 s (3H) |
| **16** | 3.05 b (1H)<br>2.84 b (1H) | 2.10 b (1H)<br>1.89 b (1H) | 1.42 b (1H)<br>0.69 b (1H) | 3.56 b (1H) | | 2.92 b (1H)<br>2.10 b (1H) | 2.70 m (2H), 1.74 m (2H),<br>1.42 m (2H), 0.93 t (7.4, 3H) | |
| **17** | 3.25 b (1H)<br>2.78 b (1H) | 2.15 b (1H)<br>1.95 b (1H) | 1.41 b (1H)<br>0.60 b (1H) | 3.54 b (1H) | | 3.01 b (1H)<br>2.15 b (1H) | 7.9 b (2H), 7.4 m (3H) | |
| **18a** | 2.93 b (2H) | 1.79 b (1H)<br>1.24 b (1H) | | 3.31 b (1H) | 1.98 b (1H)<br>1.70 b (1H) | 2.78 b (2H) | 2.60 b (2H), 1.79 b (2H)<br>1.43 m (2H), 0.94 t (7.4, 3H) | |
| **18b** | 2.7−3.0 b (2H) | 1.4−1.55 b (2H) | | 2.7−3.0 b (1H) | 1.9 b (1H)<br>1.4−1.55 b (1H) | 2.7−3.0 b (1H)<br>2.6 b (1H) | 2.76 m (2H), 1.77 m (2H),<br>1.48 m (2H), 0.94 t (7.4, 3H) | 5.21s (1H), 1.91s (3H), 1.85 s (3H) |
| **19a** | 2.99 b (2H) | 1.91 b (1H)<br>1.24 b (1H) | | 3.47 b (1H) | 2.03 b (1H)<br>1.68 b (1H) | 2.82 b (2H) | 8.0 m (2H), 7.4 m (3H) | |
| **19b** | 2.7−2.95 b (2H) | 1.4−1.7 m (2H) | | 3.1 b (1H) | 1.9 m (1H)<br>1.4−1.7 m (1H) | 2.7−2.95 b (2H) | 7.9 m (2H), 7.4 m (3H) | 5.25 s (1H), 1.94 s (3H), 1.84 s (3H) |

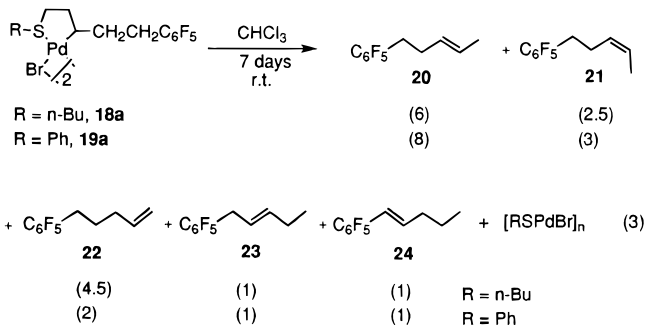
[a] $\delta$ mult $J$ values (Hz) are given in parentheses. $CDCl_3$ used as solvent. [b] The temperature used is 293 K for each complex except **17** at 273 K.

**Scheme 6**




The inversion of the sulfur atom in complexes **18b** and **19b** was studied by $^{19}$F NMR at different temperatures. Two signals for the $F_{ortho}$ atoms were observed at 243 K for each complex, and the coalescence temperatures at 282 MHz are 305 K (**18b**) and 280 K (**19b**), corresponding to $\Delta G^{\ddagger}_{305K} = 60.10 \pm 0.16$ kJ mol$^{-1}$ for **18b** and $\Delta G^{\ddagger}_{280K} = 54.36 \pm 0.16$ kJ mol$^{-1}$ for **19b**.

The decompositions of **18a** and **19a** in $CDCl_3$ solutions were analyzed by $^1$H and $^{19}$F NMR. After 7 days at room temperature 53% of the starting **18a** had decomposed, whereas 79% of **19a** had decomposed under the same conditions. Several isomers of (pentafluorophenyl)pentene are obtained: (*E*)-5-(pentafluorophenyl)-2-pentene (**20**), (*Z*)-5-(pentafluorophenyl)-2-pentene (**21**), 5-(pentafluorophenyl)-1-pentene (**22**), (*E*)-1-(pentafluorophenyl)-2-pentene (**23**), and (*E*)-1-(pentafluorophenyl)-1-pentene (**24**). They are depicted in eq 3 along with their relative ratios in parentheses; the corresponding brown insoluble palladium thiolate is also obtained.




