Study of the Evolution of η^1-η^2-Enylpalladium Complexes When the Palladium-Migration Process Is Blocked

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$\eta^1-\eta^2$-Enylpalladium complexes have been detected and/or isolated in the reaction of [PdPfBr(NCMe)$_2$] (Pf = C_6F_5) with the dienes R−CH═CH−(CH$_2$)$_n$−Y−(CH$_2$)$_m$−CH═CH$_2$ (R = H, Me; n, m = 0, 1; Y = CCl_2, $C(COOMe)_2$, CO_2, O, $SiMe_2$, SO_2). Insertion of one double bond into the Pd−aryl bond and coordination of the remaining double bond gives the above-mentioned organometallic derivatives. The dienes tested have a non-hydrogen-containing link (Y), so Pd migration to give η^3-allyl derivatives is blocked. The evolution and decomposition processes observed for the η^1-η^2-enyls reveal that β-X elimination is the main operating pathway for Y = CCl_2 (X = Cl) or Y = OCO, O, $SiMe_2$ (X = YR′). When Y = $C(COOMe)_2$ or SO_2, C−X cleavage is not observed and intramolecular insertion to give cyclic products or Pd−H elimination to generate a substituted diene predominates, respectively. From these results, a trend in C−X cleavage easiness in the presence of palladium can be estimated: C−C ≪ C−SO_2 < C−Cl < C−O (ether) < C−O (ester) ≈ C−Si.

Introduction

Different processes can follow the insertion of a double bond into the Pd−R bond to give the final organic or organometallic product (Scheme 1). When a nonconjugated diene is used, Pd migration to give η^3-allylpalladium complexes is probably the most common route and operates efficiently in the absence of excess diene (a, Scheme 1).[1−3] These functionalized palladium allyls can be converted into substituted alkenes by attack of a nucleophile or carbonylation,[4,5] in what could be described as a distant addition of R and Nu to the diene (Scheme 1).

Pd migration can be aborted by decoordination of the new olefin to generate R-substituted dienes (Scheme 1, b). This is promoted by the presence of any alkene that is a better ligand than the R diene (i.e., a less-substituted one) and coordinates preferentially.[1,2,6] Cyclization (Scheme 1, c) is also an important alternative to Pd migration and gives access to new types of organic cyclic derivatives.[7]

Another way of aborting Pd migration is to introduce a non-hydrogen-containing link in the carbon chain between both double bonds of the diene. Since Pd migration operates through Pd−H elimination−readditions, the link suppresses this route of evolution for intermediate **A** (Scheme 1) and may divert it to pathways b and c (Scheme 1) or to new reaction pathways.

To explore this idea, the following dienes were tested: R−CH═CH−(CH$_2$)$_n$−Y−(CH$_2$)$_m$−CH═CH$_2$ (R = H, n = 0, m = 1, Y = CCl_2; R = Me, n = m = 0, Y = CO_2; R = H, n = m = 0, Y = SO_2; R = H, n = m = 1, Y = $C(COOMe)_2$, O, $SiMe_2$, SO_2). Their reactions with [PdPfBr(NCMe)$_2$] (Pf = C_6F_5) give several η^1-η^2-enylpalladium intermediates, which were identified and then decomposed to study the occurrence of alternative pathways to Pd migration.

Results and Discussion

Different stabilities were found for the organometallic complexes detected in the reactions of [PdPfBr(NCMe)$_2$] (Pf = C_6F_5) with allyl−vinyl, divinyl, or diallyl dienes bearing a link lacking hydrogen in the hydrocarbon chain. For this reason, the reactions of the divinyl or allyl−vinyl dienes, which give rise to stable η^1-η^2-enylpalladium complexes, are discussed first, followed by the reactions of the diallyl diolefins, which lead to less stable organometallic derivatives. ^{1}H NMR data for the η^1-η^2-enylpalladium derivatives formed in these reactions are collected in Table 1.

Reaction with 3,3-Dichloro-1,5-hexadiene. The reaction of [PdPfBr(NCMe)$_2$] with 3,3-dichloro-1,5-hexadiene at room temperature gives the η^1-η^2-enylpalladium compound **1a** as a colorless precipitate that is quite insoluble in common organic solvents (Scheme 2). After separation of **1a**, a small amount of (*Z*)-3-chloro-6-pentafluorophenyl-1,3-hexadiene (**2**) was found in the mother liquors. The *cis* configuration of the trisubstituted double bond was confirmed by NOE experiments (NOE H^2−H^4, 4.7%). Treatment of **1a** with Tl(acac) (acac = acetylacetonate) in CH_2Cl_2 leads to the mono-

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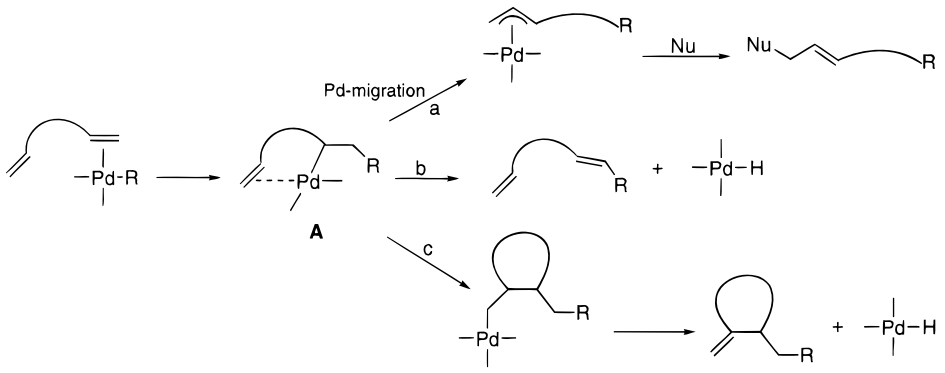
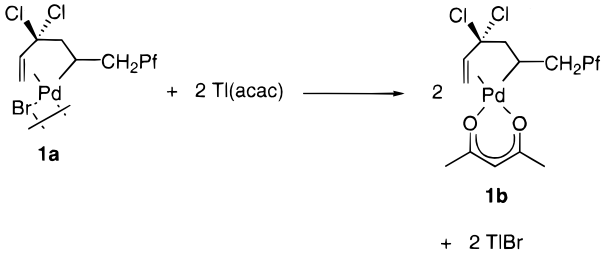
Scheme 1



meric complex **1b**, which is soluble in most organic solvents and could be studied better by NMR (eq 1).

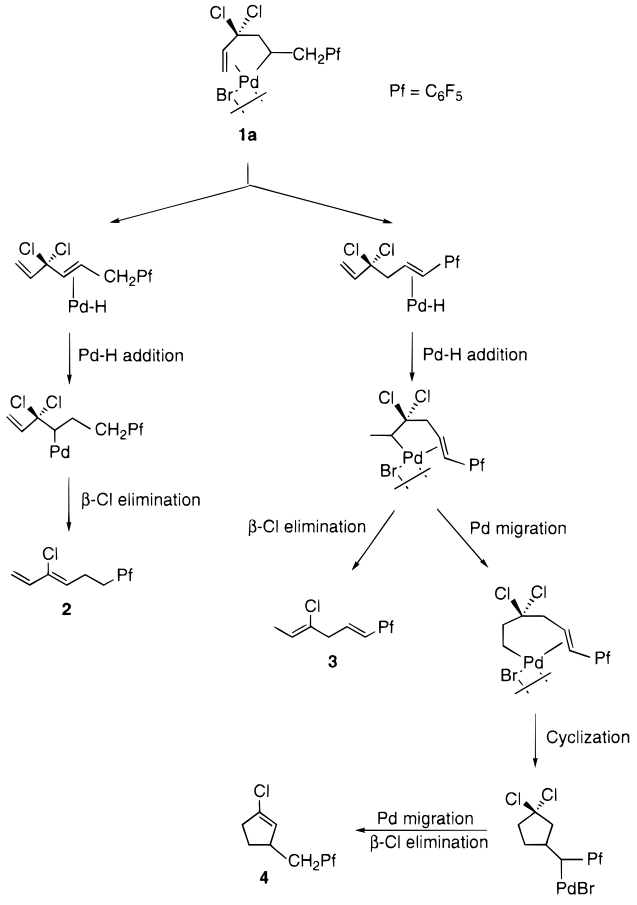


(1)

The insertion reaction was monitored by ^{19}F NMR. The reactants were mixed, and 1,3,5-trichloro-2,4,6-trifluorobenzene was added as an internal standard. When all of the starting material had been consumed, **1a** was found to account for 99% of the Pf present (less than 1% left in solution); in addition, **2** (1%) was observed. According to these data, insertion of the less-hindered allylic double bond into the Pd−Pf bond is preferred to form a stable 5.5-membered η^1-η^2 palladacycle (**1a**).[8] The formation of a small amount of **2** can be interpreted via Pd−H elimination−readdition followed by β-Cl elimination (Scheme 2).

When a suspension of **1a** in $CHCl_3$ was refluxed for 20 h, decomposition was observed and (*E*,*Z*)-4-chloro-1-(pentafluorophenyl)-1,4-hexadiene (**3**), 1-chloro-3-((pentafluorophenyl)methyl)-1-cyclopentene (**4**), and **2** in a ratio of 3:2:1, plus palladium halides, were formed (Scheme 2). The geometrical assignment of **3** was confirmed by NOE experiments (NOE H^3−H^5, 4.8%). The proposed mechanism for the decomposition is depicted in Scheme 2. Again, Pd−H elimination−readdition continues until β-Cl elimination occurs to give **2** and **3**. Thus, the process of Pd migration along the carbon chain to form an η^3-allylpalladium complex is interrupted by the CCl_2 link. Pd−Cl readdition, required for Pd−allyl formation, is not observed in the reaction in this case, even though the addition of Pd−Cl to olefin is possible.[9,10] β-Cl elimination has been previously observed in some palladium-mediated reactions[11−13] or proposed to explain the formation of some products or several isomerization processes in η^1-η^2 palladium complexes.[9,14] Cyclization from a putative 6.5-membered palladacycle followed by Pd migration and Pd−Cl elimination is also observed to give the cyclopentene derivative **4**.

