

# PGSE NMR Diffusion, Overhauser, and DFT Studies on the Salts $[\text{Pd}(\eta^3\text{-CH}_3\text{CHCHPh})(\text{dppe})](\text{anion})$

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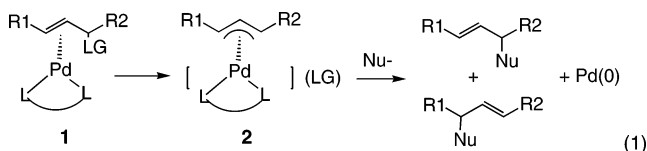
PGSE NMR diffusion, Overhauser and DFT studies on the salts  $[\text{Pd}(\eta^3\text{-CH}_3\text{CHCHPh})(\text{dppe})](\text{anion})$  (dppe = 1,2-bis(diphenylphosphino)ethane, anion =  $\text{BF}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{BARF}^-$ ,  $\text{PF}_6^-$ ) are reported. In dichloromethane solution there is little or no ion pairing for the BARF derivative, whereas the other three anions show intermediate degrees of ion pairing. In chloroform solution the  $\text{CF}_3\text{SO}_3^-$  and  $\text{BARF}^-$  salts show complete ion pairing. The  $^{19}\text{F}$ ,  $^1\text{H}$  HOESY studies reveal a selective approach of the  $\text{CF}_3\text{SO}_3^-$  and  $\text{PF}_6^-$  anions with respect to the allyl ligand. The approach brings the anion somewhat closer to the allyl phenyl ring than to the allyl methyl group. Further, the anion approaches the Pd center from the side of the two terminal allyl protons. The anions are not attracted to the allyl ligand but rather are choosing *both* an electronically (allyl phenyl vs allyl methyl) and sterically (terminal allyl protons vs central allyl proton) preferred pathway toward the P and metal atoms. This result is partially rationalized via DFT calculations.

## Introduction

There is a continuing interest in the homogeneously catalyzed allylic alkylation reaction. This reaction can be promoted by several late transition metals, including ruthenium,<sup>1</sup> rhodium,<sup>2</sup> and iridium;<sup>3</sup> however, the applications involving palladium<sup>4,5</sup> are still the most numerous. A wide variety of phosphorus, sulfur, and nitrogen chiral auxiliaries have been employed in this

Pd-catalyzed reaction with reported enantioselectivities in excess of 90% now being fairly routine.<sup>2–5</sup>

The mechanism<sup>6</sup> of the Pd-catalyzed allylic alkylation reaction is thought to involve a Pd(0) olefin complex,<sup>7–10</sup> e.g., **1**, containing the substrate-bound leaving group, LG. After oxidative addition, complex **1** (shown here as containing a chelating ligand) affords a Pd(II) allyl cationic complex, **2**, with the leaving group as the anion. This allyl cation is attacked by a nucleophile,  $\text{Nu}^-$ , to regenerate a Pd(0) species plus the two usual organic products (see eq 1). The regioselectivity of the reaction



depends on the R substituents and the remaining (usually chelating) ligands. There are now a large

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number of stable allyl complexes of Pd(II), which have been isolated and characterized.<sup>4,5,7,11–13</sup>

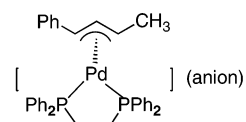
The palladium complexes **2** are of special interest, in that their structural distortions have been related to the mechanism of this catalytic reaction.<sup>14</sup> Further, there has been some discussion as to whether the anion in **2** "remembers" from which carbon it originally came; i.e., the anion formed from the leaving group is not necessarily remote from the cation.<sup>15,16</sup>

Although conductivity measurements still represent the accepted method of measuring how ions interact, there is a growing literature which suggests that the individual diffusion constants for the ions of a given salt can provide a useful alternative. This is especially true when taken together with HOESY (and/or NOESY) measurements that allow an estimation of the relative position(s) of the ions. Increasingly, one measures the individual diffusion constants using pulsed gradient spin-echo (PGSE) NMR methods<sup>17</sup> and employs <sup>19</sup>F and <sup>1</sup>H probes for the individual anions and cations, respectively.

The PGSE methodology stems from the relatively early days of NMR; hence, a substantial literature exists and the subject has been reviewed on several occasions.<sup>17</sup> The diffusion literature includes applications from the fields of biology<sup>18</sup> and polymers,<sup>19</sup> among others. Recently, studies on organometallic examples<sup>20–22</sup>

have appeared. Specifically, Macchioni et al.<sup>20</sup> and Brintzinger and co-workers<sup>21</sup> have both reported detailed PGSE studies on model zirconium complexes with relevance for polymerization catalysis. Further, we have presented PGSE studies for model palladium<sup>23</sup> (polymerization), iridium<sup>24</sup> (hydrogenation), and ruthenium<sup>25</sup> (Diels–Alder) catalysts. For a routine PGSE measurement, there are by and large no major instrumental or sample requirements (apart from a spectrometer equipped with gradients) and 1–2 mM solutions are readily measured.

