# Palladium Migration along Linear Carbon Chains: The Detection of $\eta^1$-$\eta^2$-Enyl Intermediates and the Study of Their Rearrangement

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The reactions of [PdPfBr(NCMe)$_2$] (Pf = $C_6F_5$) with stoichiometric amounts of 1,5-hexadiene, 1,6-heptadiene, or 1,7-octadiene at low temperature result in the formation of several ($\eta^1$-$\eta^2$-enyl)palladium complexes that isomerize sequentially at different temperatures depending on the ring size of the palladacycles ($T_{isom}$: 7.5- < 6.5- < 5.5-membered). These ($\eta^1$-$\eta^2$-enyl)palladium derivatives are intermediates in the Pd-migration process, arrested by coordination of the unattacked double bond. The final products of their isomerization are several isomeric Pf−($\eta^3$-allyl)palladium complexes (Pf = $C_6F_5$). The major allylic derivative in each case arises from Pd migration to the terminal double bond. Minor amounts of ($\eta^3$-allyl)palladium complexes formed by double bond switches in the process of Pd migration are also seen, but this occurs only on putative 1,5- or 1,6-diene−hydrido−palladium intermediates. A small amount of cyclic organic derivatives coming from the cyclization of ($\eta^1$-$\eta^2$-enyl)palladium intermediates is detected in each case. The use of excess diolefin gives rise to additional ($\eta^3$-allyl)palladium complexes without the Pf group and to the corresponding Pf-substituted linear dienes. These arise via displacement of the Pf dienes by the starting diolefin in a hydrido−palladium intermediate during the Pd-migration process.

## Introduction

Conjugated and nonconjugated dienes have been used to prepare ($\eta^3$-allyl)palladium derivatives by insertion of one double bond into a Pd−R bond, or by attack of an external nucleophile on the coordinated diene.[1,2] The formation of the palladium allyl is straightforward in a conjugated diene. For nonconjugated dienes Pd migration (via sequential Pd−H elimination−readdition) has to follow insertion or nucleophilic attack in order to reach the second double bond. It has been shown that the Pd atom can migrate efficiently quite "long distances",[3] and this has been used in the catalytic transformation of nonconjugated dienes.[3a,4] Nonetheless it is becoming more evident that other mechanisms, such as intramolecular insertion into the newly formed Pd−R bond (cyclization), can compete with migration in Pd-mediated reactions.[2,5−8]

$\eta^1$-$\eta^2$-Enyl derivatives forming specially favorable palladacycles can be isolated as intermediates in the process of Pd migration between distant carbons. For instance, quite stable $\eta^1$-$\eta^2$-enyl complexes are formed by insertion of 1,5-cyclooctadiene in Pd−R,[9] and other $\eta^1$-$\eta^2$-enyls with the same type of palladacycle are obtained by other methods.[10,11] Less stable $\eta^1$-$\eta^2$-enyl compounds have also been identified and/or isolated, and Pd migration to form the corresponding $\eta^3$-allyls is a more facile process in these systems.[7,12−15]

This suggests that, starting from linear nonconjugated dienes with long spacers between the double bonds, different ($\eta^1$-$\eta^2$-enyl)palladium complexes of medium stability might be formed and the Pd-migration process could be followed step by step, through the isolation or detection of the $\eta^1$-$\eta^2$-enyl intermediates, which would be snapshots in the migration of palladium.

Here we report this study made on the following linear terminal dienes: 1,5-hexadiene; 1,6-heptadiene; and 1,7-octadiene. They react with [PdPfBr(NCMe)$_2$] (Pf = $C_6F_5$) to give insertion into the Pd−Pf bond. The possibility of monitoring the reactions by $^{19}$F NMR (clean spectra with chemical shifts very sensitive to small changes in the molecule) greatly facilitates the study.[16] Preliminary results on 1,5-hexadiene were previously reported;[13] the use of a higher field instru-

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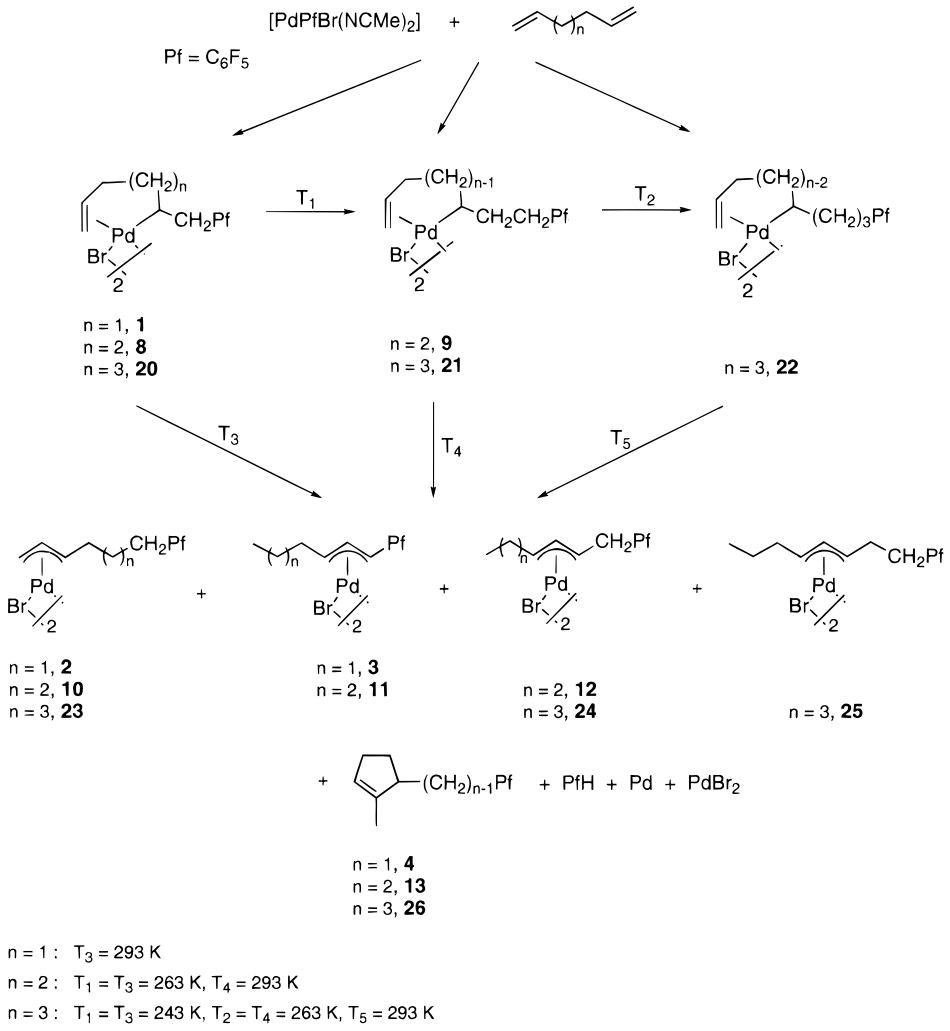
**Scheme 1**




ment has allowed for the detection of some minor products previously undetected.