Scheme 2



Reaction with Vinyl Crotonate. A mixture of complexes **5a** and **6a** (**5a**:**6a** = 7:1) can be isolated from the reaction of $[PdPfBr(NCMe)_2]$ with vinyl crotonate at room temperature (Scheme 3). In addition, products resulting from the cleavage of the ester C−O bond were found in the mother liquors (see below). Attempts to separate **5a** from **6a** failed. Inspection of the spectral data of the mixture indicated that the carbonyl oxygen

(8) The size of the η^1-η^2-enyl palladacycles is referred to as *n*.5-membered, *n* being the number of atoms in the cycle and adding 0.5 to account for the π-coordination of the double bond to the metal (see, for example: Omae, I. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 889).

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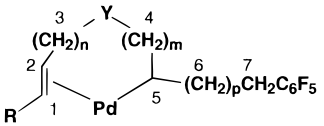
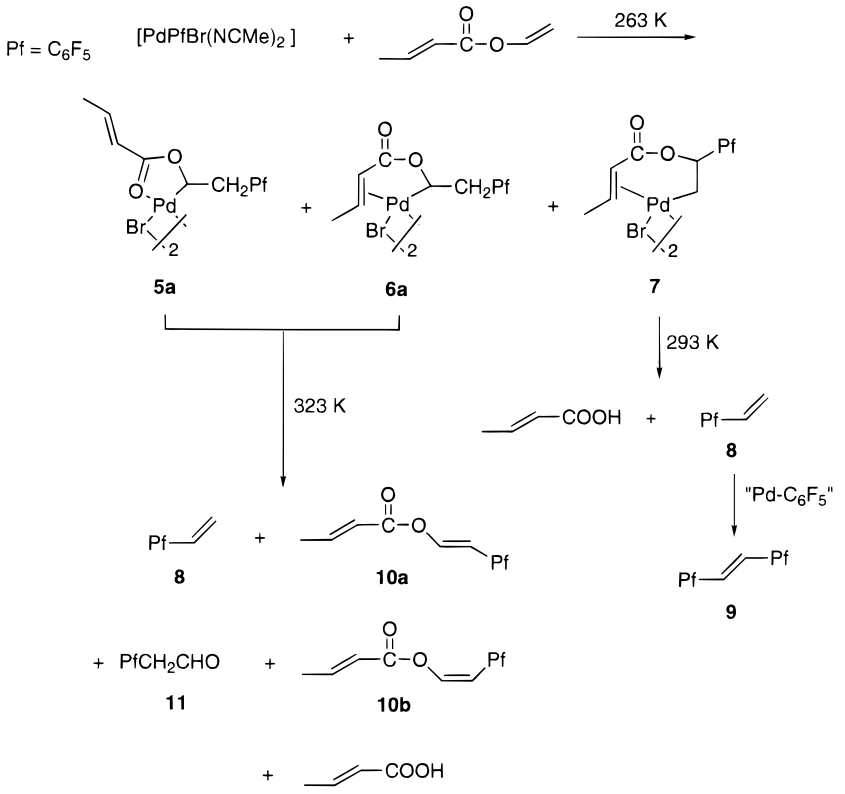
Table 1. ^{1}H NMR Data for Palladium Complexes[a−c]



compound	R (*syn*)	H^1 (*anti*)	H^2	H^3	H^4	H′^{4}	H^5	H^6	H′^{6}	H^7	H′^{7}	other
1a	4.61 b	4.61 b	4.42 d (14.3)		2.53 b	1.55 b	3.35 b			3.35 b	2.82 t (11.5)	
1b	4.31 d (8.2)	4.11 d (13.8)	5.87 ddd (13.8; 8.2; 1.8)		2.40 dd (14.8; 11.3)	1.74 ddd (14.8; 4.8; 1.8)	2.79 m			3.18 m ($J_{7-7'}$ = 11.8)	2.71 m ($J_{7-7'}$ = 11.8)	5.32 s (1H); 2.00 s (3H); 1.92 s (3H)
5a	1.93 dd (7.0; 1.6)	7.12 dq (15.6; 7.0)	5.87 m				5.87 m			3.36 b	3.36 b	
5b	1.90 dd (7.0; 1.7)	7.11 dq (15.6; 7.0)	5.87 dq (15.6; 1.7)				5.96 dd (9.0; 3.4)			3.34 dd (14.5; 9.0)	3.15 m (14.5; 3.4)	5.30 s (1H); 1.98 s (3H); 1.90 s (3H)
6a	2.07 d (5.2)	5.69 b	5.69 b				5.20 b			3.36 b	3.05 dd (15.9; 8.8)	
6b	1.94 d (6.1)	5.34 dq (13.5; 6.1)	5.50 d (13.5)				4.80 dd (8.2; 5.1)			3.22 m (14.2; 8.2)	2.95 dd (14.2; 5.1)	5.28 s (1H); 1.92 s (3H); 1.91 s (3H)
6c	1.91 d (6.9)	5.65 dq (13.3; 6.9)	5.40 d (13.3)				4.62 dd (10.0; 2.3)			3.70 dd (14.0; 2.3)	3.14 dd (14.0; 10.0)	5.37 s (1H); 1.90−1.95 (6H)[c]
12	5.57 d (8.3)	5.52 d (14.1)	6.55 dd (14.1; 8.3)				3.92 b			3.16 b	2.92 b	
14	5.50 b	4.41 b	6.00 b	3.59 b	3.59 b	2.46 b	3.25 b			3.25 b	3.04 b	
18	5.50 b	4.25 b	5.95 b	3.50−3.80 b			1.32 b	2.50 b	2.31 b	3.18 b	3.18 b	
15	5.11 d (8.7)	4.86 d (14.7)	5.92 b	4.29 db (16.2) 3.85 db (16.2)	3.05−3.20 b	2.42 b	3.47 b			2.90−3.20 mb	2.90−3.20 mb	
19	4.57 d (8.7)	4.54 d (13.3)	6.38 m	4.15 dd (12.6; 1.5) 3.92 d (12.6)			1.04 b	2.25 b	1.90 b	2.80−3.05 b	2.80−3.05 b	
16	4.95 b	3.98 b	6.30 b	1.50 b	2.00−2.50 b	2.00−2.50 b	3.05 b			2.00−2.50 b	2.00−2.50 b	0.08 s (6H)
20	5.00 b	4.01 d (15.0)	6.30 b	1.50 b			3.15 b	2.00−2.20 b	2.00−2.20 b	3.15 b	3.15 b	0.05 s (6H)
17[e]	5.10 b	5.10 b	6.32 b	2.60 b	1.94 b	1.46 b	2.95−3.50 b			2.95−3.50 b	2.95−3.50 b	
	5.33 b	5.33 b	5.81 b	2.60 b	1.21 b	0.79 b	2.95−3.50 b			2.95−3.50 b	2.95−3.50 b	

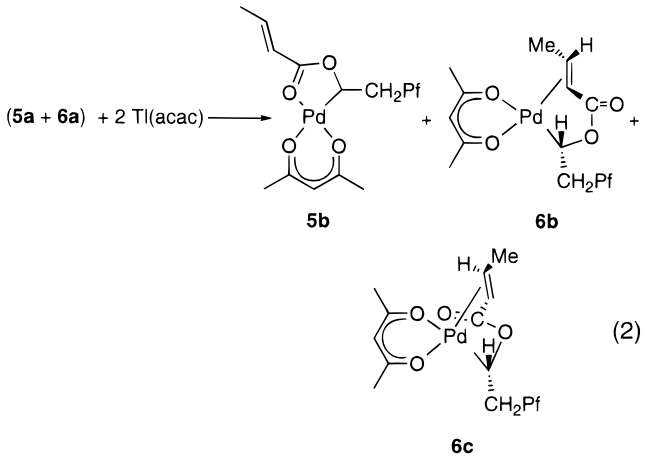
[a] **1a**,**b**: R = H; $n = p = 0$; $m = 1$; Y = CCl_2. **5a**,**b**, **6a**−**c**: R = Me; $n = m = p = 0$; Y = CO_2. **12**: R = H; $n = m = p = 0$; Y = SO_2. **14**: R = H; $n = m = 1$; $p = 0$; Y = SO_2. **18**: R = H; $n = p = 1$; $m = 0$; Y = SO_2. **15**: R = H; $n = m = 1$; $p = 0$; Y = O. **19**: R = H; $n = p = 1$; $m = 0$; Y = O. **16**: R = H; $n = m = 1$; $p = 0$; Y = $SiMe_2$. **20**: R = H; $n = p = 1$; $m = 0$; Y = $SiMe_2$. **17**: R = H; $n = m = 1$; $p = 0$; Y = $C(COOMe)_2$. [b] δ multiplicity J values (Hertz) are given in parentheses. $CDCl_3$ was used as the solvent except for with **12** (acetone-d_6). [c] The temperatures used are 293 K for complexes **1b**, **5a**,**b**, **6a**−**c**, and **12**; 273 K for **18** and **19**; 263 K for **14** and **20**; 253 K for **1a** and **17**; 243 K for **15** and **16**. [d] Signals overlapped by other compounds. [e] Data for two diasteroisomers (see ref 23).

