## Conclusions

(1) At parity of reaction conditions, the products in alkane dehydrogenation by polyoxometalates depend on both polyoxometalate and substrate. Branched alkanes undergo predominantly dehydrogenation to the corresponding alkenes.

(2) A contention with little substantiation to date, that organic radicals are intermediates in the catalytic photochemical oxidation of organic substrates by polyoxometalates, has been firmly established for the reactions investigated here. Several lines of evidence indicate conclusively that freely diffusing alkyl radicals are intermediates in the anaerobic dehydrogenation of saturated hydrocarbons.

(3) Product distribution and kinetics data are compatible with hydrogen atom abstraction (atom transfer) as the dominant pathway for attack of the polyoxotungstates excited states on alkane. Deprotonation of alkane cation radicals generated by electron transfer to yield nonthermodynamic radicals followed by subsequent oxidation and deprotonation can constitute at most a minor pathway for attack of the polyoxometalate excited state on alkane substrate.

(4) The relative rates of radical–radical disproportionation ($k_d$) and radical oxidation ($k_{ox}$) dictate the regiochemistry of the observed alkene products. Inasmuch as these relative rates can be controlled by judicious choice of the polyoxotungstate catalyst(s) and reactions conditions, the regiochemistry of alkane photochemical dehydrogenation can be controlled to a great extent.

**Acknowledgment.** We thank the National Science Foundation (Grant CHE-8715322) for support of this research. We acknowledge Dean Duncan in our group who contributed to the preparation of $Na_4W_{10}O_{32}$.

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# Synthesis and Subsequent Rearrangement of Chloro(pentafluorophenyl)-1,5-cyclooctadienepalladium(II), an Illustrative Example of Endo Attack to a Coordinated Double Bond

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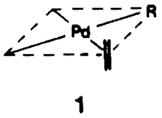
**Abstract:** $Pd(C_6F_5)Cl$(1,5-cyclooctadiene) has been prepared in high yield and characterized crystallographically: monoclinic space group $P2_1/c$, $a = 8.313$ (1) Å, $b = 7.7800$ (6) Å, $c = 22.292$ (4) Å, $\beta = 95.77$ (1)° ($Z = 4$), final $R$ of 0.024 for 2080 independent reflections. The X-ray structure reveals a high trans influence of the $C_6F_5$ groups that weakens the opposite palladium–olefin bond. This complex rearranges slowly in solution by intramolecular double bond insertion into the Pd–$C_6F_5$ bond to give an allyl complex $Pd_2(\mu\text{-}Cl)_2(6\text{-}C_6F_5\text{-}1\text{–}3\text{-}\eta^3\text{-}C_8H_{12})_2$ and $\sigma,\pi$-complex $Pd_2(\mu\text{-}Cl)_2(8\text{-}C_6F_5\text{-}1\text{:}4\text{-}5\text{-}\eta^3\text{-}C_8H_{12})_2$. A derivative of the latter, $Pd(8\text{-}C_6F_5\text{-}1\text{:}4\text{-}5\text{-}\eta^3\text{-}C_8H_{12})$(F6-acac), has been characterized crystallographically: triclinic space group $P\bar{1}$, $a = 10.360$ (3) Å, $b = 11.051$ (2) Å, $c = 11.084$ (4) Å, $\alpha = 73.70$ (2)°, $\beta = 61.41$ (2)°, $\gamma = 66.08$ (2)°, final $R$ of 0.036 for 3341 independent reflections. The rearrangement of $Pd(C_6F_5)Cl$(1,5-COD) is catalyzed by its products and slowed down in coordinating solvents. Both products are the result of an endo attack of $C_6F_5$ to COD and are formed competitively from a common intermediate.

## Introduction

The migratory insertion of olefins into metal–carbon bonds is an important reaction in transition-metal organometallic chemistry.[1] Palladium is perhaps the transition metal most widely used to induce this kind of reaction, as exemplified by the Heck reaction and related processes.[2–4] Whatever the method used to introduce R and the olefin on the palladium, eventually both groups must acquire a mutually cis arrangement as in **1** for the insertion to occur; this cis arrangement followed by olefin rotation to an "in plane" coordination allows evolution to the four-center transition state which leads to insertion.[5]



**1**

Since the intramolecular migration of R to an olefin is very facile in palladium, it is very rare to meet complexes of the type **1** which are isolable or at least detectable and yet reactive enough to undergo insertion. The very few cases reported are all of a special type in which the $\sigma$ and $\pi$ bonds to palladium are provided by the same organic moiety, thus forming a palladacycle which confers some extra stability to the molecule.[6–9]

We have reported recently that synthons of "$Pd(C_6F_5)Br$" react with diolefins to give palladium allyls as the result of an insertion of the diene into the Pd–$C_6F_5$ bond; the assumed intermediates

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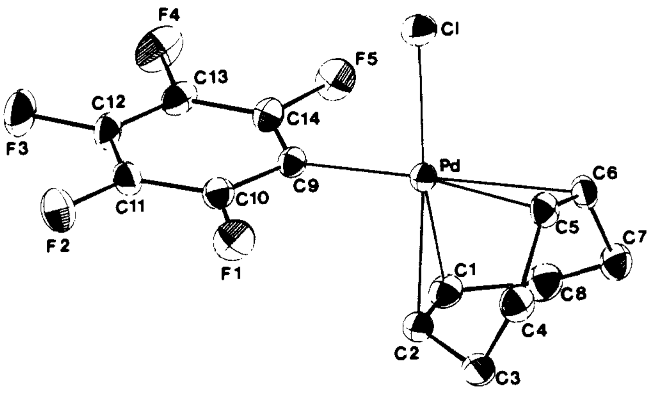

**Figure 1.** Molecular structure of **3** showing the atom numbering scheme (H atoms omited).

of the type **1** were, however, not detected.[10] We report now the synthesis of Pd($C_6F_5$)Cl(COD) (COD = 1,5-cyclooctadiene), the first complex of the type **1** which can be isolated, structurally characterized, and isomerized to two insertion products under mild conditions.

## Results

**Synthesis and characterization of Pd($C_6F_5$)Cl(COD) (3).** Pd($C_6F_5$)Cl(COD) is easily obtained in good yield by a transarylation process between $Pd(C_6F_5)_2(S)_2$ (S = tetrahydrofurane or diethyl ether)[11] and $PdCl_2(NCPh)_2$ followed by addition of 1,5-cyclooctadiene, as shown in eqs 1 and 2.

$$Pd(C_6F_5)_2(S)_2 + PdCl_2(NCPh)_2 \rightarrow \underset{\mathbf{2}}{Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(NCPh)_2} \quad (1)$$

$$Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(NCPh)_2 + COD \rightarrow \underset{\mathbf{3}}{2[Pd(C_6F_5)Cl(COD)]} \quad (2)$$

An X-ray diffraction study of Pd($C_6F_5$)Cl(COD) was undertaken in order to ascertain some features of the bonding of the diolefin to Pd and particularly to confirm the expected higher trans influence of $C_6F_5$ compared to Cl. Figure 1 shows an ORTEP drawing of this molecule. Only one other X-ray structure determination containing mutually cis Pd–olefin and σ Pd–C bonds not involved in the same chelating system, Pd($CH_2SO_2Ph$)Cl(COD),[12] has been reported.

The central palladium atom in **3** is essentially in a square-planar environment defined by the chlorine, the ipso carbon of the $C_6F_5$ group, and the midpoints of the two carbon–carbon bonds (M1 for C1–C2 and M2 for C5–C6) (Figure 1). The bond lengths and angles are given in Table I. Table II compares some parameters of this structure with those found for $PdCl_2$(COD)[12,13] and Pd($CH_2SO_2Ph$)Cl(COD).[12] A distinct feature in the structure of **3** (also observed in the related phenyl sulfonyl methanato derivative) is the long Pd–M2 distance compared to Pd–M1, reflecting a noticeable high trans influence of $C_6F_5$ compared to Cl. Other structural parameters such as the longer distance of M2 to the PdClX plane and the angles between the double bond and Pd–M (which are 90.7° for M1 and 87.5° for M2) also indicate a less efficient bonding to palladium of the double bond trans to $C_6F_5$.