The high number of isomeric (pentafluorophenyl)pentenes is again due to double bond isomerization in 5-(pentafluorophenyl)-1-pentene (**22**) catalyzed by the starting Pd complex. In fact, complex **19a** is capable of effecting the isomerization of allylpentafluorobenzene (**2**) to (*E*)-1-(pentafluorophenyl)-1-propene (**5**), as described for complex **13a**. Figure 1 shows the change in organic product distribution with time for the decomposition of **19a**, monitored by $^{19}$F and $^1$H NMR. Compound **22** is the only organic product formed when the decomposition process starts; as the reaction time increases the percentage of **22** in the mixture decreases, as it is isomerized into **21**, **23**, **24**, and especially **20** (100% is taken each time as the total amount of organic compounds, which constantly increases as the decomposition proceeds).

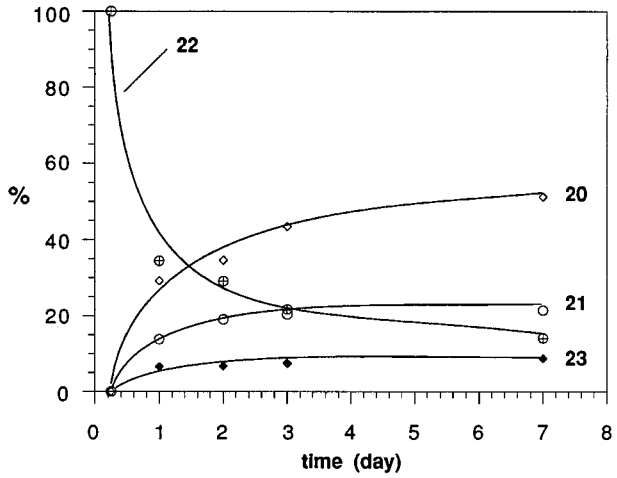



**Figure 1.**

## Discussion

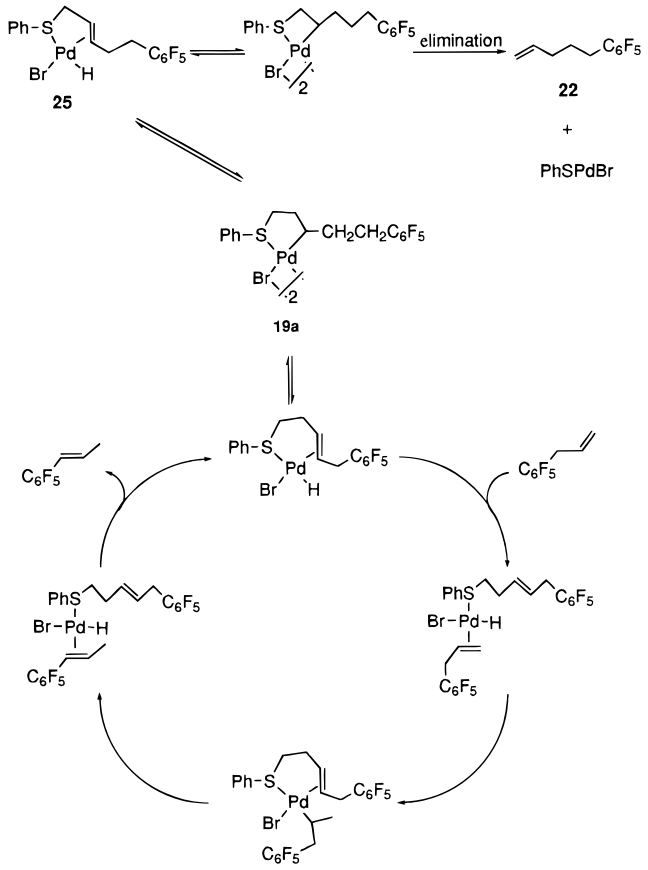
Alkenyl sulfides are potential chelating alkene−thioether ligands provided that the S-atom and the olefin are sufficiently spaced to give a stable metallacycle. However, we have not detected the formation of $\eta^2$-$\kappa S$ palladium complexes in the reactions between [Pd($C_6F_5$)Br($NCMe)_2$] and any of the alkenyl sulfides tried, not even at low temperature. The coordination of the sulfur atom is more favorable, and most probably it occurs first, but as soon as the olefin coordinates (whether as a chelate or with previous decoordination of the S we cannot say) insertion into the Pd−$C_6F_5$ bond occurs.

