# **ORGANOMETALLICS**

# How Does Palladium Coordination Affect the Electrophilicities of Allyl Cations? Development of a Robust Kinetic Method for Following Reactions of $[(\eta^3-\text{Diarylallyl})\text{Pd}(\text{PPh}_3)_2]^+$ with Nucleophiles

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**Supporting Information** 

**ABSTRACT:** Kinetics of the reactions of  $[(\eta^3-1,3-\text{diarylallyl})-\text{Pd}(\text{PPh}_3)_2]^+$  complexes with carbanions, enamines, amines, and triphenylphosphine have been investigated photometrically in dichloromethane, DMSO, and acetonitrile solutions at 20 °C. Amines were found to react both at palladium (substitution of PPh<sub>3</sub>) and at the allyl ligands, causing complex and poorly reproducible kinetics. Excellent reproducibility of the second-order rate constants for the attack at the allyl ligand was achieved when the reactions were studied in the presence of traces of PPh<sub>3</sub> and fumaronitrile. The second-order rate



constants ( $k_2$ ) for the attack of nucleophiles at the allyl ligands were found to follow the correlation log  $k_2 = s_N(N + E)$ , where  $s_N$  and N are solvent-dependent nucleophile-specific parameters and E is an electrophilicity parameter (J. Am. Chem. Soc. **2001**, 123, 9500–9512). While the electrophilicities of the free 1,3-bis(3,5-difluorophenyl)allyl (E = 6.11) and the 1,3-bis(4-dimethylaminophenyl)allyl cations (E = -7.50) differ by more than 13 orders of magnitude, the electrophilicities of the corresponding Pd(PPh\_3)<sub>2</sub> complexes were found to be almost independent of the nature of the substituents ( $E \approx -14$ ), showing that Pd(PPh\_3)<sub>2</sub> coordination reduces the electrophilic reactivities of allyl cations by 7–20 orders of magnitude.

# INTRODUCTION

The Tsuji–Trost reaction, which often proceeds under mild conditions with high regio- and stereoselectivity, is a powerful synthetic tool for asymmetric allylations of various types of nucleophiles.<sup>1</sup> These reactions have been demonstrated to proceed generally via the cationic ( $\eta^3$ -allyl)palladium complexes (1) (Scheme 1). In certain cases, for example, in the presence

Scheme 1. Typical Catalytic Cycle for Tsuji–Trost Allylations



of chloride ions, neutral ( $\eta^1$ -allyl)palladium species have also been characterized as reactive intermediates.<sup>2</sup>

Detailed mechanistic studies on the influence of leaving groups, ligands, and solvents on the formation of the allylpalladium species have been reported.<sup>3</sup> Investigations of the reactions of isolated ( $\eta^3$ -allyl)palladium complexes 1 with nucleophiles have shown that the reaction mechanism strongly depends on the nature of the ligands. Jutand et al. reported the reactions of  $[(\eta^3 - CH_2 CHCH_2)Pd(PAr_3)_2]^+$  (Ar = 4-ClC<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>)<sup>4</sup> and  $[(\eta^3$ -PhCHCHCHPh)PdL<sub>2</sub>]<sup>+</sup> (L = PPh<sub>3</sub> or  $L_2 = dppb)^5$  with morpholine and piperidine to proceed via selective attack of the amines at the allyl ligands, in agreement with earlier work by Kuhn and Mayr.<sup>6</sup> On the other hand, Crociani et al.<sup>7</sup> and Canovese et al.<sup>8</sup> observed that nucleophilic attack at the allyl ligand may be accompanied by reversible coordination of the amines to the metal center. Thus, the formation of pentacoordinated palladium species was found when iminophosphine ligands were employed,<sup>7</sup> while terdentate (S-N-S), (N-S-N), and (N-N-N) ligands and  $\alpha$ -diimines were reversibly replaced by amines.<sup>8</sup>

In recent work<sup>9</sup> we have studied the kinetics of the reactions of noncoordinated 1,3-diarylallyl cations with nucleophiles and reported that the second-order rate constants can be described by the linear free energy relationship (eq 1), where E is an

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electrophilicity parameter, N is a nucleophilicity parameter, and  $s_N$  is a nucleophile-specific sensitivity parameter (previously termed s).<sup>10</sup> As shown in Chart 1, their electrophilic reactivities differ by

Chart 1. Cationic Palladium Complexes 1(a-c) and the Corresponding Free 1,3-Diarylallyl Cations 5(a-c) with Their Electrophilicity Parameters E (from ref 9)



more than 13 orders of magnitude, corresponding to relative reaction times of 1 s vs  $10^5$  to  $10^6$  years.

$$\log k_2(20 \,^{\circ}\mathrm{C}) = s_{\mathrm{N}}(N+E) \tag{1}$$

We have now investigated the kinetics of the reactions of the corresponding  $[(\eta^3-(1,3-\text{diarylallyl})\text{Pd}(\text{PPh}_3)_2]^+$  complexes  $1(\mathbf{a}-\mathbf{c})$  (Chart 1) with a variety of nucleophiles (Table 1) in

Table 1. Nucleophiles 2(a-i) and Their Reactivity Parameters N and  $s_N$  in Different Solvents

		Nucleophiles	Solvent	$N^a$	$s_N^a$	
	2a		$CH_2Cl_2$	13.41	0.82	
	2b		$CH_2Cl_2$	15.06	0.82	
	2c		$CH_2Cl_2$	14.91	0.86	
	2d	$\sim \sim$	DMSO	13.91	0.86	
	2e	PPh <sub>3</sub>	$CH_2Cl_2$	14.33	0.65	
	2f		DMSO	15.47	0.65	
2 2	2g	Ph NH <sub>2</sub>	CH <sub>3</sub> CN	14.29	0.67	
	2h	0NH	CH₃CN	15.65	0.74	
	2i	NH	CH <sub>3</sub> CN	17.35	0.68	
<sup>a</sup> Reactivity parameters from ref 12.						

order to elucidate how Pd(PPh<sub>3</sub>)<sub>2</sub> coordination affects the electrophilic reactivities of 1,3-diarylallyl cations. While products of the reactions of  $(\eta^3$ -allyl)palladium complexes with most of these nucleophiles have previously been reported,<sup>11</sup> there have been only a few kinetic investigations.