## Results

The reactions of $[PdPfBr(NCMe)_2]$ with stoichiometric amounts of 1,5-hexadiene, 1,6-heptadiene, or 1,7-octadiene give several isomeric ($\eta^3$-allyl)palladium complexes for each diolefin. In addition, a small amount of cyclic organic derivatives is identified in each case. The formation of ($\eta^1$-$\eta^2$-enyl)palladium intermediates and their isomerization was observed when the reactions were monitored at low temperature by $^{19}F$ and $^1H$ NMR. The products observed are collected in Scheme 1.

**Reaction with 1,5-Hexadiene.** In the reaction of $[PdPfBr(NCMe)_2]$ and 1,5-hexadiene an intermediate 5.5-membered $\eta^1$-$\eta^2$-enyl complex (**1**) is formed.[17] **1** can be isolated as a white solid when the reaction is carried out at 0 °C, and it isomerizes to the ($\eta^3$-allyl)palladium species at room temperature ($k_{obs}^{298K} = 5.37 \times 10^{-5}$ $s^{-1}$).[13]

Isomerization of **1** in $CDCl_3$ was monitored by $^{19}F$ NMR at 293 K. In the first hour the ($\eta^3$-allyl)palladium complexes **2-syn** and **2-anti** are formed in a *ca.* 1:1 ratio, along with a small amount of **3** (Scheme 1, $n = 1$, $T_3 = 293$ K). The molar ratio of **2-anti** in the mixture decreases significantly after 10 h. The isomerization of **1** is complete after 32 h, and the final products **2-syn**, **2-anti**, and **3** are produced in a 13:1:2 ratio. Phosphines have been shown to promote syn−anti isomerization.[18] Addition of a small amount of $PPh_3$ to the mixture did not change this ratio, thus supporting that it actually corresponds to the equilibrium distribution of both species, the less crowded syn isomer being more abundant.

When $[PdPfBr(NCMe)_2]$ and 1,5-hexadiene are mixed at room temperature and let stand for 32 h, so that complete isomerization of the intermediate **1** occurs, the following products result: **2** (70% based on the integration of $^{19}F$ and $^1H$ NMR signals), which is a mixture of **2-syn** and **2-anti** in a 13:1 ratio; **3** (14%); 1-methyl-5-(pentafluorophenyl)-1-cyclopentene (**4**, 8%); and PfH (3%). **2-syn** can be isolated by crystallization.[13]

**Reaction with 1,6-Heptadiene.** Insertion of 1,6-heptadiene in $[PdPfBr(NCMe)_2]$ occurs efficiently at −30 °C (Scheme 1, $n = 2$). After 1 h at this temperature the insertion is complete, to give a 6.5-membered-ring $\eta^1$-$\eta^2$-enyl complex (**8**), as shown by a new $^{19}F$ resonance (*ca.* −143 ppm) typical of a Pf−C moiety.[16] Two small

(17) The size of the $\eta^1$-$\eta^2$-enyl palladacycles is referred to as *n*.5-membered, *n* being the number of atoms in the cycle and 0.5 being added to account for the $\pi$-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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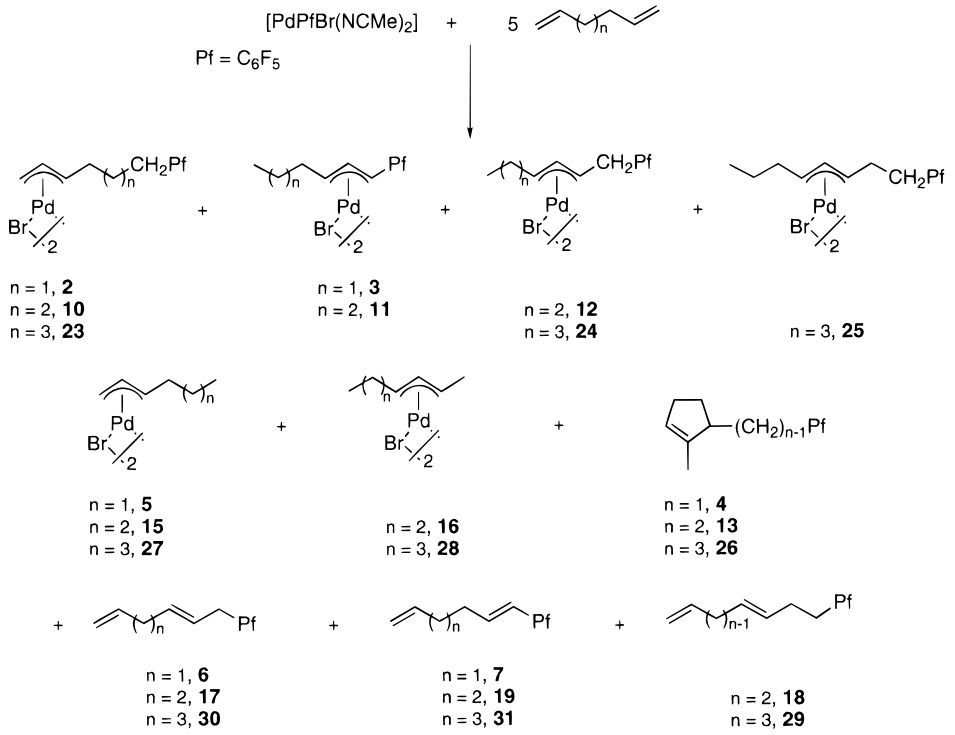
**Scheme 2**




signals (−143.2 and −144.3 ppm) are also observed, assigned to the $F_{ortho}$ atoms of the Pf groups in **9** and **10**, respectively. The spectra of **8** and **10** in the mixture can be fully analyzed. Due to overlapping of signals the $^1$H NMR spectrum of **9** could not be analyzed, but the genesis and evolution of this complex support the structure assigned in Scheme 1. When the temperature is increased to −10 °C, the simultaneous isomerization of **8** to the ($\eta^3$-allyl)palladium derivatives **10**−**12** and, in a lesser amount, to complex **9** was evident (13% **9** was found after **8** had disappeared; Scheme 1, $T_1 = T_3 = 263$ K). The rate of isomerization of **8** was measured by $^{19}$F NMR spectroscopy; it shows a first-order dependence on **8** ($k_{obs}^{263K} = 2.87 \times 10^{-4} \pm 0.08 \times 10^{-4}$ s$^{-1}$).

Complete isomerization of **9** takes 10 h at room temperature (Scheme 1, $n = 2$, $T_4 = 293$ K). This rate is similar to that observed for the analogous 5.5-membered $\eta^1$-$\eta^2$-enyl complex **1**. Three $\eta^3$-allyl complexes, **10** (57%), **11** (3%), and **12** (19%), are the final products of isomerization, plus the organic isomeric products 1-methyl-5-((pentafluorophenyl)methyl)-1-cyclopentene (**13**, 9%), and 2-methyl-1-((pentafluorophenyl)methyl)-1-cyclopentene (**14**, 5%). A small amount of PfH (3%) is also found. The major derivative **10** could be isolated as yellow crystals in cyclohexane (9%, yield).