The C=C distances in the coordinated 1,5-COD do not follow the inverse order of the Pd–M distances, and, although Pd($CH_2SO_2Ph$)Cl(COD) shows the longest Pd–M distance, it is Pd($C_6F_5$)Cl(COD) that shows the shortest C=C distances. This is probably a reflection of the fact that moving in the series Cl, $CH_2SO_2Ph$, $C_6F_5$ one goes from a π-donor ligand to a slightly π-acceptor ligand. The C5–C6 distance in **3** (1.331 Å) is the shortest in Table II and equal to the value for an uncoordinated double bond (1.337 Å); although this observation should not be overstressed, it points again to the same conclusion that the double bond trans to $C_6F_5$ should be the best candidate for decoordination if the 1,5-COD ligand were to change from $\eta^4$- to $\eta^2$-bonded.

**Table I.** Bond Lengths (Å) and Angles (deg) in $C_{14}H_{12}ClF_5Pd$ (3)

| | | | |
|---|---|---|---|
| Pd(1)–Cl(1) | 2.303 (1) | Pd(1)–C(1) | 2.182 (4) |
| Pd(1)–C(6) | 2.338 (4) | Pd(1)–C(5) | 2.281 (4) |
| Pd(1)–C(2) | 2.197 (4) | Pd(1)–C(9) | 2.011 (4) |
| F(1)–C(10) | 1.355 (5) | F(2)–C(11) | 1.344 (5) |
| F(3)–C(12) | 1.335 (5) | F(4)–C(13) | 1.348 (5) |
| F(5)–C(14) | 1.352 (5) | C(1)–C(8) | 1.506 (6) |
| C(1)–C(2) | 1.356 (6) | C(8)–C(7) | 1.504 (7) |
| C(5)–C(4) | 1.509 (6) | C(4)–C(3) | 1.528 (6) |
| C(7)–C(6) | 1.519 (6) | C(6)–C(5) | 1.331 (6) |
| C(3)–C(2) | 1.506 (6) | C(9)–C(10) | 1.379 (5) |
| C(9)–C(14) | 1.373 (5) | C(10)–C(11) | 1.378 (6) |
| C(11)–C(12) | 1.354 (7) | C(12)–C(13) | 1.372 (6) |
| C(13)–C(14) | 1.364 (6) | | |
| C(1)–Pd(1)–Cl(1) | 160.0 (1) | C(6)–Pd(1)–Cl(1) | 95.1 (1) |
| C(6)–Pd(1)–C(1) | 80.4 (2) | C(5)–Pd(1)–Cl(1) | 90.8 (1) |
| C(5)–Pd(1)–C(1) | 95.6 (2) | C(5)–Pd(1)–C(6) | 33.5 (2) |
| C(2)–Pd(1)–Cl(1) | 163.8 (1) | C(2)–Pd(1)–C(1) | 36.1 (2) |
| C(2)–Pd(1)–C(6) | 86.5 (2) | C(2)–Pd(1)–C(5) | 81.7 (2) |
| C(9)–Pd(1)–Cl(1) | 88.6 (1) | C(9)–Pd(1)–C(1) | 91.8 (2) |
| C(9)–Pd(1)–C(6) | 166.7 (2) | C(9)–Pd(1)–C(5) | 159.5 (2) |
| C(9)–Pd(1)–C(2) | 93.4 (2) | C(8)–C(1)–Pd(1) | 106.3 (3) |
| C(2)–C(1)–Pd(1) | 72.6 (2) | C(2)–C(1)–C(8) | 127.2 (4) |
| C(7)–C(8)–C(1) | 115.0 (4) | C(6)–C(7)–C(8) | 113.3 (4) |
| C(7)–C(6)–Pd(1) | 107.5 (3) | C(5)–C(6)–Pd(1) | 70.9 (2) |
| C(5)–C(6)–C(7) | 126.2 (4) | C(6)–C(5)–Pd(1) | 75.6 (2) |
| C(4)–C(5)–Pd(1) | 102.2 (3) | C(4)–C(5)–C(6) | 127.0 (4) |
| C(3)–C(4)–C(5) | 115.0 (4) | C(2)–C(3)–C(4) | 114.5 (4) |
| C(1)–C(2)–Pd(1) | 71.4 (2) | C(3)–C(2)–Pd(1) | 110.3 (3) |
| C(3)–C(2)–C(1) | 127.1 (4) | C(10)–C(9)–Pd(1) | 121.4 (3) |
| C(14)–C(9)–Pd(1) | 123.5 (3) | C(14)–C(9)–C(10) | 115.0 (4) |
| C(9)–C(10)–F(1) | 119.6 (4) | C(11)–C(10)–F(1) | 117.5 (4) |
| C(11)–C(10)–C(9) | 122.9 (4) | C(10)–C(11)–F(2) | 120.1 (5) |
| C(12)–C(11)–F(2) | 120.1 (4) | C(12)–C(11)–C(10) | 119.9 (4) |
| C(11)–C(12)–F(3) | 120.7 (5) | C(13)–C(12)–F(3) | 120.2 (5) |
| C(13)–C(12)–C(11) | 119.1 (4) | C(12)–C(13)–F(4) | 119.2 (4) |
| C(14)–C(13)–F(4) | 121.0 (4) | C(14)–C(13)–C(12) | 119.8 (4) |
| C(9)–C(14)–F(5) | 119.9 (4) | C(13)–C(14)–F(5) | 116.7 (4) |
| C(13)–C(14)–C(9) | 123.4 (4) | | |

**Table II.** Comparison of the Structures of $PdCl_2$(COD) and Pd($C_6F_5$)Cl(COD)

| | $PdCl_2$(COD) | Pd($CH_2SO_2C_6H_5$)-Cl(COD) | Pd($C_6F_5$)-Cl(COD) |
|---|---|---|---|
| Pd–M1 distance, Å | 2.092 | 2.08 | 2.082 |
| Pd–M2 distance, Å | 2.097 | 2.234 | 2.212 |
| M1–Pd–M2 "bite angle" | 83.3 | 85.4 | 85.65 |
| Cl–Pd–X angle[a] | 90.31 | 89.7 | 88.64 |
| M1 to PdClX plane, Å[a] | 0.075 | 0 | 0.069 |
| M2 to PdClX plane, Å[a] | 0.066 | 0.07 | 0.142 |
| C1–C2 distance, Å | 1.384 | 1.379 | 1.356 |
| C5–C6 distance, Å | 1.385 | 1.354 | 1.331 |

[a] X = Cl or C-atom σ-bonded to Pd.

**Isomerization of Pd($C_6F_5$)Cl(COD) and Synthesis of the Insertion Products.** Unlike Pd($CH_2SO_2Ph$)Cl(COD) which has been reported to be stable in tetrahydrofuran at reflux,[14] Pd($C_6F_5$)Cl(COD) isomerizes slowly in solution at room temperature to give two compounds which can be characterized as $Pd_2(\mu\text{-}Cl)_2$(8-$C_6F_5$-1:4-5-$\eta^3$-cyclooctenyl)$_2$ (**4**) and $Pd_2(\mu\text{-}Cl)_2$(6-$C_6F_5$-1-3-$\eta^3$-cyclooctenyl)$_2$ (**5**) (eq 3). The ratio **4**:**5** varies with the solvent used being, for instance, 50:50 in THF and 20:80 in $CH_2Cl_2$; thus the proportion of allyl complex **5** formed seems to decrease in more coordinating solvents in which, on the other hand, the insertion rate is slower.