# RESULTS AND DISCUSSION

Synthesis of the Complexes 1(a-c). The cationic Pd complexes 1a and 1b were synthesized and isolated as tetra-fluoroborate salts (1a-BF<sub>4</sub> and 1b-BF<sub>4</sub>) by treatment of the corresponding dimeric allylpalladium chlorides (5(a,b)-PdCl) with PPh<sub>3</sub> and NaBF<sub>4</sub>, as described in ref 13. The triflate 1b-OTf was obtained analogously by using NaOTf instead of NaBF<sub>4</sub> and

characterized by X-ray diffraction analysis (details, see below). Compound 1c-BF<sub>4</sub> was synthesized by the reaction of (*E*)-1, 3-bis(4-dimethylaminophenyl)allylium tetrafluoroborate (5c-BF<sub>4</sub>) with Pd(PPh<sub>3</sub>)<sub>4</sub> in dichloromethane at ambient temperature.

**Kinetic Investigations.** All kinetic measurements were performed under pseudo-first-order conditions using the nucleophiles in high excess; the reaction progress was monitored UV– vis spectroscopically at the absorbance maxima of the allyl complexes  $1(\mathbf{a}-\mathbf{c})$ . Freshly prepared solutions of electrophiles were generally required to obtain reproducible results.

Reactions with C-Nucleophiles. Even when the enamines 2a and 2b and the potassium salt of Meldrum's acid (2d) were used in high excess (10-100 equiv) over the Pd complex 1a-BF4 in order to achieve pseudo-first-order kinetics, deviations from the monoexponential decay of the absorbance at 360 nm (absorption maximum of 1a) were often observed. These deviations were explained by the UV absorptions of the  $\eta^2$ -Pd complexes 3 (Scheme 1) and their decomposition products. As fumaronitrile is a weak nucleophile, which does not react with 1a and has previously been shown to strongly coordinate to PdL<sub>2</sub>,<sup>14</sup> the kinetics of the reactions of 1a-BF<sub>4</sub> with nucleophiles were investigated in the presence of fumaronitrile. Under these conditions, the decays of the absorbances at 360 nm were generally monoexponential, when 1a-BF<sub>4</sub> was combined with more than 10 equiv of various nucleophiles, because the released Pd fragments form stable complexes with fumaronitrile, which do not significantly absorb at 360 nm. The pseudofirst-order rate constants  $(k_{obs})$ , which were obtained by least-squares fitting to the function  $A_t = A_0 e^{-k_{obs}t} + C$  (Figure 1a),



**Figure 1.** (a) Exponential decay of the absorbance  $A_t$  ( $\lambda = 360$  nm) and (b) linear correlation between the pseudo-first-order rate constants  $k_{obs}$  and the nucleophile concentration for the reaction between the enamine **2b** and **1a**-BF<sub>4</sub> ((6.2–6.3) × 10<sup>-5</sup> M) in the presence of fumaronitrile ((5.7–5.8) × 10<sup>-4</sup> M) in dichloromethane at 20 °C.

were found to be independent of the concentration of fumaronitrile. As shown in Figure 1b for the reaction of 1a-BF<sub>4</sub> with the enamine **2b**, plots of the pseudo-first-order rate constants vs the concentrations of the nucleophiles were linear with the second-order rate constants ( $k_2$ ) as slopes.

**Reactions with Triphenylphosphine.** The reaction of triphenylphosphine (2e) with 1a-BF<sub>4</sub> in CH<sub>3</sub>CN yielded a 2:1 mixture of (*E*)-(1,3-diphenylallyl)triphenylphosphonium tetrafluoroborate (6) and (*Z*)-(1,3-diphenylprop-1-en-1-yl)-triphenylphosphonium tetrafluoroborate (6') in an overall yield of 54% (Scheme 2).





As an independently synthesized sample of the allylphosphonium salt **6** was observed to isomerize to a 4:1 mixture<sup>15</sup> of **6** and **6'** in the presence of 4 mol % of  $Pd(PPh_3)_4$  in acetonitrile at rt, we assume that the reaction of 1a-BF<sub>4</sub> with PPh<sub>3</sub> proceeds via nucleophilic attack of triphenylphosphine at the allyl ligand to yield **6**, which subsequently undergoes a partial Pd-catalyzed isomerization with formation of a mixture of **6** and **6'**.

The decay of the 360 nm absorbance during the reactions of 1a-BF<sub>4</sub> with PPh<sub>3</sub> in dichloromethane, acetonitrile, and DMSO was found to be monoexponential, and the linear  $k_{obs}$  vs [PPh<sub>3</sub>] plots yielded the second-order rate constants  $k_2^{PPh_3}(CH_2Cl_2) = 0.366 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_2^{PPh_3}(CH_3CN) = 0.695 \text{ M}^{-1} \text{ s}^{-1}$ , and  $k_2^{PPh_3}(DMSO) = 0.232 \text{ M}^{-1} \text{ s}^{-1}$  at 20 °C (for details see the Supporting Information).

**Reactions with Amines.** Even when fumaronitrile was present, the reactions of the allylpalladium complex 1a-BF<sub>4</sub> with excess amines often did not follow a first-order rate law. As shown for the reaction of 1a-BF<sub>4</sub> with benzylamine (2g) in Figure 2a, up to



**Figure 2.** Complex behavior of a mixture of the allylpalladium complex **1a**-BF<sub>4</sub> and benzylamine (**2g**) in acetonitrile at 20 °C. (a) Typical decay of the absorbance at  $\lambda = 360$  nm ([**1a**-BF<sub>4</sub>] =  $1.0 \times 10^{-4}$  M, [**2g**] =  $1.5 \times 10^{-2}$  M, black line).  $k_{obs}$  values were achieved by fitting the slow parts of the absorbance decays to the monoexponential function  $A_t = A_0 e^{-k_{obs}t} + C$  (red dashed line, the fit range is shown in bold). (b) Dependence of  $k_{obs}$  on the amine concentration.

40% of the absorbance at 360 nm decayed by a very fast process, which was followed by a slower secondary reaction; the decay due to the first process increased with increasing concentration of the amine. Fitting the decays for the secondary reactions to the exponential function  $A_t = A_0 e^{-k_{obs}t} + C$  yielded the  $k_{obs}$  values, which are plotted against the amine concentrations (Figure 2b). Though the  $k_{obs}$  values are poorly reproducible, it is obvious that at low concentrations of amines these values increase with increasing amine concentrations, but do not exceed  $7 \times 10^{-3} s^{-1}$  even at high concentrations of amines, indicating changes in the reaction mechanism.

A rationalization for these observations can be derived from the UV spectra described in Figure 3. When a solution of 1a-BF<sub>4</sub> in



Figure 3. UV-vis evidence for the reversible ligand exchange in the reaction of 1a-BF<sub>4</sub> with benzylamine (2g).

acetonitrile (black dotted curve) is combined with an excess of benzylamine (**2g**), an immediate change of the UV–vis spectrum is observed (red dashed curve). Addition of trifluoroacetic acid immediately after recording the red curve restored the initial absorption spectrum (blue curve, slightly lower than the initial black curve because of dilution), which remained stable at room temperature.