**Reaction with 1,7-Octadiene.** [PdPfBr(NCMe)$_2$] and 1,7-octadiene react in $CDCl_3$ at −40 °C, as shown by the appearance of two new $^{19}$F NMR signals (*ca.* −143 and −144.5 ppm) in an approximately 2:1 ratio. When the temperature is raised to −30 °C, a clear transformation of the former $^{19}$F NMR signal (−143 ppm) to the latter one (−144.5 ppm) is observed. Thus, it is reasonable that the former corresponds to the 7.5-membered $\eta^1$-$\eta^2$-enyl palladacycle (**20**, Scheme 1, $n = 3$), and the latter to the 6.5-membered metallacycle (**21**). The starting material is consumed after 2 h at 243 K and yields **21** as the major product (64%). Other complexes, **22**−**25** (see below), account for the remaining 36% (Scheme 1, $n = 3$, $T_1 = T_3 = 243$ K). If the mixture is warmed to −10 °C, isomerization of **21** occurs, and a derivative which seems to be the 5.5-membered $\eta^1$-$\eta^2$-enyl complex **22** is observed. After 1 h at this temperature **22** was formed as the major product (50%) (Scheme 1, $n = 3$, $T_2 = T_4 = 263$ K). Complexes **20**−**22**, detected by $^{19}$F NMR, correspond to the number of $\eta^1$-$\eta^2$-enyl)palladium derivatives expected for a diene such as 1,7-octadiene. However, the structure of these ($\eta^1$-$\eta^2$-enyl)palladium intermediates could not be unequivocally supported by $^1$H NMR due to their broad signals which overlap with each other or with the signals of other compounds. Finally, extensive formation of $\eta^3$-allyl complexes is observed when the temperature is raised to 20 °C (Scheme 1, $n = 3$, $T_5 = 293$ K). After 3 h the processes of isomerization and decomposition are complete, and the final product distribution is **23** (39%), **24** (25%), **25** (17%), and **26** (8%), plus unknown organic (5%) and organometallic (6%) compounds (each one less than 2%).

**Reactions with Excess Diene.** If the reactions are carried out using excess diene (5-fold), a noticeable decrease in the percentage of $\eta^3$-allyl derivatives formed is observed, as well as the production of additional ($\eta^3$-allyl)palladium complexes lacking pentafluorophenyl. The amount of Pf-$\eta^3$-palladium allyls is similar to that of the Pf-free derivatives. Also, pentafluorophenyl diolefins are released. The products obtained for each diene are shown in Scheme 2, and the relative ratios found are collected in Table 1. Besides the products depicted in Scheme 2, two isomeric pentafluorophenyl dienes are also observed in the reaction with excess 1,7-octadiene ($n = 3$), namely, 8-(pentafluorophenyl)-2,5-octadiene (**32**) and 1-(pentafluorophenyl)-2,6-octadiene (**33**). They arise from double-bond isomerization of **29** and **30**, presumably promoted by Pd−H species.

**Table 1. Products Obtained in the Reactions of [PdPfBr(NCMe)$_2$] with Excess Diene (5-fold)[a]**

| | Pd-allyls | | | |
|---|---|---|---|---|
| diene | Pf-substituted | Pf-free | Pf dienes | other |
| 1,5-hexadiene | **2** (30), **3** (2) | **5** (30) | **6** (19), **7** (7) | **4** (10) |
| 1,6-heptadiene | **10** (15), **11** (1), **12** (8) | **15** (22), **16** (13) | **17** (18), **18** (13), **19** (3) | **13** (4) |
| 1,7-octadiene | **23** (15), **24** (9), **25** (7) | **27** (9), **28** (25) | **29** (9), **30** (7), **31** (2), **32** (3), **33** (4) | **26** (4) |

[a] Percentages are given in parentheses. A small amount of unknown products (between 2% and 7%, each one less than 2%) is formed in each case.

## Discussion

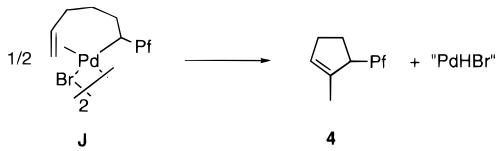
The mechanism of formation of all of the Pf-containing derivatives detected is shown in Scheme 3. Arylation of 1,5-, 1,6-, or 1,7-dienes leads to the generation of a ($\eta^1$-$\eta^2$-enyl)palladium intermediate **A**, by simple coordination of the unattacked double bond (Scheme 3, Br bridges are omitted for simplicity). **A** is an ($n$+4.5)-membered metallacycle ($n$ = 1, 2, 3 for **1**, **8**, and **20**, respectively), and its stability depends mostly on the ring size. The following order of stability is found: 5.5- > 6.5- > 7.5-membered, as shown by the temperatures at which they show comparable rates of isomerization: 293 K (5.5-membered cycle, **1**), 263 K (6.5-membered cycle, **8**), 243 K (7.5-membered cycle, **20**).

The isomerization of **A** to **B** (**9**, **21**), and that of **B** to **C** (**22**) occurs via 1,2-hydrogen shift (one-step Pd migration), which leads eventually to the final $\eta^3$-allyl derivatives. It is worth noting that 4.5-membered-ring derivatives are not detected, even though ($\eta^1$-$\eta^2$-enyl)palladium complexes of this type have been observed in the arylation of 1,4-pentadienes at low temperature.[7]

Pd migration to give a terminal ($\eta^3$-allyl)palladium complex at the initial position of the unattacked double bond (**2**, **10**, **23**) is the main mechanism for the dienes tested. Thus, rather efficient remote palladium migration is again observed here.[3] Also, internal ($\eta^3$-allyl)-palladium complexes **3**, **11**, **12**, **24**, and **25** are obtained as competitive products. The origin of these derivatives must be an intramolecular hydride transfer to the terminal double bond in the putative diene intermediates **D**, **E**, and **F** that could be formed in the course of Pd migration from the corresponding $\eta^1$-$\eta^2$ palladium complexes **A**, **B**, and **C** (Scheme 3). Once insertion has taken place (**G**, **H**, and **I**), Pd migration develops and brings about the formation of internal ($\eta^3$-allyl)palladium complexes. None of the intermediates **D**−**I** were detected. However, not every possible internal allyl derivative is formed, but only those which derive from intermediates **D** and **E** corresponding to a 1,5 or 1,6 diene (**3** for $n$ = 1; **11** and **12** for $n$ = 2; **24** and **25** for $n$ = 3). This suggests that, regardless the $\eta^2$- or $\eta^4$-coordination mode of the diolefin when insertion of the terminal double bond occurs, an $\eta^4$-diene palladium intermediate is formed at some point. Only from the relatively stable six- or seven-membered diene palladacycles is the switch of double bonds possible in the Pd-migration process.

The insertion step is fully regioselective: the Pf group always binding the less substituted carbon. The results follow the usual trend in Pd-mediated substitution of olefins by cis-addition and coincide with the previous investigation on the insertion of dienes into the Pd−Pf bond.[3,12,16] Cis addition of Pd−R bonds with opposite regiochemistry has been found, although always as a minor pathway.[4,7,19−21]

Intramolecular Heck reaction is observed in every case as a minor pathway, and cyclic organic products **4**, **13**, **14**, and **26** bearing Pf groups are generated. All of them are substituted cyclopentenes, indicating that cyclization occurs significantly only in 6.5-membered $\eta^1$-$\eta^2$-enyl palladacycles: **21** for 1,7-octadiene, **8** for 1,6-heptadiene, and an undetected $\eta^1$-$\eta^2$-enyl for 1,5-hexadiene (**J**, eq 1) which would be formed by one-step Pd migration away from the unattacked double bond.