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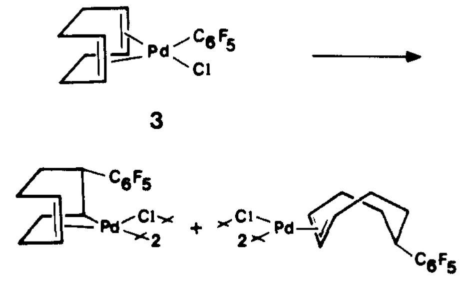


3

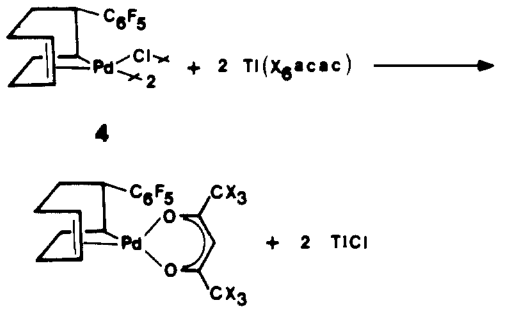
4 5

(3)

The two complexes 4 and 5 have the $C_6F_5$ group and the Pd atom on the same face of the cyclooctenyl ring (see characterization below) and are thus the result of an endo attack of the $C_6F_5$ to a cyclooctadiene double bond. They do not interconvert under the conditions used for their synthesis, and consequently neither of them is an intermediate in the formation of the other.

$Pd(C_6F_5)Br(COD)$, which was first reported some years ago[15] and is now available in high yield,[16] behaves similarly and will not be discussed; however, the slowness of these insertions at room temperature had kept the process unseen until now.

Due to the low solubility of 4, two more soluble monomeric derivatives were made, according to eq 4, to facilitate the NMR studies and to obtain single crystals.



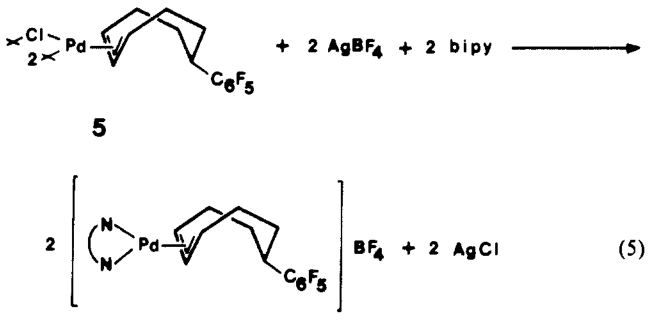
4

(4)

6 : X = H

7 : X = F

Similar derivatives of 5 are not very stable and slowly deposit palladium (probably with concomitant coupling of the $\eta^3$-allyl and acetylacetonate moieties although this was not further investigated).[17,18] For this reason $[Pd(6\text{-}C_6F_5\text{-}1\text{-}3\text{-}\eta^3\text{-}C_8H_{12})(bipy)]BF_4$ (8) was prepared according to eq 5 for characterization experiments which required a monomer.



5

(5)

8 , N–N = bipy

**Characterization of the "σ,π" Type Derivatives 4, 6 and 7.** Suitable crystals for X-ray crystallography could be obtained for 7, and Figure 2 shows an ORTEP drawing of this molecule. The bond lengths and angles are given in Table III. The palladium atom is in a square-planar environment defined by the two oxygen atoms of the hexafluoroacetylacetonato ligand, the C1 atom of the cyclooctenyl ring, and the midpoint (M1) of the coordinated double bond C4–C5. The bite angles O1–Pd–O2 and M1–Pd–C1 are 88.64° and 85.65°, respectively.

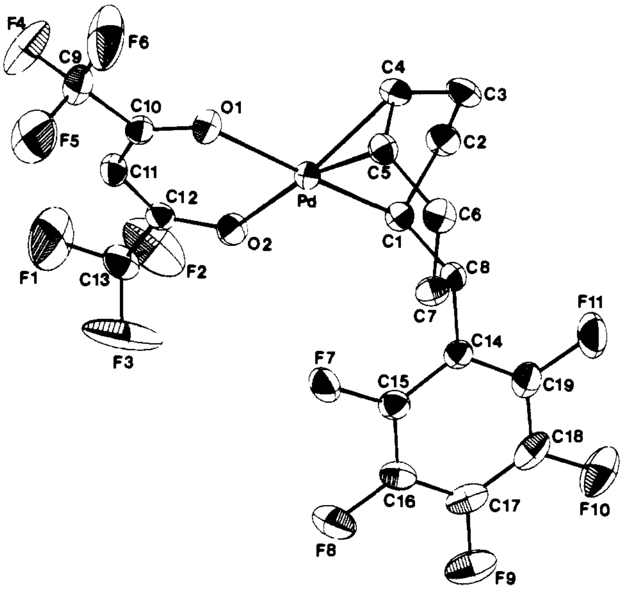


Figure 2. Molecular structure of 7 showing the atom numbering scheme (H atoms omited).

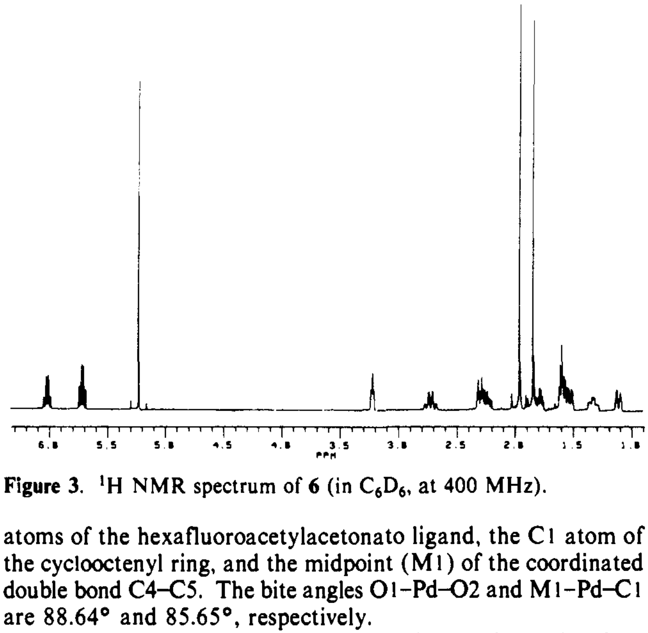
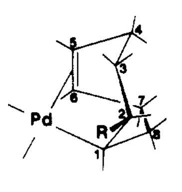


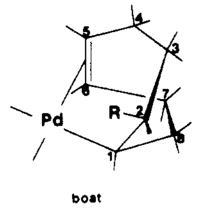
Figure 3. $^1H$ NMR spectrum of 6 (in $C_6D_6$, at 400 MHz).