Different alkenyl chain lengths have been tried: RS-$(CH_2)_n$CH=$CH_2$ ($n$ = 1−3), and this has a decisive influence on the fate of the intermediate formed after insertion. When the organometallic moiety bears S and Pd three bonds apart, $\beta$-SR elimination takes place, as shown by the behavior of the allyl sulfides tried and in the decomposition process of complexes **13a**, **14a**, **18a**, and **19a** (see below). For longer ($n$ = 2, 3) chain lengths formation of $\sigma$-yl-$\kappa S$ palladium complexes is observed. The five-membered palladacycles are the most stable rings found, and the six-membered complexes easily isomerize to five-membered palladium derivatives. The analogous reaction with a vinyl sulfide ($n$ = 0) was described in the previous paper in this issue and also gives a stable three-membered $\sigma$-yl-$\kappa S$ palladacycle.[13]

The five-membered complexes decompose in solution very slowly at room temperature or faster when strong conditions are used. According to the results of these decomposition experiments, the stabilities of the complexes follow the order **13a** > **14a** > **18a** > **19a**. The decomposition of these derivatives arises from 1, 2 hydrogen shift (Pd−H elimination−readdition) and elimination of Pd and the $\beta$-SR group to give a terminal $C_6F_5$-substituted monoolefin; the olefin can then isomerize to several positional isomers under catalysis by the starting palladium complex, as shown by the rate of formation of the different isomers in Figure 1. This catalytical process is supported by the isomerization of allylpentafluorobenzene in the presence of complexes **13a** or **19a**.

The proposed mechanism of the decomposition and catalytical activity toward olefin isomerization is depicted in Scheme 7. According to this mechanism, once PdH elimination has occurred, rotation around the Pd−olefin bond is needed in intermediate **25** for PdH

**Scheme 7**




readdition with the opposite regiochemistry. This rotation is restricted in the S-$\eta^2$-olefin palladacycle. Consequently, decoordination of the sulfur atom is expected for the process of double bond insertion into the Pd−H bond to occur. In fact, the higher unstability of the complexes with phenyl-substituted sulfides, **14a** and **19a**, can be understood as a consequence of the aromatic Ph ring weakening the coordinating ability of the sulfur atom and easing its decoordination. The higher donor ability of the *n*-Bu-substituted sulfide makes the Pd−S bond stronger, and consequently complexes **13a** and **18a** are more stable. A similar stability trend has been found for *n*-Bu- and Ph-sulfur-substituted $\sigma$-yl-$\kappa S$ palladium complexes reported in the literature.[14] On the other hand, the $CH_2$ (position 5 in Table 3) in complexes **18a** and **19a** is less sterically hindered by the $C_6F_5$ ring and the $\beta$-H elimination is probably easier than for the but-4-enyl sulfide complexes **13a** and **14a**. Hence, the stability order found is as follows: **13a**, **14a** > **18a**, **19a**.

The rates for the isomerization of complexes **16** and **17** parallel the stabilities of **18a** and **19a**, respectively; that is, the isomerization of **16** to **18a** is slower than that of **17** to **19a** in $CDCl_3$ solution. The mechanism of the isomerization is a one-step Pd-migration (1,2-hydrogen shift) most probably controlled by the decoordination of the sulfur atom, which, as discussed above, is more favorable for **17** than for **16**.

Finally, the fluxionality of the complexes **13b**, **14b**, **18b**, and **19b** is attributed to the existence of pyramidal inversion of the configuration of the sulfur atom. According to the free energy of activation values found, $\Delta G^{\ddagger}_{Tc}$, the ease of the process is **13b** ≈ **18b** < **14b** ≈ **19b**; that is, the inversion of the sulfur atom in complexes with ligand-containing *n*-Bu sulfides is more difficult than in those containing Ph sulfides. The

probable reason of this trend is that the inversion occurs through a planar transition state, which is stabilized by (3p−2p)$\pi$ conjugation between the S lone pair and the phenyl aromatic ring in the complex involving a PhS moiety.[23,24]

## Experimental Section

**General Considerations.** $^{19}$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 $\delta$ 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% aqueous solution, external reference) for $^{31}$P. Carbon and hydrogen microanalyses were carried out on a Perkin-Elmer 2400 CHN elemental analyzer.

All solvents were dried and distilled before use by standard methods. $RSCH_2CH_2CH{=}CH_2$, $RSCH_2CH_2CH_2CH{=}CH_2$ (R = *n*-Bu and Ph), *n*-$BuSCH(CH_3)CH{=}CH_2$, and *n*-$BuSCH_2$-$CH{=}CHCH_3$ were synthesized as reported in the literature.[10] Diallyl sulfide and allyl methyl sulfide were commercially available (Aldrich). $[Pd(C_6F_5)Br(NCMe)_2]$ was prepared as previously reported.[19a]

NOTE: Some of the organic products obtained are rather volatile and can be lost if evaporation is carried out under high vacuum. Thus, the use of a low vacuum water pump is recommended and when necessary it will be noted in the preparations below.