We, therefore, assume that at high concentrations of amines a rapid reversible exchange of  $Ph_3P$  by amines yields the complex 1a'-BF<sub>4</sub>, which reverts to 1a-BF<sub>4</sub> when treated with CF<sub>3</sub>COOH (Scheme 3). An analogous ligand exchange has previously been

Scheme 3. Reversible Exchange of PPh<sub>3</sub> in 1a by Amines

Ph <sub>3</sub> R PPh <sub>3</sub>	RR'NH, -PPh <sub>3</sub>	Ph₃P NHRR' ⊕
Pd <sup>⊖</sup> BF₄ Ph Ph 1a-BF₄	CF <sub>3</sub> COOH, PPh <sub>3</sub> , -RR'NH <sub>2</sub> OCOCF <sub>3</sub>	Pd ⊖ <sub>BF₄</sub> Ph Ph 1a'-BF₄

reported by Canovese et al.<sup>8</sup> As the amine complexes 1a' can be assumed to be significantly less electrophilic than 1a,<sup>16</sup> the limitation of  $k_{obs}$  at high amine concentrations (Figure 2) can be explained.

Regeneration of 1a-BF<sub>4</sub> by addition of CF<sub>3</sub>COOH (as shown in Figure 3) occurred only when CF<sub>3</sub>COOH was added immediately after the formation of 1a'-BF<sub>4</sub>. Acidification 15 min after the addition of benzylamine did not restore the original spectrum (Supplementary Figure S4 of the Supporting Information), indicating the occurrence of an irreversible process, i.e., attack of the amine at the allyl ligand of 1a or 1a'.

The formation of 1a' by ligand exchange, as depicted in Scheme 3, has also been confirmed by a cation-mode ESI mass spectrum<sup>17</sup> of the reaction mixture recorded immediately after addition of benzylamine to the acetonitrile solution of 1a-BF<sub>4</sub> (Figure 4).

On the basis of these observations, the reactions of the  $[(\eta^3-\text{allyl})\text{Pd}(\text{PPh}_3)_2]^+$  complexes with amines can be described by the mechanism depicted in Scheme 4.

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**Figure 4.** Cation-mode ESI mass spectrum recorded immediately after addition of benzylamine (12 mM) to a 0.2 mM solution of **1a**-BF<sub>4</sub> in acetonitrile. Insets: comparison between experimental (black) and calculated (red) isotopic patterns for peaks at m/z = 668 and 823. R =  $(\eta^3$ -(1,3-diphenylallyl)).

Scheme 4. Mechanism for Amination of Allylpalladium Complexes



The amine attacks the palladium complex 1a either fast and reversibly at Pd to give 1a' or slowly and irreversibly at the allyl ligand to give 3a. As the attack of amines at the allyl ligand of 1a' is significantly slower than that at 1a, this reaction is neglected in Scheme 4. In the case of low amine concentrations, the complex 1a is the predominant species in the equilibrium  $1a \Rightarrow 1a'$ , and the overall reaction rate can be described by eq 2 (n = 1).

$$-\frac{\mathrm{d}[\mathbf{1a}]}{\mathrm{d}t} = k_2 [\mathbf{1a}] [\operatorname{amine}]^n \tag{2}$$

At high amine concentrations,  $[\mathbf{1a'}]$  becomes comparable to  $[\mathbf{1a}]$ , and because of the low reactivity of  $\mathbf{1a'}$ , the reaction order n in amine concentration is lowered to  $0 \le n \le 1$ . Apart from poor reproducibility, a further complication for evaluating kinetics under these conditions is the different absorption coefficients of  $\mathbf{1a}$  and  $\mathbf{1a'}$  at 360 nm. These problems stimulated us to search for a more efficient method of determining the rates of attack of amines at the allyl ligands of  $[(\eta^3 \text{-allyl})\text{Pd}(\text{PPh}_3)_2]^+$  complexes.

Four-Component-System for Determining the Rates of the Reactions of  $[(\eta^3-\text{allyl})\text{Pd}(\text{PPh}_3)_2]^+$  with Amines. The exchange of PPh<sub>3</sub> by N ligands upon combination of 1a with amines was recognized by the change of the UV spectrum of 1a (black dashed graph vs red graph in Figure 3). In line with the small value of the equilibrium constant  $K_E (\approx 4 \times 10^{-3},$ 

Scheme 4, pp S3, S4 of the Supporting Information), addition of a small amount of PPh<sub>3</sub> to a mixture of **1a** and **1a'** restored the original spectrum of **1a** (Supplementary Figure S5 of the Supporting Information). As a consequence, the presence of a small amount of PPh<sub>3</sub> in a mixture of **1a**, **1a'**, and amines shifts the **1a**  $\rightleftharpoons$  **1a'** equilibrium toward **1a**, and the nonexponential decay of the absorbance at 360 nm observed in the absence of PPh<sub>3</sub> (Figure 5a) is replaced by the monoexponential decay



Figure 5. Decays of the absorbances at 360 nm during the reactions of 1a-BF<sub>4</sub> with benzylamine 2g (7.5 ×  $10^{-2}$  M) in the presence of fumaronitrile (5.8 ×  $10^{-4}$  M): (a) without PPh<sub>3</sub>; (b) in the presence of 1.4 ×  $10^{-3}$  M PPh<sub>3</sub> (acetonitrile, 20 °C).

shown in Figure 5b. Analogous behavior was found for reactions of diethylamine with allylpalladium complexes containing diimine ligands.<sup>8b</sup>

As discussed above for enamines, all reactions were studied in the presence of fumaronitrile in order to coordinate Pd fragments that are released during these reactions (the whole reaction can then be described with Scheme 4, where L is fumaronitrile). Since the observed rate constants were found to be independent of the fumaronitrile concentration (Supplementary Figure S6 of the Supporting Information), one can conclude that fumaronitrile is not involved in the ratedetermining step.