**J** **4** (1)

After cyclization, Pd migration follows to generate an endocyclic double bond. Combination of the "PdHBr" moiety generated in the final Pd−H elimination with the starting "PdPfBr" produces the small amount of PfH observed (eq 2).[22] Oxidative cyclization of a variety of 1,5-dienes in the presence of a Pd(II)-catalyst system has been reported,[23] and five-membered rings are common in recently developed Pd-mediated syntheses of cyclic and polycyclic systems.[5,6,8]

$$\text{"PdHBr"} + \text{"PdPfBr"} \rightarrow \text{PfH} + \text{Pd} + \text{PdBr}_2 \quad (2)$$

Besides the above mentioned ($\eta^3$-allyl)palladium complexes bearing the Pf group, use of excess diolefins leads to the production of additional ($\eta^3$-allyl)palladium derivatives not containing the Pf group. Pf-substituted dienes are also formed. Thus, the presence of an excess of starting diene promotes the displacement of the Pf-substituted dienes in the intermediate diene−palladium−hydride **D**−**F** (Scheme 3). Insertion into the Pd−H bond and subsequent Pd migration gives the $\eta^3$-allyl derivatives (**5**, **15**, and **27**). The number and structures of these $\eta^3$-allyl species are governed by the same factors observed for the Pf allyls, i.e., not only terminal but also internal allyls (complexes **16** and **28**) are formed. This effect of the addition of excess diene had been observed previously,[3,12] and the exchange of monoolefins in an $\eta^2$-alkene−hydride palladium intermediate has also been reported.[24]

## Experimental Section

**General Data.** C, H, and N elemental analyses were performed on a Perkin-Elmer 240 microanalyzer. $^1$H and $^{19}$F NMR spectra were recorded on Bruker AC-300 and ARX-300 spectrometers. Chemical shifts (in $\delta$ units, ppm) were referenced to TMS for $^1$H and $^{13}$C and to $CFCl_3$ for $^{19}$F. The spectral data were recorded at 293 K unless noted otherwise. Integration of $^{19}$F or $^1$H NMR signals was used to determine the ratios

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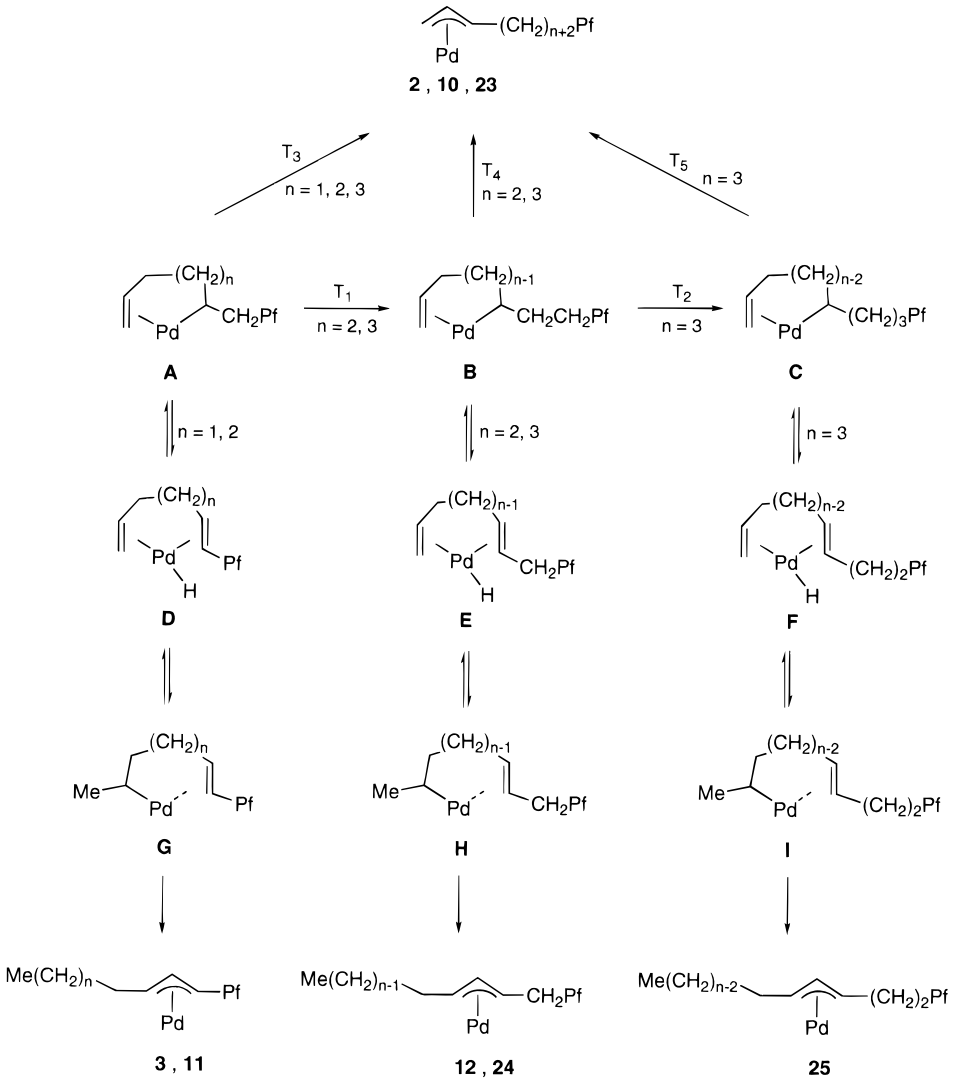
**Scheme 3**




n = 1 : $T_3$ = 293 K

n = 2 : $T_1 = T_3$ = 263 K, $T_4$ = 293 K

n = 3 : $T_1 = T_3$ = 243 K, $T_2 = T_4$ = 263 K, $T_5$ = 293 K

of products formed; a relaxation delay of at least $5T_1$ was ensured in every recording. Organic products were analyzed using a HP-5890 gas chromatograph connected to a HP-5988 mass spectrometer at an ionizing voltage of 70 eV and a quadrupole analyzer. All diolefins were purchased from Aldrich, Janssen, and Fluka Chemical Co. and used without further purification. [PdPfBr(NCMe)$_2$] was prepared as described elsewhere.[16]

**Reactions with 1,5-Hexadiene.** To a solution of [PdPfBr(NCMe)$_2$] (0.400 g, 0.918 mmol) in $CH_2Cl_2$ (20 mL) was added 1,5-hexadiene (0.110 mL, 0.918 mmol) at 0 °C. After 5 min activated carbon was added to the solution, the resulting mixture was filtered, and the filtrate was evaporated to dryness. The residue was triturated with ether, and the suspension was cooled. A white solid, **1**, was obtained (61% yield). The mother liquors were maintained at room temperature for 32 h. After eliminating Pd metal traces by filtration through Celite, the mixture was chromatographed through a silica gel column using *n*-hexane and then ether as eluents. Evaporation of the *n*-hexane solvent of the first batch gave a colorless oily residue, which contained **4** as the major component. Elution with $Et_2O$ yielded a mixture of **2** and **3**.

