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"Pd(C_6F_5)Br", a Convenient Precursor for Studying the Endo Attack of Nucleophiles on Olefins. X-ray Structure of Bis(μ-bromo)bis(4-(pentafluorophenyl)-1–3-η^3-cyclohexenyl)dipalladium(II)

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Acyclic and cyclic diolefins insert into Pd–C_6F_5 bonds of *isolable* "Pd(C_6F_5)Br" synthons to give η^3-allyl complexes. The reactions are regiospecific; the C_6F_5 in the product is always attached to one external carbon of the diene system, and the allyl moiety is formed at the position of the unattacked double bond. Furthermore, the reactions are stereospecific; the X-ray determination of the title complex (**7a**) shows that the C_6F_5 group (which was coordinated to Pd in the precursor) and the Pd atom are on the same face of the cyclohexenyl ring. **7a** crystallizes in the triclinic space group $P\bar{1}$ with a = 15.4376 (22) Å, b = 7.3616 (7) Å, c = 5.7056 (5) Å, α = 107.77 (1)°, β = 82.08 (1)°, and γ = 89.01 (2)° (Z = 1). Least-squares refinement leads to final R of 0.076 for 2064 independent reflections. Styrene reacts with these synthons to give *trans*-PhCH=CH(C_6F_5), and this reaction models, as an isolated reaction, the proposed second step in the Heck arylation reactions.

Introduction

Palladium-initiated additions of nucleophiles to unsaturated groups are currently a common and useful process in organic syntheses.[1] Olefins and dienes are prone to this type of reaction, which can follow one of two possible pathways:[2] (i) trans or exo attack, where the nucleophile (Nu) attacks externally to a coordinated double bond; (ii) cis or endo attack, where the nucleophile first coordinates to the metal, and a cis addition of the Pd–Nu bond to the double bond follows. This second path can also be looked at as an insertion of a double bond into the Pd–Nu bond.

The Heck arylation reaction[1] and the synthesis of *endo*-η^3-allylpalladium complexes in one-pot reactions (from tetrachloropalladate, a diene, and an organomercurial)[3-7] are examples of cis insertion. Although these reactions are accepted to proceed via the formation of "PdRX" intermediates (R = aryl, vinyl, acyl, methyl, etc.), these have never been isolated.

We report the reactivity of isolated "Pd(C_6F_5)Br" synthons toward styrene and some diolefins, which models (as an isolated reaction) the insertion step proposed in path ii). The regio- and stereochemical features of the insertion can be easily recognized by examining the location of the C_6F_5 group in the products.

A paper[8] has recently appeared in which some complexes of the type [PtRCl(1,2,5,9-η^4-5-methylenecyclooctene] are isolated and then isomerized into the corresponding σ,π-derivatives, [Pt(μ-Cl)$_2$(1,4,5-η^3-1-(RCH_2)-4-cycloocten-1-yl)$_2$]. The different reactivity of M–C bonds (M = Pd or Pt) toward insertion leads to different strategies in that paper and in ours. There, the higher inertness of Pt–R bonds demands an unusual "in-plane" coordinated olefin to help the insertion step. Here, the high reactivity of the Pd–R bonds demands an unusually inert Pd–C_6F_5 bond to make possible the isolation of precursors, which ensures that the R group is linked to the Pd atom before the insertion step occurs.

In the text, figures, and tables of this paper, C_6F_5 or Pf is used to represent a pentafluorophenyl group, whereas (C_6F_5-allyl) stands for any allylic group carrying one C_6F_5 group on one carbon in the chain.

Results

Synthesis of the Products. We have recently shown that $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2Br_2]$ (**1**) is an excellent precursor for complexes containing the moiety "Pd(C_6F_5)Br".[9] Dienes with poor coordinating ability such as those used in this work do not react with **1** unless easily accessible coordination sites are made available by removing half of the bromides with $AgClO_4$; then, a fast reaction takes place that leads to dimeric (η^3-C_6F_5-allyl)palladium compounds (eq 1).

$$\textit{trans,sym}\text{-}(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2Br_2] + 2AgClO_4 + 2(\text{diene}) \rightarrow \underset{\mathbf{3a\text{–}8a}}{Pd_2(\mu\text{-}Br)_2(\eta^3\text{-}C_6F_5\text{-allyl})_2} + 2AgBr + 2(NBu_4)ClO_4 \quad (1)$$

Alternatively, $[Pd(C_6F_5)Br(NCMe)_2]$ (**2**, obtained from **1**, $AgClO_4$, and NCMe) can be used as an isolable, storable, and soluble source of "Pd(C_6F_5)Br" in the reactions toward dienes (eq 2).

$$Pd(C_6F_5)Br(NCMe)_2 + \text{diene} \rightarrow \underset{\mathbf{3a\text{–}8a}}{[Pd_2(\mu\text{-}Br)_2(\eta^3\text{-}C_6F_5\text{-allyl})_2]} + 2NCMe \quad (2)$$

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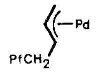
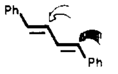
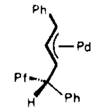
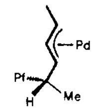
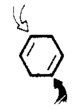
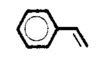
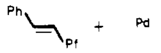
Table I. Summary of Reactivity[a]

olefin	product structure	compd
		3a, 3b
		4a, 4b
		5a
		6a
		7a, 7b
		8a, 8b
		9

[a] Dark arrow, position of attack; light arrow, central allyl carbon in product. a, Br-bridged dimer; b, acac monomer.