As triphenylphosphine may also add to the allyl ligand of 1 (*vide supra* Reactions with Triphenylphosphine), the rate constants ( $k_{obs}$ ) measured for reactions of 1 with amines in the presence of PPh<sub>3</sub> are the sum of the rate constants for the reactions of 1 with amines and PPh<sub>3</sub> (eq 3).

$$k_{\rm obs} = k_{1\psi}^{\rm amine} + k_2^{\rm PPh_3}[\rm PPh_3] \tag{3}$$

As illustrated by the open symbols in Figure 6, the rate constants  $k_{obs}$  determined at a constant amine concentration increased with increasing [PPh<sub>3</sub>]. While the strong increase of  $k_{obs}$  in the left part of Figure 6 is due to the shift of the equilibrium  $\mathbf{1a} \rightleftharpoons \mathbf{1a}'$  toward the more electrophilic complex  $\mathbf{1a}$ ,



**Figure 6.** Plot of  $k_{obs}$  vs [PPh<sub>3</sub>] for the reaction between 1a (1.1 × 10<sup>-4</sup> M) and benzylamine 2g (7.52 × 10<sup>-2</sup> M) in the presence of fumaronitrile (5.82 × 10<sup>-4</sup> M) and variable concentrations of PPh<sub>3</sub> (acetonitrile, 20 °C).

the linear increase of  $k_{obs}$  in the right part of Figure 6 reflects the attack of PPh<sub>3</sub> at the allyl ligand of 1a, which was independently determined (see above and in the Supporting Information). As illustrated by the lower plot in Figure 6, subtraction of the contribution of phosphine from  $k_{obs}$  yields a plateau for [PPh<sub>3</sub>] > 1.5 mM, where  $k_{1uplateau}^{amine}$  reflects the attack of benzylamine at the allyl ligand of complex 1a.

The value of  $k_2^{\text{amine}}$  can therefore be derived from the slope of a plot of  $k_{1\psi\text{plateau}}^{\text{amine}}$  [amine] (Figure 7).



**Figure 7.** Correlation between the first-order rate constants for the decays of the absorbance at  $\lambda = 360$  nm (absorption maximum of 1a) during the reaction of 1a ((1.4–1.5) × 10<sup>-4</sup> M) with benzylamine (2g) in the absence (open symbols) and presence of PPh<sub>3</sub> (3.2 × 10<sup>-4</sup> to 5.75 × 10<sup>-3</sup> M, filled symbols) and the amine concentration (acetonitrile, 20 °C).

Figure 7 clearly shows that  $k_{1\psi plateau}^{\text{amine}}$  correlates linearly with the concentration of amines, also in the concentration range in which the poorly reproducible values of  $k_{obs}$  measured in the absence of PPh<sub>3</sub> do not increase with increasing [amine].

It is noteworthy that completely different batches of all components were used for the kinetic measurements shown in Figure 7, which indicates excellent reproducibility of the individual rate constants  $k_{1\psi\text{plateau}}^{\text{amine}}$  and contrasts the scatter of  $k_{\text{obs}}$  determined in the absence of PPh<sub>3</sub>. Obviously, side reactions, which have different weight with different batches of reagents and are responsible for the scatter of the rate constants determined in the absence of triphenylphosphine, can completely be suppressed using the four-component kinetic method. When PPh<sub>3</sub> was present, reproducible kinetic data could also be obtained with solutions of **1a**-BF<sub>4</sub> that have been stored for several hours. Decomposition of **1a**-BF<sub>4</sub>, which is

responsible for the poor reproducibility of the kinetic data obtained in the absence of triphenylphosphine, is indicated by the change of the UV–vis spectra of solutions of 1a-BF<sub>4</sub> in acetonitrile within a few hours. Addition of 3 equiv of triphenylphosphine to such aged solutions fully regenerates the original UV–vis spectrum of 1a and, therefore, makes reliable kinetic measurements possible.

As the phosphonium ions **6** and **6'** do not react with benzylamine in the absence of Pd complexes, we can exclude that (E)-N-benzyl-1,3-diphenylprop-2-en-1-amine (7), which is the only isolable product of the reaction of **1a**-BF<sub>4</sub> with benzylamine in the presence of PPh<sub>3</sub> and fumaronitrile, is produced via initial attack of PPh<sub>3</sub> at the allyl ligand of **1a** and subsequent noncatalyzed reaction of **6**/**6'** with the amine. Since the phosphonium salts **6** and **6'** do react with benzylamine in the presence of palladium complexes, **6** and **6'** are not among the reaction products, even when high concentrations of PPh<sub>3</sub> are present in the reaction of **1a**-BF<sub>4</sub> with benzylamine.

Addition of triphenylphosphine has an even stronger effect on the reaction of 1a-BF<sub>4</sub> with piperidine (2i) than on the reaction with benzylamine discussed above. Supplementary Figure S7 of the Supporting Information as well as Figure 8



**Figure 8.** Correlation between the first-order rate constants for the decay of the absorbance at  $\lambda = 360$  nm (absorption maximum of 1a) during the reaction of 1a ((4.5–7.9) × 10<sup>-4</sup> M) with piperidine (2i) in the absence (open symbols) and presence of PPh<sub>3</sub> (3.7 × 10<sup>-4</sup> to 9.70 × 10<sup>-3</sup> M, filled symbols) and the amine concentration (acetonitrile, 20 °C).

illustrate that the problem of low reproducibility of the kinetics in the absence of  $PPh_3$  (Figure 8, open symbols) is solved when the reactions are studied in the presence of triphenylphosphine (Figure 8, filled symbols).

Similar results were found for the reactions of the complexes 1(a-c) with a variety of other amines. Only in rare cases were deviations from the second-order rate law, i.e., first-order with respect to 1 and first-order with respect to nucleophile 2, observed when PPh<sub>3</sub> was present. Thus, for reasons that presently are not exactly known,<sup>18</sup> the reaction of morpholine (2h) with 1a-BF<sub>4</sub> was found to be of mixed first- and second-order in amine concentration.

**Determination of Electrophilicity Parameters** *E* for 1(a-c). Using the four-component system developed above (additives of PPh<sub>3</sub> and fumaronitrile to mixtures of 1 and 2), rate constants for the reactions of the allylpalladium complexes 1(a-c) with a variety of C-, N-, and P-nucleophiles have been determined (Table 2).

Figure 9 shows a plot of  $(\log k_2/s_N)$  vs N (for the N and  $s_N$  values see Table 1) for the reactions of complex 1a with nucleophiles 2. As required by eq 1, the slope of 1.0 was enforced

Table 2. Second-Order Rate Constants (in  $M^{-1} s^{-1}$ ) for the Reactions of ( $\eta^3$ -Diarylallyl)palladium Complexes 1(a-c) with the Nucleophiles 2(a-i) at 20 °C (solvents are specified in Table 1) and the Resulting Electrophilicity Parameters *E* 

complex	$E^{a}$	Nu	$k_2$	$k_{\rm calc}^{\ a}$	$k_2/k_{\rm cal}$
1a	-14.14	2a	$1.99 \times 10^{-1}$	$2.51 \times 10^{-1}$	0.79
		2b	8.15	5.66	1.44
		2d	$1.49^{b,c}$	$6.32 \times 10^{-1}$	2.36
		2e	$3.66 \times 10^{-1c}$	1.33	0.28
		2f	$4.52^{d}$	7.30	0.62
		2g	$1.26^{d}$	1.26	1.00
		2h	$1.07 \times 10^{c,d,e}$	$1.31 \times 10$	0.82
		2i	$2.05 \times 10^{2d}$	$1.52 \times 10^{2}$	1.35
1b	-14.21	2a	$2.63 \times 10^{-1}$	$2.51 \times 10^{-1}$	1.05
		2d	$2.98^{b,c}$	$6.32 \times 10^{-1}$	4.71
		2f	$3.39^{d}$	7.30	0.46
		2g	$1.13^{d}$	1.13	1.00
		2i	$2.10 \times 10^{2d}$	$1.37 \times 10^{2}$	1.54
1c	-14.46	2c	2.05	2.44	0.84
		2f	5.67 <sup>f</sup>	4.54	1.25
		2g	$7.79 \times 10^{-1f}$	$7.71 \times 10^{-1}$	1.01
		2i	$6.67 \times 10^{c,e,f}$	$9.25 \times 10$	0.72