In order to measure the ratio of all products, the reaction was also carried out in an NMR tube. [PdPfBr(NCMe)$_2$] (0.025 g, 0.0574 mmol), 1,5-hexadiene (0.069 mL, 0.0574 mmol), and $CDCl_3$ (0.6 mL) were mixed at room temperature. The analysis of $^{19}$F and $^1$H NMR spectra showed that the reaction was complete after 32 h and **2** (70%), **3** (14%), **4** (8%), and PfH (3%) were formed; the yields (in parentheses) are based on the integration of $^{19}$F NMR signals.

The reaction with excess 1,5-hexadiene (5-fold) was also tried. It was monitored by $^{19}$F and $^1$H NMR, which indicated that the reaction had finished after 15 h. The following products were formed: **2** (30%, mixture of syn and anti isomers in the ratio 13:1), **3** (2%), **5** (30%, mixture of anti and syn isomers in the ratio 14:1), **4** (10%), **6** (19%), and **7** (7%). The organic derivatives could be separated from the mixture by column chromatography eluting with hexane, and they were checked by GC−MS. The separation of the two major complexes **2-syn** and **5-syn** was performed by preparative TLC using hexane/EtOAc (10:1) as eluent ($R_f$ = 0.24, **2-syn**; $R_f$ = 0.38, **5-syn**).

**1**: $^{19}$F NMR ($CDCl_3$, $\delta$, 283 K, 282 MHz) −163.0 (m, $F_{meta}$), −157.7 (t, $F_{para}$), −142.3 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 283 K, 300 MHz), 6.20 (m, 1H, $H^2$), 4.65 (d, $J$ = 8.0 Hz, 1H, $H^1$), 4.51 (d, $J$ = 14.0 Hz, 1H, $H^{1'}$), 3.52 (m, 1H, $H^5$), 3.28 (m, 1H, $H^6$), 2.86 (m, 1H, $H^{6'}$), 2.38 (m, 1H, $H^3$), 2.0 (m, 1H, $H^{3'}$), 1.55 (m, 1H, $H^4$), 0.53 (m, 1H, $H^{4'}$).[13]

**2-syn**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.2 (m, $F_{meta}$), −158.1 (t, $F_{para}$), −144.5 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.27 (m, $J$ = 6.8, 11.9 Hz, 1H, $H^2$), 3.97 (d, $J$ = 6.8 Hz, 1H, $H^1{}_{syn}$), 3.90 (m, 1H, $H^3$), 2.86 (d, $J$ = 11.9 Hz, 1H, $H^1{}_{anti}$), 2.75 (bt, $J$ = 7.2 Hz, 2H, $PfCH_2$), 1.7−1.95 (m, 4H, $H^4$, $H^5$).[13]

**2-anti**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.0 (m, $F_{meta}$), −157.9 (t, $F_{para}$), −144.4 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.25 (m, 1H, $H^2$), 4.82 (q, $J$ = 7.5 Hz, 1H, $H^3$), 4.19 (d, $J$ = 7.4 Hz, 1H, $H^1{}_{syn}$), 3.34 (d, $J$ = 13.0 Hz, 1H, $H^1{}_{anti}$), 2.69 (t, $J$ = 6.4 Hz, 2H, $H^6$), 1.6−2.0 (m, 4H, $H^4$, $H^5$).

**3**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −162.4 (m, $F_{meta}$), −153.9 (t, $F_{para}$), −140.5 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.97 (t, $J$ = 11.2 Hz, 1H, $H^2$), 4.34 (d, $J$ = 11.2 Hz, 1H, $H^1$), 4.07 (m, 1H, $H^3$), 1.60−1.95 (m, 4H, $H^4$, $H^5$), 0.99 (t, $J$ = 7.2 Hz, 3H, $H^6$).

**4**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.9 (m, $F_{meta}$), −159.1 (t, $F_{para}$), −144.3 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.21 (m, 1H, $H^2$), 4.25 (m, 1H, $H^5$), 2.35−2.58 (m, 3H, $H^3$, $H^{3'}$, $H^4$), 1.95 (m, 1H, $H^{4'}$), 1.78 (dd, $J$ = 1.2, 0.8 Hz, 3H, Me); MS (EI) *m/z* (relative intensity) 248 ($M^+$, 33), 233 (100), 181 (35), 79 (9), 51 (9), 41 (14).

**5-syn**: $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.26 (td, $J$ = 12.1, 6.6 Hz, 1H, $H^2$), 3.94 (d, $J$ = 6.6 Hz, 1H, $H^1{}_{syn}$), 3.9 (m, 1H, $H^3$), 2.85 (d, $J$ = 12.1 Hz, 1H, $H^1{}_{anti}$), 1.85 (m, 1H, $H^4$), 1.42−1.74 (m, 3H, $H^{4'}$, $H^5$, $H^{5'}$), 0.95 (t, $J$ = 7.3 Hz, 3H, $H^6$).[3b]

**5-anti**: $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.25 (m, 1H, H2), 4.86 (q, $J$ = 7.5 Hz, 1H, $H^3$), 4.15 (d, $J$ = 7.4 Hz, 1H, $H^1{}_{syn}$), 3.34 (d, $J$ = 13.0 Hz, 1H, $H^1{}_{anti}$), 1.42−1.85 (m, 4H, $H^4$, $H^5$, overlapped with signals of other compounds), 0.88 (t, $J$ = 7.3 Hz, 3H, $H^6$).

**6**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.2 (m, $F_{meta}$), −158.2 (t, $F_{para}$), −144.7 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.78 (m, 1H, $H^2$), 5.52 (m, 2H, $H^4$, $H^5$), 5.0 (m, 2H, $H^1$), 3.39 (d, $J$ = 5.0 Hz, 2H, $H^6$), 2.74 (m, 2H, $H^3$); MS (EI) *m/z* (relative intensity) 248 ($M^+$, 6), 233 (6), 181 (18), 69 (14), 67 (100), 65 (12), 41 (33).

**7**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.8 (m, $F_{meta}$), −158.2 (t, $F_{para}$), −144.2 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 6.55 (dt, $J$ = 16.8, 6.6 Hz, 1H, $H^2$), 6.28 (d, $J$ = 16.8 Hz, 1H, $H^1$), 5.80 (m, 1H, $H^5$), 5.0 (m, 2H, $H^6$), 2.32−2.45 (m, 4H, $H^3$, $H^4$); MS (EI) *m/z* (relative intensity) 248 ($M^+$, 21), 233 (11), 207 (100), 187 (82), 181 (68), 138 (11), 67 (20), 41 (15).