Table II. Analytical Data of the Compounds

compd	color	anal. found (calcd) C	H	N
2	yellow	27.50 (27.58)	1.39 (1.39)	6.41 (6.43)
3a	yellow	29.47 (29.48)	1.48 (1.48)	
3b	white	42.22 (42.24)	3.07 (3.07)	
4a	yellow	47.03 (47.21)	2.51 (2.52)	
4b	pale yellow	55.88 (56.02)	3.65 (3.66)	
5a	yellow	33.06 (33.09)	2.31 (2.31)	
6a	yellow	31.60 (31.49)	1.44 (1.44)	
7a	yellow	33.12 (33.24)	1.85 (1.86)	
7b	white	45.12 (45.10)	3.33 (3.33)	
8a	yellow	33.25 (33.24)	1.86 (1.86)	
8b	white	45.26 (45.10)	3.32 (3.33)	
9	white	62.00 (62.23)	2.62 (2.61)	

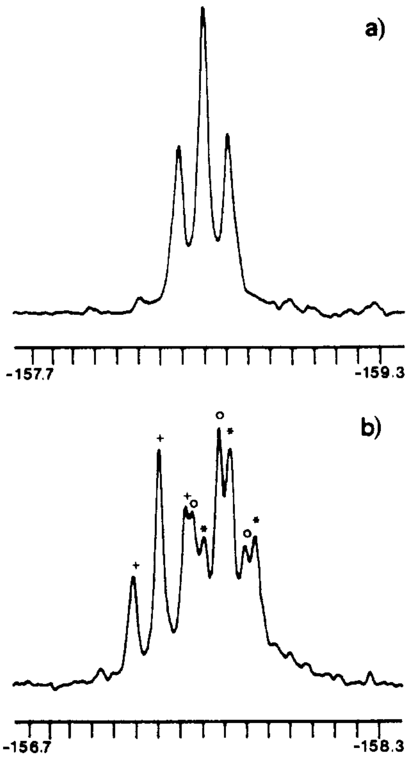


Figure 1. F^4 signal of complex **7a**: (a) at 60 °C; (b) at -50 °C.

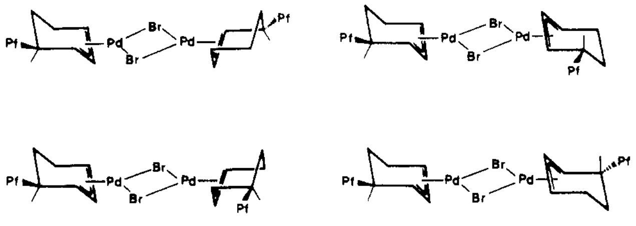


Figure 2. The four possible arrangements of two allyl moieties shown for **7a**.

To clarify some features of the NMR spectra of the dimeric (η^3-C_6F_5-allyl)palladium complexes, several monomers were obtained according to eq 3.

$$[Pd_2(\mu\text{-Br})_2(\eta^3\text{-}C_6F_5\text{-allyl})_2] + 2Tl(acac) \rightarrow 2[Pd(\eta^3\text{-}C_6F_5\text{-allyl})(acac)] + 2TlBr \quad (3)$$

3b,4b,7b,8b

Finally, when the "Pd(C_6F_5)Br" synthons used in eqs 1 and 2 are reacted with a monoolefin such as styrene, pentafluorophenylation of the styrene occurs with formation of palladium (eq 4), as expected from a typical Heck arylation.

$$\text{"Pd}(C_6F_5)\text{Br"} + PhCH{=}CH_2 \rightarrow \mathit{trans}\text{-}PhCH{=}CH(C_6F_5) + Pd + HBr \quad (4)$$

9

The olefins tested are collected in Table I. All the dienes led to (η^3-C_6F_5-allyl)palladium complexes having the structures shown in Table I. The colors and analytical data of the compounds are given in Table II.

IR and ^{19}F and ^1H NMR Spectroscopic Data. The favorable spectroscopic features of the C_6F_5 group greatly facilitate the interpretation of the results. A simple inspection of the IR spectra of the products shows that the C_6F_5 group is no longer attached to the Pd atom since its typical absorptions (1630, 1500, 1060, 950, and 780 cm^{-1}) have been replaced for those characteristic of C_6F_5 attached to carbon (1650, 1515, 1490, 1130, 990, and 950 cm^{-1}).[10] This migration is confirmed by the reduction in chemical shift separation between the ortho and the meta fluorines (ca. 40 ppm in C_6F_5–Pd systems compared to ca. 15 ppm in C_6F_5–C systems).

The ^{19}F resonance of the para fluorine (F^4) always appears as a triplet well separated from the rest of the ^{19}F resonances, and each F^4 signal corresponds to one type of C_6F_5. Hence the number of stereoisomers of any kind formed in a given reaction corresponds to the number of F^4 resonances observed. This avoids the need for cumbersome analysis of ^1H NMR spectra in mixtures.