<sup>a</sup>The *E* parameters for  $1(\mathbf{a}-\mathbf{c})$  result from the least-squares minimization of  $\Delta^2 = \sum (\log k_2 - s_N(N + E))^2$ , which uses the second-order rate constants  $k_2$  (this table) and the *N* and  $s_N$ parameters of the nucleophiles  $2(\mathbf{a}-\mathbf{i})$  listed in Table 1. *E* values with more decimals than given in this table were used for the calculation of  $k_{calc}$  by eq 1. The use of *E* parameters given in this table leads to slightly deviating results. <sup>b</sup>The kinetic data are only of moderate quality. <sup>c</sup>This value was not used for the determination of *E*. <sup>d</sup>Four-component kinetic method used. <sup>e</sup>Mixed first- and secondorder in nucleophile. <sup>f</sup>The rate constant was determined in the presence of PPh<sub>3</sub>. Fumaronitrile must not be added, as it causes immediate release of the free (*E*)-1,3-bis(4-dimethylaminophenyl)allylium ion (5c).

in the drawn correlation line. The electrophilicity parameters E (Table 2) of the allylpalladium complexes  $1(\mathbf{a-c})$  were calculated by minimizing the sum of the squared deviations  $\Delta^2 = \sum (\log k_2 - s_N(N + E))^2$  with the nonlinear solver "What's Best!"<sup>19</sup> using the rate constants listed in Table 2 and the N and  $s_N$  values derived from the reactions of corresponding nucleophiles with benzhydrylium ions (Table 1). Because of the lower accuracy of the second-order rate constants for 2d and 2h, these  $k_2$  values were not used for the determination of the E parameters. Triphenylphosphine was also not included in the correlation in order to have comparable reference nucleophiles for all three allylpalladium complexes. The proximity of these points to the correlation line implies that the calculated E values would not be significantly changed if these rate constants were included in the correlation.

It is remarkable that the second-order rate constants of reactions of 1(a-c) with C-, N-, and P-nucleophiles performed in three different solvents can be predicted within a factor of 5 by using eq 1. This observation indicates that the N and  $s_N$  values of the nucleophiles, determined on the basis of their reactions with benzhydrylium ions and therefore incorporating the solvent effects on the stabilities of the diarylmethyl cations (as the *E* values were defined as solvent-independent),<sup>10</sup> can be applied for the relatively accurate prediction of the reactivities of these nucleophiles even toward electrophiles of widely different nature.



**Figure 9.** Plot of  $(\log k_2)/s_N$  vs N for the reactions of complex 1a with the nucleophiles 2(a-i) (solvents are specified in Table 1). Open points correspond to the rate constants that were not used for the determination of *E*.

Comparison of the Allylpalladium Complexes 1(a-c) with the Free Diarylallyl Cations 5(a-c). The structural data listed in Table 3, which are based on X-ray diffraction analysis or quantum chemical calculations, show significant differences between the palladium complexes 1a and 1b and the corresponding free cations 5a and 5b. While the bond lengths in the allylic fragments of the complexes 1(a,b) and the free cations 5(a,b) are almost identical, the bonds between the terminal allyl and the aromatic carbons are significantly longer in the complexes 1(a,b) than in the free cations. Conjugative stabilization of the positive charge by the aryl rings is thus indicated to be much more important in the free diarylallyl cations 5(a,b) than in the palladium complexes 1(a,b). The smaller conjugative interaction between the aromatic rings and the allyl fragments in the complexes 1(a,b) is also reflected by the torsional angles of approximately 20° for C2-C3-C4-C5 and C2-C1-C10-C11, while they are close to 0° in the free cations 5(a-c). The planar configuration of the allyl fragment in the free cations 5(a,b) is only slightly disturbed in the Pd complexes 1(a,b), as shown by the torsional angles C1-C2-C3-C4 and C3-C2-C1-C10, which deviate by less than 5° from planarity.

Chart 2 shows that the tremendous differences in the electrophilicities of the differently substituted free allyl cations  $5(\mathbf{a}-\mathbf{c})$  are leveled in the corresponding palladium complexes  $1(\mathbf{a}-\mathbf{c})$ , all of which have similar electrophilic reactivities. Comparison of the two columns in Chart 2 shows that  $Pd(PPh_3)_2$  coordination of the highly reactive allyl cation **Sb** reduces the electrophilic reactivity by 20 orders of magnitude, while the reactivity of the stabilized allyl cation **Sc** is only reduced by 7 orders of magnitude.

Jutand et al. reported small differences between the rate constants of the reactions of  $[(\eta^3 - (CH_2CHCH_2)Pd(PAr_3)_2]^+$  and  $[(PhCHCHCHPh)Pd(PPh_3)_2]^+$  with morpholine in DMF.<sup>4,5</sup> This observation may a priori be explained by a compensation of electronic acceleration and steric retardation of the nucleophilic attack by the phenyl substituents. As the data in Chart 2 show that electronic substituent effects do not modify the electrophilicities of allylpalladium complexes, we can conclude that steric effects also play a minor role. In line with this conclusion the rate constants for the reactions of piperidine (2i) with 1(a-c) (205, 210, and 66.7 M<sup>-1</sup> s<sup>-1</sup>, Table 2) are

	Pd complexes		free cations			
	$1a^b$	1b <sup>c</sup>	5a <sup>d</sup>	5b <sup>d</sup>	5c <sup>e</sup>	$5c^d$
		Bo	ond Lengths (Å)			
<i>r</i> <sub>C1C10</sub>	1.484	1.466	1.425	1.428	1.391	1.415
$r_{\rm C3C4}$	1.473	1.476	1.425	1.428	1.413	1.415
<i>r</i> <sub>C1C2</sub>	1.397	1.403	1.391	1.390	1.386	1.392
$r_{C2C3}$	1.391	1.393	1.391	1.390	1.374	1.392
		Tors	ional Angles (deg)			
C2C3C4C5	-13.14	-19.54	0.00	-0.008	3.13	0.00
C2C1C10C11	27.48	16.09	0.00	0.00	-1.69	0.00
C1C2C3C4	-177.02	-174.94	180.00	180.00	174.37	179.99
C3C2C1C10	-175.14	179.32	0.00	-180	-177.96	180.00

Table 3. Geometrical Parameters of the  $(\eta^3$ -Diarylallyl)palladium Complexes 1(a,b) and Free Diarylallyl Cations  $5(a-c)^a$ 

<sup>*a*</sup>For the numbering of atoms see Figure 10. <sup>*b*</sup>X-ray data from ref 13. <sup>*c*</sup>X-ray data from this work. <sup>*d*</sup>B3LYP/6-31G(d,p) data from ref 9. <sup>*e*</sup>X-ray data from ref 9.



