Cyclization versus Pd−H Elimination−Readdition: Skeletal Rearrangement of the Products of Pd−C_6F_5 Addition to 1,4-Pentadienes

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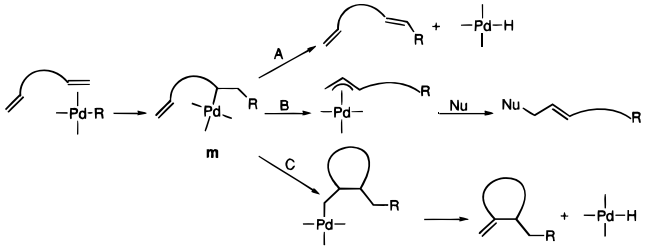
Abstract: The reactions of $[Pd(C_6F_5)Br(CH_3CN)_2]$ with 1,4-pentadiene or 3-methyl-1,4-pentadiene at low temperature afford, after insertion of one double bond into the Pd−C_6F_5 bond, two types of η^1-η^2-pentenylpalladium derivatives: the 4.5-membered palladacycles $[Pd_2(\mu\text{-Br})_2$(5-Pf-3-R-1,2,4-η^1-η^2-pentenyl)$_2]$ (Pf = C_6F_5; R = H (**2a**), Me (**2b**)) and the 5.5-membered metallacycles $[Pd_2(\mu\text{-Br})_2$(5-Pf-3-R-1,2,5-η^1-η^2-pentenyl)$_2]$ (R = H (**3a**), Me (**3b**)). Both enyls isomerize to η^3-allylic derivatives following two *competitive* pathways, i.e. (i) Pd migration or (ii) cyclopropane formation and reopening, which lead to the isomeric η^3-allylpalladium complexes $[Pd_2(\mu\text{-Br})_2$(5-Pf-3-R-1-3-η^3-pentenyl)$_2]$ (R = H (**5a**), Me (**5b**)) and $[Pd_2(\mu\text{-Br})_2$(4-Pf-3-(CH_2R)-1-3-η^3-butenyl)$_2]$ (R = H (**6a**), Me (**6b**)), respectively. After the cyclopropane formation−reopening process, $[Pd_2(\mu\text{-Br})_2$(3-CH_2Pf-1,2,5-η^1-η^2-pentenyl)$_2]$ (**8**) is also formed which isomerizes to **6b**. The reaction of a mixture of the η^1-η^2-pentenyl complexes at low temperature with CO/NaOMe gives methyl ester derivatives. Again, the formation of the major ester CH_2=CH(CH_2Pf)-CHRCOOMe involves cyclopropane formation−reopening in the enyl derivative **2**. An unusual acyl complex, [Pd-(μ-Br)(η^1-η^2-3-CH_2Pf-1-oxo-4-pentenyl)]$_2$ (**15**) containing a chelating η^2-η^1-olefin acyl moiety has been characterized.

Introduction

Palladium-mediated reactions of organic compounds have proved to be of great utility in organic synthesis and play an important role in the design of efficient and selective processes.[1] One of them is the arylation and vinylation of olefins, known as the Heck reaction. In this process a Pd−R moiety, usually formed in situ by oxidative addition of an aryl or vinyl halide to a Pd(0) complex, adds to the olefin via a *cis*-olefin−Pd−R intermediate following a well-established mechanism.[2,3] The final product of the reaction depends on the fate of the new alkyl palladium complex formed (**m**, Scheme 1). Decomposition through Pd−H elimination gives a substituted olefin (path A, Scheme 1), and this is usually observed for mono-olefins. If other double bonds are present in the molecule, subsequent Pd−H eliminations and readditions can transport the Pd atom along the hydrocarbon chain to form a stable allyl palladium derivative; this allyl can be transformed into useful organic derivatives by reaction with suitable nucleophiles (path B, Scheme 1).[1d] An alternative is the addition of the new Pd−R moiety to a second double bond in the substrate to give a cyclic compound (path C, Scheme 1). Pd−H elimination is usually the final step in these cyclizations. This intramolecular Heck reaction has been applied to polyunsaturated substrates in a cascade fashion allowing the synthesis of polycyclic organic

Scheme 1



derivatives with remarkable efficiency and atom economy.[4] The combination of the processes outlined in Scheme 1 has led to a great development of new synthetic routes.[5]

The cyclization via intramolecular Heck reaction (path C, Scheme 1) requires the coordination of the second double bond in the molecule to palladium in order to create an intermediate η^1-η^2-palladacycle. Thus the formation of a 5-membered ring from a plausible 6.5-membered η^1-η^2-palladacycle is the cyclization process most commonly observed.[4−6] Cyclizations to give ring sizes other than 5-membered are less common, but 3- to 6-membered rings have also been synthesized.[7−9] Both 3- and 5-membered rings can be described, according to Baldwin rules, as a result of favored 3-exo-trig or 5-exo-trig cyclizations, respectively.[10] The formation of 6-membered rings by an apparent 6-endo-trig cyclization has been interpreted as the result

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(1) (a) *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G., Abel, E. W., Eds.; Pergamon Press: New York, 1995; Vol. 12. (b) Hegedus, L. S. In *Organometallics in Synthesis*; Schlosser, M., Ed.; Wiley: New York, 1994; Chapter 5. (c) Larock, R. C. *Adv. Met.-Org. Chem.* **1994**, *3*, 97−224. (d) Bäckvall, J.-E. *Adv. Met. Org. Chem.* **1989**, *1*, 135−175. (e) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: New York, 1985. (f) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 8, p 854 and references therein.

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(3) Albéniz, A. C.; Espinet, P.; Jeannin, Y.; Philoche-Levisalles, M.; Mann, B. E. *J. Am. Chem. Soc.* **1990**, *112*, 6594.

(4) (a) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1993**, *115*, 9421−9438. (b) Negishi, E. *Pure Appl. Chem.* **1992**, *64*, 323−334. (c) Meyer, F. E.; Brandenburg, J.; Parsons, P. J.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1992**, 390−392. (d) Oppolzer, W.; DeVita, R. J. *J. Org. Chem.* **1991**, *56*, 6256−6257.

(5) (a) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259−281. (b) de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379−2411.

(6) (a) Trost, B. M.; Romero, D. L.; Rise, F. *J. Am. Chem. Soc.* **1994**, *116*, 4268−4278. (b) Trost, B. M.; Tanoury, G. J.; Lautens, M.; Chan, C.; MacPherson, D. T. *J. Am. Chem. Soc.* **1994**, *116*, 4255−4267. (c) Takacs, J. M.; Zhu, J.; Chandramouli, S. *J. Am. Chem. Soc.* **1992**, *114*, 773−774. (d) Trost, B. M. *Janssen Chim. Acta* **1991**, *9*, 3−9.

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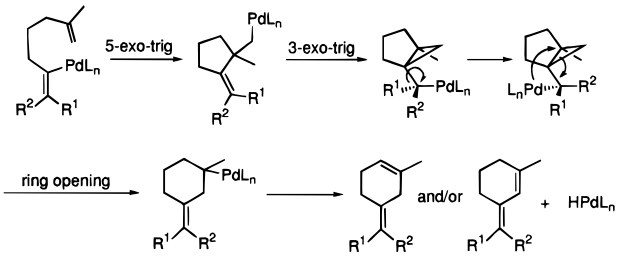
Scheme 2



of a favorable cyclopropane formation and subsequent ring opening (Scheme 2).[7c] The palladium-promoted ring opening of cyclopropanes is a well-known process.[11] The example in Scheme 2 and the reported formation of certain unexpected products show that the formation of strained cyclopropane rings might be more common than the number of isolated organic compounds containing this moiety would suggest.[7b,8c]