Table III collects the number of F^4 resonances observed at different temperatures for the complexes prepared. Several of the dimeric compounds [$Pd(\mu$-$Br)_2(\eta^3$-C_6F_5-allyl$)_2$] show two or more F^4 signals at room or below room temperature (see, for example, the spectra of **7a** in Figure 1), but these converge to one signal at higher temperatures (except for complex **4a**, where this high-temperature simplification is not reached within the limits of the solvent, $CDCl_3$). Since all the monomeric complexes [$Pd(\eta^3$-C_6F_5-allyl)(acac)] display only one F^4 signal even at low temperature, the appearance of several stereoisomers in

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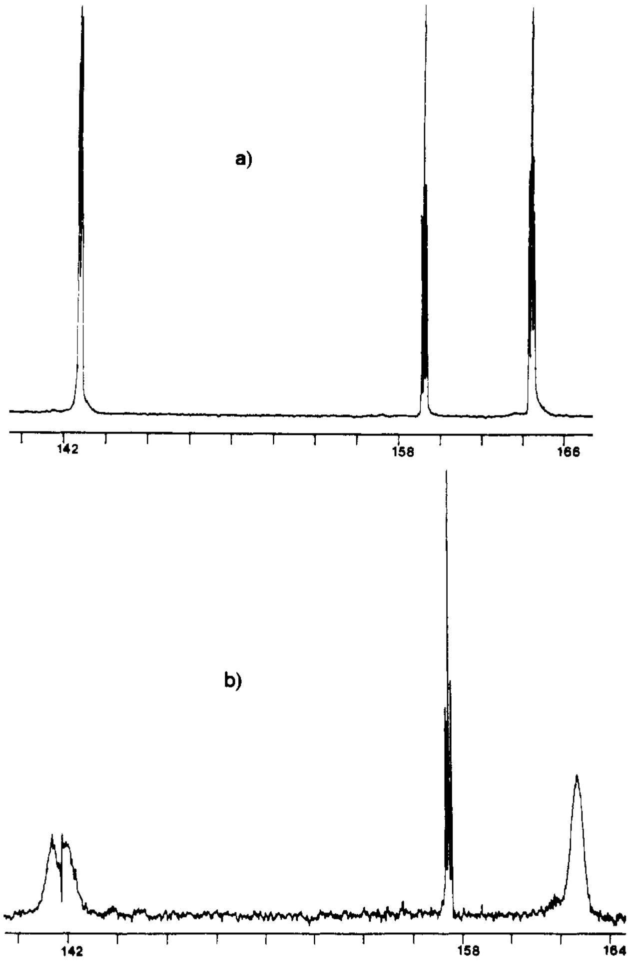

Figure 3. ^{19}F spectra VT spectra of complex **4b**: (a) at 20 °C; (b) at -50 °C.

[$Pd_2(\mu\text{-}Br)_2(\eta^3\text{-}C_6F_5allyl)_2$] must be due to their dimeric nature and to the different arrangements of two allyl moieties in the dimer (Figure 2). This can give rise to four different stereoisomers for allyl moieties lacking a symmetry plane (**3a**–**7a**) or two if the allyl moiety has a symmetry plane (**8a**).[11,12]

A second temperature-dependent process, which leads to inequivalence of the two ortho fluorines (and also of the two meta fluorines) at low temperature (see Figure 3), is observed in the monomeric complexes **4b**, **7b**, and **8b**. It is obviously related to hindrance of the rotation of the C_6F_5 group around the C_6F_5–C bond, which is enhanced in the more crowded compound **4b**. The coalescence temperature for the two ortho fluorines of **4b** was in the range -40 to -50 °C, corresponding to approximately 45 kJ mol^{-1} for the rotational barrier, according to the Eyring equation.[13] The fact that ^{19}F NMR spectra show only one stereoisomer, both in the monomers and in the high-temperature limit of the dimers, means that the reactions are regiospecific; the attack always occurs on the external carbon of the diene system, and allyl formation occurs without isomerization of the unattacked double bond (this is clearly seen in Table I, which shows the (η^3-C_6F_5-allyl)Pd structures of the resulting complexes and their relationship to the corresponding starting dienes). Moreover it means that the reaction is also stereospecific (otherwise complexes **4**–**8** should consist of two diastereoisomers). This attack is endo, as expected, and was conclusively proved for complex **7a** by X-ray molecular structure determination, as discussed below.

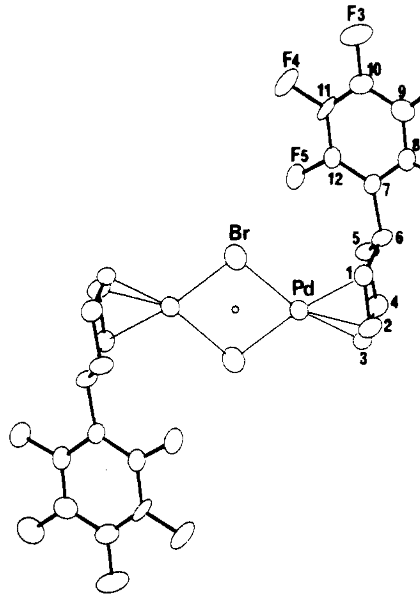

Figure 4. PLUTO drawing of complex **7a**, showing the atom numbering scheme.

Table IV collects the ^{1}H NMR parameters that have led to the structural assignments given in Table I. The spectra were interpreted with the help of double-irradiation techniques when necessary and in accordance with many previous studies on related complexes.[14-18] Syn or anti stereochemistry for linear allyls (**3a**,**b**, **4a**,**b**, **5**) and boat or chair conformations for the cyclohexenyl derivatives[17] were assigned according to the accepted criteria of coupling constant values.

^{1}H and ^{19}F NMR data for the organic compound *trans*-PhCH=CH(C_6F_5) (**9**) are given in the Experimental Section.