As we have found no diffusion data for cationic allyl complexes of Pd(II), we have prepared the relatively simple salts **3**, with BF<sub>4</sub><sup>−</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>−</sup>, BARF<sup>−</sup>, and PF<sub>6</sub><sup>−</sup> as anions, and report here our results from PGSE, Overhauser NMR, and DFT experiments. The unsym-



**3a** = BF<sub>4</sub>, **b** = CF<sub>3</sub>SO<sub>3</sub>, **c** = BARF, **d** = PF<sub>6</sub>

metrical phenyl/methyl allyl (rather than a symmetric analogue, e.g., 1,3-diphenylallyl) was chosen in the hope that the anion would express some choice with respect to its position. The chelate 1,2-bis(diphenylphosphino)ethane was chosen so as to avoid the formation of "endo" and "exo" isomers, i.e., isomeric complexes due to the two possible positions of the central allyl proton, with respect to the chelate, which are observed if the chelate ligand is unsymmetrical.

## Results and Discussion

The complexes were prepared by treating the known dinuclear Pd–allyl complex with the appropriate silver or sodium salt in acetone solution, followed by the addition of the chelating ligand (see eq 2). Details of

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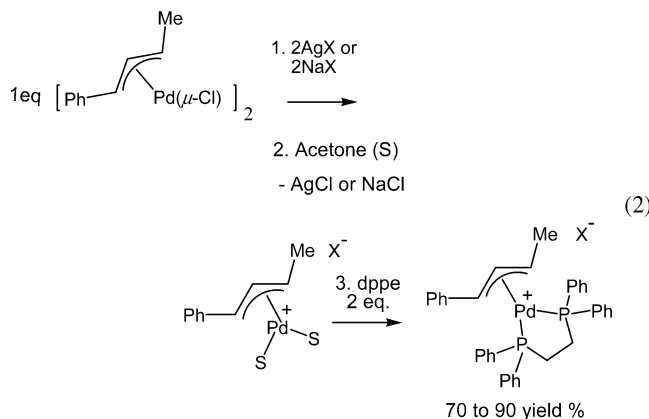
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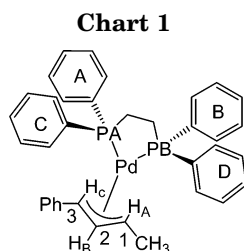
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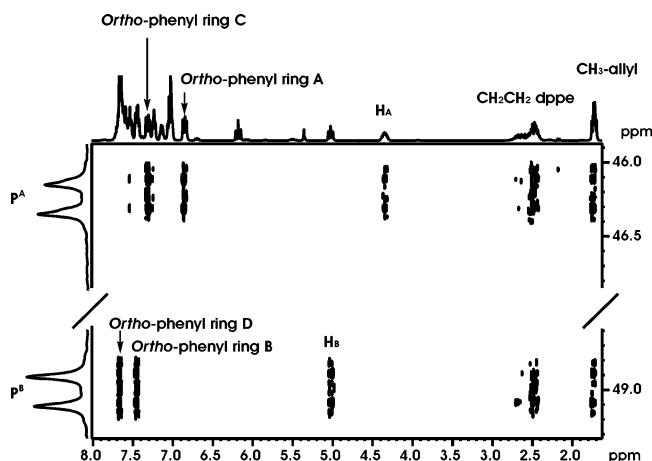
their characterization are given in the Experimental Section.



The assignment of the  $^1\text{H}$  NMR spectra for the three allyl protons of **3** was straightforward. The terminal allyl =CH resonance, close to the methyl group,  $\text{H}_\text{A}$ , was identified via its COSY and NOESY contacts. The central allyl proton,  $\text{H}_\text{B}$ , is readily assigned, as its associated  $^{13}\text{C}$  resonance appears in a characteristic<sup>26–28</sup> region at ca. 118 ppm (see Chart 1). The  $^{31}\text{P}$ ,  $^1\text{H}$  correla-



tion can then be used to assign the nonequivalent  $^{31}\text{P}$ ,  $\text{P}_\text{A}$  and  $\text{P}_\text{B}$ , spins. Specifically, one can use the relatively large  $^3J(^{31}\text{P}, ^1\text{H}(\text{allyl}))_{\text{trans}}$  value to connect a specific terminal allyl proton to the P atom in a pseudo-trans position (see Figure 1).<sup>26</sup> Moreover, the  $^{31}\text{P}$ ,  $^1\text{H}$  correlation allows the recognition and partial assignment of the four sets of P-phenyl ortho protons (also in Figure 1). These assignments are important for the discussion of the  $^{19}\text{F}$ ,  $^1\text{H}$  HOESY results. It is worth noting that the two  $^{31}\text{P}$  chemical shifts, e.g. for the anion  $\text{PF}_6^-$ ,



**Figure 1.**  $^{31}\text{P}$ ,  $^1\text{H}$  correlation for **3d** showing the geometry-dependent spin–spin interactions from the P atoms to their pseudo-trans terminal allyl protons,  $\text{H}_\text{A}$  and  $\text{H}_\text{C}$  ( $\text{CD}_2\text{Cl}_2$ ).