Scheme 3



acts as a donor atom in complex **5a**, but the propenyl double bond coordinates to palladium in **6a**. The IR spectrum (Nujol mull) shows one very intense absorption at 1655 cm^{-1} and a small one around 1740 cm^{-1}. The former can be assigned to ν(CO) of the major derivative **5a** and the latter to **6a**. A decrease in ν(CO) is expected upon coordination, compared with the 1741 cm^{-1} absorption for vinyl crotonate (CH_2Cl_2 solution). The ^1H NMR spectrum of the mixture shows the resonances of the olefinic protons H^1 and H^2 for the major compound **5a** at δ 7.12 and 5.87, respectively, very close to the corresponding resonances for free vinyl crotonate (δ 7.05 and 5.82). A broad signal at δ 5.69 appears in the ^1H NMR spectrum of the minor derivative **6a**, which was assigned to the H^1 and H^2 protons (Table 1). The large difference in chemical shifts between the olefinic protons in the propenyl moiety for free vinyl crotonate and **6a** suggests the coordination of the double bond to palladium. The appearance of broad signals in the ^1H and ^{19}F NMR of **5a** and **6a** is probably due to exchange of the two coordination modes and the presence of different arrangements of two chiral moieties in the dimer which gives rise to diastereoisomers.

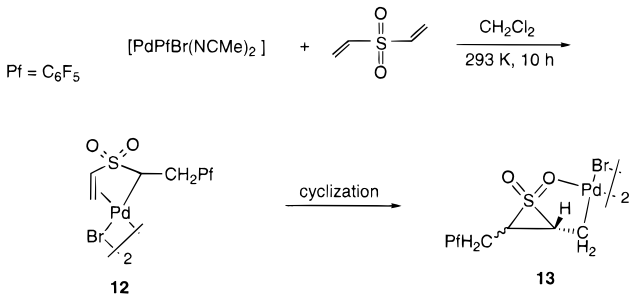
To avoid the presence of diastereoisomers derived from the dimeric structures of **5a** and **6a** and help to characterize the structures of both complexes in more detail, monomeric derivatives were obtained (**5b**, **6b**, and **6c** in a ratio of 5:4:1) by treating **5a** and **6a** with Tl(acac) (eq 2). It is interesting that almost half of **5a** changed the coordination mode from oxygen to the propenyl double bond after treatment with Tl(acac). Two isomers **6b** and **6c**, most likely arising from the presence of a chiral carbon and a coordinated prochiral double bond, are clearly observed in the ^{19}F and ^1H NMR spectra. The ^1H resonances of all olefinic protons in **6b** and **6c** display high-field shifts compared to the free ligand, as observed for **6a**.



(2)

The reaction of $[PdPfBr(NCMe)_2]$ with vinyl crotonate was monitored at low temperature by NMR (Scheme 3). Insertion of one double bond into the Pd−Pf bond was evident at −10 °C, and after 30 min, two broad $^{19}F_{ortho}$ signals (ratio of 8:3, δ values characteristic of C−Pf) appeared. With the help of ^1H NMR, the main signal can be assigned to the overlapping F_{ortho} resonances of **5a** and **6a**, derived from insertion of the terminal vinylic double bond. The minor $^{19}F_{ortho}$ signal corresponds to a compound that has two small broad signals in the ^1H NMR spectrum (δ 3.50 and 6.08 ppm) in a ratio of 2:1, which probably correspond to the $PdCH_2$ and PfCH moieties in complex **7**, i.e., a product of insertion with the opposite regiochemistry of the terminal vinylic double bond, the Pf group adding to the more substituted carbon. As the temperature was raised **7** decomposed, and its disappearance was complete at 20 °C.

Scheme 4



After 8 h at room temperature, a mixture of **5a** (63%), **6a** (9%), vinylpentafluorobenzene (**8**, 21%), *trans*-1,2-bis(pentafluorophenyl)ethylene (**9**, 7%), and crotonic acid (28%) was obtained. **8** and crotonic acid come from C−O cleavage of the β-ester moiety.[15] The bis(Pf) derivative results from arylation of **8** by residual [PdPfBr(NCMe)$_2$], followed by Pd−H elimination.

On the other hand, when **5a** and **6a** were dissolved in $CDCl_3$ and warmed at 50 °C for 1 day, they decomposed to vinylpentafluorobenzene (**8**), (*E*,*E*)-(pentafluorophenyl)vinyl crotonate (**10a**), (*E*,*Z*)-(pentafluorophenyl)-vinyl crotonate (**10b**), 2-(pentafluorophenyl)aldehyde (**11**), and crotonic acid in a ratio of 10:3:1:1:10 (Scheme 3). **10a** and **10b** are formed by Pd−H elimination. However, the dominant process is the β-elimination of a crotonato group after Pd migration to the Pf-substituted carbon, which produces **8** and crotonic acid.[11] The same type of C−O(CO) cleavage is observed in the decomposition of **7**. β-acetoxy elimination has been observed in the Pd-mediated synthesis of certain butyrolactones.[11] The small amount of product **11** observed is the result of the cleavage of the crotonate C(O)−O bond.

Only insertion of the terminal vinylic double bond is observed, but the addition of the Pd−Pf moiety can occur in either direction. The preference for the less-substituted one is clear, as shown by the ratio, (**5a** + **6a**):**7** = 8:3. Accordingly, the arylation on the terminal carbon is predominant, although a preference for the more substituted end of the olefin has been found for some heteroatom-substituted alkenes.[16,17] The results obtained are coincident with the arylation of enol esters reported by Heck[18] and the phenyl functionalization of enol acetates via tin enolates catalyzed by palladium.[19]

Reaction with Divinyl Sulfone. [PdPfBr(NCMe)$_2$] reacted with divinyl sulfone for 10 h at room temperature to form **12** and a second product with spectral data (see below) that are compatible with structure **13** (**12**:**13** = 5:1, Scheme 4). **12** was isolated as a yellow solid (61% yield). However, all attempts at isolation of **13** failed due to its instability when kept in solution and the lower solubility of **12**, which crystallizes preferentially. The reaction was also monitored at low temperature. Only **12** was formed after 3 h at 0 °C, and as the reaction time increased, **13** slowly appeared. After all of the starting materials were consumed, the amount of **13** continued to raise according to integration of the ^{19}F NMR signals, which confirms that complex **13** is produced by isomerization of **12** (Scheme 4).

13 is a mixture of two isomers in a 1.7:1 ratio from integration of the ^{19}F NMR signals. The ^{1}H NMR spectrum of **13** in acetone-d_6 shows two pairs of ABX systems (one pair per isomer in the ratio found in the ^{19}F NMR spectrum), which can be assigned to $PfCH_2$-CH and $PdCH_2CH$ moieties, respectively. The two diastereoisomers observed are derived from the two asymmetric carbons present in the complex which are formed in a slightly stereoselective cyclization step, as the ratio of the isomers implies. **13** is a rare example of an organometallic derivative containing a complexed episulfone. The latter is an important intermediate in the Ramberg−Bäcklund transformation of halosulfones.[20] Other palladacycles containing a SO_2 unit are also uncommon. A four-membered ring palladacycle has been reported;[21] a 4.5-membered cyclic allyl sulphinato complex was detected at low temperature.[22]

Reaction with Diallyl Substrates. The reactions of [PdPfBr(NCMe)$_2$] with the diallyl substrates CH_2=CH−(CH_2)−Y−(CH_2)−CH=CH_2 gave, at low temperature, the corresponding 6.5-membered η^1-η^2-enyl derivatives (Scheme 5, Y = SO_2, **14**, T = 263 K; Y = O, **15**, T = 243 K; Y= $SiMe_2$, **16**, T = 243 K; Y = $C(COOMe)_2$, **17**, T = 253 K).[23] When the temperature was raised, decomposition of these derivatives was observed as well as isomerization to the 5.5-membered η^1-η^2-enyl complexes **18** (Y = SO_2), **19** (Y = O), and **20** (Y= $SiMe_2$). The decomposition process is faster than isomerization for **17**, and the corresponding 5.5-membered enyl complex was not observed. The organometallic derivatives detected follow several routes of decomposition, often operating simultaneously. However, a main pathway can be identified in each case, which depends on the nature of Y. The pathways are as follows (Scheme 5 and Table 2):

(i) Cyclization. This was observed in the decomposition of **17** (Y = $C(COOMe)_2$); cyclization, Pd migration, and, finally, Pd−H elimination gives the endocyclic cyclopentene derivative **21**.[24] The PdHBr species generated in the final Pd−H elimination just described is responsible for two side reactions. First, efficient H-transfer to the σ-alkylpalladium derivative formed after cyclization occurs, and it gives the saturated derivative **22** (mixture of two diasteroisomers in a 1:1 ratio, by ^{19}F

(15) C−O cleavage of the β-ester moiety in compound **7** gives **8** and a crotonato group. This group can be converted into crotonic acid by the HBr formed in the decomposition of the "HPdBr" species generated in the formation of **9** and probably by the small amount of HCl present in the $CDCl_3$ used as solvent, since the quantity of the compounds handled in the monitored experiments, and so the amount of crotonato formed, is very small.