X-ray Structure of Bis(μ-bromo)bis(4-(pentafluorophenyl)-1-3-η^3-cyclohexenyl)dipalladium(II) (7a). A PLUTO[19] drawing of the complex is shown in Figure 4. Atomic coordinates for the non-hydrogen atoms are listed in Table V, and selected distances and bond angles in Table VI. The dimer is situated at a crystallographic symmetry center.

Each palladium atom is bonded to one η^3-allyl moiety and two bridging bromines. The two allyl moieties have a trans arrangement, and the two Pd atoms and the two Br atoms are coplanar; a search of the Cambridge Crystallographic Database[20] of molecular frames of the (μ-Cl-η^3-allyl-Pd(II)) type showed that trans arrangement of the two allyls is associated with planar dimers, whereas cis arrangement is associated with butterfly-shaped dimers (dihedral angles of 49.5–54.8°).

The plane defined by the two Pd atoms and the two Br atoms makes an angle of 74.2 (8)° with both C1,C2,C3

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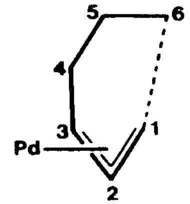
Table III. ^{19}F NMR Data of the Complexes at Different Temperatures^{a,b}

compd	T, °C	F_{para}^{c}	F_{meta}	F_{ortho}	compd	T, °C	F_{para}^{c}	F_{meta}	F_{ortho}
3a	20^d	−156.4 (t)	−162.3 (m)	−143.4 (m)			−156.0 (t)		
3b	20^d	−157.6 (t)	−163.0 (m)	−143.4 (m)	**7a**	60	−158.5 (t)	−163.9 (m)	−141.0^e
4a	60	−158.0 (t)	−163.0^e	−142.5^e		20	−157.9^e		
		−158.1 (t)					−157.4 (t)		
	20	−157.7^e				−50	−157.4 (t)		
		−156.6^e					−157.2 (t)		
	−40	−157.2 (t)			**7b**	20^d	−159.0 (t)	−164.2 (m)	−141.8 (m)
		−157.4 (t)			**8a**	20	−157.0 (t)	−162.8 (m)	−142.1 (m)
4b	20^d	−158.8 (t)	−164.0 (m)	−142.3 (m)		−55	−156.2 (t)		
5a	20^d	−158.2 (t)	−163.5 (m)	−143.7 (m)			−156.3 (t)		
6a	20	−157.3 (t)	−163.4 (m)	−137.8 (m)	**8b**	20^d	−158.7 (t)	−163.3 (m)	−142.8 (m)
	−55	−156.3 (t)							

[a] Measured on a Varian XL-200. Chemical shifts are given in δ, with reference to CFCl$_3$. [b] F_{meta} and F_{ortho} are given only when high-temperature simplification is reached. [c] $^3J_{F-F}$ = 20 Hz. [d] The same F_{para} pattern is found in the range 60 to −50 °C. [e] Broad resonance due to unresolved overlapping of signals.

Table IV. ^{1}H NMR Data for the (η^3-C$_6$F$_5$-allyl) Complexes^a



3a,b: $R_1 = R_1' = R_4 = R_4'$ = H
4a,b: R_1 = H; R_1' = Ph; R_4 = H; R_4' = Ph
5a: R_1 = H; R_1' = Me; R_4 = H; R_4' = Me
6a: R_1' = H; R_4 = H; R_4' = C$_6$F$_5$; $R_5 = R_5'$ = H
7a,b: R_1' = H; R_4 = H; R_4' = C$_6$F$_5$; $R_5 = R_5' = R_6 = R_6'$ = H
8a,b: R_1' = H; $R_4 = R_4'$ = H; R_5 = H; R_5' = C$_6$F$_5$; $R_6 = R_6'$ = H

compd	R_1(anti)	R_1'(syn)	H_2	H_3	R_4	R_4'	R_5	R_5'	R_6	R_6'	other
3a	2.97 (dt) (12, 1)	4.09 dd (7, 1)	5.45 ddd (12, 11, 7)	3.89 m^b (11, 10.1, 4.9)	3.37 m^b (14.5, 4.9, 2^c)	3.12 m^b (14.5, 10.1, 2^c)	3.12 m^b				
3b	2.8 dt (12, 1)	3.78 dd (7, 1)	5.45 m (12, 10.5, 7)	3.54 m^b (10.5, 9.2, 5.8)	3.20 m^b (15, 5.8, 2^c)	3.00 m^b (15, 9.2, 2^c)					5.36 s [1 H], 1.99 s [3 H], 1.94 s [3 H]
4a	4.70^d (11)	7.4–7.2 m	5.72^d (11)	4.5^d	4.70^d (9)	7.4–7.2 m					
4b	4.55 d (10.8)	7.3–7.5 m	5.71 dd^e (10.8)	4.19 m	4.79 d (8.8)	7.3–7.5 m					5.21 s [1 H], 1.73 s [3 H], 1.70 s [3 H]
5a	3.93 m (10.9, 6.3)^f	1.45 d (6.3)	5.42 dd^e (10.9)	3.88 m (10.9, 6.1)^f	3.60 m	1.52 d (7.1)					
6a		5.46 m^g	5.71 dd^e (2.8)	5.24 m^g	2.96 d (6.3)		1.62 dd (18.6, 6.3)	2.42 d (18.6)			
7a^h		5.05^d	5.53 m	5.20^d	3.26 m			1.5–2.5 m [4 H]			
7b		4.67 m	5.66 dd^e (6.6)	4.97 m	3.24 m			2.0–2.6 m [4 H]			5.27 s [1H], 1.98 s [3 H], 1.8 s [3 H]
8a		5.40 dd (6.3, 5.6)	5.59 t (6.3)	5.40 dd (6.3, 5.6)	2.35 m^i (17.9, 11.9)	2.13 m^i (17.9, 5.6, 5.6)	2.78 m (11.9, 5.6)		2.35 m^i	2.13 m^i	
8b		5.03 m (6, 4.5, 3)	5.70 t (6)	5.03 m (6, 4.5, 3)		2.1 m [4 H]	2.73 m		2.1 m [4 H]		5.3 s [1 H], 1.9 s [6 H]