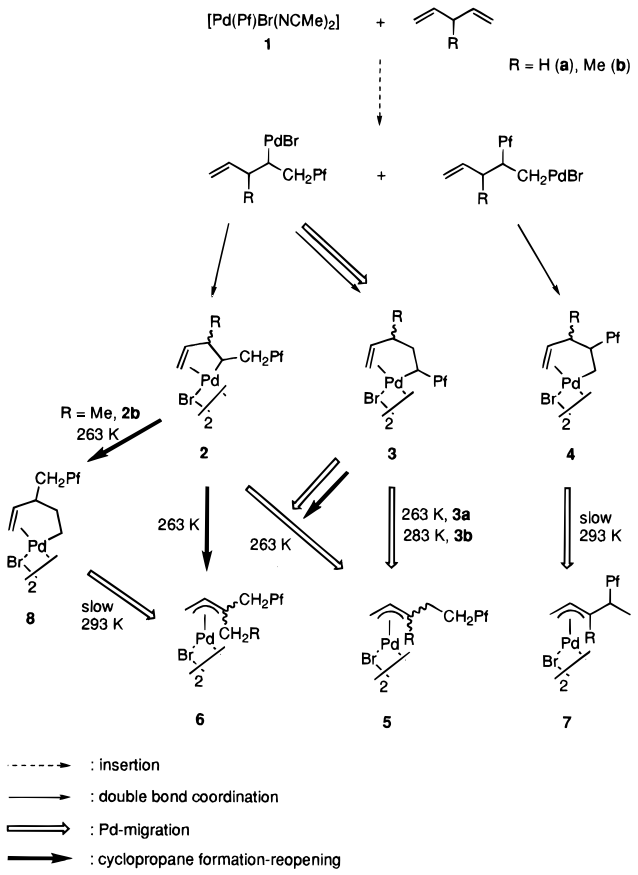
On the other hand, Pd−H elimination is a rapid reaction that can compete with the cyclization path and even abort it. The formation of a 5-membered ring seems to operate efficiently even when Pd−H elimination could occur.[4−6] In contrast, cyclopropane formation has only been accomplished when the Pd−H elimination pathway is blocked.[7]

We have used previously [Pd(C_6F_5)Br(CH_3CN)$_2$] as a model compound for the study of the Heck reaction.[3,12] In this paper we describe its reactions with 1,4-pentadiene or 3-methyl-1,4-pentadiene which afford unprecedented examples of competition of cyclopropane formation−ring opening and Pd−H elimination (pathways B and C in Scheme 1).

Results

The reactions of 1,4-pentadiene and 3-methyl-1,4-pentadiene with [Pd(C_6F_5)Br(CH_3CN)$_2$] (**1**) were analyzed. Similar behavior was observed for both dienes and accordingly the reactions will be described together and the differences will be pointed out where necessary. The reactions led eventually (sometimes after days) to the formation of the allyl complexes **5**−**7** (Scheme 3). Two obvious features prompted us to carry out deeper studies: first, the formation of **6** which involves an unexpected rearrangement of the carbon skeleton of the diene; and second, the observation of some quite stable intermediates even at room temperature. Consequently, the reactions were monitored by ^{19}F and ^{1}H NMR spectroscopy under temperature control so that further intermediates could be observed.

Scheme 3



(i) Insertion. When **1** and the diene were mixed in $CDCl_3$ at 243 K (Pd:diene ratio 1:1) coordination of some of the diene to palladium seemed to occur immediately: a new broad signal at δ 6 (1,4-pentadiene) or 6.4 (3-methyl-1,4-pentadiene) was observed in the ^{1}H NMR spectrum in both cases (compared to the multiplet at δ 5.8 for the free dienes); new F_{ortho} resonances at about δ −121, close in chemical shift to the signals of the starting material **1**, are also observed. However, as most of the diene added remains unreacted, its ^{1}H NMR signals hide any other new resonances, and full identification of these presumed Pd−diene derivatives could not be carried out.

Insertion of one double bond into the Pd−C_6F_5 moiety occurs slowly at this temperature giving rise to distinct F_{ortho} resonances at about δ −143 ppm which are typical for C_6F_5−C moieties.[3,12] They correspond to the η^1-η^2-pentenylpalladium derivatives **2** and **3** (Scheme 3). Compound **2** arises from coordination of the second double bond to palladium in the putative η^1-alkylpalladium intermediate formed by insertion. If elimination and readdition of Pd−H moves the Pd atom one carbon further, coordination of the uninserted double bond gives **3**.[13] A third type of η^1-η^2-pentenyl complex, **4**, was detected coming from the less favored addition of the Pd−C_6F_5 moiety to the double bond with opposite regiochemistry, i.e. the pentafluorophenyl group adding to the internal carbon. Although we have not observed before this type of addition in the reaction of dienes with "PdC_6F_5Br" synthons,[12] minor products resulting from R attack to the most substituted carbon of the double bond have been detected by other authors when certain dienes are subjected to the Heck reaction.[14]

(7) Cyclopropane ring formation: (a) Liu, C.-H.; Cheng, C.-H.; Cheng, M.-C.; Peng, S.-M. *Organometallics* **1994**, *13*, 1832−1839. (b) Rawal, V. H.; Michoud, C. *J. Org. Chem.* **1993**, *58*, 5583. (c) Owczarczyk, Z.; Lamaty, F.; Vawter, E. J.; Negishi, E. *J. Am. Chem. Soc.* **1992**, *114*, 10091−10092. (d) Grigg, R.; Sridharan, V.; Sukirthalingam, S. *Tetrahedron Lett.* **1991**, *32(31)*, 3855−3858. (e) Meyer, F. E.; Parsons, P. J.; de Meijere, A. *J. Org. Chem.* **1991**, *56*, 6487−6488. (f) Grigg, R.; Dorrity, M. J.; Malone, J. F.; Sridharan, V.; Sukirthalingam, S. *Tetrahedron Lett.* **1990**, *31(9)*, 1343−1346. (g) Zhang, Y.; Negishi, E. *J. Am. Chem. Soc.* **1989**, *111*, 3454−3456.

(8) Cyclohexane ring formation: (a) Dankwardt, J. W.; Flippin, L. A. *J. Org. Chem.* **1995**, *60*, 2312−2313. (b) Tietze, L. F.; Schimpf, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1089−1091. (c) Grigg, R.; Stevenson, P.; Worakun, T. *Tetrahedron* **1988**, *44*, 2033−2048. (d) References 4c, 6b, and 7a.

(9) Cyclobutane ring formation: Carpenter, N. E.; Kucera, D. J.; Overman, L. E. *J. Org. Chem.* **1989**, *54*, 5846−5848.

(10) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734−736.

(11) (a) Donaldson, W. A. *Adv. Met.-Org. Chem.* **1991**, *2*, 269−293. (b) Fischetti, W.; Heck, R. F. *J. Organomet. Chem.* **1985**, *293*, 391−405. (c) Larock, R. C.; Varaprath, S. *J. Org. Chem.* **1984**, *49*, 3432−3435. (d) Green, M.; Hughes, R. P. *J. Chem. Soc., Dalton Trans.* **1976**, 1880−1889.

(12) (a) Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *Organometallics* **1995**, *14*, 2977−2986. (b) Albéniz, A. C.; Espinet, P. *Organometallics* **1991**, *10*, 2987−2988. (c) Albéniz, A. C.; Espinet, P.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1990**, *9*, 1079−1085.

(13) The allyl derivative **5** is also observed in a very small ratio at 243 K. Pd migration operating on the η^1-alkylpalladium intermediate before double bond coordination accounts for the formation of this derivative.

(14) (a) Bender, D. D.; Stakem, F. G.; Heck, R. F. *J. Org. Chem.* **1982**, *47*, 1278−1284. (b) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146−151.

The ratio of the three compounds was evaluated by the ratio of their ^{19}F resonances at 243 K. For 1,4-pentadiene **2a:3a:4a** = 9.3:3.5:1, whereas for 3-methyl-1,4-pentadiene **2b:3b:4b** = 8:8:1. Both **2b** and **3b** appear as a 1:1 mixture of two diastereoisomers (**2b$_1$**, **2b$_2$**, **3b$_1$**, and **3b$_2$**) clearly shown by their distinct ^{19}F resonances. They arise from the non-stereoselective formation of two asymmetric carbons in the insertion step (Pd-substituted and Me-substituted carbons). Only broad signals were observed for **4b** which may contain the two diastereoisomers also expected in this case. Although only one asymmetric carbon is present in the structure of **2a**, two equally populated diastereoisomers were clearly observed in its ^1H NMR spectrum (only one set of signals with an unusual multiplicity pattern was shown by their ^{19}F NMR spectrum due to very close chemical shift values). They must be the two diastereoisomers expected from coordination of the *re* and *si* faces of the prochiral double bond to palladium; in fact a slight excess of reactant diene promotes rapid exchange between faces and the coalescence of the resonances of the two diastereoisomers. This source of diastereoisomerism is also present in the rest of the compounds **2**−**4** but the corresponding duplication of signals was not actually observed, probably because in the corresponding experiments some free diene in excess was efficiently producing their conversion.

The ^{19}F and ^1H NMR spectral data for these complexes are given in the Experimental Section. The simplicity of the pentafluorophenyl pattern in the ^{19}F NMR spectra (three typical multiplets) and the wide chemical shift range (which makes overlapping of signals very rare) provide a fast and useful check of the number of compounds in mixtures and facilitate to monitor their evolution as has been previously described.[12c] ^1H homonuclear correlations and decoupling experiments were used to fully identify all the complexes. For **3a** the ^1H resonances are hidden by the major derivatives **2a$_1$** and **2a$_2$**, but are revealed by integration in a ratio consistent with the ^{19}F spectrum of the mixture. Besides this, the structure proposed for **3a** is based on those of **3b$_1$** and **3b$_2$**, formed in the reaction of the analogous diene 3-methyl-1,4-pentadiene.