**Table 1.**  $^{13}\text{C}$  NMR Allyl Data (ppm) for Several of the Pd Complexes

	$\text{CF}_3\text{SO}_3$	BArF	$\text{PF}_6$
C1	86.8	85.9	86.6
C2	118.1	117.5	118.0
C3	89.6	89.0	89.6

**Table 2.** Detailed NMR Data for the  $\text{PF}_6^-$  Salt **3d**<sup>a</sup>

	$\delta$	assignt	$\delta$	assignt
$^1\text{H}$	6.85	ortho arom dppe ring A	$^{13}\text{C}$	132.3 ortho arom dppe ring A
	7.45	ortho arom dppe ring B		131.8 ortho arom dppe ring B
	7.31	ortho arom dppe ring C		
	7.65	ortho arom dppe ring D		132.4 ortho arom dppe ring D
	7.24	meta arom dppe ring A		
	7.62	meta arom dppe ring B		
	7.54	meta arom dppe ring C		
	7.71	meta arom dppe ring D		
	7.46	para arom dppe ring A		
	7.66	para arom dppe ring D		
	7.02	ortho arom allyl		
	1.73	$\text{CH}_3$	18.7	$\text{CH}_3$
	4.35	$\text{CHMe}$ allyl $\text{H}_\text{A}$	86.6	$\text{CHMe}$ allyl
	6.18	$\text{CHCHCH}$ allyl $\text{H}_\text{B}$	118.0	$\text{CHCHCH}$ allyl
	5.06	$\text{CHPh}$ allyl $\text{H}_\text{C}$	89.6	$\text{CHPh}$ allyl
	2.46–2.68	$\text{CH}_2\text{CH}_2$ dppe	28.8	$\text{CH}_2\text{CH}_2$ dppe
			28.2	$\text{CH}_2\text{CH}_2$ dppe
$^{31}\text{P}$	46.3	$\text{P}_\text{A}$ , $^2J_{\text{PP}} = 39.9$ Hz		
	49.0	$\text{P}_\text{B}$ , $^2J_{\text{PP}} = 39.9$ Hz		
	–143.2	$\text{PF}_6^-$ , $^2J_{\text{FP}} = 710$ Hz		
$^{19}\text{F}$	–73.7	$\text{PF}_6^-$ , $^1J_{\text{PF}} = 710$ Hz		

<sup>a</sup>  $^1\text{H}$  (700 and 500 MHz),  $^{13}\text{C}$  (125 MHz),  $^{31}\text{P}$  (202 MHz), and  $^{19}\text{F}$  (376 MHz) NMR spectra were recorded in  $\text{CD}_2\text{Cl}_2$  at 299 K.

$\delta$  46.3 and 49.0, as well as the two terminal allyl  $^{13}\text{C}$  chemical shifts,  $\delta$  86.6 and 89.6, are rather similar (see Table 1), suggesting that there is little imbalance in the bonding of the allyl group to the palladium atom. Detailed NMR data for **3d** are given in Table 2.

**Diffusion Data.** PGSE diffusion data for the four salts **3** are shown in Table 3. In the following discussion, we will refer to a hydrodynamic radius,  $r_\text{H}$ , which we derive from the Stokes–Einstein relation (eq 3). Use of

$$D = (kT)/(6\eta\pi r_\text{H}) \quad (3)$$

$k$  = Boltzmann constant,  $T$  = temperature,  $\eta$  = viscosity of the solvent

the  $r_\text{H}$  value allows one to circumvent the effect of viscosity on the  $D$  values, while introducing a more readily understood structural aspect.

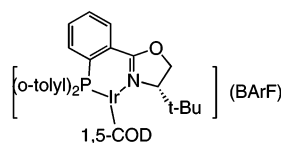
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**Table 3.** <sup>1</sup>H (Cations) and <sup>19</sup>F (Anions) Diffusion Results<sup>a</sup> for the Pd–Allyl Complexes

Salt		CD <sub>2</sub> Cl <sub>2</sub>		CDCl <sub>3</sub>	
		D <sup>a</sup>	r <sub>H</sub> <sup>b</sup>	D <sup>a</sup>	r <sub>H</sub> <sup>b</sup>
<b>3a</b> , BF <sub>4</sub>	Cations	9.51	5.6		
	Anion	12.99	4.1		
<b>3b</b> , CF <sub>3</sub> SO <sub>3</sub>	Cation	9.35	5.7	6.99	5.9
	Anion	11.14	4.8	6.99	5.9
<b>3c</b> , BArF	Cations	9.51	5.6	5.43	7.5
	Anion ( <sup>1</sup> H)	8.51	6.2	5.59	7.3
	Anion ( <sup>19</sup> F <sup>d</sup> )	8.67	6.1		
<b>3d</b> , PF <sub>6</sub>	Cations	9.36	5.7		
	Anion	13.38	4.0		