[a] δ mult. J values (hertz) are given in parentheses. [b] ABX pattern. [c] $^4J_{F-H}$. [d] Broad resonance due to unresolved overlapping of signals. [e] Apparent triplet. [f] J values measured from double-irradiation experiments. [g] Apparent singlet. [h] Spectrum recorded at 60 °C. [i] AB pattern.

Table V. Final Atomic Coordinates

atom	*x/a*	*y/b*	*z/c*
Pd	0.42759 (4)	0.65677 (9)	0.75735 (11)
Br	0.54819 (7)	0.70172 (15)	0.43593 (22)
C(1)	0.3197 (6)	0.6801 (14)	1.0455 (15)
C(2)	0.3737 (7)	0.8387 (17)	1.1049 (19)
C(3)	0.3769 (6)	0.9502 (14)	0.9438 (18)
C(4)	0.2975 (7)	0.9890 (13)	0.8331 (20)
C(5)	0.2450 (6)	0.8141 (13)	0.7613 (18)
C(6)	0.2342 (6)	0.7104 (13)	0.9608 (18)
C(7)	0.1826 (5)	0.5317 (12)	0.8956 (16)
C(8)	0.1229 (6)	0.5006 (14)	1.0797 (16)
C(9)	0.0707 (7)	0.3459 (15)	1.0413 (21)
C(10)	0.0797 (7)	0.2135 (13)	0.8080 (21)
C(11)	0.1391 (7)	0.2390 (13)	0.6219 (18)
C(12)	0.1896 (6)	0.3957 (13)	0.6665 (18)
F(1)	0.1101 (4)	0.6273 (10)	1.3130 (11)
F(2)	0.0129 (5)	0.3253 (11)	1.2261 (14)
F(3)	0.0306 (6)	0.0623 (10)	0.7644 (17)
F(4)	0.1478 (5)	0.1100 (9)	0.3915 (13)
F(5)	0.2460 (4)	0.4039 (9)	0.4721 (11)

Table VI. Selected Interatomic Distances (Å) and Angles (deg) for 8a

Pd–Br	2.528 (1)	C(7)–C(8)	1.376 (13)
Pd–Br′	2.529 (1)	C(7)–C(12)	1.372 (12)
Pd–C(1)	2.138 (9)	C(8)–C(9)	1.387 (15)
Pd–C(2)	2.075 (9)	C(8)–F(1)	1.358 (10)
Pd–C(3)	2.172 (9)	C(9)–C(10)	1.376 (14)
C(1)–C(2)	1.430 (16)	C(9)–F(2)	1.332 (14)
C(2)–C(3)	1.404 (18)	C(10)–C(11)	1.365 (15)
C(3)–C(4)	1.515 (16)	C(10)–F(3)	1.337 (13)
C(4)–C(5)	1.515 (16)	C(11)–C(12)	1.382 (14)
C(5)–C(6)	1.546 (16)	C(11)–F(4)	1.354 (10)
C(1)–C(6)	1.502 (15)	C(12)–F(5)	1.330 (12)
C(6)–C(7)	1.524 (13)		
Br–Pd–Br′	89.83 (4)	C(3)–C(4)–C(5)	111.4 (9)
Pd–Br–Pd′	90.17 (4)	C(4)–C(5)–C(6)	112.6 (8)
C(1)–C(2)–C(3)	114.8 (9)	C(1)–C(6)–C(7)	113.6 (8)
C(2)–C(3)–C(4)	122.0 (10)	C(2)–C(1)–C(6)	117.6 (9)

planes. The cyclohexenyl ring shows a $^2C_5$ chair conformation; the plane defined by C1,C3,C4,C6 makes an angle of 32.9 (9)° with the allyl plane C1,C2,C3 and of 41.8 (7)° with the plane C4,C5,C6. *The C_6F_5 ring is attached to C6, and Pd and C_6F_5 are situated in a cis arrangement in the cyclohexenyl ring, as expected for an endo attack.* The C_6F_5 plane is twisted 31.8 (2)° with respect to the central plane. The allyl angle at C2 (114.8°) can be compared with that found in the only other cyclohexenyl structure studied (114.8°);[21] this angle in cyclic allyls seems to be determined mostly by the ring size, ranging from 91° in cyclobutenyl compounds[22] to 123.5° in cycloheptenyl derivatives.[21]