The cyclooctenyl ring has the chair-like conformation 9 as preferred to the boat-like conformation 10. A chair-like conformation has been assigned to $Pd_2(\mu\text{-}Cl)_2(1{:}4\text{-}5\text{-}\eta^3\text{-}exo\text{-}7\text{-}chlorocyclooctenyl)_2$,[19] while a boat-like conformation has been found crystallographically for $Pd_2(\mu\text{-}Cl)_2(1{:}4\text{-}5\text{-}\eta^3\text{-}exo\text{-}8\text{-}(\alpha\text{-}chloroethyl)cyclooctenyl)_2$.[20] The endo attachment of the $C_6F_5$ group in our complexes probably forces a chair-like conformation which gives more room to this bulky group than the boat-like conformation.



chair

9 , R = $C_6F_5$



boat

10 , R = $C_6F_5$

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**Table III.** Bond Lengths (Å) and Angles (deg) in $C_{19}H_{13}F_{11}O_2Pd$ (7)

| | | | |
|---|---|---|---|
| Pd(1)–C(4) | 2.166 (4) | Pd(1)–C(5) | 2.166 (4) |
| Pd(1)–O(1) | 2.169 (3) | Pd(1)–O(2) | 2.077 (3) |
| Pd(1)–C(1) | 2.022 (4) | C(2)–C(3) | 1.510 (8) |
| C(1)–C(2) | 1.534 (6) | C(4)–C(5) | 1.383 (6) |
| C(3)–C(4) | 1.505 (7) | C(6)–C(7) | 1.521 (7) |
| C(5)–C(6) | 1.506 (7) | C(8)–C(1) | 1.536 (6) |
| C(7)–C(8) | 1.548 (6) | C(9)–C(10) | 1.529 (7) |
| C(8)–C(14) | 1.518 (6) | C(9)–F(5) | 1.342 (7) |
| C(9)–F(4) | 1.284 (6) | C(10)–C(11) | 1.395 (7) |
| C(9)–F(6) | 1.262 (7) | C(11)–C(12) | 1.378 (7) |
| C(10)–O(1) | 1.248 (5) | C(12)–O(2) | 1.246 (5) |
| C(12)–C(13) | 1.526 (6) | C(13)–F(2) | 1.305 (7) |
| C(13)–F(1) | 1.290 (7) | C(14)–C(15) | 1.388 (6) |
| C(13)–F(3) | 1.228 (6) | C(15)–C(16) | 1.374 (6) |
| C(14)–C(19) | 1.380 (6) | C(16)–C(17) | 1.363 (7) |
| C(15)–F(7) | 1.344 (5) | C(17)–C(18) | 1.374 (8) |
| C(16)–F(8) | 1.339 (6) | C(18)–C(19) | 1.382 (7) |
| C(17)–F(9) | 1.339 (6) | C(19)–F(11) | 1.351 (6) |
| C(18)–F(10) | 1.335 (6) | | |
| O(1)–Pd(1)–C(5) | 91.7 (2) | O(1)–Pd(1)–C(1) | 176.3 (2) |
| O(2)–Pd(1)–C(4) | 157.1 (2) | O(2)–Pd(1)–C(5) | 165.0 (2) |
| O(2)–Pd(1)–C(1) | 89.8 (2) | O(2)–Pd(1)–O(1) | 88.8 (1) |
| C(5)–Pd(1)–C(4) | 37.2 (2) | C(1)–Pd(1)–C(4) | 81.2 (2) |
| C(1)–Pd(1)–C(5) | 90.5 (2) | O(1)–Pd(1)–C(4) | 98.9 (2) |
| C(2)–C(1)–Pd(1) | 103.8 (3) | C(8)–C(1)–Pd(1) | 115.0 (3) |
| C(2)–C(1)–C(8) | 112.8 (4) | C(3)–C(2)–C(1) | 109.6 (4) |
| C(5)–C(4)–Pd(1) | 71.4 (3) | C(3)–C(4)–Pd(1) | 109.5 (3) |
| C(3)–C(4)–C(5) | 124.1 (5) | C(4)–C(5)–Pd(1) | 71.4 (3) |
| C(6)–C(5)–Pd(1) | 113.7 (3) | C(6)–C(5)–C(4) | 124.9 (5) |
| C(7)–C(6)–C(5) | 115.8 (4) | C(1)–C(8)–C(7) | 115.8 (4) |
| C(14)–C(8)–C(1) | 110.5 (4) | C(14)–C(8)–C(7) | 111.0 (4) |
| C(2)–C(3)–C(4) | 109.5 (4) | F(4)–C(9)–C(10) | 114.3 (5) |
| F(5)–C(9)–C(10) | 109.8 (5) | F(5)–C(9)–F(4) | 103.0 (5) |
| F(6)–C(9)–C(10) | 113.7 (5) | F(6)–C(9)–F(4) | 110.9 (6) |
| F(6)–C(9)–F(5) | 104.0 (6) | C(11)–C(10)–C(9) | 116.3 (4) |
| O(1)–C(10)–C(9) | 114.9 (4) | O(1)–C(10)–C(11) | 128.7 (4) |
| C(12)–C(11)–C(10) | 124.8 (4) | C(13)–C(12)–C(11) | 117.5 (4) |
| O(2)–C(12)–C(11) | 130.2 (4) | O(2)–C(12)–C(13) | 112.3 (4) |
| F(1)–C(13)–C(12) | 114.6 (5) | F(2)–C(13)–C(12) | 111.7 (4) |
| F(2)–C(13)–F(1) | 99.7 (5) | F(3)–C(13)–C(12) | 113.9 (4) |
| F(3)–C(13)–F(1) | 109.4 (6) | F(3)–C(13)–F(2) | 106.3 (6) |
| C(15)–C(14)–C(8) | 122.6 (4) | C(19)–C(14)–C(8) | 122.3 (4) |
| C(19)–C(14)–C(15) | 115.1 (4) | C(16)–C(15)–C(14) | 122.9 (4) |
| F(7)–C(15)–C(14) | 119.5 (4) | F(7)–C(15)–C(16) | 117.6 (4) |
| C(17)–C(16)–C(15) | 120.0 (5) | F(8)–C(16)–C(15) | 120.2 (5) |
| F(8)–C(16)–C(17) | 119.7 (5) | C(18)–C(17)–C(16) | 119.4 (5) |
| F(9)–C(17)–C(16) | 120.2 (6) | F(9)–C(17)–C(18) | 120.3 (5) |
| C(19)–C(18)–C(17) | 119.4 (5) | F(10)–C(18)–C(17) | 120.5 (5) |
| F(10)–C(18)–C(19) | 120.1 (6) | C(18)–C(19)–C(14) | 123.2 (5) |
| F(11)–C(19)–C(14) | 119.6 (5) | F(11)–C(19)–C(18) | 117.3 (5) |
| C(10)–O(1)–Pd(1) | 122.4 (3) | C(12)–O(2)–Pd(1) | 124.2 (3) |

The coordination of the double bond C4–C5 to Pd is such that the midpoint M1 is practically in the least-squares coordination plane of Pd (distance 0.009 Å to this plane) and C4–C5 makes an angle of 90° with the line Pd–M1, but the double bond is titled around the Pd–M1 line so as to give more room to the longer Pd–C1–C8–C7–C6–C5 cycle than to the shorter Pd–C1–C2–C3–C4 one.

The $^1H$ NMR spectra (Figure 3 and Experimental Section, assignments based on $^1H$–$^1H$ and $^{13}C$–$^1H$ correlations and INEPT experiments) of **4**, **6**, and **7** suggest that the chair-like conformation **9** is maintained in solution,[19] and the VT $^{19}F$ NMR spectra show a barrier to the rotation of $C_6F_5$ corresponding to a $\Delta G = 45.8$ KJ/mol, similar to that found in related derivatives[10] and for the rotation of other bulky groups.[21]

**Characterization of the $\eta^3$-Allyl Type Derivatives 5 and 8.** An X-ray characterization of **5** was attempted, but a disorder problem precluded full solution of the structure. The $C_6F_5$ groups and the C6 atoms were not disordered, however, and they were found placed as expected for the all-boat conformation **11**. Fortunately, this all-boat conformation is maintained in solution and can be conclusively proved by NMR spectroscopy. The $^1H$ NMR spectrum of **5** (Figure 4) is that expected for a symmetric 1–3-$\eta^3$-*endo*-6-$C_6F_5$-cyclooctenyl ring; the observation of large vicinal coupling constants, well over the values expected for conformationally averaged couplings, supports a rigid conformation, and the couplings observed (assigned with the help of $^1H$–$^1H$ correlation and homodecoupling experiments and given in the Experimental Section) indicate the all-boat conformation **11**. This is further supported by NOE experiments in which H2 and H6 show a mutual NOE effect both in the dimer **5** (2.8%) and in the monomer **8** (4%); the latter was prepared and studied in order to discount the possibility **12** where a NOE effect could perhaps be observed for H2 and H6 of different cyclooctenyl rings.