**4a** Anion = CF<sub>3</sub>SO<sub>3</sub>**4b** Anion = BArF both in CDCl<sub>3</sub>

	D <sup>a</sup>	r <sub>H</sub> <sup>b</sup>	D <sup>a</sup>	r <sub>H</sub> <sup>b</sup>
Cation	7.04	5.9	5.70	7.3
Anion	7.05	5.9	( <sup>1</sup> H) 5.63 ( <sup>19</sup> F) 5.59	7.4

<sup>a</sup> 10<sup>-10</sup> m<sup>2</sup> s<sup>-1</sup> 2 mM solutions. Estimated using the diffusion coefficient of HDO in D<sub>2</sub>O as reference. *D* values are ±2%. <sup>b</sup> Viscosity,  $\eta$  (299 K) for CH<sub>2</sub>Cl<sub>2</sub>: 0.414 kg s<sup>-1</sup> m<sup>-1</sup>.

On the basis of earlier measurements,<sup>29</sup> one now expects almost identical *D* values for the cation and anion in CDCl<sub>3</sub> solutions: i.e., >90% ion pairing. Indeed, in this solvent, the anion and cation of **3b** are moving at about the same rate, on the basis of their respective *D* values (see Figure 2), suggesting that a tight ion pair represents the correct description for these CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> and BArF<sup>-</sup> salts. The BArF ion pair is, as expected, considerably larger, on the basis of its *r*<sub>H</sub> value. For comparison we show related data for the salts **4a,b** in the same

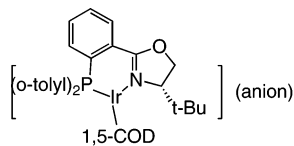
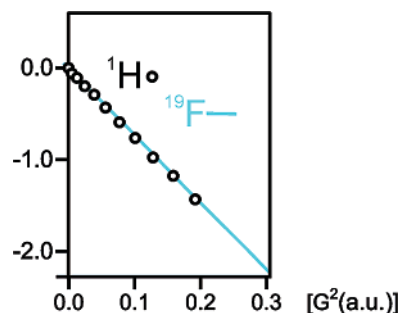
**4a** Anion = CF<sub>3</sub>SO<sub>3</sub>    **4b** Anion = BArF

table and note that, perhaps by coincidence, the two salts have almost the same *D* and *r*<sub>H</sub> values for these

**Figure 2.** Diffusion data for the chloroform solution of **3b**, showing identical slopes for the cation and anion.

two anions. Interestingly, there are five phenyl rings in **3** and five “rings” in **4** and, as we have shown,<sup>22e</sup> the presence of such rings strongly affects translation. In any case, the *r*<sub>H</sub> values provide an estimation of the size of these salts in CDCl<sub>3</sub>.

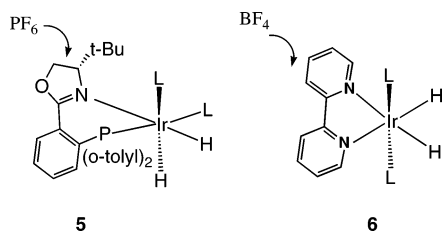
In dichloromethane solution, the anions and cations of **3** are moving at very different rates, on the basis of their respective *D* values; consequently, the ion pairing is not 100%. However, the *D* (and *r*<sub>H</sub>) values for the anions suggest substantial partial ion pairing for the

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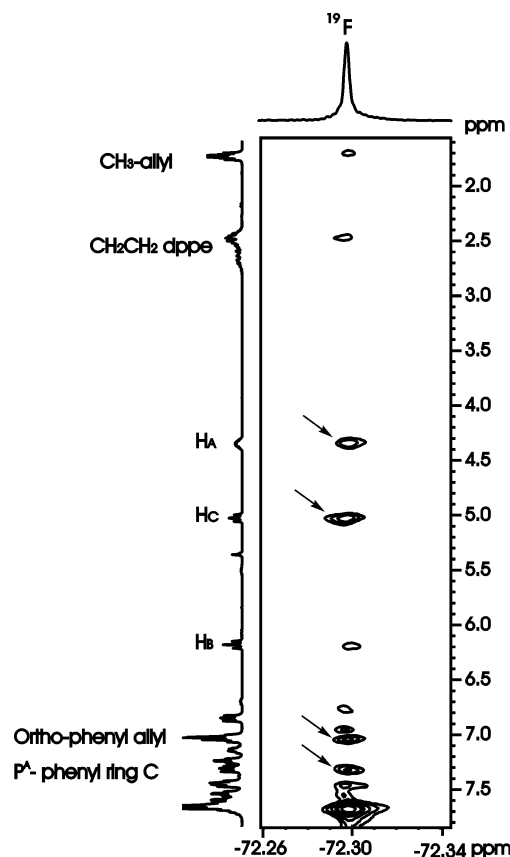
three anions  $\text{BF}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ , and  $\text{PF}_6^-$  but little or no ion pairing for the  $\text{BARf}^-$  anion. Reasonable estimates for the  $r_{\text{H}}$  values of the solvated anions in methanol solution are 2.5–2.8 Å for  $\text{BF}_4^-$  and  $\text{PF}_6^-$  and 3.0–3.3 Å for  $\text{CF}_3\text{SO}_3^-$ ; i.e., much smaller than the values observed for **3** in dichloromethane solution. For  $\text{BARf}^-$  in methanol, 5.8–6.1 Å represents a reasonable range. Therefore, an observed value of 4.8 Å for the triflate of **3b** indicates substantial ion pairing. This  $r_{\text{H}}$  value for the  $\text{CF}_3\text{SO}_3^-$  anion of 4.8 Å is somewhat large: e.g., for **4a** the analogous value in dichloromethane is 4.3 Å.<sup>30</sup> The translation of the cation is not strongly affected by the anion, and an  $r_{\text{H}}$  value of ca. 5.6 Å seems a reasonable estimate for this solvated ion.