Figure 10. X-ray structure of complex 1b-OTf. The triflate anion and acetone (cosolvent for crystallization), which were found in the unit cell, are omitted in this figure and are depicted in the Supporting Information.

Chart 2. Electrophilicities of Complexes 1(a-c) and the Corresponding Free 1,3-Diarylallyl Cations 5(a-c)



similar to that for the reaction of piperidine with the  $[(\eta^3-1-phenylallyl)Pd(PPh_3)_2]^+$  complex<sup>6</sup> (30.9 M<sup>-1</sup> s<sup>-1</sup>).<sup>20</sup>

Since the reactivities of the allylpalladium complexes  $[(\eta^3 \text{-RCH-CHCHR})\text{PdL}_2]^+$  are obviously not related to the reactivities of the free allyl cations [RCHCHCHR]<sup>+</sup>, the designation of the former species as "palladium-stabilized allyl cations" may be misleading.

As bimolecular reactions at room temperature take place only within acceptable times, when  $k_2$  (20 °C) > 10<sup>-5</sup> M<sup>-1</sup> s<sup>-1</sup>, one

can derive that nucleophiles with N > 9 are suitable substrates for Tsuji–Trost reactions via  $[(\eta^3-\text{allyl})\text{Pd}(\text{PPh}_3)_2]^+$  complexes. Weaker nucleophiles may react, however, if another reaction mechanism is followed or other ligands are used, e.g., in reactions with indoles<sup>21</sup> ( $N \approx 5-7$ ), which have been suggested<sup>21a</sup> to proceed via the precoordination of the indole to the metal.

#### CONCLUSIONS

Contrary to previous assumptions,<sup>5</sup> secondary and primary amines were found to attack not only the allyl ligand but also the central metal in reactions with  $[(\eta^3-\text{allyl})\text{Pd}(\text{PPh}_3)_2]^+$  complexes. Since the products of the latter reaction, in which one PPh<sub>3</sub> ligand is reversibly replaced by an amine molecule, are considerably less electrophilic than the Pd(PPh<sub>3</sub>)<sub>2</sub>-coordinated species, complex kinetics were encountered. Small amounts of PPh<sub>3</sub> were shown to suppress the ligand exchange, giving rise to the high reproducibility of the kinetic measurements of these reactions.

Substitution of the previously reported<sup>12–16</sup> nucleophilespecific parameters N and  $s_N$  and the second-order rate constants  $k_2$  for the reactions of  $1(\mathbf{a-c})$  with various nucleophiles in the correlation log  $k_2 = s_N(N + E)$  (eq 1) allowed us to derive the electrophilicities  $E \approx -14$  for the  $[(\eta^3 \text{-diarylallyl})$ -Pd(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> almost independent of the nature of the substituents and to compare them with the reactivities of other important classes of electrophiles<sup>22</sup> (Figure 11).

### EXPERIMENTAL SECTION

Materials for Kinetic Measurements. Dichloromethane (p.a. grade) was subsequently treated with concentrated sulfuric acid, water, 10% NaHCO<sub>3</sub> solution, and again water. After predrying with anhydrous CaCl<sub>2</sub>, it was freshly distilled over CaH<sub>2</sub>. Acetonitrile (HPLC grade) and DMSO (99.7% purity) were used as received.

**NMR Spectroscopy.** In the <sup>1</sup>H and <sup>13</sup>C NMR spectra chemical shifts are expressed in  $\delta$  (ppm) and refer to CD<sub>2</sub>Cl<sub>2</sub> ( $\delta_{\rm H}$  5.32,  $\delta_{\rm C}$  54.00), DMSO ( $\delta_{\rm H}$  2.50,  $\delta_{\rm C}$  39.50), and CD<sub>3</sub>CN ( $\delta_{\rm H}$  1.94,  $\delta_{\rm C}$  1.39) as internal standards. The coupling constants are given in Hz. Abbreviations used are s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). In the case of <sup>13</sup>C NMR spectra, these abbreviations refer to the multiplicity in hydrogen decoupled spectra, and the hydrogen multiplicity (based on DEPT or HSQC experiments) is shown as CH<sub>3</sub>, CH<sub>2</sub>, CH, or C to avoid ambiguity.

 $(\tilde{E})$ -5,5'-(3-Chloroprop-1-ene-1,3-diyl)bis(1,3-difluorobenzene) (5b-Cl). Prepared from (E)-1,3-bis(3,5-difluorophenyl)prop-2en-1-ol (4.58 g, 16.2 mmol) and thionyl chloride (2.71 g, 22.8 mmol)

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**Figure 11.** Comparison of the electrophilicities of the allylpalladium complexes 1(a-c) and electron-deficient  $\pi$ -systems of similar reactivity.<sup>22</sup>

in dichloromethane (20 mL) using the procedure from ref 23: 3.82 g (12.7 mmol, 78%); colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 599 MHz):  $\delta$  5.54 (d, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 1 H, ArCHCHCH(Cl)Ar), 6.41 (dd, <sup>3</sup>J<sub>HH</sub> = 15.6, 7.7 Hz, 1 H, ArCHCHCH(Cl)Ar), 6.57 (d, <sup>3</sup>J<sub>HH</sub> = 15.6 Hz, 1 H, ArCHCHCH(Cl)Ar), 6.71-6.81 (m, 2 H, H<sub>Ar</sub>), 6.89-6.93 (m, 2 H, H<sub>Ar</sub>), 6.98-7.02 ppm (m, 2 H, H<sub>Ar</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 151 MHz):  $\delta$  61.2 (t,  $J_{CF}$  = 2.2 Hz, CH), 103.4 (s, CH), 103.8 (t,  $J_{CF}$  = 25.5 Hz, CH), 103.9 (t,  $J_{CF}$  = 2.9 Hz, CH), 104.1 (t,  $J_{CF}$  = 25.2 Hz, CH), 109.6 (dd,  $J_{CF}$  = 20.3, 5.3 Hz, CH), 110.5 (dd,  $J_{CF}$  = 20.8, 5.6 Hz, CH), 138.7 (t,  $J_{CF}$  = 9.5 Hz, C), 143.3 (t,  $J_{CF}$  = 8.7 Hz, C), 163.0 (dd,  $J_{CF}$  = 251, 12.0 Hz, C), 163.2 ppm (dd,  $J_{CF}$  = 249, 13.6 Hz, C).