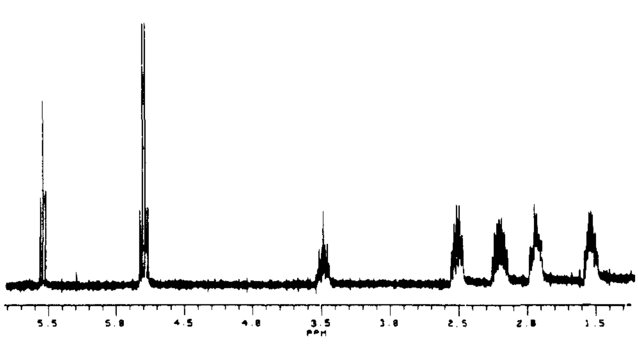
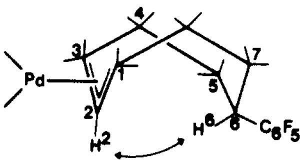
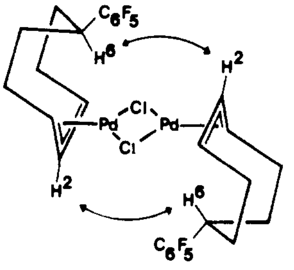


**Figure 4.** $^1H$ NMR spectrum of **5** (in $CDCl_3$, at 400 MHz).

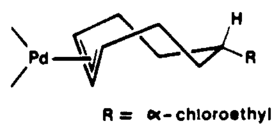


**11**



**12**

It is interesting to note that in a related structure **13** the cyclooctenyl ring shows a boat-chair conformation.[22] It seems that the conformation adopted is that producing a minimum interaction of the ring with the bulky substituents.



**13**

**Kinetic Measurements.** The slow rate of insertion allowed to follow the reaction **3** → **4** + **5** by $^{19}F$ NMR spectroscopy and the results are plotted in Figure 5. In the first experiment (a) it was observed that the rate of reaction (as measured by the disappearance of the starting complex) is slow at the beginning, increases as the reaction proceeds, and slows down when most of the starting material has been consumed. Since this behavior is typical of a product-catalyzed reaction, an additional experiment (b) was studied starting with a mixture of pure **3** and added **4**

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(21) Hanack, M. "*Conformation Theory*", *Org. Chem. Series of Monographs*; Academic Press: New York, 1965; Vol. 3.

(22) Parra-Hake, M.; Rettig, M. F.; Wing, R. M. *Organometallics* **1983**, *2*, 1013.

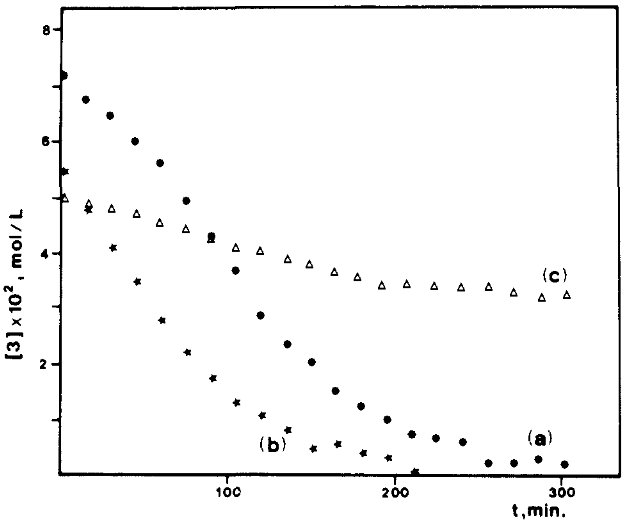


Figure 5. Kinetics of the reaction 3 → 4 + 5: (a) starting from 3, in deuteriochloroform; (b) starting from 3 + (4 + 5), in deuteriochloroform; and (c) starting from 3, in deuterioacetone.

+ 5; in this case the disappearance of 3 is fast in the beginning, as can bee seen in Figure 5.

The rate of insertion is affected by the solvent and, Figure 5 experiment (c) shows how it is much slower when carried out in acetone.

The rate of isomerization 4 → 5 was also checked. No isomerization could be detected in the times and temperature conditions used for the synthesis and the kinetic measurements. This $\sigma,\pi \rightarrow$ allyl isomerization is known for other cyclooctenylpalladium systems and is also very slow.[19,20] In our case only 20% of 4 was isomerized to 5 after 80 h in refluxing $CHCl_3$.

## Discussion

The results presented above fit well in the simplified mechanism depicted in Scheme I. For the first time a palladium complex containing a Pd–C and a Pd–olefin bond mutually cis and not involved in the same palladacycle has been isolated, characterized, and isomerized by endo olefin insertion. The kinetic stability of the starting complex 3 is remarkable. Since other diolefins insert quite rapidly into the Pd–$C_6F_5$ bond,[10] this kinetic stability is to be attributed mainly to the chelating nature of 1,5-COD. In light of Hoffmann's calculations that the double bond needs to rotate to an in plane coordination in order to produce insertion,[5] and since such a situation cannot be reached in an $\eta^4$-COD system, complex 3 will need to change to an $\eta^2$-COD system for the insertion to occur. Consequently, the slow rate of the insertion process can be attributed to the high activation energy involved in the ($\eta^4$-COD) → ($\eta^2$-COD) transformation that must be the rate-determining step.

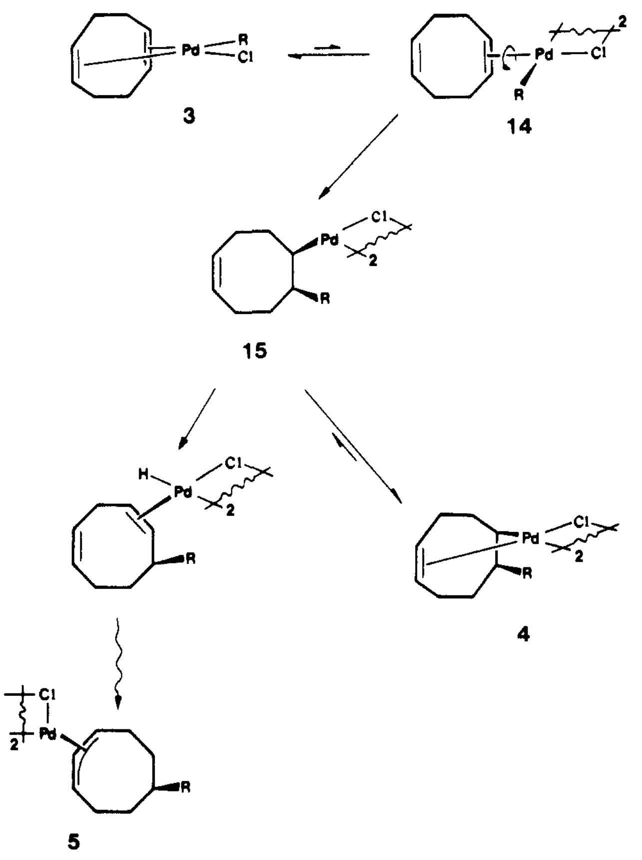
The displacement of one double bond (that trans to $C_6F_5$, as suggested by the molecular structure determination of 3) could occur initially by substitution for a molecule of solvent (eq 6) or by self-dimerization (eq 7). Although a faster mechanism (discussed below) takes control progressively of the reaction and soon hides this slow-rate process, it can be noted that if the initial mechanism were that of eq 6 one would expect an increase in the initial rate with increasing coordinating ability of the solvent, which is not observed.

$$Pd(C_6F_5)Cl(\eta^4\text{-COD}) + S \rightarrow Pd(C_6F_5)Cl(\eta^2\text{-COD})(S) \quad (6)$$

$$2[Pd(C_6F_5)Cl(\eta^4\text{-COD})] \rightarrow \underset{\mathbf{14a}}{Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(\eta^2\text{-COD})_2} \quad (7)$$