**Overhauser Data.** Using  $^{19}\text{F}$ , $^1\text{H}$  HOESY<sup>31,32</sup> or NOESY methods, several groups have reported that external anions tend to take up positions remote from the coordinated anionic ligands. For example, in the oxazoline<sup>33</sup> and bipyridine<sup>34</sup> Ir(III) hydride cationic complexes containing fairly large ligands, L, the external anion avoids the relatively small hydride and chooses to approach the metal via the oxazoline, as in **5**, or via the bipy, as in **6**. Moreover, there are additional

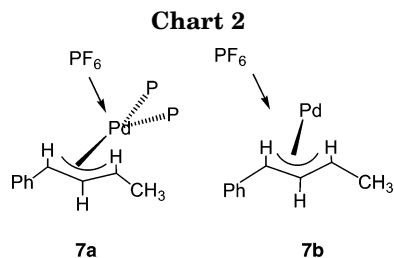


reports which suggest that the anion makes only a selective approach toward the cation, i.e., the anion does not move freely around the periphery of the cation. Consequently, it was of interest to see how the  $\text{CF}_3\text{SO}_3^-$  and  $\text{PF}_6^-$  anions behaved in **3**.

A section of the 2-D HOESY spectrum for **3d** in dichloromethane solution is shown in Figure 3. There are a number of medium-to-strong contacts involving the allyl protons, and these arise primarily from the two terminal allyl protons and the two ortho phenyl allyl resonances (see arrows). One finds a weak cross-peak from the central allyl proton, a weak interaction to the  $\text{CH}_2\text{--CH}_2$  backbone, and another weak contact to the methyl group. Of the two terminal allyl protons, that closest to the phenyl reveals the strongest interaction. The strongest contact in the spectrum arises from a series of overlapping phenyl protons at ca. 7.7 ppm. From the diffusion data, we know that there is incom-



**Figure 3.**  $^{19}\text{F}$ , $^1\text{H}$  HOESY for **3d**, showing a relatively large number of selective contacts from the anion to the cation (10 mM,  $\text{CD}_2\text{Cl}_2$ ). Only half of the  $^{19}\text{F}$  doublet is shown.



plete ion pairing, so that the strongest cross-peak could arise from the anion floating around the periphery of the phenyl array. This would explain the weak interactions with the ethylene backbone and the allyl methyl group. However, the selectivity observed with respect to the terminal allyl protons suggests (a) a steric preference in which the anion approaches the allyl ligand preferentially from the side containing the two terminal allyl protons (see **7a** in Chart 2) (and not the two syn allyl substituents) and (b) that the approach seems to favor the phenyl—rather than the methyl—side of the allyl anion (see **7b** in Chart 2). The pathway moves the anion toward the Pd atom, as we shall show on the basis of the DFT results.

The same pattern of cross-peaks is observed in the 2-D HOESY of the triflate analogue **3b** in dichloromethane solution, although the intensities are significantly weaker, since the triflate  $\text{CF}_3$  group is slightly more remote from the cation. We show in Figure 4 the HOESY spectrum for the triflate salt **3b** in  $\text{CDCl}_3$ , a solvent which affords 100% ion pairing (see Table 3). Although this solvent is not routinely used in allylic alkylation chemistry, it was of interest to seek possible