(ii) Isomerization. As the temperature increases, isomerization of compounds **2** and **3** is observed and was followed by ^{19}F NMR spectroscopy (Scheme 3). Thus **2a** and **3a** disappear at similar rates, and this is clearly observed at 263 K (25% conversion after 10 min; half conversion after 30 min). **2b$_1$** and **2b$_2$** also isomerize clearly at this temperature (30% conversion after 10 min; half conversion after 20 min), but a noticeable disappearance rate is reached for **3b$_1$** and **3b$_2$** only at a higher temperature (283 K, 15% conversion after 10 min; half conversion after 40 min). The final products of the isomerization are compounds **5** and **6**, but during the isomerization of the mixture of **2b** and **3b**, the formation of a third compound, **8**, which isomerizes to the η^3-allyl complex **6b** at room temperature, is also observed. The final η^3-allyls are formed as a mixture of syn and anti isomers, the less hindered syn isomer (i.e. the isomer with the bulkier substituent syn to the central allylic proton) being more abundant in all cases. The following ratios are observed: **5a-syn:5a-anti** = 9:1; **5b-syn:5b-anti** = 1.5:1; **6a-syn:6a-anti** = 2:1; **6b-syn:6b-anti** = 3.3:1 (Scheme 3). Compound **6a** had been obtained previously as a minor product from the reaction of $[Pd(C_6F_5)Br(CH_3CN)_2]$ with isoprene.[12a]

Also the η^1-η^2-pentenyl derivatives **4a** and **4b** isomerize through Pd−H elimination−readditions leading to the corresponding η^3-allylpalladium complexes **7a** and **7b**. The processes occur very slowly and take 25 days at room temperature for completion.

Table 1. Final Products (%) of the Reaction of **1** and Pentadienes (PD)[a]

diene	Pd:diene ratio	**5**	**6**	**7**	organic deriv	**5/6**[b]
1,4-PD	1:1	45.5	43.6	9.2		1.04
1,4-PD	1:5	87.1	5.3	6.2		16.4
3-Me-1,4-PD	1:1	47.5	44	3.1	3.1	1.08
3-Me-1,4-PD	1:5	55.1	32.5	2.9	9.4	1.7

[a] Percent determined from integration of ^{19}F NMR signals. [b] Ratio of both products.

Crystallization and chromatographic separation by preparative TLC were tried on the final mixture of η^3-allylpalladium derivatives obtained in the reactions. The complexes are very soluble in organic solvents and only **5a-syn** (7% yield) and **5b-syn** (10% yield) could be isolated as yellow solids by crystallization from their respective mixtures using diethyl ether/*n*-hexane at −20 °C. Partial separation of the allylic compounds was carried out by preparative TLC. Details of these separations, analyses, and ^{19}F and ^1H NMR data are given in the Experimental Section.

The ratio diene:Pd used in the reaction affects the ratio of final products obtained and relevant data are collected in Table 1. Experiments using Pd:diene = 1:5 were carried out. Although the low-temperature distribution **2:3:4** was not significantly different from that found in the 1:1 experiment, remarkable effects were observed in the isomerization step. Excess of 1,4-pentadiene increases dramatically the ratio **5a/6a**. The ratio **5b/6b** changes in the same way when excess 3-methyl-1,4-pentadiene is used but the effect is less important. In this case a C_6F_5-substituted diene is also formed in about 10% yield, which was identified as 3-((pentafluorophenyl)-methyl)-1,4-pentadiene (**9**) along with the non-pentafluorophenyl-containing derivative di(μ-bromo)bis(3-methyl-1-3-η^3-pentenyl)dipalladium(II) (**10**).[15] It has been observed before that excess diene favors decoordination of the double bond from palladium during Pd migration to give substituted dienes and the non-substituted palladium allyl.[12a,16,17]

(iii) Carbonylation Experiments. Carbonylation of palladium organometallic derivatives is a well-known reaction of wide applicability.[18] In order to further support the structure of the η^1-η^2-pentenyl complexes formed at low temperature, trapping reactions of these derivatives with CO were tried. The rates of the different reactions in Scheme 3 are such that it is not possible to obtain a solution containing only **2**, **3**, and **4**. Thus mixtures containing about 85−90% of these derivatives in the ratio indicated above and about 10−15% of either **1**, **5**, or both (depending on the temperature and reaction time) were

(15) Small amounts of organic C_6F_5-disubstituted derivatives (3%) are also produced in the course of the reaction of $[Pd(C_6F_5)Br(CH_3CN)_2]$ and 3-methyl-1,4-pentadiene (ratio 1:1). They were identified as a mixture of *(E)*- and *(Z)*-1,5-bis(pentafluorophenyl)-3-methyl-2-pentene (**11**), *E*:*Z* = 2:1. They are the result of insertion of the unsubstituted double bond of 1-(pentafluorophenyl)-3-methyl-1,4-pentadiene into the Pd−C_6F_5 bond and subsequent H transfer to form the monoolefin. 1-(Pentafluorophenyl)-3-methyl-1,4-pentadiene is generated in turn from insertion of 3-methyl-1,4-pentadiene into the Pd−C_6F_5 bond followed by Pd−H elimination. These products do not form when excess diene is used in the reaction.

(16) Larock, R. C.; Takagi, K. *J. Org. Chem.* **1984**, *49*, 2701−2705.

(17) An increase of the amount of syn complex is found for complexes **5a** and **6a** when excess diene is used (**5a-syn:5a-anti** = 9:1, Pd:diene = 1:1; **5a-syn:5a-anti** = 19.2:1, Pd:diene = 1:5; **6a-syn:6a-anti** = 2:1, Pd:diene = 1:1; **6a-syn:6a-anti** = 3.8:1, Pd:diene = 1:5). It is well-know that the interconversion syn−anti is promoted by free ligands and, even if the coordination ability of dienes is not very high, the ratio observed when excess diolefin is used must be closer to the thermodynamic syn−anti distribution. No noticeable change in the syn:anti ratio is found with time or excess diene for derivatives **b** (3-methyl-1,4-pentadiene).

(18) (a) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation: Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991. (b) Reference 1c, Chapter 8, pp 341−400.

obtained and used for carbonylation. Apparently there is no noticeable conversion of **2** or **3** into **5** during the reaction. The carbonylation products of **1** and **5** in the presence of NaOMe are $C_6F_5CO_2Me$, *p*-$MeOC_6F_4CO_2Me$ (both from **1**), and $C_6F_5(CH_2)_2CR{=}CHCH_2CO_2Me$ (from **5**), which can be easily discounted from the spectra, and the fate of the other 85−90% is discussed below.

When a mixture of the η^1-η^2-pentenyl complexes obtained in the reaction of $[Pd(C_6F_5)Br(CH_3CN)_2]$ with 1,4-pentadiene in $CHCl_3$ at 243 K, i.e. **2a:3a:4a** = 9.3:3.5:1, was reacted with CO and a methanolic solution of NaOMe, metallic palladium precipitated immediately. Working up of the solution afforded a mixture of the following C_6F_5-substituted methyl esters (Scheme 4): methyl 3-((pentafluorophenyl)methyl)-4-pentenoate (**12a**); methyl 2-((pentafluorophenyl)methyl)-4-pentenoate (**13a**); and methyl 3-(pentafluorophenyl)-5-hexenoate (**14a**). The ratio of these derivatives was **12a:13a:14a** = 9.5:3.3:1.

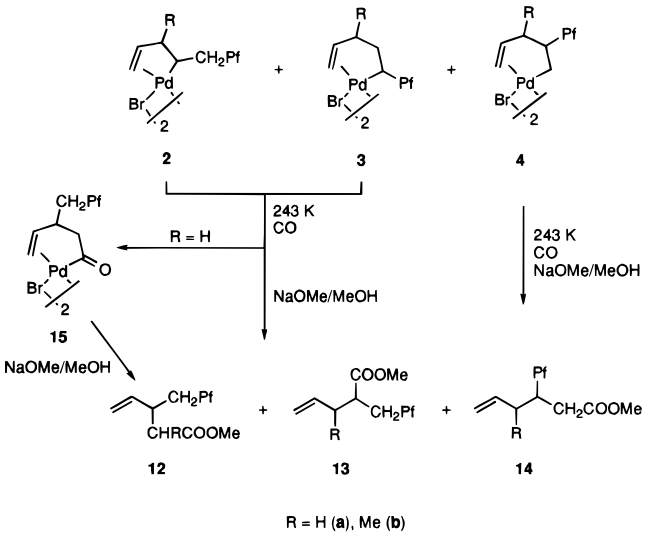
The structure of the major derivative **12a** reflects a skeletal rearrangement of the starting compounds. ^{1}H COSY and heteronuclear ^{1}H−^{13}C correlation experiments helped in the assignment. The last experiment determined the presence of a CH_2COOMe moiety (cross peak between a δ 2.43 proton and a δ 39.1 carbon) which is consistent with the structure of ester **12a**. Esters **13a** and the minor **14a** are the result of direct carbonylation of the Pd complexes **2a** and **4a**, respectively, i.e. formal substitution of Pd by a carbomethoxy group.[19]

The carboxylic ester expected from direct CO insertion into the η^1-η^2-enyl complex **3a**, methyl 2-(pentafluorophenyl)-5-hexenoate, was not observed in the final mixture; this ester was independently synthesized by standard organic methods and its ^{1}H and ^{19}F NMR spectra compared with those corresponding to the carbonylation mixture, where no coincidences were found.