[Pd(1,3-bis(3,5-difluorophenyl)-π-allyl)( $\mu$ -Cl)]<sub>2</sub> (5b-PdCl). Prepared from palladium(II) chloride (400 mg, 2.26 mmol), 5b-Cl (2.70 g, 8.98 mmol), and lithium chloride (405 mg, 9.55 mmol) following the procedure described in ref 24: 834 mg (1.02 mmol, 90%); yellow powder; mp 247.8–249.2 °C (dec). <sup>1</sup>H NMR (DMSO, 400 MHz):  $\delta$  5.20 (d, <sup>3</sup>*J*<sub>HH</sub> = 11.8 Hz, 4 H, ArCHCHCHAr), 7.09 (t, *J* = 11.8 Hz, 2 H, ArCHCHCHAr), 7.17–7.34 (m, 4 H, H<sub>Ar</sub>), 7.40–7.64 ppm (m, 8 H, H<sub>Ar</sub>). <sup>13</sup>C NMR (DMSO, 101 MHz):  $\delta$  80.7 (s, CH), 103.4 (t, *J*<sub>CF</sub> = 26.0 Hz, CH), 109.5 (s, CH), 111.4–111.6 (m, CH), 141.5 (t, *J*<sub>CF</sub> = 10.1 Hz, C), 162.7 ppm (dd, *J*<sub>CF</sub> = 245.1, 13.5 Hz, C). <sup>19</sup>F NMR (DMSO, 376 MHz):  $\delta$  –110.7 to –110.4 ppm (m). HRMS (ESI+, acetonitrile–water as eluents): calcd 453.0201 (C<sub>19</sub>H<sub>15</sub>F<sub>4</sub>N<sub>2</sub><sup>106</sup>Pd<sup>+</sup>, [C<sub>6</sub>H<sub>3</sub>F<sub>2</sub>CHCHCHC<sub>6</sub>H<sub>3</sub>F<sub>2</sub>Pd(CH<sub>3</sub>CN)<sub>2</sub>]<sup>+</sup>), found 453.0202.

(*E*)-[( $\eta^3$ -1,3-Bis(3,5-difluorophenyl)allyl)Pd(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (1b-BF<sub>4</sub>). Synthesized according to ref 17 from 5b-PdCl (420 mg, 0.516 mmol), triphenylphosphine (542 mg, 2.07 mmol), and NaBF<sub>4</sub> (568 mg, 5.17 mmol): 605 mg (0.615 mmol, 60%); yellow powder; mp 170–172 °C (dec). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  5.45–5.51 (m, 2 H, ArCHCHCHAr), 6.38–6.51 (m, 7 H, ArCHCHCHAr, H<sub>Ar</sub>), 7.11–7.16 (m, 12 H, *o*-PPh<sub>3</sub>), 7.19–7.23 (m, 12 H, *m*-PPh<sub>3</sub>), 7.34–7.38 ppm (m, 6 H, *p*-PPh<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 101 MHz):  $\delta$  91.1 (t,  $J_{CP}$  = 15.0 Hz, CH), 103.7 (t,  $J_{CF}$  = 25.6 Hz, CH), 111.3–111.9 (m, CH), 113.8 (t,  $J_{CP}$  = 7.3 Hz, CH), 129.3–129.4 (m, CH), 129.6 (d,  $J_{CP}$  = 22.1 Hz, C), 131.5 (s, CH), 134.1–134.2 (m, CH), 139.4–139.6 (m, C), 163.2 ppm (dd,  $J_{CF}$  = 248, 13.0 Hz, C). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz):  $\delta$  27.5 ppm. <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 376 MHz):  $\delta$  –150.63 to –150.62 (m, 3 F, BF<sub>4</sub>), –150.58 to –150.57 (m, 1 F, BF<sub>4</sub>), –110.32 to –110.28 ppm (m, 4 F, F<sub>Ar</sub>). HRMS (ESI+): calcd 895.1492 (C<sub>51</sub>H<sub>39</sub>F<sub>4</sub>P<sub>2</sub><sup>-106</sup>Pd<sup>+</sup>), found 895.1498.

( $\dot{E}$ )-[( $\eta^3$ -1,3-Bis(3,5-difluorophenyl)allyl)Pd(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>TfO<sup>-</sup> (1b-OTf). Analogous to 1b-BF<sub>4</sub>. From 5b-PdCl (186 mg, 0.228 mmol), PPh<sub>3</sub> (242 mg, 0.923 mmol), and sodium triflate (393 mg, 2.28 mmol): 205 mg (0.196 mmol, 43%); yellow needles; mp 206.5–208.5 °C (dec). To obtain crystals suitable for X-ray diffraction analysis, 1b-OTf was recrystallized from acetone–Et<sub>2</sub>O.

(E)- $[(\eta^3-1, 3-Bis(4-(dimethylamino)phenyl)allyl)Pd-$ (PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (1c-BF<sub>4</sub>). Pd(PPh<sub>3</sub>)<sub>4</sub> (871 mg, 0.754 mmol) and 5c- $BF_4$  (268 mg, 0.732 mmol) were mixed in the solid state followed by addition of dichloromethane (10 mL). The resulting solution was stirred for 10 min at rt; then pentane (ca. 50 mL) was added. After 2 h of cooling (4 °C), the precipitate was filtered, washed with pentane, and dried in vacuo to yield 1c-BF<sub>4</sub>: 476 mg (0.477 mmol, 65%); red powder; mp 162.0–164.0 °C (dec). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  2.91 (s, 12 H, 2 × NMe<sub>2</sub>), 5.48–5.53 (m, 2 H, ArCHCHCHAr), 6.11 (t,  ${}^{3}J_{HH}$  = 12.4 Hz, 1 H, ArCHCHCHAr), 6.26–6.28 (m, 4 H,  $H_{Ar}$ ), 6.71–6.73 (m, 4 H,  $H_{Ar}$ ), 7.00–7.04 (m, 12 H, *o*-PPh<sub>3</sub>), 7.13–7.17 (m, 12 H, *m*-PPh<sub>3</sub>), 7.32–7.36 ppm (m, 6 H, *p*-PPh<sub>3</sub>). <sup>13</sup>C NMR  $(CD_2Cl_2, 101 \text{ MHz}): \delta 40.5 \text{ (s, CH}_3), 98.7 \text{ (t, } J_{CP} = 11.7 \text{ Hz, CH}),$ 101.3 (t,  $J_{CP}$  = ca. 6 Hz, CH), 112.4 (s, CH), 122.0 (t,  $J_{CP}$  = 4.1 Hz, C), 129.1-129.2 (m, CH), 130.0 (s, CH), 130.9 (s, CH), 131.2 (d,  $J_{CP}$  = 19.3 Hz, C), 134.0–134.1 (m, CH), 151.4 ppm (s, C). HRMS (ESI, positive): calcd 909.2713 ( $C_{55}H_{53}N_2P_2^{106}Pd^+$ ), found 909.2721.