**Reactions with 1,6-Heptadiene.** [$PdPfBr(NCMe)_2$] (0.200 g, 0.459 mmol) was mixed with 1,6-heptadiene (0.062 mL, 0.459 mmol) in $CH_2Cl_2$ (20 mL). After 10 h the dark yellow solution was treated with activated carbon, the resulting mixture filtered, and the filtrate evaporated to dryness. Yellow **10** was obtained by adding cyclohexane to the residue and cooling (9% yield). The mother liquors were evaporated to dryness, and the residue was separated into two batches by column chromatography, using silica gel and eluting with *n*-hexane first and then diethyl ether. The first batch contained **13** and **14** as major components; the second one included **10**, **11**, **12**, and **16**. Both batches were analyzed by $^1$H and $^{19}$F NMR with the help of $^1$H−$^1$H COSY. $^{13}$C NMR and $^1$H−$^{13}$C COSY were also used to identify the organic derivatives.

The reaction was monitored by NMR at low temperature. An NMR tube was charged with [$PdPfBr(NCMe)_2$] (0.025 g, 0.0574 mmol) and $CDCl_3$ (0.6 mL) and cooled to −30 °C. 1,6-Heptadiene (0.008 mL, 0.0574 mmol) was added. After 1 h at this temperature **8**, **9**, and **10** had formed in the ratio 40:5:1, based on integration of $^{19}$F resonances. The temperature was increased to −10 °C, and isomerization of **8** occurred. Finally, the reaction mixture was warmed to room temperature. After 10 h, analysis of $^1$H and $^{19}$F NMR spectra indicated that the final products were **10** (57%), **11** (3%), **12** (19%), **13** (9%), **14** (5%), and $C_6F_5H$ (3%). The yields in parentheses are based on the integration of $^1$H and $^{19}$F NMR signals.

The rate constant for the isomerization of **8** was measured by recording $^{19}$F NMR spectra every 10 min at 263 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 1 standard deviation in the slope of the best fit line multiplied by Student's factor $t_{1-\alpha}(f)$.[25]

The reaction of [$PdPfBr(NCMe)_2$] (0.025 g, 0.0574 mmol) with excess 1,6-heptadiene (0.039 mL, 0.287 mmol) was also studied. After 5 h the reaction was complete, and the final product mixture contained **10** (15%), **11** (1%), **12** (8%), **15** (22%), **16** (13%), **13** (4%), **17** (18%), **18** (13%), and **19** (3%). Silica gel column chromatography was employed to separate the organic compounds and the palladium complexes by using hexane and ether as eluents, respectively. The $^1$H NMR spectra of the mixture of ($\eta^3$-allyl)palladium complexes were assigned with the help of $^1$H−$^1$H COSY. The Pf-substituted diolefins were identified by $^1$H, $^{19}$F NMR, $^1$H−$^1$H COSY, and GC−MS. **10** could be separated out from the organometallic mixture by preparative TLC in hexane/EtOAc (20:1). $R_f$ = 0.18 for **10** and 0.25 for the rest of the palladium complexes.

**8**: $^{19}$F NMR ($CDCl_3$, 243 K, $\delta$, 282 MHz), −162.6 (b, $F_{meta}$), −157.6 (b, $F_{para}$), −142.8 (b, $F_{ortho}$); $^1$H NMR ($CDCl_3$, 243 K, $\delta$, 300 MHz), 6.11 (b, 1H, $H^2$), 5.08 (bd, $J$ = 8.4 Hz, 1H, $H^1$), 4.42 (bd, $J$ = 15.0 Hz, 1H, $H^{1'}$), 3.69 (b, 1H, $H^6$), 3.06 (dd, $J$ = 13.4, 7.3 Hz, 1H, $H^7$), 2.42 (b, 1H, $H^{7'}$), 2.10 (b, 2H, $H^3$), 1.72 (b, 2H, $H^4$), 1.20 (b, 1H, $H^5$), 0.44 (bd, $J$ = 14.1 Hz, 1H, $H^{5'}$).

**9**: $^{19}$F NMR ($CDCl_3$, 243 K, $\delta$, 282 MHz), −162.6 (b, $F_{meta}$), −157.6 (b, $F_{para}$), −143.2 (b, $F_{ortho}$).

**10**: Anal. Calcd for $C_{26}H_{24}F_{10}Br_2Pd_2$: C, 34.71; H, 2.69. Found: C, 34.76; H, 2.71. $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz): −163.3 (m, $F_{meta}$), −158.4 (t, $F_{para}$), −144.7 (m, $F_{ortho}$). $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz): 5.27 (td, $J$ = 11.8, 6.8 Hz, 1H, $H^2$), 3.96 (d, $J$ = 6.6 Hz, 1H, $H^1{}_{syn}$), 3.89 (m, $J$ = 11.8, 7.4, 4.4 Hz, 1H, $H^3$), 2.85 (d, $J$ = 11.8 Hz, 1H, $H^1{}_{anti}$), 2.70 (t, $J$ = 6.5 Hz, 2H, $H^7$), 1.90 (m, $J$ = 4.4 Hz, 1H, $H^4$), 1.76 (m, $J$ = 7.4 Hz, 1H, $H^{4'}$), 1.48−1.70 (m, 4H, $H^5$, $H^6$).

**11**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −162.9 (m, $F_{meta}$), −153.9 (t, $F_{para}$), −140.5 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.96 (t, $J$ = 11.3 Hz, 1H, $H^2$), 4.33 (d, $J$ = 11.3 Hz, 1H, $H^1$), 4.08 (m, $J$ = 11.3 Hz, 1H, $H^3$), 1.3−1.9 (m, 6H, $H^4$, $H^5$, $H^6$), 0.92 (t, $J$ = 7.3 Hz, 3H, $H^7$).

**12**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −162.3 (m, $F_{meta}$), −156.6 (t, $F_{para}$), −143.4 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.29 (t, $J$ = 10.6 Hz, 1H, $H^3$), 3.89 (m, $J$ = 10.6 Hz, 1H, $H^4$), 3.65 (m, $J$ = 10.6, 7.0, 6.9 Hz, 1H, $H^2$, ABX system), 3.31 (dd, $J$ = 14.6, 6.9 Hz, 1H, $H^1$, ABX system), 3.04 (dd, $J$ = 14.6, 7.0 Hz, 1H, $H^{1'}$, ABX system), 1.45−1.95 (m, 4H, $H^5$, $H^6$), 0.93 (t, $J$ = 7.3 Hz, 3H, $H^7$).

**13**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.4 (m, $F_{meta}$), −158.4 (t, $F_{para}$), −143.6 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.42 (b, 1H, $H^2$), 2.94 (bd, $J$ = 13.7 Hz, 1H, $PfCH\ H'$), 2.68 (m, 1H, $H^5$), 2.50 (dd, $J$ = 13.7, 12.1 Hz, 1H, $PfCHH'$), 2.1−2.35 (m, 2H, $H^3$)*, 1.86 (m, 1H, $H^4$), 1.76 (m, 3H, Me)*, 1.54 (m, 1H, $H^{4'}$); $^{13}$C NMR ($CDCl_3$, $\delta$, 74.5 MHz), 126.1 ($C^2$), 31.9 ($C^3$), 29.7 ($C^4$), 26.3 ($PfCH_2$), 21.8 ($C^5$), 14.7 (Me); MS (EI) *m/z* (relative intensity) 262 ($M^+$, 2), 181 (12), 81 (100), 79 (26), 77 (6), 53 (8), 41 (6); (*) overlapped with signals of other compounds.