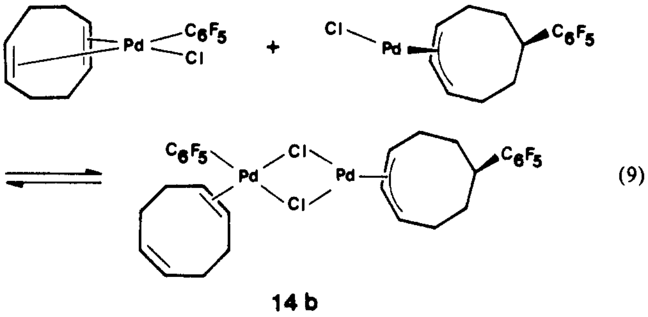
The presence of the products 4 + 5 increases the rate of reaction very noticeably. It is well-known that allyl–palladium dimers rearrange easily in solution due to the lability and easy splitting of the bridge system in these complexes.[23,24] Hence the formation

Scheme I



of split species from 5 (and perhaps from 4) provides a lower activation energy path for the otherwise slower $\eta^4 \rightarrow \eta^2$ step (eqs 8 and 9). Since the solvent will compete with 3 for the split species

$$Pd_2(\mu\text{-}Cl)_2(6\text{-}C_6F_5\text{-}1\text{-}3\text{-}\eta^3\text{-}C_8H_{12})_2 \rightarrow 2[Pd(6\text{-}C_6F_5\text{-}1\text{-}3\text{-}\eta^3\text{-}C_8H_{12})Cl] \quad (8)$$



(9)

14 b

$$Pd(6\text{-}C_6F_5\text{-}1\text{-}3\text{-}\eta^3\text{-}C_8H_{12})Cl + S \rightarrow Pd(6\text{-}C_6F_5\text{-}1\text{-}3\text{-}\eta^3\text{-}C_8H_{12})Cl(S) \quad (10)$$

(eq 10), better coordinating solvents are expected to produce lower rates of reaction, as observed.

Formula 14 in Scheme I stands for either 14a, dominant in the slow initial stage, or 14b (and perhaps its $\sigma,\pi$-isomer), dominant once enough 4 + 5 has been formed. In any case there is a Pd($\eta^2$-COD) moiety with the coordinated double bond cis to $C_6F_5$, which can now readily rotate to a in plane olefin coordination and undergo insertion as proposed by Hoffmann,[5] to give 15 in a comparatively fast reaction since 14 is not detected. This is followed, again in fast processes, either by double bond coordination to give 4 or by palladium–hydride elimination–readdition[19,22,25,26] to give 5. Since 4 can be converted into 5 only very slowly and under more energic conditions, it is clear that 4 is a

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(23) Tibbetts, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1969**, *91*, 1108.

(24) Van Leeuwen, P. W. N. M.; Lukas, J.; Praat, A. P.; Appelmann, M. *J. Organomet. Chem.* **1972**, *38*, 199.

(25) Larock, R. C.; Mitchell, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 180.

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

kinetically competing product, whereas **5** is the thermodynamic product. The isomerization **4** → **5** can take place only via **15** and involves opening the palladacycle, a high-energy process that explains the slowness of isomerization. The observation that the ratio **4**:**5** apparently increases with increasing coordination ability of the solvent can again be understood considering the molecule of solvent as a competitor for the vacant coordination site in **15** which affects more negatively the Pd–hydride elimination than the double bond coordination.

It is worth remarking that, to the best of our knowledge, this is the first occasion that simultaneous formation of both allyl- and $\sigma,\pi$-palladium products is observed. Since the isomerization $\sigma,\pi \rightarrow$ allyl is very slow, this means that the $\sigma,\pi$-compound is not an intermediate in the formation of the allyl complex, rather both isomers **4** and **5** are formed from a common intermediate, **15**.

## Concluding Remarks

The isomerization of $Pd(C_6F_5)Cl(COD)$ into its insertion products is possibly the best example available to date illustrating the different steps in the insertion of olefins into Pd–R bonds. Although the preliminary mechanistic studies reveal themselves to be more complicated than it was anticipated, the results prove or strongly support the main intermediates proposed for this kind of reaction, as follows: (i) The insertions are accepted to occur on an intermediate with the double bond and the R group mutually cis, that in this case has been isolated and characterized crystallographically. (ii) The slowness of isomerization supports the need of evolution to an in plane coordination of the double bond previously to insertion. (iii) Although the intermediate product of insertion **15** has not been detected, the observation that the $\sigma,\pi$- and the allyl complexes are competing products strongly points to this common intermediate.

Finally the formation of two different long lived products warns of the possibility of complication in organic syntheses based on an endo (or an exo) attack to coordinated olefins when the olefin is not a simple one.

## Experimental Section

**General Considerations.** C, H, and N analyses were carried out on a Perkin-Elmer 240 microanalyzer. IR spectra were recorded (in the range 4000–200 cm$^{-1}$) on a Perkin-Elmer 883 spectrometer; $^{19}F$ NMR spectra were recorded on Varian XL-200 (200 MHz for $^1H$) and Bruker WP-80 instruments, and $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker WH400 (400 MHz for $^1H$). Chemical shifts are reported in $\delta$ units, parts per million (ppm), downfield from $Me_4Si$ for $^1H$ and $^{13}C$ and from $CFCl_3$ for $^{19}F$.

Literature methods were used to prepare $(NBu_4)_2Pd_2(\mu\text{-}Br)_2(C_6F_5)_4$[27] and $PdCl_2(NCPh)_2$.[28] 1,5-Cyclooctadiene, pure commercial, was used without further purification.

**Bis($\mu$-chloro)bis(pentafluorophenyl)bis(benzonitrile)dipalladium(II) (2).** To a solution of $AgClO_4$ (0.75 g, 3.6 mmol) in dry THF (10 mL) was added $(NBu_4)_2Pd_2(\mu\text{-}Br)_2(C_6F_5)_4$ (2.75 g, 1.8 mmol). The mixture was stirred in the dark for 30 min. The insoluble AgBr was filtered off, and the resulting solution was evaporated to dryness. The residue was taken up in $Et_2O$ (30 mL), and the solution was filtered to remove the insoluble $(NBu_4)ClO_4$. To the colorless $Et_2O$–filtrate was added $PdCl_2(NCPh)_2$ (1.38 g, 3.6 mmol), and the suspension was stirred. After 1 h the suspension had turned into an orange-red solution, which was filtered through Kieselgur, and the solvent was evaporated. Ten drops of NCPh were added to the residue, and it was triturated with *n*-hexane (4 × 5 mL). The resulting yellow solid (**2**) was then filtered, washed with *n*-hexane, and air-dried: yield 2.96 g (90%); IR 2281 cm$^{-1}$ (s, $\nu_{CN}$), 327 cm$^{-1}$ (m, $\nu_{Pd-Cl}$). Anal. Calcd for $C_{26}H_{10}Cl_2F_{10}N_2Pd_2$: C, 37.89; H, 1.22; N, 3.40. Found: C, 38.01; H, 1.24; N, 3.39.

**(Pentafluorophenyl)chloro-1,5-$\eta^4$-cyclooctadienepalladium(II) (3).** To a solution of $Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(NCPh)_2$ (1.5 g, 1.82 mmol) in $CH_2Cl_2$ (25 mL) was added 1,5-cyclooctadiene (0.223 mL, 2 mmol). After 2 min of stirring the solution was filtered through Kieselgur, and the solvent was vacuum-evaporated. Cold $Et_2O$ (5 mL) was added to the residue, and the yellow solid (**3**) was filtered, washed with a mixture $Et_2O$–hexane (1:2), and air dried: yield 1.44 g (95%); IR 1560 cm$^{-1}$ (m, $\nu_{C=C}$), 322 cm$^{-1}$ (m, $\nu_{Pd-Cl}$); $^{19}F$ NMR −122.3 (m, $F_{ortho}$), −158.9 (t, 19.2 Hz, $F_{para}$), and −162.5 (m, $F_{meta}$); $^1H$ NMR 6.27 (m, 2 H), 5.65 (m, 2 H), and 2.9–2.6 (m, 8 H); $^{13}C$ NMR 124.5, 107.6, 31.68 and 28.3. Anal. Calcd for $C_{14}H_{12}ClF_5Pd$: C, 40.31; H, 2.90. Found: C, 40.43; H, 2.79.