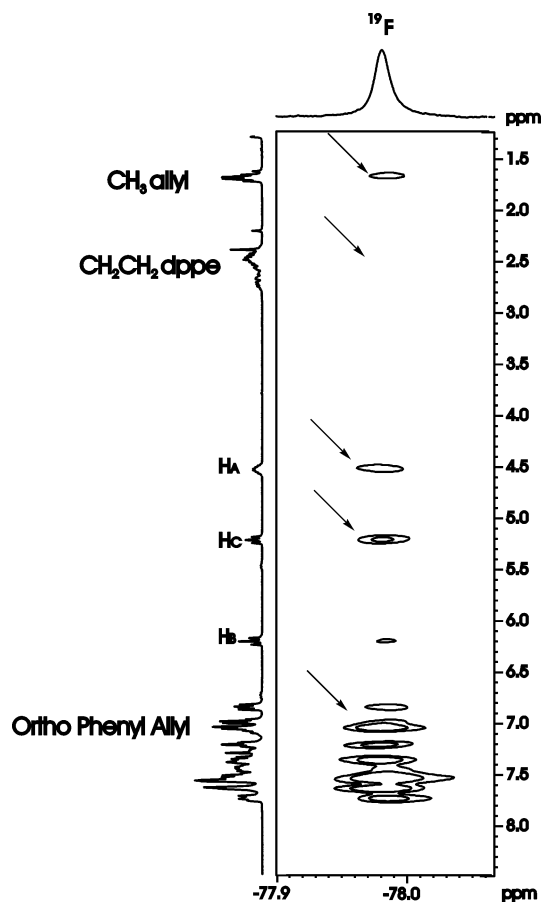
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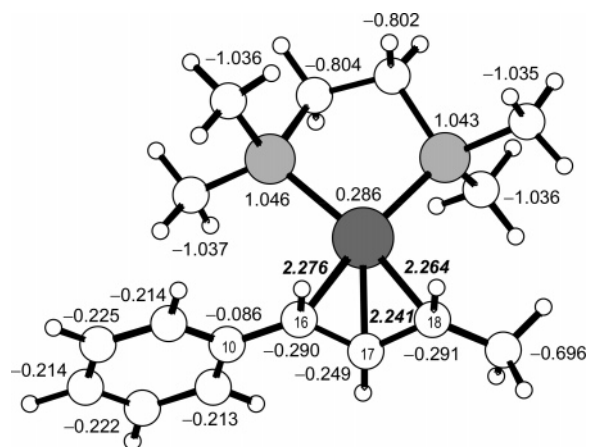


**Figure 4.**  $^{19}\text{F}$ ,  $^1\text{H}$  HOESY for **3b** (10 mM in  $\text{CDCl}_3$ ), showing a larger number of stronger (relative to **3d**) selective contacts from the triflate anion to the allyl cation.

changes in the relative position of the anion. The spectrum clearly shows that (a) there are more cross-peaks than for **3b** in dichloromethane, but about the same number as in Figure 3, for the  $\text{PF}_6^-$  in dichloromethane, (b) the allyl selectivity, in terms of the relative intensities, is still present, i.e., the cross-peaks to the two terminal allyl protons are more intense, and (c) there are now no interactions with the  $\text{CH}_2\text{CH}_2$  phosphine moiety. We conclude that the increased ion pairing in  $\text{CDCl}_3$  has compensated for the more remote triflate  $\text{CF}_3$  group but that little else has changed.

**DFT Results.** DFT studies on allyl complexes have proven to be informative in describing asymmetric allyl bonding of the  $\eta^3$ -PhCHCHCH<sub>2</sub> anionic ligand in Cp complexes of ruthenium.<sup>35</sup> Consequently, we have carried out DFT/B3LYP calculations<sup>36</sup> on the model cationic complex  $[\text{Pd}(\eta^3\text{-PhCHCHCHCH}_3)](\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)^+$ , which contains methyl, rather than phenyl, substituents on the phosphine. The optimized geometry is represented in Figure 5 and corresponds to a typical<sup>37</sup> Pd(II) square-planar complex.

The calculated Pd–C(allyl) separations (see Figure 5) do not suggest significant distortion and thus are in



**Figure 5.** Optimized geometry of the cation  $[\text{Pd}(\eta^3\text{-PhCHCHCHCH}_3)](\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)^+$  with the calculated NPA charges indicated for the heavy atoms. The Pd–C(allyl) bond distances (Å) are represented in bold and italics. The Pd (dark gray) and the P atoms (light gray) are shaded.

agreement with the observed  $^{13}\text{C}$  data from the terminal allyl carbons. Also, the two Pd–C bonds stemming from the two terminal allyl carbon atoms are equivalent from the electronic point of view, as shown by the corresponding Wiberg indices:<sup>38</sup> 0.28 for Pd–C16 and 0.30 for Pd–C18.

The atomic charges, calculated by means of natural population analysis (NPA),<sup>39</sup> are also shown in Figure 5, along with a numbering scheme, for the relevant atoms. The charges on the terminal allyl carbons,  $-0.290$  for C16 and  $-0.291$  for C18, do not differ much; however, the negative charge for the phenyl ipso carbon,  $-0.086$  for C10, is much smaller than that found on the allyl methyl carbon,  $-0.696$  for C19. Still, one should not overlook the fact that the P atoms carry a great deal of the positive charge (ca.  $+1.04$  for each atom). Consequently, it would seem that the approach of the anion via a pathway closer to the allyl phenyl ring arises from electronic and not steric considerations and involves the differing allyl substituents rather than the allyl carbons themselves. The anions are not attracted to the allyl ligand but rather are choosing both an electronically (allyl phenyl vs allyl methyl) and sterically (terminal allyl protons vs. central allyl proton) preferred pathway toward the P and metal atoms.