**Reaction of $[Pd(C_6F_5)Br(NCMe)_2]$ with Diallyl Sulfide.** To a solution of $[Pd(C_6F_5)Br(NCMe)_2]$ (0.400 g, 0.918 mmol) in $CH_2Cl_2$ (20 mL) was added diallyl sulfide (0.118 mL, 0.918 mmol). After 8 h of stirring a dark brown precipitate was filtered (mixture of **3**, $PdBr_2$, PdS, and Pd). The filtrate was evaporated to dryness carefully using a water pump. The orange residue was chromatographed through a silica gel column eluting with *n*-hexane and then diethyl ether. A colorless oily residue formed after careful evaporation of the solvent of the first fraction, which was a mixture of **2**, **4**, and **5** (ratio 33:9:1) by analyses of its $^{1}$H and $^{19}$F NMR spectra and GC−MS. The white solid **4** can be isolated by evaporating off (oil pump) the more volatile compounds **2** and **5**. The second fraction (ether used as eluent) afforded orange crystals, **6**, after concentration of the solution to 1 mL, addition of *n*-hexane (3 mL), and cooling (yield: 15% based on Pd).

**3**: $^{1}$H NMR (DMSO-$d_6$, $\delta$, 300 MHz) 5.8 (m, 1H), 5.1 (m, 2H), 3.1 (m, 2H).

**4**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz) −162.4/−163.2 (m, $F_{meta}$), −156.3/−156.5 (t, $F_{para}$), −143.4/−143.9 (m, $F_{ortho}$); $^{1}$H NMR ($CDCl_3$, $\delta$, 300 MHz) 6.56 (dt, $J$ = 16.4, 6.6 Hz, 1H, $H^2$), 6.40 (d, $J$ = 16.4 Hz, 1H, $H^1$), 3.66 (d, $J$ = 6.6 Hz, 2H, $H^3$). Anal. Calcd for $C_{15}H_4F_{10}$: C, 48.15; H, 1.08. Found: C, 48.26; H, 1.12.

**5:** $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz) −163.9 (m, $F_{meta}$), −158.5 (t, $F_{para}$), −144.5 (m, $F_{ortho}$); $^{1}$H NMR ($CDCl_3$, $\delta$, 300 MHz) 6.56 (dq, $J$ = 16.2, 6.5 Hz, 1H, $H^2$), 6.27 (dq, $J$ = 16.2, 1.6 Hz, 1H, $H^1$), 1.94 (dd, $J$ = 6.5, 1.6 Hz, 3H, $H^3$); MS (El) *m*/*z* (relative intensity) 208 ($M^+$, 100), 189 (22), 187 (28), 181 (79), 169 (14), 158 (15).

**6:** $^{1}$H NMR ($CDCl_3$, $\delta$, 300 MHz) 5.98 (m, 2H, $H^2$), 5.35 (m, 4H, $H^1$), 3.62 (d, $J$ = 6.9 Hz, 4H, $H^3$); MS (EI) *m*/*z* (relative intensity) 252 ($M^+$, 71), 250 (100), 248 (53), 215 (21), 108 (25). Anal. Calcd for $C_6H_{10}PdS_2$: C, 28.52; H, 3.99. Found: C, 28.55; H, 3.95.

When $[Pd(C_6F_5)Br(NCMe)_2]$ (1 mol) and diallyl sulfide (0.5 mol) were mixed in $CH_2Cl_2$, the same procedure as above was used. A mixture of organic compounds **2**, **4**, and **5** in a ratio 9:7.5:1 and a black solid mixture of $PdBr_2$, PdS, and Pd were obtained.

**Reaction of $[Pd(C_6F_5)Br(NCMe)_2]$ with Allyl Methyl Sulfide.** The same procedure as above was used. When the equimolar amounts of the reactants were employed, the final products were a mixture of organic compounds **2**, **4**, and **5** (ratio 2.5:2.6:1) and a dark brown solid (mixture of $[MeSPdBr]_n$, $PdBr_2$, PdS, and Pd).

$[MeSPdBr]_n$: $^{1}$H NMR (DMSO-$d_6$, $\delta$, 300 MHz) 2.1 (s, Me).