Discussion

Two different starting materials are used to prepare (η^3-C_6F_5-allyl)palladium complexes from diolefins. One of them, $[Pd(C_6F_5)Br(NCMe)_2]$ (**2**), can be isolated and is fairly stable in the solid state, but its ^1H NMR spectrum in $CDCl_3$ [δ 2.10 (s, 3 H, free MeCN), 2.25 (s, 3 H, coordinated MeCN)] and its IR spectrum in $CHCl_3$ (see Experimental Section) show that it dimerizes in solution, losing MeCN (eq 5), as observed before for $[PdCl_2(NCPh)_2]$.[23,24]

$$2[Pd(C_6F_5)Br(NCMe)_2] \rightarrow \textit{trans,sym}\text{-}[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(NCMe)_2] + 2MeCN \quad (5)$$

The other starting material has been referred to as "*$Pd(C_6F_5)Br$*" solutions.[9] Solid $[Pd(C_6F_5)Br]_n$ was first prepared by using the "metal atom technique" by Klabunde et al.,[25] who also studied its behavior in some solvents. Since our method to prepare these "$Pd(C_6F_5)Br$" solutions is just a new access to the same reagent by a more conventional and higher yield method, the nature of these solutions should be interpreted in light of Klabunde's findings, coincident with our own experience. It seems that the degree of polymerization of the species in solution depends on the competition between the solvent as a ligand and the bridging ability of Br (and perhaps C_6F_5); whereas $[Pd(C_6F_5)Br(OEt_2)_2]$ appears to be dominant in diethyl ether solution, trimers or other polymers seem more probable in other solvents.[25] Moreover, the composition of the solids isolated from these solutions depends on the coordinating ability of the solvent, its volatility, and the efficiency in pumping or washing it off. Bearing this in mind, we will use the general formulation $[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(S)_2]$, which also includes the MeCN complex, to avoid duplication of equations.

Upon addition of dienes or styrene to the precursors, a double bond inserts into the $Pd-C_6F_5$ bond, leading to (η^3-C_6F_5-allyl)palladium complexes or, respectively, *trans*-PhCH=CH(C_6F_5). These reactions are regio- and stereospecific (endo attack) and model the second step of reactions such as olefin arylation catalyzed by palladium complexes (Heck reaction).

There is no doubt that at least one of the two double bonds of the diene must coordinate to the palladium cis to the C_6F_5 group, in order to give rise to an insertion reaction.[26] This situation can be reached from **2** by displacing NCMe, which is easily lost: it has been shown previously that olefins[27] and dienes[28] displace both nitrile ligands from $[PdCl_2(NCPh)_2]$ to give complexes $[PdCl_2(olefin)]_n$ or $[PdCl_2(diene)]_n$. When starting from "$Pd(C_6F_5)Br$" solutions, a poorly coordinating solvent should be displaced even more easily to give *trans,sym*-$[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(\eta^2\text{-}diene)_2]$ (eq 6).

$$\textit{trans,sym}\text{-}[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(L)_2] + 2(diene) \rightarrow \textit{trans,sym}\text{-}[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(\eta^2\text{-}diene)_2] + 2L \quad (6)$$

L = MeCN or solvent

The question arises whether the second double bond also coordinates to the palladium to give the monomeric intermediate $[Pd(C_6F_5)Br(\eta^4\text{-}diene)]$ rather than the dimer $[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(\eta^2\text{-}diene)_2]$. Typically chelating dienes such as 1,5-cyclooctadiene, norbornadiene, 1,5-hexadiene,[29] and probably some substituted cyclopentadienes[30] (these because of special steric and electronic features) are known to give monomeric $[PdCl_2(\eta^4\text{-}diene)]$ compounds, but conjugated dienes such as *cis,trans*-1,3-cyclooctadiene[31,32] or 1,3-butadiene[32] prefer the dimeric structure $[Pd_2(\mu\text{-}Cl)_2Cl_2(\eta^2\text{-}diene)_2]$ in solution, according to molecular weight determinations. Thus the dienes used in this work look prone to produce dimeric *trans,sym*-$[Pd_2(\mu\text{-}Br)_2$-

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$(C_6F_5)_2(\eta^2\text{-diene})_2]$ intermediates rather than monomeric $(\eta^4\text{-diene})$ complexes.

The proposed intermediates *trans-sym*-$[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(\eta^2\text{-diene})_2]$ have the moiety "*cis*-$Pd(C_6F_5)(\eta^2\text{-diene})$" from which both the "in-plane" coordination and the Pd migration[33-36] (via palladium hydride elimination–readdition) that has to follow the insertion step in the case of 1,4-cyclohexadiene can proceed easily; the regioselectivity in allyl formation would be a consequence of this uncoordinated double bond acting as a sink of palladium during its migration. Finally, a monoolefin such as styrene cannot give rise to an allylic system, and the insertion is followed by hydride elimination and decomposition of the unstable palladium hydride to $PhCH{=}CH(C_6F_5)$, Pd, and HBr.

Bäckvall has provided some convincing evidence in favor of $(\eta^4\text{-diene})$ complexes of conjugated dienes as the species undergoing exo attack in trans acetoxypalladiations[37] even in systems known to form $(\eta^2\text{-diene})$ complexes in the solid state and in solution. This is not in contradiction with our suggestion of $(\eta^2\text{-diene})$ complexes as the species undergoing endo attack, since the "in-plane" coordination (which looks geometrically very problematic for η^4-bonded conjugated dienes) is a requirement for the four-center covalent addition occurring in an endo attack but not for the nucleophilic exo attack. The possibility of a conversion $(\eta^2\text{-diene})$ dimer $\rightleftharpoons 2(\eta^4\text{-diene})$ monomer for any diolefin can provide the preferred species for exo attacks (either η^4 or η^2 species) and for endo attacks (η^2 species in the cases we have considered here).