**Reaction of 1a-BF**<sub>4</sub> with Triphenylphosphine (2e). Triphenylphosphine (553 mg, 2.11 mmol) was added to a solution of 1a-BF<sub>4</sub> (315 mg, 0.346 mmol) in acetonitrile (10 mL). After 1 h of stirring (rt), the precipitate was filtered off, and the filtrate was dried in vacuo. Diethyl ether (50 mL) was added to the solid residue, and the resulting slurry was placed in an ultrasonic bath for 20 min. The remaining solid was filtered and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O, yielding a 2:1 mixture of (*E*)-(1,3-diphenylallyl)triphenylphosphonium tetrafluoroborate (6) and (*Z*)-(1,3-diphenylprop-1-en-1-yl)triphenylphosphonium tetrafluoroborate (6'). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of 6' were obtained comparing the spectra of the mixture with those of isolated 6.<sup>9</sup>

**6**': <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ 3.62 (dd, <sup>3</sup>*J*<sub>HH</sub> = 7.5, <sup>4</sup>*J*<sub>HP</sub> = 3.0 Hz, 2 H, CH<sub>2</sub>), 6.93–7.02 (m, 3 H, ==CH, H<sub>Ar</sub>), 7.05–7.10 (m, 2 H, H<sub>Ar</sub>) overlapped with H<sub>Ar</sub> of **6**), 7.26–7.36 (m, 5 H, H<sub>Ar</sub> overlapped with H<sub>Ar</sub> of **6**), 7.38–7.45 (m, 7 H, *o*-PPh<sub>3</sub>, H<sub>Ar</sub>, overlapped with H<sub>Ar</sub> of **6**), 7.62–7.70 (m, 6 H, *m*-PPh<sub>3</sub>, overlapped with *m*-PPh<sub>3</sub> of **6**), 7.83–7.88 ppm (m, 3 H, *p*-PPh<sub>3</sub> overlapped with *p*-PPh<sub>3</sub> of **6**). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 101 MHz): δ 38.0 (d, *J*<sub>CP</sub> = 14.4 Hz, CH<sub>2</sub>), 117.4 (d, *J*<sub>CP</sub> = 88.9 Hz, C), 124.5 (d, *J*<sub>CP</sub> = 77.9 Hz, C), 127.7 (*s*, CH), 129.0 (*s*, CH), 129.6 (*s*, CH), 130.4 (d, *J*<sub>CP</sub> = 2.5 Hz, CH), 130.08–130.13 (m, overlapped with resonance of **6**, CH), 130.7 (m, overlapped with resonance of **6**, CH), 130.1 (d, *J*<sub>CP</sub> = 3.0 Hz, CH), 137.2 (d, *J*<sub>CP</sub> = 10.1 Hz, C), 157.4 ppm (d, *J*<sub>CP</sub> = 10.1 Hz, CH). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz): δ 24.5 ppm.

**Isomerization of 6 in the Presence of Pd(PPh\_3)\_4.**  $Pd(PPh_3)_4$ (8.4 mg, 7.3  $\mu$ mol) and 6 (104 mg, 0.192 mmol) were mixed in the solid state, and acetonitrile (10 mL) was added. After 15 h of stirring (ambient temperature), the reaction mixture was freed from the solvent, yielding a 4:1 mixture of 6 and 6' (based on <sup>1</sup>H NMR).

Reaction of 1a-BF<sub>4</sub> with Benzylamine (2g) in the Presence of Triphenylphosphine and Fumaronitrile. A solution containing benzylamine (151 mg, 1.41 mmol), triphenylphosphine (185 mg, 0.706 mmol), and fumaronitrile (17 mg, 0.22 mmol) in acetonitrile (5 mL) was added to a solution of 1a-BF<sub>4</sub> (199 mg, 0.218 mmol) in the same solvent (5 mL). After 1 h of stirring (rt), the precipitate was filtered off and the filtrate was dried in vacuo. (*E*)-*N*-Benzyl-1, 3-diphenylprop-2-en-1-amine (7) was found to be the only allylic product in the crude mixture (<sup>1</sup>H NMR). Column chromatography (MPLC, silica gel, isohexane–EtOAc = 93:7, flow rate 25 mL/min)

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afforded 7 (35.4 mg, 0.118 mmol, 54%), the  $^{1}$ H and  $^{13}$ C NMR spectra of which agreed with literature data.<sup>24,25</sup>

Isomerization of 6 in the Presence of Benzylamine (2g). The phosphonium salt 6 (29.6 mg, 54.6  $\mu$ mol) was dissolved in CD<sub>3</sub>CN (0.5 mL). Then a solution of benzylamine (43.6 mg, 0.407 mmol) in the same solvent (0.2 mL) was added. <sup>1</sup>H and <sup>31</sup>P NMR spectra of the reaction mixture taken 2 and 5 min after mixing, respectively, showed resonances corresponding to a mixture of 6, 6', and benzylamine. After 24 h, no traces of 7 were found, and the ratio between 6 and 6' (ca. 1:5) remained unchanged.

Reaction of 6 with Benzylamine in the Presence of Pd(PPh<sub>3</sub>)<sub>4</sub>. The phosphonium salt 6 (29.3 mg, 0.0540 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (7.3 mg, 6.1  $\mu$ mol) were dissolved in CD<sub>3</sub>CN (0.5 mL). Then a solution of benzylamine (39.6 mg, 370  $\mu$ mol) in the same solvent (0.2 mL) was added. The <sup>1</sup>H NMR spectrum of the reaction mixture taken 20 min after mixing showed resonances corresponding to a mixture of 7, 6, and 6' in a ratio of ca. 1:0.3:0.6. After a reaction time of 6 h, the 7:6:6' ratio reached 1:0.04:0.13.

## ASSOCIATED CONTENT

#### **S** Supporting Information

Details of kinetic and ESI experiments and of the determination of the equilibrium constant  $K_{\rm E}$ , supplementary figures, copies of the NMR spectra of new compounds, and crystallographic data in CIF format for **1b**-OTf. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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