**Reactions of $[Pd(C_6F_5)Br(NCMe)_2]$ with *n*-Butyl 1-Buten-3-yl Sulfide and with *n*-Butyl But-2-enyl Sulfide.** Two NMR tubes were charged with $[Pd(C_6F_5)Br(NCMe)_2]$ (0.025 g, 0.0574 mmol) and *n*-butyl 2-methylallyl sulfide (0.0105 mL, 0.0574 mmol) or $[Pd(C_6F_5)Br(NCMe)_2]$ (0.025 g, 0.0574 mmol) and *n*-butyl but-2-enyl sulfide (0.0096 mL, 0.0574 mmol) in $CDCl_3$ (0.6 mL), respectively. The reactions were monitored by $^{1}$H and $^{19}$F NMR for 24 h. The final products were analyzed.

**7**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.5 (m, $F_{meta}$), −158.4 (t, $F_{para}$), −144.7 (m, $F_{ortho}$); $^{1}$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.5 (m, 2H, $H^2$, $H^3$), 3.37 (dd, $J$ = 5.3, 1.5 Hz, 2H, $H^1$), 1.64 (dd, $J$ = 5.9, 1.2 Hz, 3H, $H^4$); MS (El) *m*/*z* (relative intensity) 222 ($M^+$, 67), 207 (71), 194 (25), 187 (45), 181 (100), 161 (15), 93 (14), 41 (14).

**8**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz) −164.0 (m, $F_{meta}$), −158.5 (t, $F_{para}$), −144.3 (m, $F_{ortho}$); $^{1}$H NMR ($CDCl_3$, $\delta$, 300 MHz) 5.5−5.6 (m, 2H, $H^2$, $H^3$), 3.44 (d, $J$ = 7.4 Hz, 2H, $H^1$), 1.74 (d, $J$ = 6.8 Hz, 3H, $H^4$); MS (El) *m*/*z* (relative intensity) 222 ($M^+$, 82), 207 (75), 187 (55), 181 (100), 93 (24), 69 (32), 41 (98).

**9**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz) −162.4, 163.3 (m, $F_{meta}$), −156.5, 157.0 (t, $F_{para}$), −143.1, 143.4 (m, $F_{ortho}$); $^{1}$H NMR ($CDCl_3$, $\delta$, 300 MHz) 6.76 (dd, $J$ = 16.3, 7.5 Hz, 1H, $H^2$), 6.38 (d, $J$ = 16.3 Hz, 1H, $H^1$), 4.10 (qui, $J$ = 7.3 Hz, 1H, $H^3$), 1.55 (d, $J$ = 7.3 Hz, 3H, Me); MS (El) *m*/*z* (relative intensity) 388 ($M^+$, 13), 373 (25), 187 (7), 181 (100), 161 (9), 143 (9), 13 (8), 93 (8).

**10**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz) −162.9, 163.4 (m, $F_{meta}$), −157.2, 157.4 (t, $F_{para}$), −143.9, 144.3 (m, $F_{ortho}$); $^{1}$H NMR ($CDCl_3$, $\delta$, 300 MHz) 6.50 (dt, $J$ = 16.0, 6.9 Hz, 1H, $H^2$), 6.26 (d, $J$ = 16.0 Hz, 1H, $H^1$), 2.91 (t, $J$ = 7.3 Hz, 2H, $H^4$), 2.56 (q, $J$ = 7.3 Hz, 2H, $H^3$); MS (El) *m*/*z* (relative intensity) 388 ($M^+$, 14), 207 (100), 187 (52), 181 (77), 161 (16), 93 (8).

**12**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz) −163.1 (m, $F_{meta}$), −158.2 (t, $F_{para}$), −143.3 (m, $F_{ortho}$); $^{1}$H NMR ($CDCl_3$, $\delta$, 300 MHz) 5.9 (m, 1H, $H^2$), 5.0 (m, 2H, $H^1$), 3.82 (qui, $J$ = 6.9 Hz, 1H, $H^3$), 1.5 (d, $J$ = 6.9 Hz, Me); MS (El) *m*/*z* (relative intensity) 222 ($M^+$, 94), 207 (100), 187 (84), 181 (72).

**Preparation of 13a.** *n*-Butyl but-3-enyl sulfide (0.079 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) at room temperature. After 2 h of stirring, the solution was evaporated to dryness. On addition of ether (2 mL) and then *n*-hexane (3 mL) and cooling a yellow precipitate formed, which was filtered, washed with ether/*n*-hexane (2:3), and air-dried to give a yellow solid **13a** (85% yield).