Concluding Remarks

The results discussed in this work support the accepted mechanism of endo attack to coordinated olefins by providing a nice example of a nucleophile (C_6F_5) coordinated to palladium which undergoes olefin insertion to give a product (**7a**) where the palladium atom and the nucleophile are in the same face of the ring in a cyclic diene. Intermediates having one double bond and the nucleophile mutually cis seem to be most reasonable, whereas coordination of the second double bond in these intermediates seems unnecessary, if not inconvenient. The pentafluorophenylation of styrene corresponds exactly to the proposed second step of the Heck arylation reactions.

Experimental Section

General Considerations. Carbon, hydrogen, and nitrogen 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 599 spectrometer; ^{19}F and ^1H NMR spectra were recorded on Varian XL-200 (200 MHz for ^1H) and Bruker WH250 (250 MHz for ^1H) instruments. Chemical shifts are reported in δ units (parts per million, ppm) downfield from Me_4Si for ^1H and from $CFCl_3$ for ^{19}F.

Literature methods were used to prepare $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2Br_2]$.[9] Cyclopentadiene was prepared by thermal cleavage of commercial dicyclopentadiene. All other diolefins were pure commercial grades and were used without further purification.

Preparation of the Complexes. Some general syntheses are described. The yields reported refer to isolated pure products. In addition the remaining mother liquors were evaporated to dryness, and the residues were analyzed by NMR techniques, finding that they contained only the same complexes isolated as pure samples and some $(NBu_4)ClO_4$.

Table VII. Crystal Analysis Parameters at Room Temperature

Crystal Data	
formula	$C_{24}H_{16}F_{10}Br_2Pd_2$
cryst habit	yellow plate
cryst size, mm	0.50 × 0.43 × 0.10
sym	triclinic, $P\bar{1}$
unit-cell determination	least-squares fit from 79 rflns ($\theta < 45°$)
unit-cell dimens	a = 15.4376 (22), b = 7.3616 (7), c = 5.7056 (5) Å, α = 107.77 (1), β = 82.08 (1), γ = 89.01 (2)°
packing: V (Å^3), Z, D_c (g cm^{-3}), M, $F(000)$, μ (cm^{-1})	610.4 (1), 1, 2.359, 866.98, 412, 169.47
Experimental Data	
technique	four-circle diffractometer bisecting geometry graphite-oriented monochromator, Cu Kα $\omega/2\theta$ scans, scan width 1.6° detector apertures 1.0 × 1.0°
total measmts	up to 65° in θ
speed	1 min/rfln
no. rflns	
indep	2064
obsd	2014 [$3\sigma(I)$ criterion]
std rflns:	2 rflns/90 min no variation
max-min trans factors	1.715–0.381[a]
Solution and Refinement	
solution	Patterson
refinement	least-squares on F_{obs}, full matrix
no. of variables	172 (hydrogen parameters fixed)
degrees of freedom	1842
ratio of freedom	11.7
H atoms	difference synthesis
final shift/error	0.01
weighting scheme	empirical as to give no trends in $\langle w\Delta^2F\rangle$ vs $\langle\lvert F_{obs}\rvert\rangle$ or $\langle \sin\theta)/\lambda\rangle$
max thermal value	$U_{11}[F4]$ = 0.079 (2) Å^2
final ΔF peaks	1.23 e Å^{-3} near the Br atom
final R and R_w	0.076, 0.101
computer and programs	VAX 11/750 XRAY76 system[b]
scattering factors	International Tables for X-Ray Crystallography[c]

[a] Reference 40. [b] Reference 41. [c] Reference 42.

Bis(acetonitrile)bromo(pentafluorophenyl)palladium(II) (2). $AgClO_4$ (0.13 g, 0.63 mmol) and **1** (0.42 g, 0.31 mmol) were stirred in NCMe (ca. 10 mL) for 45 min. A yellow precipitate (AgBr) appeared, which was filtered off, and the resulting solution was evaporated to dryness. The residue was extracted with Et_2O (50 mL), and $(NBu_4)ClO_4$, which is only sparingly soluble in this solvent, was removed. The Et_2O solution was evaporated, and several drops of NCMe were added. The yellow oil formed was treated with several portions of n-hexane until a yellow solid appeared. This product (**2**) was filtered and air-dried (0.25 g, 91% yield); IR (ν_{CN} region,[38,39] Nujol mull) 2332 (m), 2323 (s), 2304 (m), 2295 (s) cm^{-1}, $(CHCl_3)$ 2330 (s) and 2301 (w) (trans,sym dimer), 2294 (m) and 2256 (s) cm^{-1} (free MeCN); ^1H NMR $(CDCl_3)$ δ 2.1 (s, 3 H, free MeCN), 2.25 (s, 3 H).

Bis(μ-bromo)bis(4-(pentafluorophenyl)-1,4-diphenyl-1–3-η^3-butenyl)dipalladium(II) (4a). To a suspension of $AgClO_4$ (0.2 g, 0.96 mmol) in CH_2Cl_2 (30 mL) were added 1,4-diphenylbutadiene (0.2 g, 0.96 mmol) and **1** (0.65 g, 0.48 mmol). After 8 h of stirring, the precipitate (mainly AgBr) was filtered, and the resulting solution evaporated to dryness. The residue was extracted with 100 mL of Et_2O, and the insoluble $(NBu_4)ClO_4$ was

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removed. Evaporation of this Et_2O clear solution to ca. 5 mL and cooling afforded a yellow product (**4a**), which was filtered and air-dried (0.34 g, 63% yield).