**14**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.4 (m, $F_{meta}$), −158.7 (t, $F_{para}$), −143.8 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 3.43 (b, 2H, $PfCH_2$), 2.2−2.3 (m, 4H, $H^3$, $H^5$)*, 1.76 (m, 3H, Me)*, 1.73 (m, 2H, $H^4$); $^{13}$C NMR (CDCl3, $\delta$, 74.5 MHz), 38.4, 35.2 ($C^3$, $C^5$), 21.5 ($PfCH_2$), 21.2 ($C^4$), 13.8 (Me); MS (EI) *m/z* (relative intensity) 262 ($M^+$, 21), 247 (5), 181 (39), 81 (100), 79 (24), 53 (9), 41 (7); (*) overlapped with signals of other compounds.

**15**: $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.27 (m, 1H, $H^2$)*, 3.95 (d, $J$ = 6.4 Hz, 1H, $H^1{}_{syn}$), 3.90 (m, 1H, $H^3$)*, 2.83 (d, $J$ = 11.4 Hz, 1H, $H^1{}_{anti}$), 1.45−1.95 (m, 6H, $H^4$, $H^5$, $H^6$)*, 0.94 (t, $J$ = 7.3 Hz, 3H, $H^7$);[3b] (*) overlapped with signals of other compounds.

(25) (a) Spiridonov, V. P.; Lopatkin, A. A. *Tratamiento Matemático de Datos Fisico-Químicos*; Mir: Madrid, 1983. (b) Graham, R. C. *Data Analysis for the Chemical Sciences*; VCH: New York, 1993.

**16**: $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.17 (t, $J$ = 11.1 Hz, 1H, $H^3$), 3.77 (m, $J$ = 11.1 Hz, 2H, $H^2$, $H^4$), 1.45−1.95 (m, 4H, $H^5$, $H^6$), 1.40 (d, $J$ = 6.4 Hz, 3H, $H^1$), 0.89 (t, $J$ = 7.3 Hz, 3H, $H^7$).

**17**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.3 (m, $F_{meta}$), −158.3 (t, $F_{para}$), −144.8 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.8 (m, 1H, $H^2$)*, 5.46−5.53 (m, 2H, $H^5$, $H^6$), 4.9−5.05 (m, 2H, $H^1$)*, 3.38 (d, $J$ = 5.3 Hz, 2H, $H^7$), 2.1 (m, 4H, $H^3$, $H^4$); MS (EI) *m/z* (relative intensity) 262 ($M^+$, 2), 181 (13), 81 (100), 79 (64), 67 (18), 54 (23), 53 (44), 51 (12), 41 (62); (*) overlapped with signals of other compounds.

**18**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.5 (m, $F_{meta}$), −158.4 (t, $F_{para}$), −144.5 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.8 (m, 1H, $H^2$)*, 5.4−5.45 (m, 2H, $H^4$, $H^5$), 4.9−5.05 (m, 2H, $H^1$)*, 2.76 (t, $J$ = 7.2 Hz, 2H, $H^7$), 2.71 (m, $J$ = 5.0, 2.0 Hz, 2H, $H^3$), 2.28 (td, $J$ = 7.2, 5.9 Hz, 2H, $H^6$); MS (EI) *m/z* (relative intensity) 262 ($M^+$, 1), 221 (6), 181 (39), 151 (7), 81 (100), 79 (14), 53 (14), 51 (9), 41 (33); (*) overlapped with signals of other compounds.

**19**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.9 (m, $F_{meta}$), −158.3 (t, $F_{para}$), −144.3 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 6.54 (dt, $J$ = 16.2, 7.0 Hz, 1H, $H^2$), 6.27 (d, $J$ = 16.2 Hz, 1H, $H^1$), 5.8 (m, 1H, $H^6$)*, 4.9−5.05 (m, 2H, $H^7$)*, 2.33 (m, 2H, $H^3$), 2.14 (m, 2H, $H^5$), 1.68 (qi, $J$ = 7.4 Hz, 2H, $H^4$); MS (EI) *m/z* (relative intensity) 262 ($M^+$, 4), 181 (23), 81 (63), 79 (66), 77 (17), 67 (59), 65 (24), 54 (50), 53 (44), 51 (22), 41 (100); (*) overlapped with signals of other compounds.

**Reactions with 1,7-Octadiene.** An NMR tube was charged with [PdPfBr(NCMe)$_2$] (0.025 g, 0.0574 mmol) and $CDCl_3$ (0.5 mL) and then cooled to −40 °C. 1,7-Octadiene (0.0085 mL, 0.0574 mmol) was added, and the reaction was monitored by $^{19}$F NMR. The temperature was increased in 10 °C steps, and the different isomerization processes were observed. The spectra showed that the reaction was complete after 3 h at 293 K, and the final mixture was analyzed by $^1$H and $^{19}$F NMR and found to contain **23** (39%), **24** (25%), **25** (17%), and **26** (8%), plus unknown organic (5%) and organometallic (6%) compounds (each one less than 2%). The yields in parentheses are based on the integration of $^{19}$F NMR signals.

When the reaction was carried out with a larger amount of starting materials, column chromatography (silica gel) could be used to separate the organic compounds obtained, eluting with *n*-hexane. Further verification and assignment of spectra for the palladium complexes and **26** were accomplished by $^1$H−$^1$H COSY experiments and (for **26**) GC−MS. Attempts at isolation as solids of the organometallic compounds failed due to their high solubility.

Excess 1,7-octadiene (0.085 mL, 0.575 mmol) was added to [PdPfBr(NCMe)$_2$] (0.050 g, 0.115 mmol) in $CDCl_3$ (0.6 mL). The reaction was complete after 2 h at room temperature as shown by $^{19}$F NMR. A mixture containing **23** (15%), **24** (9%), **25** (7%), **27** (9%), **28** (25%), **26** (4%), **29** (9%), **30** (7%), **31** (2%), **32** (3%), **33** (4%), and unknown organics (4%) and organometallics (2%) was obtained. The organic compounds could be separated by column chromatography. Assignment of $^1$H NMR spectra was accomplished by using $^1$H−$^1$H COSY.

**20**: $^{19}$F NMR ($CDCl_3$, $\delta$, 243 K, 282 MHz), −161.6 (m, $F_{meta}$), −156.7 (t, $F_{para}$), −142.8 (m, $F_{ortho}$).

**21**: $^{19}$F NMR ($CDCl_3$, $\delta$, 243 K, 282 MHz), −162.6 (m, $F_{meta}$), −157.8 (t, $F_{para}$), −144.5 (m, $F_{ortho}$).

**22**: $^{19}$F NMR ($CDCl_3$, $\delta$, 263 K, 282 MHz), −163.1 (m, $F_{meta}$), −158.4 (t, $F_{para}$), −144.4 (m, $F_{ortho}$).

**23**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.4 (m, $F_{meta}$), −158.6 (t, $F_{para}$), −144.8 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.25 (m, 1H, $H^2$), 3.94 (d, $J$ = 6.6 Hz, 1H, $H^1{}_{syn}$), 3.90 (m, 1H, $H^3$), 2.83 (d, $J$ = 11.9 Hz, 1H, $H^1{}_{anti}$)*, 2.68 (t, $J$ = 7.5 Hz, 2H, $H^8$), 1.96−1.50 (m, 8H, $H^4$, $H^5$, $H^6$, $H^7$)*; (*) overlapped with signals of other compounds.