**13a**: Anal. Calcd for $C_{28}H_{32}Br_2F_{10}Pd_2S_2$: C, 33.79; H, 3.24. Found: C, 33.91; H, 3.27.

**Preparation of 14a**. Complex **14a** was prepared from phenyl but-3-enyl sulfide following the same procedure used to prepare **13a**. A yellow solid, **14a,** was obtained (88% yield).

**14a**: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, $\delta$, 75.4 MHz) 144.9 (bd, $^{1}J_{CF}$ = 244.1 Hz, $C_6F_5$), 139.5 (bd, $^{1}J_{CF}$ = 240.4 Hz, $C_6F_5$), 137.3 (bd, $^{1}J_{CF}$ = 251.0 Hz, $C_6F_5$), 132.8 (Ph), 132.2 ($C^1$Ph), 129.9 (Ph), 129.5 (Ph), 112.8 (b, $C_6F_5$), 52.0 ($C^3$), 41.3 ($C^1$), 38.0 ($C^2$), 27.9 ($C^4$). Anal. Calcd for $C_{32}H_{24}Br_2F_{10}Pd_2S_2$: C, 37.12; H, 2.34. Found: C, 37.07; H, 2.39.

**Preparation of 18a.** Complex **18a** was prepared from *n*-butyl pent-4-enyl sulfide by the same procedure used to prepare **13a**, but changing the reaction time to 30 h. The preparation afforded a yellow solid **18a** (68% yield).

**18a**: Anal. Calcd for $C_{30}H_{36}Br_2F_{10}Pd_2S_2$: C, 35.21; H, 3.55. Found: C, 35.46; H, 3.59.

**Preparation of 19a.** Complex **19a** was prepared from phenyl pent-4-enyl sulfide by the same procedure used to prepare **13a**, but changing the reaction time to 4 h. A yellow solid **19a** was obtained (77% yield).

(23) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365−414.
(24) Abel, E. W.; Bhargava, S. K.; Orrell, K. G.; Sik, V.; Williams, B. L. *Tetrahedron* **1982**, *1*(3), 289.

**19a**: Anal. Calcd for $C_{34}H_{28}Br_2F_{10}Pd_2S_2$: C, 38.40; H, 2.63. Found: C, 38.36; H, 2.68.

**Preparation of 13b.** To a solution of **13a** (0.060 g, 0.06 mmol) in $CH_2Cl_2$ (10 mL) was added Tl(acac) (0.037 g, 0.12 mmol). After 1 h, the white precipitate formed was filtered off. The light yellow filtrate was evaporated to dryness. The residue was triturated with ether (2 mL) and *n*-hexane (2 mL). A light yellow solid **13b** formed (69% yield).

**13b.** Anal. Calcd for $C_{19}H_{23}F_5O_2PdS$: C, 44.15; H, 4.45. Found: C, 44.09; H, 4.38.

The synthesis of **14b**, **18b**, and **19b** was accomplished by the same method described above for **13b**, starting from **14a**, **18a**, and **19a** respectively.

**14b**: yellow solid (67% yield). Anal. Calcd for $C_{21}H_{19}F_5O_2SPd$: C, 46.98; H, 3.57. Found: C, 46.34; H, 3.60.

**18b**: obtained as a yellow oily residue (75% yield).

**19b:** yellow oily residue (79% yield).

All monomeric complexes were analyzed by $^1H$ and $^{19}F$ NMR. The inversion of the sulfur atom in each monomer was studied at different temperatures by $^{19}F$ NMR. Rate constants were determined at the coalescence temperature using the equation $k = (\pi/2^{1/2})\cdot\delta\nu$.[25] Uncertainties in the rate constant were calculated assuming a $\delta\nu$ variation of ± 0.35 Hz. The rate constants are given as follows: $k = 69.3 \pm 1.5\ s^{-1}$ for **13b**; $k = 165.4 \pm 1.5\ s^{-1}$ for **14b**; $k = 320.9 \pm 1.5\ s^{-1}$ for **18b**; $k = 416.8 \pm 1.5\ s^{-1}$ for **19b**. Free energies of activation were calculated using the Eyring equation in the form $\Delta G^{\ddagger} = -2.3RT\log(K_BT/hk_{obs})$. Error was calculated using the above-mentioned uncertainty in $k_{obs}$ and a temperature variation of ±0.4 K.[25]

**Decomposition of 13a**. An NMR tube was charged with **13a** (0.030 g, 0.03 mmol) and $CDCl_3$ (0.6 mL). Analysis of the $^1H$ and $^{19}F$ NMR spectra showed that 2% of **13a** decomposed to 4-(pentafluorophenyl)-1-butene (**11**) after 7 days at room temperature. However, the rate of the decomposition increased to 13% when **13a** (0.060 g, 0.06 mmol) in $CHCl_3$ (15 mL) was refluxed for 12 h.