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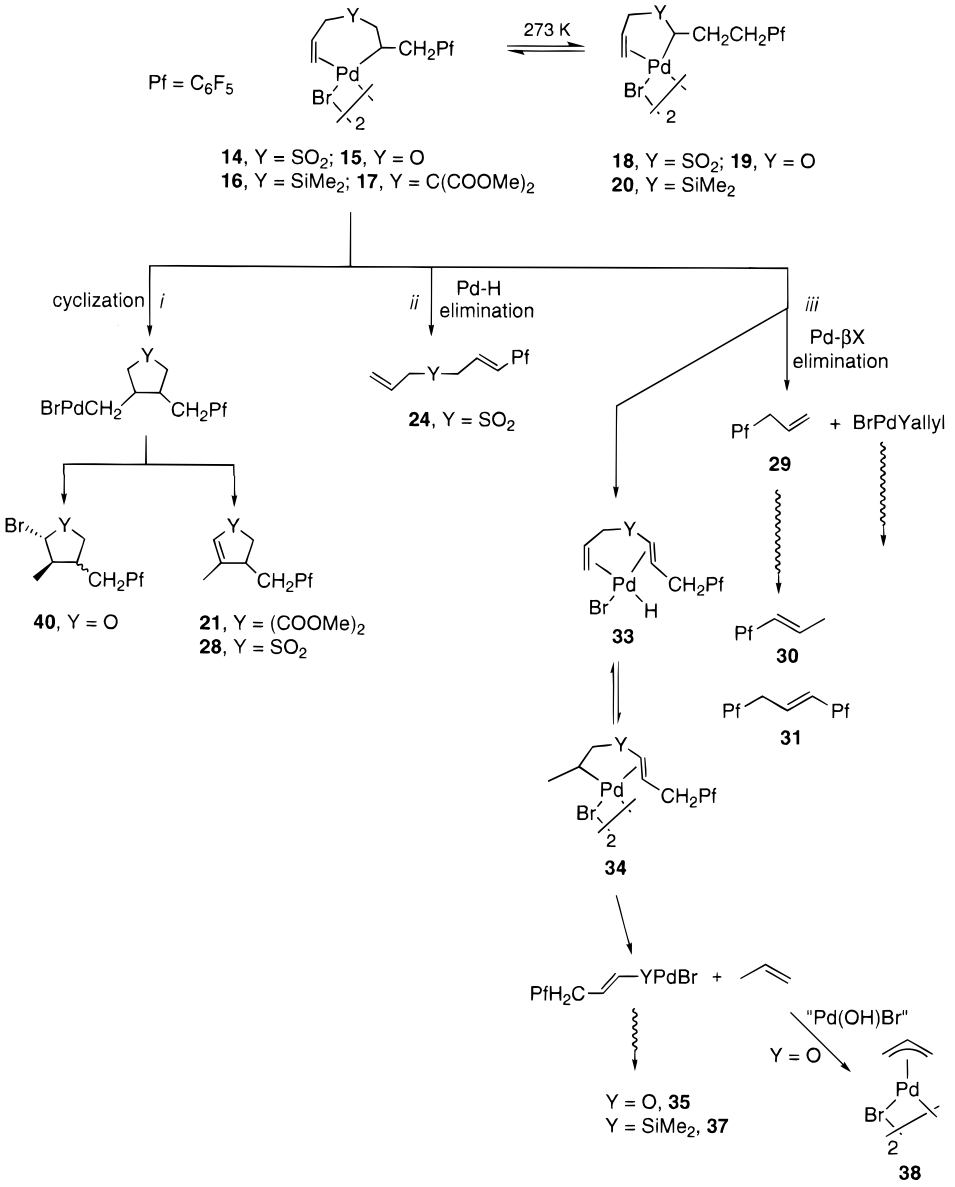
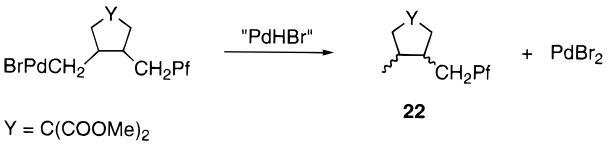
(23) Diastereoisomers were observed as two broad signals in the ^{19}F NMR spectrum of **14** and **17**, probably as a result of the prochiral nature of the double bond and the dimeric nature of the complexes. The diastereomeric ratios are 1:0.6 (**14**) and 1:0.8 (**17**).

(24) The cyclization reactions of dimethyl diallylmalonate have been studied, see: (a) Hegedus, L. S. In *Organometallics in Synthesis*; Schlosser, M., Ed.; Wiley: Chichester, 1994; Chapter 5. (b) Larock, R. C. *Adv. Met.−Org. Chem.* **1994**, *3*, 97. (c) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 38. (d) Grigg, R.; Mitchell, T. R. B.; Ramasubbu, A. *J. Chem. Soc., Chem. Commun.* **1979**, 669.

Scheme 5

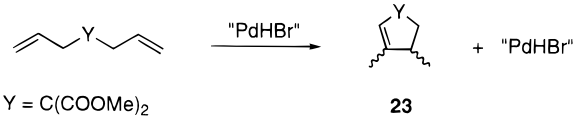


NMR, eq 3).[25,26] Second, dimethyl diallylmalonate



(3)

starting material inserts into the Pd−H bond to yield, through the same route just described for **21**, the Pf-free cyclopentene **23** (eq 4). H-transfer to the starting "PdPfBr" species is also observed, and some PfH is formed.[25]



(4)

(ii) Pd−H Elimination. This was observed in the decomposition of complexes **14** and **18** (Y = SO_2), which afford **24** as the main product. **24** undergoes further transformations under the decomposition conditions to give **25** through double-bond isomerization and **26** by hydrogenation of the terminal double bond (both processes produced by Pd−H species generated in the formation of **24**)[25] and **27** by arylation of **24** by "PdPfBr" species (Scheme 6 and Table 2). The amount of compound **24** and its derivatives **25**−**27** accounts for 79% of the reaction products, which reveals Pd−H elimination as the preferred decomposition route. The regiochemistry of **27** was inequivocally assigned by a ^{1}H−^{19}F heteronuclear NOE experiment: 4.1% NOE was found between the ortho fluorines of the Pf group and H^1 of the (pentafluorophenyl)allyl group. The coincidence of the chemical shifts of its olefinic protons and the alkene signals for **24**, **25**, and **26** leads to the regiochemistry shown in the schemes. Other processes

(25) Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *Organometallics* **1997**, *16*, 4030.

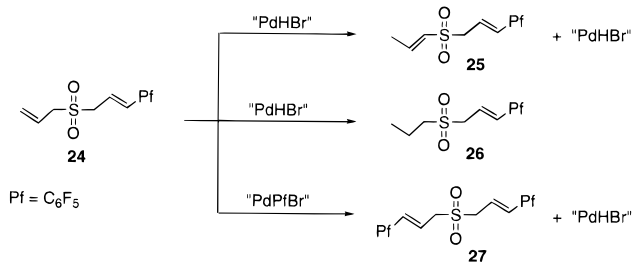
(26) The absence of olefinic protons in the ^{1}H NMR spectrum and GC-MS support this proposal, even though the ^{1}H NMR spectrum of **22** was difficult to assign because of heavy overlapping of its signals with other compounds.

Table 2. Products Obtained in the Decomposition of η^1:η^2-Enyl Derivatives 14−20[a]

	Y = SO_2	Y = O[b]	Y = $SiMe_2$[c]	Y = $C(COOMe)_2$
cyclization	**28** (7%)	**40** (11%)		**21** (56%)
				22 (13%)
				23 (31%)
Pd−H elimination	**24** (16%)			
	25 (32%)			
	26 (19%)			
	27 (12%)			
	32 (4%)			
β-X elimination	**30** (5%)	**29** (10%)	**29** (60%)	
	31 (5%)	**31** (3%)	**30** (15%)	
		35 (29%)	**31** (4%)	
		38 (28%)	**37** (15%)	
		propanal (7%)	**39** (6%)	

[a] See Scheme 5 for compound structure; percentages are given in parentheses. [b] **19** (5%) and 7% of unidentified compounds were also found in the final mixture. [c] Only Pf-containing products are given.

Scheme 6



are also observed, i.e., cyclization of **14** to give **28** (Scheme 5) and C−S cleavage (β-X elimination) to form **29**. **29** can also evolve to **30** and **31** through the same processes depicted in Scheme 6.[27]

(iii) C−X Cleavage (β-X Elimination).[28] This is the main decomposition pathway for derivatives **15** and **19** (Y = O) and for **16** and **20** (Y = $SiMe_2$). β-X elimination in **15** or **16** gives **29** (and/or its derivatives **30** and **31**, Table 2) and the corresponding "PdBrX" species that react to give propanal (Y = O, X = $OCH_2CH{=}CH_2$) or, by hydrolysis−polymerization and cleavage of the Si−allyl bond, dimethylpolysiloxanes and propene (Y = $SiMe_2$, X = $Si(Me)_2CH_2CH{=}CH_2$).[29]

Alternatively, C−X cleavage can occur from the undetected η^1-η^2-enyl derivatives **34** (Scheme 5) that arise from double-bond switch in a 1,5-diene-hydridopalladium intermediate (**33**) generated in turn by Pd−H elimination from **15** or **16**.[1] The process gives propene and the corresponding "PdBr(PfX)" species that react to give the 3-(pentafluorophenyl)propanal species **35** (Y = O) or dimethyl(3-(pentafluorophenyl)propenyl)-bromosilane species **36**. **36** reacts further by hydrolysis and dimerization to yield 1,1,3,3-tetramethylbis((*E*)-3-(pentafluorophenyl)propenyl)disiloxane **37** (Y = $SiMe_2$) as the final product observed. For diallyl ether (Y = O), the propene produced in this process reacts further to give the η^3-propenylpalladium complex **38**, which can be crystallized from the reaction mixture.[30,31]

β-X elimination is the only decomposition pathway observed for diallyldimethylsilane and the main route for diallyl ether. However, a small amount of cyclic derivative **40** (as a mixture of two diastereoisomers) is observed for the latter diene (about 11% of the decomposition products). Cyclization, Pd migration, and reductive elimination of alkyl and Br explains the formation of **40**. The actual mutual arrangement of H^2 and H^3 could not be determined since the values of the vicinal coupling constants between them (4.7 and 3.1 Hz for each isomer) are not unequivocal.[32] However, oxidative addition of RX (R = allyl) to Pd(0) under similar reaction conditions to those used here proceeds with retention of configuration at the C center.[33] Thus, the reverse reaction, reductive elimination of RBr, should also occur with retention of configuration, giving **40** with the configuration depicted in Scheme 5. The two diastereoisomers observed arise from the nonfixed configuration at the third chiral carbon in the cycle.