When CO was bubbled through a mixture of **2a**, **3a**, and **4a** in the usual ratio (which also contained **5a-syn** in about 12%) at low temperature in the absence of the methanolic NaOMe solution, an intermediate acyl derivative di(μ-bromo)bis(η^1-η^2-(3-((pentafluorophenyl)methyl)-1-oxo-4-pentenyl)dipalladium(II) (**15**), along with other products, was formed. Repeated crystallizations of the mixture from Et_2O/*n*-hexane afforded a yellow solid in 25% yield, containing **15** as the major component (60%), unreacted **5a-syn**, and what seemed to be the acyl derivatives resulting from insertion of CO into the Pd−C bond of the η^1-η^2-pentenyl derivatives **2a** and **4a**. These two acyl derivatives could not be identified though, since their ^{1}H NMR signals were hidden by the major derivative **15**; however their presence was clear in the ^{19}F NMR spectrum of the mixture.

Although **15** is stable at room temperature in the solid state and moderately stable in $CHCl_3$ solution we could not isolate it pure. It was characterized in the mixture by an intense ν(CO) absorption in the IR spectrum at 1763 cm^{-1} and a ^{13}C resonance at δ 206 ppm, showing clearly the presence of an acyl moiety. Although palladium acyl derivatives are well-known[20] and some of them are stabilized through chelation,[21] **15** exhibits a less

Scheme 4



R = H (**a**), Me (**b**)

common η^2-η^1-olefin−acyl chelating ligand. **15** undergoes nucleophilic cleavage by OMe^- to give the ester derivative **12a**, thus supporting the assigned structure and showing its intermediacy in the carbonylation reaction (Scheme 4).

The carbonylation reaction was also carried out with a mixture of the η^1-η^2-enyl complexes derived from the reaction of $[Pd(C_6F_5)Br(NCMe)_2]$ with 3-methyl-1,4-pentadiene, i.e. **2b**, **3b**, and **4b** (ratio 8:8:1). When this mixture, in $CDCl_3$ at 243 K, was reacted with CO and a methanolic solution of NaOMe, black palladium precipitated immediately. Working up of the solution afforded a mixture of the following C_6F_5-substituted methyl esters (Scheme 4): methyl 2-methyl-3-((pentafluorophenyl)methyl)-4-pentenoate (**12b**), methyl 3-methyl-2-((pentafluorophenyl)methyl)-4-pentenoate (**13b**), and methyl 4-methyl-3-(pentafluorophenyl)-5-hexenoate (**14b**), each of them as a 1:1 mixture of two diastereoisomers; the ratio of the esters was **12b:13b:14b** = 11:5:1. The presence of **12b** shows that a rearrangement of the carbon chain has occurred, as it was observed for **12a**. The ester derivatives **13b** and **14b** are the result of formal substitution of Pd by a carbomethoxy group in the η^1-η^2-enyl complexes **2b** and **4b**. The structure of **13b** was further supported by the presence of a small coupling constant between the olefinic proton H^4 and the methyl group on the adjacent carbon (Me^3), clearly seen in the ^{1}H COSY spectrum of the mixture. This coupling was not detected for the major derivative **12b**. Again, the methyl ester corresponding to the 5.5-membered metallacycle **3b** was not observed (see above).

Discussion

The insertion of 1,4-pentadiene or 3-methyl-1,4-pentadiene into the Pd−C_6F_5 bond gives a chance to observe several η^1-η^2-pentenyl complexes **2**−**4** and their evolution to give η^3-allyl complexes (Scheme 3). Complexes **5** and **7** are the allyls expected from simple Pd−H elimination−readdition, but the generation of **6** needs a skeletal rearrangement of the carbon chain.

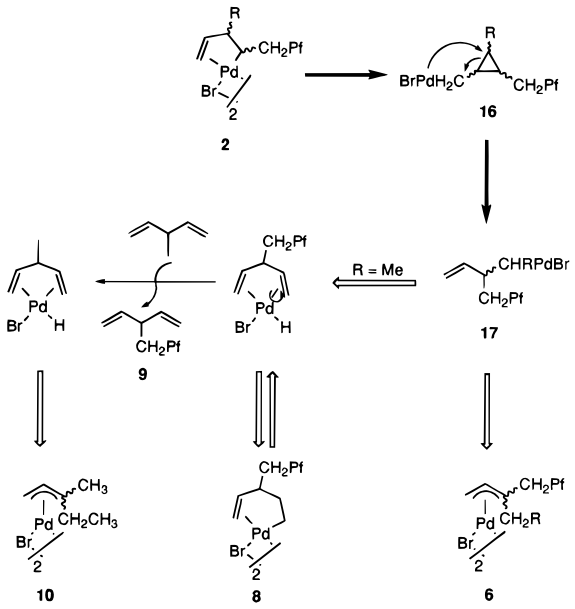
The formation of complexes **6** and, when 3-methyl-1,4-pentadiene is used, the η^1-η^2-pentenyl complex **8** occurs via cyclopropane formation and reopening as shown in Scheme 5. Cyclization to give an intermediate cyclopropylmethyl−palladium derivative (**16**), which could not be detected, followed by concerted ring opening to **17** and by Pd migration leads to complexes **6**. Alternatively, 1,2-hydrogen shift in **17** and double bond coordination leads to complex **8**. Chloropalladation of or Pd−R addition to methylenecyclopropanes has been shown

(19) Derivative **14a** could not be completely identified, but it is clearly seen in the ^{19}F NMR spectrum of the mixture and also in the ^{1}H NMR spectrum (Me resonance of the ester group) in the same relative ratio. **14a** is also present when a mixture of the η^3-pentenyl derivatives obtained from isomerization of the enyl mixture (in which **4a** is still present) is subjected to the carbonylation reaction.

(20) (a) Van Asselt, R.; Gielens, E. E. C. G.; Rülke, R. E.; Vrieze, K.; Elsevier, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 977−985. (b) Tóth, I.; Elsevier, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 10388−10389. (c) Cavinato, G.; Toniolo, L. *J. Organomet. Chem.* **1990**, *398*, 187−195. (d) Brumbaugh, J. S.; Sen, A. *J. Am. Chem. Soc.* **1988**, *110*, 803−816. (e) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115−4127. (f) Booth, G.; Chatt, J. *J. Chem. Soc. A* **1966**, 634−638.

(21) Hegedus, L. S.; Siirala-Hansén, K. *J. Am. Chem. Soc.* **1975**, *97*, 1184−1188.

Scheme 5

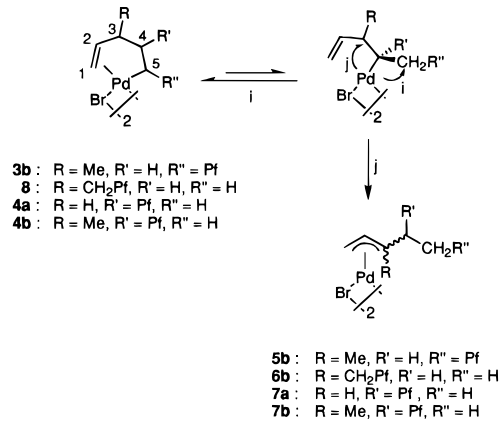


to give η^3-allylpalladium derivatives following the same ring-opening mechanism.[11] Thus, facile C−C bond formation and subsequent C−C cleavage produces the rearrangement of the carbon chain. The formation of compound **9** when excess diene is used arises from Pd−H elimination in the η^1-enyl intermediate **17** and substitution of the diene by 3-methyl-1,4-pentadiene (Scheme 5). Pd−H addition to the latter gives the η^3-allylpalladium derivative di(μ-bromo)bis(3-methyl-1-3-η^3-pentenyl)dipalladium(II) (**10**).