**11**: $^{19}F$ NMR ($CDCl_3$, $\delta$, 282 MHz) −163.5 (m, $F_{meta}$), −158.3 (t, $F_{para}$), −144.5 (m, $F_{ortho}$); $^1H$ NMR ($CDCl_3$, $\delta$, 300 MHz) 5.8 (m, 1H, $H^2$), 5.0 (m, 2H, $H^1$), 2.80 (tt, $J = 7.3$ Hz, $^4J_{HF} = 1.6$ Hz, 2H, $H^4$), 2.34 (q, $J = 7.3$ Hz, 2H, $H^3$); MS (El) *m*/*z* (relative intensity) 222 ($M^+$, 26), 181 (100), 161 (10), 93 (8), 41 (58).

The same procedure was used to study of the decomposition of **14a**, **18a**, and **19a**. All organic products were identified by $^1H$ and $^{19}F$ NMR and GC−MS. In the case of **14a** and **19a**, a brown solid $[PhSPdBr]_n$ was isolated.

$[PhSPdBr]_n$: $^1H$ NMR (DMSO-$d_6$, $\delta$, 300 MHz), 8.1 (b, 2H, Ph), 7.3 (b, 3H, Ph). Anal. Calcd for $C_6H_5BrSPd$: C, 24.39; H, 1.71. Found: C, 25.05; H, 1.70.

**15**: $^{19}F$ NMR ($CDCl_3$, $\delta$, 282 MHz) −163.2 (m, $F_{meta}$), −158.0 (t, $F_{para}$), −144.0 (m, $F_{ortho}$); $^1H$ NMR ($CDCl_3$, $\delta$, 300 MHz) 6.60 (dt, $J = 16.3$, 6.5 Hz, 1H, $H^2$), 6.26 (dt, $J = 16.3$ Hz, $^4J_{HF} = 1.6$ Hz, 1H, $H^1$), 2.3 (m, 2H, $H^3$)*, 1.11 (t, $J = 7.5$ Hz, 3H, $H^4$); MS (El) *m*/*z* (relative intensity) 222 ($M^+$, 2), 181 (100), 161 (3), 142 (8), 85 (17), 71 (26), 57 (77), 43 (100), 41 (66).

*: overlapped with signals of other compounds.

**20**: $^{19}F$ NMR ($CDCl_3$, $\delta$, 282 MHz) −163.7 (m, $F_{meta}$), −158.5 (t, $F_{para}$), −144.6 (m, $F_{ortho}$); $^1H$ NMR ($CDCl_3$, $\delta$, 300 MHz) 5.4 (m, 2H, $H^2$, $H^3$), 2.74 (tt, $J = 7.0$ Hz, $^4J_{HF} = 1.5$ Hz, 2H, $H^5$), 2.25 (m, 2H, $H^4$), 1.62 (dd, $J = 3.5$, 1.2 Hz, 3H, $H^1$); MS (El) *m*/*z* (relative intensity) 236 ($M^+$, 9), 181 (12), 161 (4), 93 (2), 55 (100), 43 (2), 41 (5).

**21**: $^{19}F$ NMR ($CDCl_3$, $\delta$, 282 MHz) −163.5 (m, $F_{meta}$), −158.4 (t, $F_{para}$), −144.6 (m, $F_{ortho}$); $^1H$ NMR ($CDCl_3$, $\delta$, 300 MHz) 5.5 (m, 2H, $H^2$, $H^3$), 2.7−2.8 (m, 2H, $H^5$)*, 2.34 (q, $J = 7.4$, 2H, $H^4$), 1.53 (dm, $J = 6.7$ Hz, 3H, $H^1$); MS (El) *m*/*z* (relative intensity) 236 ($M^+$, 7), 194 (20), 181 (12), 71 (9), 57 (23), 55 (100), 43 (22), 41 (20).

*: overlapped with signals of other compounds.

**22**: $^{19}F$ NMR ($CDCl_3$, $\delta$, 282 MHz) −163.5 (m, $F_{meta}$), −158.6 (t, $F_{para}$), −144.8 (m, $F_{ortho}$); $^1H$ NMR ($CDCl_3$, $\delta$, 300 MHz) 5.8 (m, $J = 16.9$, 10.2, 6.2 Hz, 1H, $H^2$), 4.95−5.1 (m, $J = 16.9$, 10.2 Hz, 2H, $H^1$), 2.7−2.8 (m, 2H, $H^5$)*, 2.2−2.3 (m, 2H, $H^3$)*, 1.68 (qui, $J = 7.3$ Hz, 2H, $H^4$); MS (El) *m*/*z* (relative intensity) 236 ($M^+$).