Conclusions

η^1-η^2-Enylpalladium derivatives are obtained either by direct coordination of the unattacked double bond to palladium or by one-step Pd migration and then coordination of the second double bond. 6.5-, 5.5-, and 4.5-membered η^1-η^2-enylpalladacycles are observed, and although the actual stability of these derivatives depends on the particular complex, the 6.5-membered complexes are clearly the least stable.

Since the Pd-migration mechanism is blocked for the unsaturated substrates used, the formation of η^3-allyl derivatives is prevented unless other mechanisms transport the Pd atom past the block to reach the second double bond. No η^3-allylpalladium complexes were found, indicating that Pd migration is the only efficient mechanism to form these complexes.

(27) A small amount of starting diallyl sulfone is catalytically isomerized to 2,3-dihydro-3,4-dimethylthiophene-1,1-dioxide (**32**, 4%) by "PdHBr" through insertion into Pd−H bonds and cyclization.

(28) For other examples of palladium β-X elimination, see ref 10 and for X = Cl, refs 11 and 12. X = OR: b) Nguefack, J.-F.; Bolitt, V.; Sinou, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1893. (c) Duan J.-P.; Cheng, C.-H. *Tetrahedron Lett.* **1993**, *34*, 4019. X = OH: (d) Hosokawa, T.; Sugafuji, T.; Yamanaka, T.; Murahashi, S. *J. Organomet. Chem.* **1994**, *470*, 253. X = SiR_3: (e) Ikenaga, K.; Kikukawa, K.; Matsuda, T. *J. Org. Chem.* **1987**, *52*, 1276. (f) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1986**, 51, 5286. (g) Ikenaga, K.; Kikukawa, K.; Matsuda, T. *J. Chem. Soc. Perkin Trans.* **1986**, 1959.

(29) (a) Kliegman, J. M. *J. Organomet. Chem.* **1971**, *29*, 73. (b) Sommer, L. H.; Tyler, L. J.; Whitmore, F. C. *J. Am. Chem. Soc.* **1948**, *70*, 2872.

(30) The reaction of $[PdCl_4]^{2-}$ with allyl ether to form palladium(II)−allyl complex **38** and propenal has also been reported, see: Pietropaolo, R.; Faraone, F.; Sergi, S.; Pietropaolo, D. *J. Organomet. Chem.* **1972**, *42*, 177.

(31) A small amount of 2-(pentafluorophenyl)propene (**39**) was found in the reaction with diallyldimethylsilane (Y = $SiMe_2$), which probably comes from insertion of the allylic double bond into the Pd−C_6F_5 bond with opposite regiochemistry, that is, C_6F_5 binds to the more substituted double bond; subsequent Pd migration of one carbon and β-SiR_3 elimination gives **39** and allyl(dimethyl)bromosilane.

(32) Tedder, J. M.; Nechvatal, A.; Murray, A. W.; Carnduff, J. *Basic Organic Chemistry*; Wiley: Chichester, 1970; p 181.

(33) Kurosawa, H.; Ogoshi, S.; Kawasaki, Y.; Murai, S.; Miyoshi, M.; Ikeda, I. *J. Am. Chem. Soc.* **1990**, *112*, 2813.

β-X elimination (C−X cleavage, X ≠ C, H) occurs for most of the substrates employed either as the main decomposition route or as a side reaction. Pd−X readdition (X ≠ H) does not take place in any case. The ease of β-X elimination follows the order C−C ≪ C−SO_2 < C−Cl < C−O (ether) < C−O (ester) ≈ C−Si.

Experimental Section

General Considerations. $[Pd(C_6F_5)Br(NCMe)_2]$[34] and the dienes 3,3-dichloro-1,5-hexadiene,[35] diallyl ether,[36] and diallyl sulfone[37] were prepared by literature methods. Other ligands were purchased from Aldrich and Lancaster Chemical Co. and used without further purification. Solvents were dried employing the usual desiccants and distilled before use. ^{1}H and ^{19}F NMR spectra were obtained on Bruker AC-300 and ARX-300 spectrometers at 293 K unless otherwise noted. ^{1}H and ^{13}C chemical shifts were referenced to TMS and ^{19}F chemical shifts to $CFCl_3$. Infrared spectra (Nujol mulls) were recorded on a Perkin-Elmer 883 spectrometer. Elemental analyses were performed on a Perkin-Elmer 240 microanalyzer. Organic products were analyzed using an HP-5890 gas chromatograph connected to an HP-5988 mass spectrometer at an ionizing voltage of 70 eV and a quadrupole analyzer; chemical ionization using methane at 230 eV was also used. Evaporation of solvents was carried out using a water pump to avoid evaporation of low-boiling organic derivatives of interest.

Monitoring Reaction of $[Pd(C_6F_5)Br(NCMe)_2]$ with Dienes at Low Temperature by NMR (General Method). $[Pd(C_6F_5)Br(NCMe)_2]$ (0.025 g, 0.0574 mmol) in $CDCl_3$ (0.6 mL) was charged in an NMR tube and cooled down, and the diolefin (0.0574 mmol) was added. The reaction was monitored by alternatively taking ^{1}H and ^{19}F NMR spectra on a Bruker AC-300 spectrometer with a thermostated multinuclear QNP probe head operating in the FT mode. The temperature was slowly increased (10 °C at a time) to observe the reaction course. ^{1}H homonuclear correlation experiments were carried out at low temperature for the assignment of some derivatives when necessary. The final products were analyzed by ^{1}H and ^{19}F NMR and GC-MS. The yields for the products were determined by integration of the ^{1}H and ^{19}F NMR signals.

Reaction with 3,3-Dichloro-1,5-Hexadiene. To a solution of $[Pd(C_6F_5)Br(NCMe)_2]$ (0.089 g, 0.20 mmol) in CH_2Cl_2 (2 mL) was added 3,3-dichloro-1,5-hexadiene (0.034 mL, 0.20 mmol). After 1 h of stirring, the white precipitate, **1a**, was filtered, washed with CH_2Cl_2, and air dried (71% yield). The mother liquors were evaporated to dryness and extracted with *n*-hexane, and the insoluble residue "PdBrCl" was filtered off. After evaporation of the solvent, a colorless oily residue, **2**, was obtained.

1a. Anal. Calcd for $C_{24}H_{16}Br_2Cl_4F_{10}Pd_2$: C, 28.58; H, 1.60. Found: C, 28.80; H, 1.61. IR (cm^{-1}, Nujol mull, C_6F_5): 1659, 1522, 1503, 1119, 1030, 949 cm^{-1}. ^{19}F NMR ($CDCl_3$, δ, 282 MHz, 253 K): −161.5 (b, F_{meta}), −155.7 (b, F_{para}), −142.2 (b, F_{ortho}).

2. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −163.1 (m, F_{meta}), −157.6 (t, F_{para}), −144.4 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 6.35 (dd, J = 16.5, 10.5 Hz, 1H, H^2), 5.75 (t, J = 7.4 Hz, 1H, H^4), 5.57 (d, J = 16.5 Hz, 1H, H^1), 5.20 (d, J = 10.5 Hz, 1H, $H^{1'}$), 2.84 (t, J = 7.3 Hz, 2H, H^6), 2.62 (q, J = 7.3 Hz, 1H, H^5); MS (EI) m/z (relative intensity): 282 (M^+, 10), 181 (14), 103 (21), 101 (65), 65 (100), 51 (6).

Preparation of (Acetylacetonato){η^1-η^2-3,3-dichloro-6-(pentafluorophenyl)-1-hexen-5-yl}palladium(II) (1b). Tl(acac) (0.026 g, 0.086 mmol) was added to a suspension of **1a** (0.041 g, 0.043 mmol) in CH_2Cl_2 (15 mL). After 1 h of stirring, the white precipitate (TlBr) was filtered. The filtrate was evaporated to dryness, and diethyl ether (2 mL) was added. The mixture was cooled down, and a white solid, **1b**, was obtained (72% yield).

1b. Anal. Calcd for $C_{17}H_{15}Cl_2F_5O_2Pd$: C, 38.99; H, 2.88. Found: C, 38.66; H, 2.84. ^{19}F NMR ($CDCl_3$, δ, 282 MHz); −162.9 (m, F_{meta}), −157.8 (t, F_{para}), −143.3 (m, F_{ortho}).

Decomposition of 1a. A suspension of **1a** (0.030 g, 0.030 mmol) in $CHCl_3$ (15 mL) was refluxed for 20 h. The brown precipitate (PdBrCl) was filtered off. Upon evaporation of the solvent, a colorless residue formed, which was a mixture of **3**, **4**, and **2** in a ratio of 3:2:1.

3. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −163.5 (m, F_{meta}), −157.2 (t, F_{para}), −143.6 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 6.56 (dt, J = 16.3, 6.7 Hz, 1H, H^2), 6.37 (dt, J = 16.3, 1.4 Hz, 1H, H^1), 5.65 (qt, J = 6.6, 1.1 Hz, 1H, H^5), 3.25 (db, J = 6.7 Hz, 2H, H^3), 1.76 (dt, J = 6.6, 1.2 Hz, 3H, H^6). MS (EI) m/z (relative intensity): 282 (M^+, 0.2), 181 (6), 103 (32), 101 (100), 65 (88), 51 (5).

4. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −162.8 (m, F_{meta}), −157.4 (t, F_{para}), −143.3 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 5.56 (m, 1H, H^2), 3.03 (m, 1H, H^3), 2.78−2.73 (m, 2H, CH_2Pf), 2.54 (m, 2H, H^5), 2.15 (m, 1H, H^4), 1.68 (m, 1H, $H^{4'}$). MS (EI) m/z (relative intensity): 282 (M^+, 41), 247 (45), 231 (13), 187 (16), 181 (100), 123 (11), 101 (11), 77 (15), 65 (22), 53 (13), 51 (10).

Reaction with Vinyl Crotonate. Vinyl crotonate (0.055 mL, 0.459 mmol) was added to $[Pd(C_6F_5)Br(NCMe)_2]$ (0.200 g, 0.459 mmol) dissolved in CH_2Cl_2 (10 mL). After 8 h of stirring, activated carbon was added and the suspension filtered. The solvent was evaporated, and the residue was chromatographed through a silica gel column. The first batch obtained using *n*-hexane as the eluent gave, after evaporation of the solvent, a colorless oily residue; it was a mixture of **8** and **9**. A small amount of white solid **9** separated after removal of **8** by suction. A second batch was obtained with diethyl ether as the eluent. Concentration of the solution to ca. 2 mL afforded a yellow solid, **5a** mixed with 12% of **6a** (total yield 44%). An aqueous KOH solution (1 M) was added to the mother liquors, and the mixture was vigorously stirred. The aqueous phase was neutralized with aqueous HCl solution (1 M) and then extracted with diethyl ether. The organic phase was dried with $MgSO_4$, and the solvent was evaporated. A white residue, crotonic acid, was found.

5a mixed with 12% of **6a**. Anal. Calcd for $C_{24}H_{16}Br_2F_{10}O_4Pd_2$: C, 30.96; H, 1.72. Found: C, 30.98; H, 1.70. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): **5a** −162.8 (b, F_{meta}), −156.5 (b, F_{para}), −142.8 (b, F_{ortho}); **6a** −162.3 (b, F_{meta}), −155.8 (b, F_{para}), −142.8 (b, F_{ortho}).

The reaction was examined by NMR at low temperature (−10 °C), and complex **7** was detected; the final products are **5a** (63%), **6a** (9%), **8** (21%), **9** (7%) and crotonic acid (yields were determined by integration of the ^{1}H or ^{19}F NMR signals and based on vinyl crotonate).

7. ^{19}F NMR ($CDCl_3$, δ, 282 MHz, 263 K): −162.7 (b, F_{meta}), −156.2 (b, F_{para}), −141.3 (b, F_{ortho}).

Reaction of 5a and 6a with Tl(acac). To a mixture of **5a** and **6a** (0.040 g, 0.042 mmol) in $CHCl_3$ (5 mL) was added Tl(acac) (0.026 g, 0.084 mmol). A white precipitate (TlBr) was formed immediately, and it was filtered after 30 min. By evaporation of the solvent, a light yellow oily residue was obtained, which was a mixture of **5b**, **6b**, and **6c** with a ratio of 5:4:1. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): **5b** −163.4 (m, F_{meta}), −157.9 (t, F_{para}), −143.2 (m, F_{ortho}); **6b** −163.2 (m, F_{meta}), −157.3 (t, F_{para}), −143.4 (m, F_{ortho}); **6c** −163.1 (m, F_{meta}), −157.6 (t, F_{para}), −143.2 (m, F_{ortho}).

Decomposition of 5a and 6a. The mixture of **5a** and **6a** (0.030 g, 0.032 mmol) in $CHCl_3$ (2 mL) was warmed at 55 °C

(34) Albéniz, A. C.; Espinet, P.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1990**, *9*, 1079.
(35) Seyferth, D.; Murphy, G. J.; Mauzé, B. *J. Am. Chem. Soc.* **1977**, *99*, 5317.
(36) Olson, W. T.; Hipsher, H. F.; Buess, C. M.; Goodman, I. A.; Hart, I.; Lamneck, J. H., Jr.; Gibbons, L. C. *J. Am. Chem. Soc.* **1947**, *69*, 2451.
(37) Hirano, M.; Tomaru, J.-I.; Morimoto, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3752.

for 1 day. After the black precipitate was filtered and the solvent evaporated, a colorless residue was obtained, which contained **8**, **10a**, **10b**, and **11** in a ratio of 10:3:1:1, and crotonic acid.

10a. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −163.1 (m, F_{meta}), −157.2 (t, F_{para}), −141.6 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 8.18 (d, J = 13.0 Hz, 1H, Pf−CH=C*H*), 7.20 (m, J = 15.6, 7.1 Hz, 1H, Me−C*H*=CH), 6.35 (d, J = 13.0 Hz, 1H, Pf−C*H*=CH), 5.95 (dq, J = 15.6, 1.6 Hz, 1H, Me−CH=C*H*), 1.97 (dd, J = 7.1, 1.6 Hz, 3H, *Me*−CH=CH). MS (EI) *m*/*z* (relative intensity): 278 (M^+, 2), 181 (6), 161 (3), 69 (100), 41 (18).

10b. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −162.3 (m, F_{meta}), −156.1 (t, F_{para}), −138.4 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 7.57 (d, J = 7.0 Hz, 1H, Pf−CH=C*H*), 7.15 (m, 1H, Me−C*H*=CH), 5.90 (m, 1H, Me−CH=C*H*), 5.63 (dt, J = 7.0, $^4J_{F-H}$ = 1.2 Hz, 1H, Pf−C*H*=CH), 1.95 (m, 3H, *Me*−CH=CH). MS (EI) *m*/*z* (relative intensity): 278 (M^+, 0.8), 181 (5), 161 (3), 69 (100), 41 (16).

11. ^{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, Pf−CH_2). MS (EI) *m*/*z* (relative intensity): 210 (M^+, 31), 181 (100), 161 (24), 132 (19), 93 (17).

Reaction with Divinyl Sulfone. To a solution of [Pd(C_6F_5)Br($NCMe)_2$] (0.200 g, 0.459 mmol) in CH_2Cl_2 (10 mL) was added divinyl sulfone (0.046 mL, 0.459 mmol). After 10 h at room temperature, a mixture of **12** and **13** had formed in a ratio of 5:1, as shown by the ^{19}F NMR spectrum in CH_2Cl_2 (a capillary tube with acetone-d_6 was used as external lock solvent). The solvent was reduced to ca. 0.5 mL and n-hexane was added (2 mL). A yellow solid, **12**, was obtained (61% yield).

12. Anal. Calcd for $C_{20}H_{12}Br_2F_{10}O_4Pd_2S_2$: C, 25.47; H, 1.28. Found: C, 25.32; H, 1.29. IR (SO_2): 1303 (s), 1128 (s), 991−966 (sb) cm^{-1}. ^{19}F NMR (acetone-d_6, δ, 282 MHz): −163.9 (b, F_{meta}), −157.7 (b, F_{para}), −141.4 (b, F_{ortho}).

13$_1$. ^{19}F NMR (acetone-d_6, δ, 282 MHz): −164.9 (m, F_{meta}), −160.6 (t, F_{para}), −142.2 (m, F_{ortho}). ^{1}H NMR (acetone-d_6, δ, 300 MHz): 3.05 (m, 2H, Pf−C*H*H′C*H*), 2.56 (b, 1H, Pf−CH*H*′CH), 2.15 (b, 1H, Pd−C*H*H′CH), 1.8−2.0 (m, 2H, Pd−CH*H*′C*H*).

13$_2$. ^{19}F NMR (acetone-d_6, δ, 282 MHz), −164.9 (m, F_{meta}), −160.6 (t, F_{para}), −142.2 (m, F_{ortho}). ^{1}H NMR (acetone-d_6, δ, 300 MHz), 3.1 (m, 2H, Pf−C*H*H′C*H*), 2.47 (b, 1H, Pf−CH*H*′CH), 2.3 (b, 1H, Pd−C*H*H′CH), 1.8−2.0 (m, 2H, Pd−CH*H*′C*H*).

Reaction with Diallyl Sulfone. [Pd(C_6F_5)Br($NCMe)_2$] (0.030 g, 0.0689 mmol) and diallyl sulfone (0.0087 mL, 0.0689 mmol) were mixed at −30 °C in $CDCl_3$ (0.6 mL), and the reaction was monitored by ^{1}H and ^{19}F NMR. Complexes **14** and **18** were detected and identified. After 2 days at room temperature, a black precipitate had formed, which was filtered, and the products contained in the filtrate were analyzed: **24** (32%), **25** (16%), **26** (19%), **27** (12%), **28** (7%), **32** (4%), **30** (5%), and **31** (5%) (the yields are based on diallyl sulfone).