The isomerization of the 4.5-membered η^1-η^2-pentenylpalladium complex **2b** at 263 K yields complexes **5b**, **6b**, and **8** simultaneously (Scheme 3). This means that cyclization (which yields **6b** and **8**) and decoordination of the double bond followed by Pd migration (that yields **5b**) are competitive pathways operating on derivative **2b** with almost equal efficiency, as indicated by the ratio **5b**:(**6b** + **8**) ≈ 1:1.05. A preference for the Pd-migration pathway is observed in the isomerization of the 5.5-membered pentenylpalladium derivative **3b** at 283 K; the ratio after the disappearance of **3b** is **5b**:(**6b** + **8**) ≈ 1:0.87. Since the cyclopropane formation process, an intramolecular Heck reaction, must occur from **2**, it seems that a certain amount of **3b** forms **2b** and then undergoes the above-mentioned rearrangement.

Several η^1-η^2-pentenyl complexes have been detected in this work and it is worth noting their different rates of isomerization which roughly follow the order **2a** ≈ **2b** ≈ **3a** > **3b** > **8** > **4a** ≈ **4b**. The 4.5-membered η^1-η^2-pentenyl complexes **2** isomerize faster than most of the η^1-η^2-pentenyl complexes with one extra chain link. This is consistent with the higher strain of the palladacycle in the former, which should make double bond decoordination easier; this decoordination is probably needed for Pd migration to proceed.[3,12a] However, the very different rates found for **3a**, **3b**, **4**, and **8** (all containing a 5.5-membered metallacycle) reveal that the strain of the metallacycle is not the main factor that controls their stability toward Pd migration. Other steps such as bond rotation around the C^4−C^5 bond, to arrange Pd and a β-H syn to each other, may also become rate determining (Scheme 6).[22] In fact the most stable derivatives are complexes **4**, with only one β-H available to Pd−H elimination and a bulky pentafluorophenyl group which may

Scheme 6



hinder rotation to reach a syn Pd−H arrangement easily. After the first Pd−H elimination−readdition, Pd gets bound to C^4 and again C−C bond rotation to reach a syn Pd−H alignment is needed. This is more difficult for the C-3 substituted complexes. Thus, the backward β-H^5 elimination (i, Scheme 6) becomes competitive with the β-H^3 elimination (j, Scheme 6), slowing down the isomerization process to η^3-allyl.

Should decoordination of the double bond in the η^1-η^2-pentenyl complexes **2** occur, this would prevent isomerization through the cyclization pathway. This decoordination is induced by addition of an excess diene which can act as a competing ligand. The effect is quite remarkable for 1,4-pentadiene and the ratio Pd-migration:cyclization products is increased to 16.4:1. The influence is less important in 3-methyl-1,4-pentadiene and the amount of Pd-migration products raises only moderately (Table 1). The less favorable Pd migration for the latter (just discussed) and small differences in the coordination ability of the two dienes can account for the different effects.

It can be said that, in general, the presence of substituents on the diene carbon chain makes Pd−H elimination more difficult, in favor of the cyclization process. In the limit, cyclopropane formation is the only available isomerization path for 4.5-membered η^1-η^2-palladacycles when Pd−H elimination is not possible, i.e. when palladium is bound to a quaternary carbon, or when a *trans*-Pd−H arrangement is fixed in a cyclic derivative or by intramolecular coordination. It is worth noting that the examples of cyclopropane formation in Pd-mediated cyclizations in the literature, where usually excess of the unsaturated substrate is used, have been observed only when the Pd−H elimination path is blocked.[7] To our knowledge, this is the first report on competitive Pd−H elimination and cyclopropane formation.

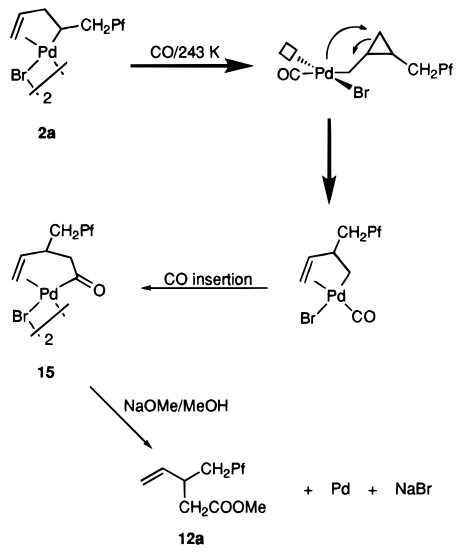
The presence of CO seems to promote the cyclization path, since the major methyl ester formed by reaction of the η^1-η^2-pentenyl mixture (**2**, **3**, and **4**) with carbon monoxide and NaOMe is **12**. This ester results from cyclopropane formation and reopening, which gives a new η^1-η^2-pentenyl palladium derivative (Scheme 7). Then CO insertion into the Pd−σ-C bond gives the acylpalladium complex **15** which could be isolated. Nucleophilic attack by OMe^- on **15** gives the methyl ester derivative **12**.

The ester derivatives coming from direct insertion of CO into the Pd−C bond of the enyl derivatives **2** and **4** (**13** and **14**, respectively) were also identified, but the ester corresponding to the analogous reaction on complexes **3** was not detected. As electronegative substituents decrease the ease of insertion of CO into a metal−carbon bond,[23] the presence of a pentafluo-

(22) Goddard, R.; Green, M.; Hughes, R. P.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1976**, 1890−1899.

(23) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986; pp 251−252.

Scheme 7



rophenyl group attached to the carbon atom bound to palladium in complexes **3** seems to slow down the insertion process rendering the Pd−H elimination−readdition competitive. This should move the Pd atom to an adjacent carbon to form **2**, where cyclization or CO insertion, to give esters **12** and **13**, occurs.

Conclusions

Unstable η^1-η^2-pentenyl palladium derivatives, formed by insertion of a double bond of 1,4-pentadiene or 3-methyl-1,4-pentadiene into the Pd−C_6F_5 bond, can be stabilized at low temperature. Two competitive processes are found in their evolution to give η^3-allyls, namely, (i) Pd migration and (ii) cyclopropane formation from 4.5-membered η^1-η^2-palladacycles and reopening. The latter result proves that the intramolecular Heck reaction to give cyclopropanes can occur at a rate comparable with that of Pd−H elimination. This competition is observed for the first time and brings about chain rearrangements otherwise unexpected. CO coordination seems to promote the cyclization path.

Experimental Section

General Comments. ^{19}F and ^{1}H NMR spectra were recorded on Bruker ARX-300 and AC-300 spectrometers. Chemical shifts (in δ units, ppm) are reported downfield from $SiMe_4$ for ^{1}H and ^{13}C and from $CFCl_3$ for ^{19}F. Mixtures of organic products were analyzed using a HP-5890 gas chromatographer connected to a HP-5988 mass spectrometer at an ionizing voltage of 70 eV and a quadrupole analyzer. High-resolution MS were recorded in a Fisons UG-Autospec spectrometer. Carbon, hydrogen, and nitrogen analyses were carried out on a Perkin-Elmer 240 microanalyzer. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer.

$[Pd(C_6F_5)Br(NCMe)_2]$ was prepared as described elsewhere.[12c] Diolefins were purchased from Aldrich and used without further purification.

Variable-Temperature Experiments. Reaction of $[Pd(C_6F_5)Br(NCMe)_2]$ with 3-Methyl-1,4-pentadiene. A 5-mm NMR tube was charged with a solution of $[Pd(C_6F_5)Br(NCMe)_2]$ (0.050 g, 0.115 mmol) in $CDCl_3$ (0.6 mL) and cooled to −30 °C. 3-Methyl-1,4-pentadiene (0.014 mL, 0.115 mmol) was added to this solution and the reaction was monitored by ^{19}F and ^{1}H NMR. After 2 h at this temperature insertion of the olefin into the Pd−C_6F_5 bond had occurred and compounds **2b**, **3b**, and **4b** were formed. The temperature was then raised to −10 °C and the mixture was kept for 2 h at this temperature; isomerization of **2b** was observed. The mixture was warmed to 10 °C and after 4 h isomerization of **3b** was complete. The temperature was finally increased to 20 °C and after 2 days total disappearance of **8** occurred. **4b** completely isomerized after 25 days. The mixture was worked up to separate **5b**, **6b**, **7b**, and the small amount of organic derivatives formed. The solvent was evaporated and the residue was chromatographed on a silica column (neutral, 230−400 mesh) and eluted with *n*-hexane. This operation afforded a mixture of the C_6F_5− organic derivatives (*E*)- and (*Z*)-**11**. Elution with Et_2O yielded the Pd−allyl compounds, which could be further separated by preparative TLC as reported below.