**24**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −162.3 (m, $F_{meta}$), −156.7 (t, $F_{para}$), −143.4 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.27 (t, $J$ = 11.3 Hz, 1H, $H^3$), 3.8 (m, $J$ = 11.3 Hz, 1H, $H^4$)*, 3.64 (m, $J$ = 11.3 Hz, 1H, $H^2$)*, 3.30 (dd, $J$ = 14.4, 4.4 Hz, 1H, $H^1$), 3.03 (dd, $J$ = 14.4, 9.7 Hz, 1H, $H^{1'}$), 1.96−1.28 (m, 6H, $H^5$, $H^6$, $H^7$)*, 0.88 (t, $J$ = 6.8 Hz, 3H, $H^8$); (*) overlapped with signals of other compounds.

**25**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −162.9 (m, $F_{meta}$), −157.5 (t, $F_{para}$), −143.9 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.07 (t, $J$ = 11.0 Hz, 1H, $H^4$), 3.8 (m, $J$ = 11.0 Hz, 1H, $H^5$)*, 3.64 (m, $J$ = 11.0 Hz, 1H, $H^3$)*, 2.98−2.83 (m, 2H, $H^1$)*, 2.16 (m, 1H, $H^2$), 1.90 (m, 1H, $H^{2'}$)*, 1.78−1.28 (m, 4H, $H^6$, $H^7$)*, 0.91 (t, $J$ = 6.7 Hz, 3H, $H^8$); (*) overlapped with signals of other compounds.

**26**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.5 (m, $F_{meta}$), −158.8 (t, $F_{para}$), −145.2 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.37 (bs, 1H, $H^2$), 2.68 (t, $J$ = 7.3 Hz, 2H, $PfCH_2$), 2.2−2.4 (m, 3H, $H^3$, $H^5$), 2.14 (m, 1H, $H^4$), 1.85 (m, 1H, $PfCH_2CH$ H′), 1.66 (m, 3H, Me), 1.60 (m, 1H, $H^{4'}$), 1.38 (m, 1H, $PfCH_2CH$*H′*); MS (EI) *m/z* (relative intensity) 276 ($M^+$, 2), 95 (23), 81 (100), 79 (22), 67 (10), 53 (10), 41 (9).

**27**: $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.25 (m, 1H, $H^2$)*, 3.93 (d, $J$ = 7.2 Hz, 1H, $H^1{}_{syn}$), 3.90 (m, 1H, $H^3$)*, 2.83 (d, $J$ = 11.9 Hz, 1H, $H^1{}_{anti}$)*, 1.96−1.28 (m, 8H, $H^4$, $H^5$, $H^6$, $H^7$)*, 1.11 (t, $J$ = 7.5 Hz, 3H, $H^8$);[3b] (*) overlapped with signals of other compounds.

**28**: $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.17 (t, $J$ = 10.5 Hz, 1H, $H^3$), 3.8 (m, $J$ = 10.5 Hz, 2H, $H^2$, $H^4$)*, 1.96−1.28 (m, 6H, $H^5$, $H^6$, $H^7$)*, 1.40 (d, $J$ = 6.0 Hz, 3H, $H^1$), 0.88 (t, $J$ = 6.8 Hz, 3H, $H^8$)*;[3b] (*) overlapped with signals of other compounds.

**29**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.2−163.7 (m, $F_{meta}$), −158.6 (t, $F_{para}$), −144.8 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.78 (m, 1H, $H^2$)*, 5.35−5.55 (m, 2H, $H^5$, $H^6$)*, 4.95 (m, 2H, $H^1$)*, 2.75 (t, $J$ = 7.3 Hz, 2H, $H^8$), 2.3 (m, 2H, $H^7$)*, 1.95−2.1 (m, 4H, $H^3$, $H^4$)*; MS (EI) *m/z* (relative intensity) 276 ($M^+$, 0.2), 181 (100), 95 (91), 67 (40), 54 (12), 41 (33); (*) overlapped with signals of other compounds.

**30**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.2−163.7 (m, $F_{meta}$), −158.4 (t, $F_{para}$), −144.4 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.78 (m, 1H, $H^2$)*, 5.35−5.55 (m, $J$ = 5.4 Hz, 2H, $H^6$, $H^7$)*, 4.95 (m, 2H, $H^1$)*, 3.37 (d, $J$ = 5.4 Hz, 2H, $H^8$), 1.95−2.1 (m, $J$ = 7.2 Hz, 4H, $H^3$, $H^5$)*, 1.44 (qi, $J$ = 7.2 Hz, 2H, $H^4$); MS (EI) *m/z* (relative intensity) 276 ($M^+$, 2), 234 (19), 219 (20), 181 (83), 95 (100), 82 (22), 67 (47), 55 (93), 54 (44), 53 (21), 41 (37); (*) overlapped with signals of other compounds.

**31**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −164.0 (m, $F_{meta}$), −158.4 (t, $F_{para}$), −144.3 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 6.54 (dt, $J$ = 15.9, 6.6 Hz, 1H, $H^2$), 6.26 (d, $J$ = 15.9 Hz, 1H, $H^1$), 5.78 (m, 1H, $H^7$)*, 4.95 (m, 2H, $H^8$)*, 2.3 (m, $J$ = 6.6 Hz, 2H, $H^3$)*, 1.95−2.1 (m, 2H, $H^6$)*, 1.6 (m, 4H, $H^4$, $H^5$); MS (EI) *m/z* 276 ($M^+$); (*) overlapped with signals of other compounds.

**32**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.2−163.7 (m, $F_{meta}$), −158.7 (t, $F_{para}$), −144.8 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.35−5.55 (m, 4H, $H^2$, $H^3$, $H^5$, $H^6$)*, 2.71 (t, $J$ = 7.3 Hz, 2H, $H^8$), 2.7 (m, 2H, $H^4$), 2.3 (m, 2H, $H^7$)*, 1.66 (m, 3H, $H^1$)*; MS (EI) *m/z* 276 ($M^+$); (*) overlapped with signals of other compounds.

**33**: $^{19}$F NMR ($CDCl_3$, $\delta$, 282 MHz), −163.2−163.7 (m, $F_{meta}$), −158.5 (t, $F_{para}$), −144.4 (m, $F_{ortho}$); $^1$H NMR ($CDCl_3$, $\delta$, 300 MHz), 5.35−5.55 (m, 4H, $H^2$, $H^3$, $H^6$, $H^7$)*, 3.43 (d, $J$ = 6.2 Hz, 2H, $H^1$), 1.95−2.1 (m, 4H, $H^4$, $H^5$)*, 1.66 (m, 3H, $H^8$)*; MS (EI) *m/z* (relative intensity) 276 ($M^+$, 7), 194 (10), 181 (94), 95 (91), 82 (30), 81 (24), 67 (56), 55 (100), 54 (44), 53 (23), 41 (38); (*) overlapped with signals of other compounds.

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