**Table IV.** Experimental Data for the Crystallographic Analysis of **3**

| | |
|---|---|
| formula | $C_{14}H_{12}ClF_5Pd$ |
| mw | 417.09 |
| crystal system | monoclinic |
| space group | $P2_1/c$ |
| *a*, Å | 8.313 (1) |
| *b*, Å | 7.7800 (6) |
| *c*, Å | 22.292 (4) |
| $\beta$, deg | 95.77 (1) |
| *V*, Å$^3$ | 1434.4 (5) |
| *Z* | 4 |
| $\rho_{calc}$, g cm$^{-3}$ | 1.93 |
| reflections for lattice parameters (no., range) | 25<br>15–16 |
| *F*(000) | 748 |
| temperature, °C | 18 |
| crystal size, mm | 0.50 × 0.30 × 0.25 |
| diffractometer | CAD4 Enraf Nonius |
| radiation | Mo K$\alpha$ |
| monochromator | graphite |
| scan type | $\omega$–$2\theta$ |
| scan width | 1.0 + 0.34 tan $\theta$ |
| $\theta$ range, deg | 1–25 |
| standard reflections | two, measured every 2 h |
| $\mu$, cm$^{-1}$ | 15.07 |
| absorption correction, min.–max | 1.00–1.25 |
| Nb of measured reflections | 2520 |
| Nb of reflections used $I \geq 3\sigma(I)$ | 2080 |
| Min.–max height in final $\Delta\rho$, e A$^{-3}$ | −0.41–0.35 |
| Nb of refined parameters | 228 |
| merging R | 0.022 |
| $R = [\sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert]$ | 0.024 |
| $R = [\sum w(\Delta F)^2/\sum wF_o^2]$ | 0.026 |
| $w = 1$ | |

**Bis($\mu$-chloro)bis(8-(pentafluorophenyl)-1:4-5-$\eta^3$-cyclooctenyl)dipalladium(II) (4).** $Pd(C_6F_5)Cl(1,5\text{-}\eta^4\text{-}COD)$ (1.148 g, 2.75 mmol) was dissolved in THF (40 mL). The yellow solution was stirred, and after 36 h a white precipitate appeared. The suspension was stirred for 12 h more, and the white precipitate (**4**) was filtered, washed with THF, and air dried (0.5 g, 43%): $^{19}F$ NMR −141.2 (b, $F_{ortho}$), −159.1 (t, 21 Hz, $F_{para}$), and −163.4 (m, $F_{meta}$); $^1H$ NMR 6.01 (m, 8.0, 8.0 and 7.5 Hz, H4), 6.00 (m, H5), 3.53 (m, H1), 3.08 (m, H7), 2.6–2.35 (m, 4 H, H2 + H6 + H7′ + H8), 2.2–2.1 (m, 2 H, H3 + H3′), 1.90 (m, H6′), 1.22 (m, H2′). Anal. Calcd for $C_{28}H_{24}Cl_2F_{10}Pd_2$: C, 40.31; H, 2.90. Found: C, 40.41; H, 2.98.

**Bis($\mu$-chloro)bis(6-(pentafluorophenyl)-1–3-$\eta^3$-cyclooctenyl)palladium(II) (5).** $Pd(C_6F_5)Cl(1,5\text{-}\eta^4\text{-}COD)$ (1.25 g, 2.99 mmol) was dissolved in $CH_2Cl_2$ (50 mL). The yellow solution was stirred at room temperature for 60 h. The solvent was then removed in vacuo, and $Et_2O$ (10 mL) was added. The resulting yellow solid was filtered and air dried (1.12 g, 90%). The crude product, a mixture of **5** (80%) and **4** (20%), was dissolved in $CHCl_3$ (10 mL); the slow diffusion of *n*-hexane into this solution allowed us to obtain pure **5** as big yellow crystals which could be separated manually from **4** powder. $^{19}F$ NMR −143.2 (m, $F_{ortho}$), −158.4 (t, 20 Hz, $F_{para}$), and −163.3 (m, $F_{meta}$); $^1H$ NMR 5.55 (t, 7.5 Hz, H2), 4.81 (m, 7.5, 7.5, and 7.5 Hz, H1 + H3), 3.50 (tt, 12.5 and 4 Hz, H6), 2.52 (m, 15.5, 7.5, 7, and 2 Hz, H4 + H8), 2.20 (m, 15.5, 12.5, 7.5, and 6.5 Hz, H4′ + H8′), 1.95 (m, 14, 12.5, 6.5, and 1.5 Hz, H5 + H7), 1.55 (m, 14, 12.5, 4, and 4 Hz, H5′ + H7′). Anal. Calcd for $C_{28}H_{24}Cl_2F_{10}Pd_2$: C, 40.31; H, 2.90. Found: C, 40.48; H, 2.96.

**(8-(Pentafluorophenyl)-1:4-5-$\eta^3$-cyclooctenyl)(acetylacetonato)palladium(II) (6).** To a suspension of $Pd_2(\mu\text{-}Cl)_2(8\text{-}C_6F_5\text{-}1,4,5\text{-}\eta^3\text{-}C_8H_{12})_2$ (0.3 g, 0.36 mmol) in $CH_2Cl_2$ (15 mL) was added Tlacac (0.22 g, 0.72 mmol). The mixture was stirred for 30 min, and the suspension was filtered to remove the white flocculant precipitate (TlCl). The colorless filtrate was evaporated to dryness, and cold *n*-hexane (5 mL) was added affording a white product (**6**) which was filtered and air dried (0.23 g, 68%). $^{19}F$ NMR −142.2 (b, $F_{ortho}$), −160.3 (t, 21 Hz, $F_{para}$), and −164.4 (m, $F_{meta}$); $^1H$ NMR 6.01 (m, 8.8, 8.8, and 8.8 Hz, H4), 5.70 (m, 8.8, 8.8, and 6 Hz, H5), 5.21 (s, C*H* acac), 3.21 (m, 3.6 and 3.6 Hz, H1), 2.71 (m, 13, 13, 13, and 3.2 Hz, H7), 2.29 (m, 13, 3.6, and 3.6 Hz, H8), 2.24 (m, 13.6, 9.4, and 10.8 Hz, H2), 1.47 ( s, $CH_3$ acac), 1.82 (s, $CH_3$ acac), 1.78 (m, 13, 8.8, 4, and 3.2 Hz, H6′), 1.6–1.55 (m, 2 H, H3 + H3′), 1.51 (m, 13, 4, 2.8, and 2.8 Hz, H7′), 1.32 (m, 13, 13, 6, and 2.8 Hz, H6), 1.10 (m, 13.6, 3.6, 3.6, and 2.4 Hz, H2′); $^{13}C$ NMR 187, 190 (C=O), 106.1

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(27) (a) Usón, R.; Forniés, J. *Organometallic Syntheses* **1986**, *3*, 161. (b) Usón, R.; Forniés, J.; Martínez, F.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1980**, 888.

(28) Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 218.