$2b_1$: ^{19}F NMR ($CDCl_3$, δ, 263 K, 282 MHz), −162.1 (m, F_{meta}), −156.1 (t, F_{para}), −142.9 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 263 K, 300 MHz), 5.00 (m, 2H, H^1, $H^{1'}$), 4.62 (m, 1H, H^2), 3.17 (m, H^3), 1.12 (d, 3H, J = 7 Hz, Me^3).

$2b_2$: ^{19}F NMR ($CDCl_3$, δ, 263 K, 282 MHz), −163.1 (m, F_{meta}), −156.3 (t, F_{para}), −143.4 (b, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 263 K, 300 MHz), 4.50−4.30 (H^1, $H^{1'}$, H^2), 2.55 (H^3), 0.89 (d, 3H, J = 6.5 Hz, Me^3).

$3b_1$: ^{19}F NMR ($CDCl_3$, δ, 283 K, 282 MHz), −162.0 (m, F_{meta}), −156.2 (t, F_{para}), −143.1 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 283 K, 300 MHz), 4.75 (d, 1H, J = 15.5 Hz, H^1), 4.37 (m, $H^{1'}$, H^2), 3.00 (H^5), 2.55 (b, H^3), 2.33 (H^4), 1.65 ($H^{4'}$), 0.95 (d, 3H, J = 6.5 Hz, Me^3).

$3b_2$: ^{19}F NMR ($CDCl_3$, δ, 283 K, 282 MHz), −162.5 (m, F_{meta}), −157.0 (t, F_{para}), −143.2 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 283 K, 300 MHz), 4.63 (d, 1H, J = 14.5 Hz, H^1), 4.37 (m, $H^{1'}$, H^2), 2.05 (H^5), 1.72 (H^3), 1.30 (H^4), 1.1 ($H^{4'}$), 0.77 (d, 3H, J = 5.5 Hz, Me^3).

4b: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −162.3 (b, F_{meta}), −156.3 (b, F_{para}), −140.5 (b, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.76 (dd, 1H, J = 15, 8.5 Hz, H^2), 4.93 (bd, 1H, J = 8.5 Hz, H^1), 4.87 (d, 1H, J = 15 Hz, $H^{1'}$), 3.70 (m, 1H, J = 12, 5.5 Hz, H^4), 3.50 (H^5), 2.45 (m, 1H, $H^{5'}$), 2.35 (m, 1H, H^3), 1.35 (Me^3).

5b-syn: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −162.6 (m, F_{meta}), −157.2 (t, F_{para}), −144.2 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.03 (dd, 1H, J = 12.7, 7.2 Hz, H^2), 3.99 (d, 1H, J = 7.2 Hz, H^1-syn), 3.23 (d, 1H, J = 12.7 Hz, H^1-anti), 3.05 (m, H^5), 2.80 (m, $H^{5'}$), 2.25 (m, H^4), 2.15 (m, $H^{4'}$), 1.32 (s, 3H, Me^3).

5b-anti: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −162.6 (m, F_{meta}), −157.0 (t, F_{para}), −144.5 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.09 (dd, 1H, J = 12.6, 7.4 Hz, H^2), 3.87 (d, 1H, J = 7.4 Hz, H^1-syn), 3.01 (d, 1H, J = 12.6 Hz, H^1-anti), 3.03 (m, H^5), 2.90 (m, $H^{5'}$), 2.05 (m, H^4), 1.73 (m, $H^{4'}$), 1.64 (s, 3H, Me^3).

6b-syn: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −161.9 (m, F_{meta}), −155.7 (t, F_{para}), −141.4 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.33 (dd, 1H, J = 12.6, 7.4 Hz, H^2), 3.98 (d, 1H, J = 7.4 Hz, H^1-syn), 3.52 (d, 1H, J = 15 Hz, $CH_2C_6F_5$), 3.16 (bd, 2H, H^1-anti, $CH_2C_6F_5$), 1.40 (m, 1H, H^4), 1.28 (t, 3H, J = 6.5 Hz, Me^5), 1.13 (m, 1H, $H^{4'}$).

6b-anti: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −162.3 (m, F_{meta}), −156.4 (t, F_{para}), −140.5 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.15 (dd, 1H, J = 12.8, 7.5 Hz, H^2), 4.10 (d, 1H, J = 7.5 Hz, H^1-syn), 3.48 (d, 1H, J = 12.8 Hz, H^1-anti), 2.80 (m, $CH_2C_6F_5$), 1.90 (m, 1H, H^4), 1.60 (m, $H^{4'}$), 1.11 (t, 3H, J = 7.3 Hz, Me^5).

7b: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −162.0 (m, F_{meta}), −156.2 (t, F_{para}), −142.7 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.47 (dd, 1H, J = 12, 7 Hz, H^2), 4.08 (d, 1H, J = 7 Hz, H^1-syn), 3.80 (m, H^4), 3.29 (d, 1H, J = 12 Hz, H^1-anti), 1.59 (d, J = 7 Hz, Me^5), 1.14 (s, Me^3).

8: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −162.4 (m, F_{meta}), −156.7 (t, F_{para}), −143.2 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.87 (m, 1H, H^2), 4.69 (d, 1H, J = 14 Hz, $H^{1'}$), 4.65 (d, 1H, J = 6.6 Hz, H^1), 2.90 (m, H^3), 2.71 (d, 2H, J = 6.6 Hz, $CH_2C_6F_5$), 2.46 (m, 1H, H^5), 2.28 (m, 1H, $H^{5'}$), 1.69 (H^4), 0.66 (dt, 1H, J = 11, 4.5 Hz, $H^{4'}$).

(E)-**11**: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −163.6 (m, F_{meta}), −163.2 (m, F_{meta}), −158.4 (t, F_{para}), −158.3 (t, F_{para}), −144.7 (m, F_{ortho}), −144.6 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.04 (t, 1H, J = 7.5 Hz, H^2), 3.34 (d, 2H, J = 7.5 Hz, H^1), 2.79 (tt, 2H, J = 7.5 Hz, $^4J_{F-H}$ = 1.5 Hz, H^5), 2.24 (m, 2H, J = 7.5 Hz, H^4), 1.79 (s, 3H, Me^3); MS(EI) *m*/*z* (relative intensity), 416 (M^+, 6), 235 (36), 207 (41), 181 (100), 41 (50). HRMS calcd for $C_{18}H_{10}F_{10}$, *m*/*z* 416.0623; found, 416.0632.

(Z)-**11**: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −163.1 (m, F_{meta}), −158.2 (t, F_{para}), −157.8 (t, F_{para}), −144.9 (m, F_{ortho}), −144.6 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.23 (t, 1H, J = 6.5 Hz, H^2),

3.27 (d, 2H, J = 6.5 Hz, H^1), 2.82 (tt, 2H, J = 7.5 Hz, $^4J_{F-H}$ = 1.5 Hz, H^5), 2.42 (m, 2H, J = 7.5 Hz, H^4), 1.76 (q, 3H, J = 1.3 Hz, Me^3); MS (EI) m/z (relative intensity), 416 (M^+), 235 (81), 221 (27), 207 (48), 181 (100), 41 (21).

The same procedure was used in the reaction of $[Pd(C_6F_5)Br(NCMe)_2]$ and excess 3-methyl-1,4-pentadiene and the reaction was monitored by ^{19}F NMR spectroscopy. Column chromatography separation of the residue containing the reaction mixture afforded compound **9**, which was isolated as a colorless oil from the *n*-hexane eluted fraction. When Et_2O was used as eluent a second batch was obtained which contained a mixture of the allylic derivatives **5b**, **6b**, **7b**, and the C_6F_5-free di(μ-bromo)bis(3-methyl-1-3-η^3-pentenyl)dipalladium(II) (**10**).

9: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −163.4 (m, F_{meta}), −157.7 (t, F_{para}), −143.1 (m, F_{ortho}); ^1H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.76 (m, 2H, J = 17.2, 10.4, 7.5 Hz, H^2 + H^4), 5.02 (dt, 2H, J = 10.4, 1.1 Hz, H^1 + H^5), 4.97 (dt, 2H, J = 17.2, 1.1 Hz, $H^{1'}$ + $H^{5'}$), 3.00 (m, 1H, J = 7.5, 7.7 Hz, H^3), 2.80 (d, 2H, J = 7.7 Hz, $CH_2C_6F_5$). MS(EI) m/z (relative intensity), 248 (M^+, 0.9), 181 (5), 68 (6), 67 (100), 65 (20), 41 (30). HRMS calcd for $C_{12}H_9F_5$, m/z 248.0624; found, 248.0629.