*: overlapped with other signals of compounds.

**23**: $^{19}F$ NMR ($CDCl_3$, $\delta$, 282 MHz) −163.5 (m, $F_{meta}$), −158.3 (t, $F_{para}$), −144.3 (m, $F_{ortho}$); $^1H$ NMR ($CDCl_3$, $\delta$, 300 MHz) 5.3−5.45 (m, 2H, $H^2$, $H^3$)*, 3.36 (d, $J = 6.6$ Hz, 2H, $H^1$), 2.0 (qui, $J = 7.2$ Hz, 2H, $H^4$), 0.95 (t, $J = 7.2$ Hz, 3H, $H^5$); MS (El) *m*/*z* (relative intensity) 236 ($M^+$, 22), 207 (20), 194 (100), 187 (29), 181 (34), 55 (37), 41 (13).

*: overlapped with other of other compounds.

**24**: $^{19}F$ NMR ($CDCl_3$, $\delta$, 282 MHz) −163.3 (m, $F_{meta}$), −158.2 (t, $F_{para}$), −144.8 (m, $F_{ortho}$); $^1H$ NMR ($CDCl_3$, $\delta$, 300 MHz) 6.55 (dt, $J = 14.0$, 7.0 Hz, 1H, $H^2$), 6.27 (dt, $J = 14.0$ Hz, $^4J_{HF} = 1.4$ Hz, 1H, $H^1$), 2.11 (qui, $J = 7.2$ Hz, 2H, $H^3$), 1.2 (m, 2H, $H^4$), 0.96 (t, $J = 7.2$ Hz, 3H, $H^5$); MS (El) *m*/*z* (relative intensity) 236 ($M^+$, 1), 194 (4), 170 (7), 85 (22), 71 (35), 57 (80), 55 (32), 43 (100), 41 (75).

**Isomerization of Allylpentafluorobenzene Catalyzed by 13a.** An NMR tube was charged with **13a** (0.020 g, 0.02 mmol), $CDCl_3$ (0.6 mL), and allylpentafluorobenzene (0.0062 mL, 0.04 mmol). The analysis of $^1H$ and $^{19}F$ NMR indicated that 50% of allylpentafluorobenzene had isomerized to **5** after 7 days.

The isomerization of allylpentafluorobenzene was also performed in the presence of complex **19a** by the same procedure described above. Twenty-two percent of **2** was isomerized to **5** after 8 h at room temperature. However, **19a** began to decompose at this point.

**Formation and Isomerization of 16.** An NMR tube was charged with $[Pd(C_6F_5)Br(NCMe)_2]$ (0.025 g, 0.0574 mmol), $CDCl_3$ (0.6 mL), and *n*-butyl pent-4-enyl sulfide (0.0107 mL, 0.0574 mmol) at room temperature. The arylation of the alkenyl sulfide was complete after 30 min and complex **16** formed; it was identified by $^1H$ and $^{19}F$ NMR. Eighty-three percent of **16** had isomerized to **18a** after 1 day.

**Formation and Isomerization of 17.** To a solution of $[Pd(C_6F_5)Br(NCMe)_2]$ (0.04 g, 0.0918 mmol) in $CDCl_3$ (0.6 mL) in an NMR tube was added phenyl pent-4-enyl sulfide (0.0166 mL, 0.0918 mmol) at 273 K. **17** formed after 1 h and was identified by $^1H$ and $^{19}F$ NMR. The solution was warmed to 293 K, and isomerization of **17** to **19a** was observed. After 3 h at this temperature 95% of **17** had been converted.

The rate constant was measured by recording $^{19}F$ NMR spectra every 10 min at 293 K (relaxation delays of at least $5T_1$'s were used). A plot of ln[signal integral] *versus* time gave the first-order rate constant. The reported uncertainty in the isomerization rate corresponds to one standard deviation in the slope of the best fit line multiplied by the Student's factor $t_{1-\alpha}(f)$.[26] The free energy of activation was calculated using the Eyring equation in the form $\Delta G^{\ddagger} = -2.3RT\log(K_BT/hk_{obs})$. Error was calculated using the above-mentioned uncertainty in $k_{obs}$ and a temperature variation of ±0.4 K.[25]

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