The compounds in the above-mentioned mixture could be separated in several batches when the reaction was carried out using higher amounts of the starting materials. To [Pd(C_6F_5)Br($NCMe)_2$] (0.200 g, 0.459 mmol) in CH_2Cl_2 (10 mL) was added allyl sulfone (0.058 mL, 0.459 mmol). After 2 days of stirring, a palladium mirror appeared on the flask wall. Activated carbon was added to the black suspension, it was filtered, and the filtrate was evaporated to dryness. The residue was triturated with *n*-hexane and separated by column chromatography (silica gel). A first batch, eluting with *n*-hexane, afforded a colorless oily residue, which was **31** mixed with **30**. The use of diethyl ether as the eluent afforded a second batch. Evaporation of the solvent to ca. 2 mL and cooling led to a white solid (**27**, 11% yield). After the separation of **27**, its mother liquors were subjected to preparative TLC using diethyl ether as the eluent. Two batches were obtained, with R_f = 0.90 (**24**, **25**, and **26**) and 0.75 (**28** and **32**).

14. ^{19}F NMR ($CDCl_3$, δ, 282 MHz, 243 K): −161.4/−163.0 (b, F_{meta}), −155.5/−157/6 (b, F_{para}), −143.2/−142.2 (b, F_{ortho}).[21]

18. ^{19}F NMR ($CDCl_3$, δ, 282 MHz, 273 K): −162.9 (b, F_{meta}), −157.9 (b, F_{para}), −138.3 (b, F_{ortho}).

24. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −162.6 (m, F_{meta}), −154.2 (t, F_{para}), −142.4 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 6.63 (d, J = 16.3 Hz, 1H PfC*H*=CHCH_2−), 6.57 (dd, J = 16.3, 6.0 Hz, 1H, PfCH=C*H*CH_2−), 5.95 (m, J = 17.1, 10.0, 7.4 Hz, 1H, CH_2=C*H*CH_2−), 5.56−5.43 (m, J = 17.1, 10.0 Hz, 2H, CH_2=CHCH_2−), 3.90 (d, J = 6.0 Hz, 2H, PfCH=CHCH_2−), 3.75 (d, J = 7.4 Hz, 2H, CH_2=CHCH_2−). MS (EI) *m*/*z* (relative intensity): 312 (M^+, 3), 207 (100), 187 (43), 181 (41), 138 (6), 41 (46).

25. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −162.5 (m, F_{meta}), −154.5 (t, F_{para}), −142.6 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 6.92 (dq, J = 15.1, 7.0 Hz, 1H, MeC*H*=CH−), 6.56 (d, J = 16.3 Hz, 1H, PfC*H*=CHCH_2−), 6.48 (dd, J = 16.3, 6.7 Hz, 1H, PfCH=C*H*CH_2−), 6.32 (dq, J = 15.1, 1.5 Hz, 1H, MeCH=C*H*−), 3.88 (d, J = 6.7 Hz, 2H, PfCH=CHCH_2−), 1.97 (dd, J = 7.0, 1.5 Hz, 3H, *Me*CH=CH−). MS (EI) *m*/*z* (relative intensity): 312 (M^+, 2), 207 (100), 187 (43), 181 (30), 41 (12).

26. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −162.6 (m, F_{meta}), −154.3 (t, F_{para}), −142.5(m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 6.64 (d, J = 16.2 Hz, 1H, PfC*H*=CHCH_2−), 6.58 (dd, J = 16.2, 6.0 Hz, 1H, PfCH=C*H*CH_2−), 3.91 (d, J = 6.0 Hz, 2H, PfCH=CHCH_2−), 2.98 (m, 2H, −CH_2CH_2Me), 1.90 (m, J = 7.4 Hz, 2H, −CH_2CH_2Me), 1.08 (t, J = 7.4 Hz, 3H, −CH_2CH_2*Me*). MS (EI) m/z (relative intensity): 314 (M^+, 1), 312 (22), 247 (8), 233 (9), 220 (7), 181 (100), 41 (10).

27. Anal. Calcd for $C_{18}H_8F_{10}O_2S$: C, 45.20; H, 1.67. Found: C, 44.82; H, 1.68. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −162.3 (m, F_{meta}), −153.9 (t, F_{para}), −142.4 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 6.67 (d, J = 16.2 Hz, 1H, PfC*H*=CH-CH_2−), 6.60 (dd, J = 16.2, 6.0 Hz, 1H, PfCH=C*H*CH_2−), 3.96 (d, J = 6.0 Hz, 2H, PfCH=CHCH_2−). MS (EI) *m*/*z* (relative intensity): 478 (M^+, 0.7), 207 (100), 187 (35), 181 (29), 138 (5).

28. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −161.1 (m, F_{meta}), −154.7 (t, F_{para}), −142.8 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 6.43 (m, J_{H^5-Me} = 1.3 Hz, 1H, H^5), 3.31 (dd, J = 12.5, 7.8 Hz, 1H, H^2), 3.28 (m, $J_{3-PfCHH'}$ = 9.1, $J_{3-2'}$ = 1.5 Hz, 1H, H^3), 3.18 (d, J = 14.5 Hz, 1H, PfC*H*H′−), 3.03 (dd, J = 12.5, 1.5 Hz, 1H, H$^{2'}$), 2.93 (dd, J = 14.5, 9.1 Hz, 1H, PfCH*H*′−), 2.10 (d, J = 1.3 Hz, 3H, Me). MS (EI) *m*/*z* (relative intensity): 312 (M^+, 26), 233 (13), 181 (100), 161 (6), 67 (7), 65 (7), 41 (13).

30. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −163.9 (m, F_{meta}), −158.5 (t, F_{para}), −144.5 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 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 (EI) *m*/*z* (relative intensity): 208 (M^+, 100), 189 (22), 187 (28), 181 (79), 169 (14), 158 (15).

31. ^{19}F NMR ($CDCl_3$, δ, 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 ($CDCl_3$, δ, 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). MS (EI) *m*/*z* (relative intensity): 374 (M^+, 53), 355 (17), 205 (16), 193 (27), 187 (34), 181 (100), 163 (25), 161 (17), 143 (18).

32. ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 6.30 (m, $J_{H^5-Me^4}$ = 1.6 Hz, 1H, H^5), 3.50 (dd, J = 13.3, 8.0 Hz, 1H, H^2), 3.00 (m, J = 8.0, 7.1, 4.0 Hz, 1H, H^3), 2.95 (dd, J = 13.3, 4.0 Hz, 1H, H$^{2'}$), 1.99 (d, J = 1.6 Hz, 3H, Me^4), 1.32 (d, J = 7.1 Hz, 3H, Me^3). MS (EI) *m*/*z*: 146 (M^+).

Reaction with Diallyl Ether. An NMR tube charged with [Pd(C_6F_5)Br($NCMe)_2$] (0.030 g, 0.0689 mmol) and $CDCl_3$ (0.6 mL) was cooled to −30 °C, and diallyl ether (0.0084 mL, 0.0689 mmol) was added. The behavior of the reaction at low temperature was monitored by NMR, and complexes **15** and **19** were identified. Finally, the temperature was increased to 20 °C, and after 1 day, the mixture of products formed was shown to be **19** (5%), **29** (10%), **31** (3%), **35** (29%), **38** (28%), **40** (11%), propanal (7%), and an unknown component (7%).

15. ^{19}F NMR ($CDCl_3$, δ, 282 MHz, 243 K): −162.4/−163.2 (m, F_{meta}), −156.3/−156.5 (t, F_{para}), −143.4/−143.9 (m, F_{ortho}).

19. ^{19}F NMR ($CDCl_3$, δ, 282 MHz, 273 K): −162.4(b, F_{meta}), −157.2 (b, F_{para}), −142.6 (b, F_{ortho}).

To separate and identify the products, the reaction was repeated using a higher amount of reactants. To [$Pd(C_6F_5)$-$Br(NCMe)_2$] (0.086 g, 0.20 mmol) in CH_2Cl_2 (10 mL) was added diallyl ether (0.024 mL, 0.20 mmol). After 1 day of stirring, activated carbon was added and the suspension filtered. The yellow filtrate was evaporated to dryness, and diethyl ether (5 mL) was added; after cooling down the mixture, a yellow solid bis(μ-bromo)-bis(η^3-propenyl)dipalladium(II) (**38**) appeared (23%). The mother liquors were evaporated to dryness and chromatographed on a silica gel column. With *n*-hexane, a mixture of **31** and **29** was obtained. When diethyl ether was used as the eluent, two more batches were obtained, which were formed by **35** and **40**, mixed with some unidentified compounds, the first one, and a small amount of **15**, **38**, and **19**, the second one. Finally, CH_2Cl_2 was used as the eluent, and a small amount of **38** was obtained again.

29. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −163.5 (m, F_{meta}), −158.1 (t, F_{para}), −144.7 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 5.87 (m, 1H, H^2), 5.1 (m, 2H, H^1), 3.43 (d, J = 6.2 Hz, 2H, H^3). MS (EI) *m*/*z* (relative intensity): 208 (M^+, 97), 189 (24), 187 (38), 181 (100), 169 (24), 161 (22), 158 (18).

35. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −162.7 (m, F_{meta}), −157.2 (t, F_{para}), −144.0 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 9.81 (b, 1H, −C*H*O), 3.02 (t, J = 7.9 Hz, 2H, $PfCH_2$-CH_2−), 2.79 (dd, J = 7.9, 0.7 Hz, 2H, $PfCH_2CH_2$−). MS (EI) *m*/*z* (relative intensity): 224 (M^+, 46), 181 (100), 168 (35), 163 (54), 99 (25), 75 (22), 56 (60).