**Comment.** These results suggest that the anions associated with the relatively simple  $\eta^3$ -CH<sub>3</sub>CHCHCHPh palladium cation do indeed partially occupy a preferred position. The anion approaches via a pseudo-fifth coord-

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dination position but chooses to come from the direction associated with the two terminal allyl hydrogen atoms, rather than approach the allyl via the central allyl proton. There is no evidence that the anion is positioned behind the plane of the allyl, remote from the palladium, in an area where a nucleophile might possibly approach a coordinated allyl ligand. Of course, the preparation and subsequent study of **3** allows ample time for equilibration of the various positions occupied by the anion(s). In a catalytic allylic alkylation reaction, it is possible that the leaving group, as the anion, does not migrate far before the nucleophile, Nu<sup>-</sup>, which is present in large excess, attacks the allyl. Consequently, one cannot extrapolate our results to catalysis. Nevertheless, the combined PGSE, NOE, DFT approach provides a fairly clear qualitative picture of how the ions interact in these palladium salts.

## Experimental Section

**General Procedure (NMR).** <sup>1</sup>H, <sup>31</sup>P, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were recorded on Bruker Avance 250, 300, 400, 500, and 700 NMR spectrometers. Chemical shifts are quoted in parts per million (ppm) downfield of TMS. Deuterated solvents were dried by distillation over molecular sieves and stored in the presence of molecular sieves under N<sub>2</sub>.

**Diffusion.** All the measurements were performed on a Bruker Avance spectrometer, 400 MHz, equipped with a microprocessor-controlled gradient unit and a multinuclear inverse probe with an actively shielded Z-gradient coil. In general, the gradient shape is rectangular and its length was 1.75 ms. Its strength was increased by steps of 4% during the course of the experiment. The time between midpoints of the gradients was 167.75 ms for all experiments. The experiments were carried out at a set temperature of 299 K within the NMR probe. However, these parameters were altered for the <sup>1</sup>H diffusion measurement of the BARF compound in CD<sub>2</sub>Cl<sub>2</sub>, where the gradient shape length was set to 2.00 ms and the time between midpoints of the gradients was 68 ms.

As indicated in Table 3, the diffusion values were measured using 2 mM CDCl<sub>3</sub> and CD<sub>2</sub>Cl<sub>2</sub> solutions. Cation diffusion rates were measured using the <sup>1</sup>H signal from the ortho proton of the aromatic, whereas the anion *D* values were obtained from the <sup>19</sup>F and <sup>1</sup>H resonances (where available) of the boron substituent. The error coefficient for the *D* values is ±0.06.

**HOESY.** <sup>19</sup>F, <sup>1</sup>H HOESY spectra were measured using 10 mM solutions in CD<sub>2</sub>Cl<sub>2</sub>, at 299 K with mixing times of 0.8 s.

**Computational Details.** The calculations were performed using the Gaussian 98 software package<sup>40</sup> and the B3LYP hybrid functional. This functional includes a mixture of Hartree–Fock<sup>41</sup> exchange with DFT<sup>36a</sup> exchange correlation, given by Becke's three-parameter functional<sup>36b</sup> with the Lee, Yang, and Parr correlation functional, which includes both local and nonlocal terms.<sup>36c,d</sup> The LanL2DZ basis set<sup>42</sup> augmented with an f-polarization function<sup>43</sup> was used for the Pd

atom, and the same basis set augmented with a d-polarization function<sup>44</sup> was used for the P atom; the remaining elements were described by a standard 4-31G(d)<sup>45</sup> basis set. The optimization was performed without symmetry constraints. A natural population analysis (NPA)<sup>39</sup> and the resulting Wiberg indices<sup>38</sup> were used to study the electronic structure and bonding of the optimized species.

**[Pd( $\eta^3$ -Me(CH)<sub>3</sub>Ph)(dppe)][PF<sub>6</sub>].** To 1 equiv of [Pd( $\mu$ -Cl)-( $\eta^3$ -Me(CH)<sub>3</sub>Ph)]<sub>2</sub> (64 mg, 545.8 g mol<sup>-1</sup>, 1.18 × 10<sup>-4</sup> mol) was added 2 equiv of the AgPF<sub>6</sub> salt (59.1 mg, 252 g mol<sup>-1</sup>, 2.35 × 10<sup>-4</sup> mol). The mixture of solids was placed under vacuum and purged with nitrogen three times. Then 2–4 mL of acetone was added, and the yellow mixture was stirred under nitrogen for ca. 2 h. After this time, the dark yellow solution was filtered through Celite and 2 equiv of dppe in CH<sub>2</sub>Cl<sub>2</sub> (94 mg, 398 g mol<sup>-1</sup>, 2.36 × 10<sup>-4</sup> mol) added to the filtrate (still under nitrogen). The solution was then stirred for 1 h. The yellow solution that resulted was filtered over Celite and the solid rinsed with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed under vacuum to yield a bright yellow solid. Yield: 144 mg, 1.85 × 10<sup>-4</sup> mol, 78.7%. MS (ESI; *m/z*): M<sup>+</sup> 634.9, M – allyl<sup>+</sup> 504.9.