5a (70% yield) and **6a** (76% yield) were prepared similarly.

Bis(μ-bromo)bis(5-(pentafluorophenyl)-1-3-η^3-cyclohexenyl)dipalladium(II) (8a). Method A: From 1. To a suspension of $AgClO_4$ (0.22 g, 1.06 mmol) in CH_2Cl_2 (40 mL) were added 1,4-cyclohexadiene (0.1 mL, 1.06 mmol) and **1** (0.716 g, 0.53 mmol). The mixture was stirred at room temperature for 8 h, and the resulting precipitate (AgBr) was filtered. Evaporation of the solution to ca. 10 mL led to a yellow product (**8a**), which was filtered, washed with CH_2Cl_2, and air-dried (0.25 g, 55% yield). The remaining solution was evaporated to dryness, and EtOH (20 mL) was added, affording an additional amount of **8a** which was filtered, washed with EtOH, and air dried (0.15 g), total yield 87%.

3a (85% yield) and **7a** (88% yield) were prepared similarly.

Method B: From 2. To a solution of **2** (0.2 g, 0.46 mmol) in CH_2Cl_2 (20 mL) was added 1,4-cyclohexadiene (0.04 mL, 0.46 mmol). The mixture was stirred for 5 min. The yellow solution was evaporated, and *n*-hexane (5 mL) was added. A yellow product (**8a**) was obtained, which was filtered and air-dried (0.18 g, 90% yield).

3a–**7a** were also obtained by this same procedure in excellent yields (85–90%).

(4-(Pentafluorophenyl)-1–3-η^3-butenyl)(2,4-pentanedionato)palladium(II) (3b). To a solution of **3a** (0.1 g, 0.12 mmol) in CH_2Cl_2 (ca. 10 mL) was added Tl(acac) (0.075 g, 0.24 mmol). A white precipitate appeared immediately. The suspension was stirred for 15 min, and the precipitate was filtered off; the colorless solution obtained was evaporated to dryness, and *n*-hexane was added. A white product (**3b**) was obtained, filtered, and air-dried (0.07 g, 70% yield).

4b (60% yield), **7b** (51% yield), and **8b** (55% yield) were prepared similarly. **3b**, **7b**, and **8b** were stored at −20 °C because they decompose slowly at room temperature.

Preparation of *trans*-PhCH═CH(C_6F_5) (9). To a suspension of $AgClO_4$ (0.076 g, 0.366 mmol) in CH_2Cl_2 (20 mL) were added styrene (0.042 mL, 0.366 mmol) and **1** (0.247 g, 0.183 mmol). During the reaction a Pd mirror appeared. After the mixture was stirred for 6 h, activated charcoal was added, and the suspension was filtered off. The solution obtained was evaporated to ca. 1 mL and cooled, affording white needles of **9** in 45% yield; ^{19}F NMR (200 MHz, $CDCl_3$) δ −143.7 (m, F_{ortho}), −157.5 (t, F_{para}), −163.9 (m, F_{meta}); ^1H NMR (200 MHz, $CDCl_3$) δ 6.98 (d, 2 H, J = 16.8 Hz), 7.43 (d, 2 H), 7.55–7.35 (m, Ph).

Safety Note. Although we have not had any problems using perchlorate salts, it is well-known that they are potentially explosive. Thus, *great caution* should be exercised when handling these materials.

X-ray Structure Determination of 7a. Crystals of **8a** suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of the complex. Crystal data and details of data collection and structure solution and refinement are collected in Table VII. An empirical absorption correction was applied.[40]

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Registry No. 1, 124351-22-0; 2, 125475-73-2; 3a, 125494-79-3; 3b, 125475-74-3; 4a, 125494-80-6; 4b, 125475-75-4; 5a, 125494-81-7; 6a, 125475-76-5; 7a, 125475-77-6; 7b, 125475-78-7; 8a, 125475-79-8; 8b, 125475-80-1; 9, 19292-25-2; Tl(acac), 15525-62-9; 1,3-butadiene, 106-99-0; 1,4-diphenylbutadiene, 886-65-7; 2,4-hexadiene, 592-46-1; 1,3-cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; styrene, 100-42-5.

Supplementary Material Available: Tables of thermal anisotropic parameters and hydrogen coordinates, atomic coordinates, bond distances and angles, least-squares planes and dihedral angles, ring puckering coordinates, asymmetry parameters, and torsion angles (7 pages); a listing of structure factors (9 pages). Ordering information is given on any current masthead page.

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Magnetic Circular Dichroism of Cyclic π-Electron Systems. 29.[1] Bicyclic Phospholium and Arsolium Cations with P–S, As–S, P–N, and As–N pπ-Bonding

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Electronic absorption and magnetic circular dichroism are reported for five bicyclic heterocycles derived from the phospholium and arsolium cations containing P–S, P–N, As–S, and As–N bonds. The spectra are analyzed in terms of the perimeter model and semiempirical calculations and are perfectly compatible with a delocalized aromatic π-electron system with pπ-bonding over the heterocyclic moiety.

Introduction

We have recently reported the synthesis of cationic heteronaphthalenic systems, which contain the first examples of pπ-bonding between sulfur and the heavier elements of group 15.[3-7] Spectroscopic (NMR, IR, and mass

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