10: ^1H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.11 (dd, 1H, J = 13, 7.5 Hz, H^2), 3.93 (d, 1H, J = 7.5 Hz, H^1-syn), 3.13 (d, 1H, J = 13 Hz, H^1-anti), 1.68 (m, H^4), 1.42 (m, $H^{4'}$), 1.30 (s, 3H, Me^3), 1.14 (t, 3H, J = 7.6 Hz, Me^5).

The reaction of $[Pd(C_6F_5)Br(NCMe)_2]$ with 1,4-pentadiene was monitored as described above for 3-methyl-1,4-pentadiene. The temperature was lowered down to 223 K for complete identification of the less stable compounds. The following complexes were identified:

2a$_1$: ^{19}F NMR ($CDCl_3$, δ, 223 K, 282 MHz), −161.9 (m, F_{meta}), −155.9 (t, F_{para}), −142.7 (m, F_{ortho}); ^1H NMR ($CDCl_3$, δ, 223 K, 300 MHz), 4.60 (b, 1H, H^2), 4.35 (b, 2H, H^1 + $H^{1'}$), 3.10 (H^4), 2.60 ($CH_2C_6F_5$), 1.80 (b, 1H, H^3), 0.25 (b, 1H, $H^{3'}$).

2a$_2$: ^{19}F NMR ($CDCl_3$, δ, 223 K, 282 MHz), −161.9 (m, F_{meta}), −155.9 (t, F_{para}), −142.7 (m, F_{ortho}); ^1H NMR ($CDCl_3$, δ, 223 K, 300 MHz), 4.90 (b, 2H, H^1 + H^2), 4.60 (b, 1H, $H^{1'}$), 3.00−2.80 (3H, H^4, $CH_2C_6F_5$), 1.10 (b, 1H, H^3), 0.80 (b, 1H, $H^{3'}$).

3a: ^{19}F NMR ($CDCl_3$, δ, 223 K, 282 MHz), −161.0 (m, F_{meta}), −156.3 (t, F_{para}), −143.2 (m, F_{ortho}); ^1H NMR ($CDCl_3$, δ, 223 K, 300 MHz), 4.90 (b, 2H, H^1 + H^2), 4.60 (b, 1H, $H^{1'}$), 3.00−2.80 (3H, H^5, H^3, $H^{3'}$), 2.75, 2.55 (2H, H^4, $H^{4'}$).

4a: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −162.4 (m, F_{meta}), −156.7 (t, F_{para}), −143.1 (m, F_{ortho}); ^1H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 6.04 (1H, H^2), 4.98 (d, 1H, J = 15.1 Hz, H^1), 4.92 (d, 1H, J = 8.5 Hz, $H^{1'}$), 3.58 (m, 1H, H^5), 3.09 (m), 2.87 (m), (H^3 + $H^{3'}$), 2.40 (m, 1H, H^4), 2.10 (m, 1H, $H^{5'}$).

5a-syn: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −162.7 (m, F_{meta}), −157.2 (t, F_{para}), −143.9 (m, F_{ortho}); ^1H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.23 (m, 1H, J = 11.2, 6.7 Hz, H^2), 4.01 (d, 1H, J = 6.7 Hz, H^1-syn), 3.84 (m, 1H, J = 11.8, 8.7, 5 Hz, H^3), 2.95 (m, 2H, H^5 + $H^{5'}$), 2.91 (d, 1H, J = 11.8 Hz, H^1-anti), 2.23 (m, 1H, H^4), 2.00 (m, 1H, $H^{4'}$).

5a-anti: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −162.9 (m, F_{meta}), −157.1 (t, F_{para}), −144.1 (m, F_{ortho}); ^1H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.20 (m, H^2), 4.80 (m, 1H, H^3), 4.17 (d, 1H, J = 7 Hz, H^1-syn), 3.29 (d, 1H, J = 13 Hz, H^1-anti), 2.80 (m, H^5 + $H^{5'}$), 2.00 (H^4), 1.55 ($H^{4'}$).

6a-syn: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −161.9 (m, F_{meta}), −155.7 (t, F_{para}), −141.7 (m, F_{ortho}); ^1H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.37 (dd, 1H, J = 12.8, 7.5 Hz, H^2), 4.05 (dd, 1H, J = 7.5, 1.2 Hz, H^1-syn), 3.23 (dd, 1H, J = 12.8, 1.2 Hz, H^1-anti), 3.45 (m), 3.23 (m, J = 16 Hz, H^4 + $H^{4'}$), 1.20 (s, 3H, Me^3).

6a-anti: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −162.1 (m, F_{meta}), −156.0 (t, F_{para}), −140.8 (m, F_{ortho}); ^1H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.14 (dd, 1H, J = 13, 7.5 Hz, H^2), 4.11 (dd, 1H, J = 7.5, 1.6 Hz, H^1-syn), 3.46 (dd, 1H, J = 13, 1.6 Hz, H^1-anti), 3.06 (m), 2.80 (m, 2H, J = 14.5 Hz, H^4 + $H^{4'}$), 1.51 (s, 3H, Me^3).

7a: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −162.5 (m, F_{meta}), −157.0 (t, F_{para}), −143.0 (m, F_{ortho}); ^1H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.52 (m, 1H, J = 11.5, 7 Hz, H^2), 4.08 (d, 1H, J = 7 Hz, H^1-syn), 4.10 (m, H^3), 3.70 (m, 1H, H^4), 2.97 (d, 1H, J = 11.5 Hz, H^1-anti), 1.54 (d, 3H, J = 7.2 Hz, Me^4).

Separation of the η^3-Allylpalladium Derivatives. Reaction of $[Pd(C_6F_5)Br(NCMe)_2]$ with 1,4-Pentadiene. To a solution of $[Pd(C_6F_5)Br(NCMe)_2]$ (0.15 g, 0.344 mmol) in CH_2Cl_2 (6 mL) was added 1,4-pentadiene (0.0356 mL, 0.344 mmol). The mixture was stirred at room temperature for 6 h, the resulting yellow-orange solution was filtered through Celite, and the filtrate was evaporated to dryness. Diethyl ether (2 mL) was added to the residue and the resulting solution was cooled. **5a-syn** crystallized as yellow solid which was filtered, washed with cold Et_2O, and air dried (0.01 g, 7% yield).

5a-syn: Anal. Calcd for $C_{22}H_{16}Br_2F_{10}Pd_2$: C, 31.34; H, 1.91. Found: C, 31.16; H, 1.93.

The mother liquors were kept at room temperature for 25 days and the mixture of **5a**, **6a**, and **7a** was separated by preparative TLC using a silica plate and a hexane:ethylacetate 10:1 mixture as eluent; two batches were obtained which contained (1) **6a-syn** and **7a** (R_f = 0.22) and (2) **5a-syn**, **5a-anti**, and **6a-anti** (R_f = 0.17). These mixtures could not be further separated.

The reaction of $[Pd(C_6F_5)Br(NCMe)_2]$ with 3-methyl-1,4-pentadiene was carried out following the same procedure. **5b-syn** was crystallized from Et_2O/*n*-hexane (10% yield). Anal. Calcd for $C_{24}H_{20}Br_2F_{10}Pd_2$: C, 33.09; H, 2.31. Found: C, 33.06; H, 2.39. Preparative TLC was performed as described above and afforded (batch 1) **6b-syn**, **6b-anti**, and **7b** (R_f = 0.20) and (batch 2) **5b-syn**, **5b-anti**, and **6b-anti** (R_f = 0.14). These mixtures could not be further separated.

Synthesis of the Pentafluorophenyl-Substituted Methyl Esters. Synthesis of Derivatives 12a, 13a, and 14a. 1,4-Pentadiene (0.007 mL, 0.07 mmol) was added to a solution of $[Pd(C_6F_5)Br(NCMe)_2]$ (0.030 g, 0.07 mmol) in $CHCl_3$ (3 mL) at 243 K. The mixture was kept at this temperature for 2 h. NaOMe (0.023 g, 0.42 mmol) suspended in MeOH (3 mL) was added to the mixture and CO was bubbled through the solution for 20 min. Metallic palladium precipitated which was filtered off and the filtrate was evaporated to dryness. The residue was chromatographed on a silica column (neutral, 230−400 mesh) and eluted with Et_2O; this operation afforded a mixture of **12a** (65%), **13a** (20%), and **14a** (7%) plus C_6F_5−COOMe (2%) and the ester methyl 6-(pentafluorophenyl)-3-hexenoate (6%) derived from the linear η^3-allyl complex **5a**. The isolated mixture of esters was analyzed by GC-MS and NMR spectroscopy.