**Table V.** Experimental Data for the Crystallographic Analysis of 7

| | |
|---|---|
| formula | $C_{19}H_{13}F_{11}O_2Pd$ |
| mw | 588.7 |
| crystal system | triclinic |
| space group | $P\bar{1}$ |
| $a$, Å | 10.360 (3) |
| $b$, Å | 11.051 (2) |
| $c$, Å | 11.084 (4) |
| $\alpha$, deg | 73.70 (2) |
| $\beta$, deg | 61.41 (2) |
| $\gamma$, deg | 66.08 (2) |
| $V$, Å$^3$ | 1012 (1) |
| $Z$ | 2 |
| $\rho_{calc}$, g cm$^{-3}$ | 1.93 |
| reflections for lattice parameters (no., range) | 25<br>21–22 |
| $F$(000) | 576 |
| temperature, °C | 18 |
| crystal size, mm | 0.60 × 0.45 × 0.40 |
| diffractometer | Philips PW 1100 |
| radiation | Mo K$\alpha$ |
| monochromator | graphite |
| scan type | $\omega$–2$\theta$ |
| scan width | 1.1 + 0.34 tan $\theta$ |
| $\theta$ range, deg | 1–25 |
| standard reflections | two, measured every 2 h |
| $\mu$, cm$^{-1}$ | 10.14 |
| absorption correction, min.–max | 1.00–1.30 |
| Nb of measured reflections | 3522 |
| Nb of reflections used $I > 3\sigma(I)$ | 3341 |
| Min.–max height in final, e A$^{-3}$ | –0.60–0.97 |
| Nb of refined parameters | 340 |
| $R = [\sum\|F\|/\sum\|F_o\|]$ | 0.036 |
| $R = [\sum w(\Delta F)^2/\sum wF_o^2]$ | 0.038 |
| $w = 1$ | |

(C4), 100.1 (CH, acac), 98 (C5), 56.5 (C1), 43.3 (C8), 42.2 (C2), 39.7 (C7), 29, 28.1 ($CH_3$, acac), 26.5 (C6), 25.1 (C3). Anal. Calcd for $C_{19}H_{19}F_5O_2Pd$: C, 47.47; H, 3.98. Found: C, 47.62; H, 3.78.

Pd(8-$C_6F_5$-1,4,5-$\eta^3$-$C_8H_{12}$)($F_6$-acac) (**7**) was prepared as described above for **6** except that the corresponding amount of Tl($F_6$-acac) was used: yield 70%; $^1$H NMR 6.53 (7, 7.5, 7.5, and 8 Hz, H4), 6.05 (s, $F_6$-acac), 5.97 (m, 8, 6, and 6 Hz, H5), 3.49 (m, H1), 1.26 (m, H2). Anal. Calcd for $C_{19}H_{1}3F_{11}O_2Pd$: C, 38.76; H, 2.22. Found: C, 39.01; H, 2.16.

**(6-(Pentafluorophenyl)-1–3-$\eta^3$-cyclooctenyl)(2,2′-bipyridyl)palladium(II) Tetrafluoroborate (8).** To a solution of $AgBF_4$ (0.018 g, 0.092 mmol) in acetone (10 mL) was added $Pd_2(\mu\text{-}Cl)_2(6\text{-}C_6F_5\text{-}1\text{–}3\text{-}\eta^3\text{-}C_8H_{12})_2$ (0.038 g, 0.046 mmol), and the mixture was stirred in the dark for 25 min. The solution was filtered to remove the white AgCl formed, and bipy (0.014 g, 0.092 mmol) was added to the resulting yellow filtrate. The solution turned colorless instantaneously and was stirred for 30 min. The solvent was removed, and $Et_2O$ (10 mL) was added to the residue affording a white product (**8**) which was filtered, washed with $Et_2O$, and air-dried (0.057 g, 85%). $^{19}$F NMR −143.3 (m, $F_{ortho}$), −154.3 (s, $BF_4$), −158.1 (t, 21 Hz, $F_{para}$), and −163.1 (m, $F_{meta}$); $^1$H NMR 9.2–7.8 (8 H, bipy), 6.23 (t, 8 Hz, H2), 5.23 (m, 8, 8, and 8 Hz, H1 + H3), 3.78 (tt, 12.5 and 4 Hz, H6), 2.83 (m, 15.2, 8.6, 6.5, and 2 Hz, H4 + H8), 2.52 (m, 15.2, 12.8, 8, and 6.5 Hz, H4′ + H8′), 2.05 (m, 14, 12.5, 7, and 2 Hz, H5 + H7), 1.78 (m, H5′ + H7′)9 Anal. Calcd for $C_{24}H_{20}BF_{10}N_2Pd$: C, 46.00; H, 3.23; N, 4.47. Found: C, 45.66; H, 3.19; N 4.43.

**Isomerization Reaction 4 → 5.** $Pd_2(\mu\text{-}Cl)_2(8\text{-}C_6F_5\text{-}1,4,5\text{-}\eta^3\text{-}C_8H_{12})_2$ (0.1 g, 0.12 mmol) was suspended in $CHCl_3$ (20 mL). The suspension was maintained at reflux for 80 h. After this time the suspension had turned from white to pale yellow. The solid, which was filtered off, and the filtrate were analyzed by $^{19}$F NMR. The total **4**:**5** ratio was 80:20.

**Kinetics.** All the reactions were monitored by $^{19}$F NMR spectroscopy by observing the disappearance of 3.

**(a) Isomerization of 3 in $CDCl_3$.** Pd($C_6F_5$)Cl(COD) (0.0157 g) was dissolved in 0.5 mL of $CDCl_3$, and the resulting yellow solution was immediately placed into the probe of the spectrometer (temperature = 35 °C) at which time data collection was initiated. Data points were taken every 15 min with 2.5 min acquisition time.

**(b) Isomerization of 3 + (4 + 5) in $CDCl_3$.** Pd($C_6F_5$)Cl(COD) (0.0125 g) and 0.0032 g of **4** + **5** (**4**:**5** = 20:80) were dissolved in 0.5 mL of $CDCl_3$. The rate of disappearance of **3** was monitored by the same method used in (a).

**(c) Isomerization of 3 in $(CD_3)_2CO$.** Pd($C_6F_5$)Cl(COD) (0.0104 g) was dissolved in 0.5 mL of $(CD_3)_2CO$. The yellow solution was immediately placed into the probe of the spectrometer ($T$ = 35 °C) at which time collection was initiated. Data points were collected as in (a).

**Crystal Structure Determination of 3 and 7.** Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane into an acetone solution of **3** and by slow evaporation of a $CH_2Cl_2$/*n*-hexane solution of **7**.

Details of the crystallographic analyses are given in Table IV for compound **3** ($C_{14}H_{12}ClF_5Pd$) and in Table V for compound **7** ($C_{19}H_{13}F_{11}O_2Pd$).

The structures were solved by the Patterson method and subsequent Fourier maps. An empirical absorption correction was applied, by using the $\psi$-scan of two reflections.

Hydrogens were found on a difference map and refined with an overall isotropic thermal parameter.

Refinements were carried out by using a full matrix for compound **3** and in two blocks for compound **7**.

Scattering factors with anomalous dispersion correction were taken from CRYSTALS;[29] a secondary extinction correction was applied. For compound **7** the largest peaks in the least difference map were in the vicinity of the $CF_3$ groups which showed a rather high thermal agitation.

**Acknowledgment.** We acknowledge the CICYT for economical support (Project PB86-0028), the Ministerio de Educación y Ciencia for a grant (to A.C.A.), and the Departamento de Química Inorgánica de la Universidad de Zaragoza for the use of their NMR facilities.

**Supplementary Material Available:** Tables of atomic positional and thermal parameters and anisotropic thermal parameters for 3 and 7 (4 pages); a listing of observed and calculated structure factors for 3 and 7 (21 pages). Ordering information is given on any current masthead page.

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(29) Carruthers, J. R.; Watkin, D. J. CRYSTALS, an advanced crystallographic computer program; Chemical Cristallography Laboratory, Oxford University: Oxford, U.K., 1985.