**[Pd( $\eta^3$ -Me(CH)<sub>3</sub>Ph)(dppe)][CF<sub>3</sub>SO<sub>3</sub>].** To 1 equiv of [Pd( $\mu$ -Cl)-( $\eta^3$ -Me(CH)<sub>3</sub>Ph)]<sub>2</sub> (60 mg, 545.8 g mol<sup>-1</sup>, 1.1 × 10<sup>-4</sup> mol) was added 2 equiv of the AgCF<sub>3</sub>SO<sub>3</sub> salt (58 mg, 256.9 g mol<sup>-1</sup>, 2.3 × 10<sup>-4</sup> mol). Both solids were placed under vacuum and purged with nitrogen three times. Then, 2–4 mL of acetone was added, and the yellow mixture was stirred under nitrogen for ca. 2 h. After this time, the yellow solution was filtered through Celite and 2 equiv of dppe in CH<sub>2</sub>Cl<sub>2</sub> (94 mg, 398 g mol<sup>-1</sup>, 2.36 × 10<sup>-4</sup> mol) was added to the filtrate (still under nitrogen). The solution was then stirred for 2 h. The resulting pale yellow solution was filtered over Celite and the filtrate rinsed with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed under vacuum to yield a pale yellow solid. Yield: 128 mg, 1.63 × 10<sup>-4</sup> mol, 74.1%. MS (MALDI; *m/z*): M<sup>+</sup> 635, M – allyl<sup>+</sup> 505, M<sup>-</sup> 149. Anal. Calcd: C, 56.6; H, 4.49. Found: C, 55.9; H, 4.54.

**[Pd( $\eta^3$ -Me(CH)<sub>3</sub>Ph)(dppe)][BF<sub>4</sub>].** To 1 equiv of [Pd( $\mu$ -Cl)-( $\eta^3$ -Me(CH)<sub>3</sub>Ph)]<sub>2</sub> (32 mg, 545.8 g mol<sup>-1</sup>, 5.86 × 10<sup>-5</sup> mol) was added 2 equiv of the AgBF<sub>4</sub> salt (23 mg, 195 g mol<sup>-1</sup>, 1.17 × 10<sup>-4</sup> mol). Both solids were evacuated under vacuum and purged with nitrogen three times. Then, 2 mL of acetone was added, and the yellow mixture was stirred under nitrogen for about 1 h. After this time, the yellow solution was filtered through Celite and 2 equiv of dppe (94 mg, 398 g mol<sup>-1</sup>, 2.35 × 10<sup>-4</sup> mol) was added to the filtrate (still under nitrogen). The solution was then stirred for another 1 h. The resulting solution was filtered through Celite and the filtrate rinsed with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed under vacuum to yield a pale yellow solid. Yield: 38.7 mg, 5.36 × 10<sup>-5</sup> mol, 45.7%.

**[Pd( $\eta^3$ -Me(CH)<sub>3</sub>Ph)(dppe)][BARF].** To 1 equiv of [Pd( $\mu$ -Cl)-( $\eta^3$ -Me(CH)<sub>3</sub>Ph)]<sub>2</sub> (30 mg, 545.8 g mol<sup>-1</sup>, 5.5 × 10<sup>-5</sup> mol) was added 2 equiv of the NaBARF salt (59 mg, 534.99 g mol<sup>-1</sup>, 1.1 × 10<sup>-4</sup> mol). Both solids were evacuated under vacuum and purged with nitrogen three times. Then, 4 mL of acetone was added, and the yellow mixture was stirred under nitrogen for about 1 h. After this time, the dark yellow solution was filtered over Celite and 2 equiv of dppe (44 mg, 398 g mol<sup>-1</sup>, 1.1 × 10<sup>-4</sup> mol) was added to the filtrate (still under nitrogen). Then

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the solution was stirred for another 1 h. The resulting yellow solution was filtered through Celite and the filtrate rinsed with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed under vacuum to yield a dark yellow solid. Yield: 149 mg,  $1.0 \times 10^{-4}$  mol, 90.4%. MS (*m/z*): M<sup>+</sup> 635, M – allyl<sup>+</sup> 505, M<sup>-</sup> 863.

The palladium salts were stored under nitrogen in the refrigerator.

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lyzed Reactions” is kindly acknowledged. P.S.P. also thanks the Swiss National Science Foundation and the ETH Zurich for support and the Johnson Matthey Co. for the loan of metal salts.

**Supporting Information Available:** Atomic coordinates for the optimized structure of [Pd( $\eta^3$ -PhCHCHCH<sub>3</sub>)-(Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>)]<sup>+</sup>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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