12a: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −163.1 (m, F_{meta}), −157.2 (t, F_{para}), −142.9 (m, F_{ortho}); ^1H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.64 (m, 1H, H^4), 4.98 (d, 1H, J = 11 Hz, H^5), 4.93 (d, 1H, J = 17 Hz, $H^{5'}$), 3.66 (s, 3H, COOMe), 2.80−2.70 (m, 3H, H^3, $CH_2C_6F_5$), 2.43 (d, 2H, H^2, $H^{2'}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, 293 K, 74.5 MHz), 172.0 (C^1), 138.5 (C^4), 116.8 (C^5), 51.7 (COO*Me*), 40.5 (C^3), 39.1 (C^2), 27.4 (*C*$H_2C_6F_5$). MS(EI) m/z (relative intensity), 294 (M^+, 1.2), 181 (45), 74 (70), 71 (100), 59 (47), 41 (21). HRMS calcd for $C_{13}H_{11}O_2F_5$, m/z 294.0679; found, 294.0678.

13a: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −162.8 (m, F_{meta}), −156.8 (t, F_{para}), −143.1 (m, F_{ortho}); ^1H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.73 (m, 1H, J = 17.1, 13.7, 10, 7.1, H^4), 5.10 (bd, 1H, J = 17.1, 1.4 Hz, $H^{5'}$), 5.07 (bd, 1H, J = 10 Hz, H^5), 3.64 (s, 3H, COOMe), 3.00−2.90 (m, 2H, $CH_2C_6F_5$), 2.80 (m, H^2), 2.42 (m, H^3), 2.30 (m, $H^{3'}$). MS(EI) m/z (relative intensity), 294 (M^+, 7), 220 (33), 181 (100), 113 (22), 74 (22), 71 (70), 59 (48), 54 (25). HRMS calcd for $C_{13}H_{11}O_2F_5$, m/z 294.0679; found, 294.0680.

14a: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −162.8 (m, F_{meta}), −156.9 (t, F_{para}), −142.4 (m, F_{ortho}); ^1H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 3.62 (s, 3H, COOMe).

A mixture of complexes **12b**, **13b**, and **14b** was obtained by mixing 3-methyl-1,4-pentadiene (0.028 mL, 0.23 mmol) and $[Pd(C_6F_5)Br(NCMe)_2]$ (0.100 g, 0.23 mmol) in CH_2Cl_2 (5 mL) at 253 K and letting it stand at this temperature for 1 h; carbonylation of this mixture as described above gave a mixture of the ester derivatives: **12b** (55%), **13b** (24%) (each of them as a 1:1 diastereomeric mixture), **14b**, (5%) plus C_6F_5−COOMe (7%) and several unidentified compounds (9% total, each one less than 4%). The isolated mixture of esters was analyzed by GC-MS and NMR.

12b$_1$: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −163.5 (m, F_{meta}), −157.67 (t, F_{para}), −143.1 (m, F_{ortho}); ^1H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.64 (m, 1H, H^4), 4.95 (dd, 1H, J = 10.2, 1.6 Hz, H^5), 4.80

(dd, 1H, J = 16.8, 1.4 Hz, $H^{5'}$), 3.67 (s, 3H, COOMe), 2.90−2.65 ($CH_2C_6F_5$),[24] 2.65−2.45 (m, H^2, H^3),[24] 1.23 (d, 3H, J = 7 Hz, Me^2).

12b₂: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −163.5 (m, F_{meta}), −157.7 (t, F_{para}), −143.3 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.51 (m, 1H, H^4), 4.98 (dd, 1H, J = 10.2, 1.6 Hz, H^5), 4.81 (dd, 1H, J = 16.9, 1.5 Hz, $H^{5'}$), 3.70 (s, 3H, COOMe), 2.90−2.65 ($CH_2C_6F_5$),[24] 2.65−2.45 (m, H^2, H^3),[24] 1.16 (d, 3H, J = 6.8 Hz, Me^2). **12b₁** + **12b₂**: MS(EI) *m*/*z* (relative intensity), 308 (M^+, 0.3), 181 (34), 127 (10), 88 (100), 71 (54), 67 (21), 59 (37), 55 (21). HRMS calcd for $C_{14}H_{13}O_2F_5$, *m*/*z* 308.0836; found, 308.0842.

13b₁: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −163.0 (m, F_{meta}), −157.15 (t, F_{para}), −143.2 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.77 (m, 1H, J = 17.5, 10.2, 7.7 Hz, H^4), 5.06 (m, 1H, J = 17.5, 1 Hz, $H^{5'}$), 5.04 (m, 1H, J = 10.2, 1 Hz, H^5), 3.59 (s, 3H, COOMe), 3.00, 2.90−2.65 (H^2, $CH_2C_6F_5$),[24] 2.65−2.45 (H^3),[24] 1.12 (d, 3H, J = 6.8 Hz, Me^3).

13b₂: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −163.0 (m, F_{meta}), −157.2 (t, F_{para}), −143.5 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.70 (m, 1H, H^4), 5.13 (dd, 1H, J = 17.5, 1.4 Hz, $H^{5'}$), 5.11 (dd, 1H, J = 10.2, 1.6 Hz, H^5), 3.60 (s, 3H, COOMe), 3.00, 2.90−2.65 (H^2, $CH_2C_6F_5$),[24] 2.65−2.45 (H^3),[24] 1.04 (d, 3H, J = 6.4 Hz, Me^3). **13b₁** + **13b₂**: MS(EI) *m*/*z* (relative intensity), 308 (M^+, 0.6), 253 (14), 181 (27), 127 (61), 95 (33), 67 (38), 59 (38), 55 (100), 53 (22), 51 (10). HRMS calcd for $C_{14}H_{13}O_2F_5$, *m*/*z* 308.0836; found, 308.0840.

14b: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −163.1 (m, F_{meta}), −157.1 (t, F_{para}), −141.3 (m, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 5.50 (m, H^5), 4.86 ($H^{6'}$), 4.83 (H^6), 3.66 (s, COOMe, **14b₁**), 3.65 (COOMe, **14b₂**), 2.90−2.45 (H^2, $H^{2'}$, H^3), 1.18 (d, 3H, J = 6.9 Hz, Me^4, **14b₁**), 1.11 (d, 3H, J = 6.6 Hz, Me^4, **14b₂**). MS(EI) *m*/*z* (relative intensity), 308 (M^+, 1.8), 181 (64), 85 (68), 74 (87), 67 (63), 50 (100), 55 (74), 53 (48), 41 (54). HRMS calcd for $C_{14}H_{13}O_2F_5$, *m*/*z* 308.0836; found, 308.0832.

(24) Overlapped with the signals of the other diastereoisomer.

Synthesis of Di(μ-bromo)bis(η¹-η²-(3-((pentafluorophenyl)methyl)-1-oxo-4-pentenyl)dipalladium(II) (15). $[Pd(C_6F_5)Br(NCMe)_2]$ (0.100 g, 0.23 mmol) was dissolved in CH_2Cl_2 (5 mL) and the solution was cooled at 243 K. 1,4-Pentadiene (0.0357 mL, 0.345 mmol) was added and the mixture was stirred for 2.5 h. CO was bubbled through the yellow solution for 5 min and the mixture was slowly warmed to room temperature and then filtered through Celite. The solvent was completely evaporated and the residue was dissolved in Et_2O (0.5 mL); *n*-hexane (1 mL) was slowly added to the solution and the mixture was cooled. A yellow solid crystallized which was filtered, washed with *n*-hexane, and air dried: yield 0.025 g. The solid is a mixture of **15** (60%) and other organometallic derivatives (see Results).

15: ^{19}F NMR ($CDCl_3$, δ, 293 K, 282 MHz), −162.1 (m, F_{meta}), −156.0 (t, F_{para}), −141.6 (b, F_{ortho}); ^{1}H NMR ($CDCl_3$, δ, 293 K, 300 MHz), 6.35 (b, 1H, H^4), 4.62 (d, 1H, J = 8.3 Hz, H^5), 4.03 (d, 1H, J = 12.5 Hz, $H^{5'}$), 3.30−2.70, 2.40 (5H, H^2, $H^{2'}$, H^3, $CH_2C_6F_5$). ^{13}C-{^{1}H} NMR ($CDCl_3$, δ, 293 K, 74.5 MHz), 206 (C^1), 145 (d, $^1J_{C-F}$ = 244 Hz, C_6F_5 C_{ortho}), 140 (d, $^1J_{C-F}$ = 254 Hz, C_6F_5 C_{para}), 137.5 (d, $^1J_{C-F}$ = 248 Hz, C_6F_5 C_{meta}), 112 (t, $^3J_{C-F}$ = 16.2 Hz, C_6F_5 C_{ipso}), 109.1 (C^4), 72.0 (C^5), 50.8b (C^2), 37.2 (C^3), 28.3b ($CH_2C_6F_5$).

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