38. Anal. Calcd for $C_6H_{10}Br_2Pd_2$: C, 15.85; H, 2.22. Found: C, 16.03; H, 2.19. ^{1}H NMR ($CDCl_3$, δ, 300 MHz), 5.45 (m, 1H, H^2), 4.23 (d, J = 6.9 Hz, 2H, H-*syn*), 3.11 (d, J = 12.3 Hz, 2H, H-*anti*).

40_1. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −162.5 (m, F_{meta}), −157.1(t, F_{para}), −143.5 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 5.18 (d, J = 4.7 Hz, 1H, H^2), 3.97 (t, J = 7.6 Hz, 1H, H^5), 3.57 (dd, J = 8.8, 7.6 Hz, 1H, $H^{5'}$), 2.95−2.80 (m, J = 13.9 Hz, 1H, PfC*H*H′−), 2.68 (dd, J = 13.9, 8.5 Hz, 1H, PfCH*H*′−), 2.25 (m, 1H, H^4), 1.90 (m, 1H, H^3), 0.94 (d, J = 6.7 Hz, 3H, Me). MS (EI) *m*/*z* (relative intensity): 265 (M^+ − Br, 14), 194 (28), 181 (94), 84 (25), 55 (100), 43 (33), 41 (64).

40_2. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −162.5 (m, F_{meta}), −157.2(t, F_{para}), −143.6 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 4.87 (d, J = 3.1 Hz, 1H, H^2), 4.00 (dd, J = 8.3, 7.8 Hz, 1H, H^5), 3.76 (dd, J = 8.3, 7.5 Hz, 1H, $H^{5'}$), 2.95−2.80 (m, 2H, −CH_2 Pf)*, 2.06 (m, 1H, H^4), 1.90 (m, 1H, H^3)*, 1.01 (d, J = 7.3 Hz, 3H, Me) (asterisk indicates signals overlapped with those of **40_1**). MS: coincident with MS for **40_1**.

Reaction with Diallyldimethylsilane. The reaction was carried out at −30 °C in an NMR tube which was charged with [$Pd(C_6F_5)Br(NCMe)_2$] (0.030 g, 0.0689 mmol), $CDCl_3$ (0.6 mL), and diallyldimethylsilane (0.0126 mL, 0.0689 mmol). The temperature was slowly increased, and complexes **16** and **20** were identified. After 10 h at room temperature, the black precipitate was filtered through Celite and the final mixture contained **29** (60%), **30** (15%), **31** (4%), **37** (15%), **39** (6%), propene and −$(Me_2Si)_n$−O (n = 4, 5, and 6) (yields are based on C_6F_5).

16. ^{19}F NMR ($CDCl_3$, δ, 282 MHz, 243 K): −161.9 (b, F_{meta}), −156.8 (b, F_{para}), −143.4 (b, F_{ortho}).

20. ^{19}F NMR ($CDCl_3$, δ, 282 MHz, 263 K): −162.8 (b, F_{meta}), −157.8 (b, F_{para}), −143.5 (b, F_{ortho}).

Higher amounts of [$Pd(C_6F_5)Br(NCMe)_2$] (0.180 g, 0.413 mmol) and diallyldimethylsilane (0.076 mL, 0.413 mmol) in CH_2Cl_2 (5 mL) were used to carry out the reaction at room temperature. After 10 h, the palladium metal formed was filtered off and the filtrate was evaporated to dryness. The residue was separated by silica gel column chromatography. Elution with *n*-hexane and evaporation of the solvent gave a colorless oily residue, which was a mixture of **29**, **30**, **31**, **37**, **39**, and silicone polymers. By removing the more volatile compounds by suction, **37** mixed with **31** were obtained. Diethyl ether was employed as the second eluent, and it afforded a small amount of **38**.

36. ^{19}F NMR ($CDCl_3$, 263 K, δ, 282 MHz): −162.3 (m, F_{meta}), −156.7 (t, F_{para}), −143.6 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, 263 K, δ, 300 MHz): 6.27 (dt, J = 15.1, 5.0 Hz, 1H, $PfCH_2C$*H*=CH−), 5.72 (d, J = 15.1 Hz, 1H, $PfCH_2CH$=C*H*−), 3.55 (d, J = 5.0 Hz, 2H, $PfCH_2CH$=CH−), 0.60 (s, 6H, Me).

37. ^{19}F NMR ($CDCl_3$, 293 K, δ, 282 MHz): −163.2 (m, F_{meta}), −157.7 (t, F_{para}), −144.2 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, 293 K, δ, 300 MHz): 6.07 (dt, J = 18.4, 5.7 Hz, 1H, $PfCH_2C$*H*=CH−), 5.60 (dt, J = 18.4, 1.5 Hz, 1H, $PfCH_2CH$=C*H*−), 3.48 (dd, J = 5.7, 1.5 Hz, 2H, $PfCH_2CH$=CH−), 0.09 (s, 6H, Me). MS (EI) *m*/*z* (relative intensity): 546 (M^+, 5), 531 (12), 365 (20), 181 (42), 169 (40), 155 (100), 151 (80), 137 (21), 77 (17).

39. ^{19}F NMR ($CDCl_3$, 293 K, δ, 282 MHz): −163.2 (m, F_{meta}), −157.1 (t, F_{para}), −142.6 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, 293 K, δ, 300 MHz): 5.50 (s, 1H, H^1), 5.16 (s, 1H, $H^{1'}$), 2.08 (s, 3H, Me). MS (EI) *m*/*z* (relative intensity): 208 (M^+, 100), 195 (40), 193 (42), 181 (64), 143 (51), 123 (33), 86 (35), 84 (46).

−$(Si(Me_2)$-O$)_n$−. MS (EI) *m*/*z* (relative intensity): n = 4, 281 (M^+ − Me, 100), 265 (8), 249 (6), 193 (7), 73 (6); n = 5, 355 (M^+ − Me, 93), 267 (49), 251 (7), 73 (100), 45 (8); n = 6, 429 (M^+ − Me, 5), 341 (14), 325 (5), 147 (13), 73 (100), 45 (6).

Reaction with Dimethyl Diallylmalonate. [$Pd(C_6F_5)$-$Br(NCMe)_2$] (0.030 g, 0.0689 mmol), dimethyl diallylmalonate (0.014 mL, 0.0689 mmol), and $CDCl_3$ (0.6 mL) were mixed in an NMR tube at −20 °C. The reaction was monitored, and complex **17** was identified. After 1 h at room temperature, a mixture of organic derivatives was obtained which contained **21** (56% or 47%), **23** (31% or 26%), and **22** (13% or 11%) (the yields in parentheses were determined by integration of the ^{1}H and ^{19}F NMR signals and are based on dimethyl diallylmalonate or C_6F_5, respectively). In addition, pentafluorobenzene (16%) (based on C_6F_5) was found in the solution.

17. ^{19}F NMR ($CDCl_3$, δ, 282 MHz, 253 K): −162.4/−163.0 (b, F_{meta}), −157.1/−157.5 (b, F_{para}), −142.3/−143.2 (b, F_{ortho}).[21]

21. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −162.8 (m, F_{meta}), −157.4 (t, F_{para}), −143.3 (m, F_{ortho}). ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 5.56 (m, $J_{H^1-Me^2}$ = 1.0 Hz, 1H, H^2), 3.74 (s, 3H, −COO*Me*), 3.69 (s, 3H, −COO*Me*′), 2.95 (m, 2H, H^4, PfC*H*H′−), 2.56 (m, 1H, PfCH*H*′−), 2.55 (dd, J = 13.7, 7.9 Hz, 1H, H^5), 2.03 (dd, J = 13.7, 5.6 Hz, 1H, $H^{5'}$), 1.83 (d, J = 1.0 Hz, 3H, Me^3). ^{13}C NMR ($CDCl_3$, δ, 75 MHz): 124.1 (C^2), 52.7 (COO*C*H_3), 47.3 (C^4), 37.4 (C^5), 26.3 ($PfCH_2$−), 14.5 (Me^3). MS (EI) *m*/*z* (relative intensity): 378 (M^+, 22), 318 (82), 259 (76), 181 (100), 165 (86), 137 (45), 79 (67), 77 (80), 59 (72).

23. ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 5.41 (m, $J_{H^1-Me^2}$ = 1.1 Hz, 1H, H^2), 3.72 (s, 3H, −COO*Me*), 3.70 (s, 3H, −COO*Me*′), 2.78 (m, 2H, H^4, H^5), 1.92 (dd, J = 14.8, 5.6 Hz, 1H, $H^{5'}$), 1.72 (d, J = 1.1 Hz, 3H, Me^3), 1.05 (d, J = 6.8 Hz, 3H, Me^4). ^{13}C NMR ($CDCl_3$, δ, 75 MHz): 121.8 (C^2), 52.6 (−COO*C*H_3), 41.9 (C^4), 40.5 (C^5), 18.9 (Me^3), 14.6 (Me^4). MS (EI) *m*/*z* (relative intensity): 212 (M^+, 5), 153 (29), 152 (41), 93 (100), 77 (30), 59 (20).

22. ^{19}F NMR ($CDCl_3$, δ, 282 MHz): −163.0 (m, F_{meta}), −157.8/−157.7* (t, F_{para}), −143.5/−143.6* (m, F_{ortho}) (asterisk indicates two signals corresponding to both diastereoisomers). MS (EI) *m*/*z* (relative intensity): 380 (M^+, 20), 261 (45), 221 (48), 181 (100), 139 (76), 107 (45), 79 (77), 59 (94).

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