

# Insertions of Allenes into Palladium–Carbon Bonds of Complexes Containing Bidentate Nitrogen Ligands. Structural and Mechanistic Studies

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Received September 16, 1996<sup>⊗</sup>

The insertion reactions of the allenes propadiene and 1,2-heptadiene in the Pd–C bond of complexes  $(\bar{N} \bar{N})\text{Pd}(\text{R})\text{X}$  ( $\bar{N} \bar{N} = 8\text{-PQ}$ , *p*-An-BIAN, *i*-Pr-DAB, *p*-An-DAB, *i*-Pr-PyCa; R = Me, C(O)Me, C(O)Ph, C(O)*i*-Pr; X = Cl, Br) have been investigated. An X-ray crystal structure determination of  $(8\text{-PQ})\text{Pd}\{(1\text{-}3\text{-}\eta)\text{-2-methylpropenyl}\}\text{Cl}$  exhibited the unexpected monodentate coordination of the nitrogen ligand. The monodentate coordination in apolar solvents and bidentate coordination in polar solvents was demonstrated by means of NOE NMR experiments. Kinetic measurements revealed that the reactions are first order in the palladium concentration and occur via an allene concentration independent and dependent pathway. Reactions of complexes containing flexible bidentate nitrogen ligands were retarded by additional free bidentate nitrogen ligand indicating that initial dissociation of a nitrogen donor is an important step in the reaction. We have strong indications that the migration of the R group to the precoordinated allene is the rate-determining step. Instead of mass-law retardation by excess  $\text{X}^-$  ( $\text{X} = \text{Cl}^-, \text{Br}^-$ ), an enhancement of the reaction has been observed in case of the complexes  $(8\text{-PQ})\text{Pd}(\text{Me})\text{Cl}$ ,  $(8\text{-PQ})\text{Pd}(\text{Me})\text{Br}$ , and  $(i\text{-Pr-DAB})\text{Pd}(\text{C}(\text{O})\text{-Me})\text{Cl}$ . Flexible bidentate nitrogen ligands greatly enhance the reaction, owing to the easy formation of an accessible site on the metal center. The insertion of allenes into the Pd–C bonds of complexes containing rigid bidentate nitrogen ligands probably proceeds via initial allene association followed by either halide or nitrogen dissociation and subsequent migration of the R group to the precoordinated allene.

## Introduction

Insertions of unsaturated hydrocarbons into metal–carbon bonds are very important in transition metal catalyzed processes.<sup>1,2</sup> A special case is the copolymerization of carbon monoxide and alkenes, leading to the formation of polyketones, homogeneously catalyzed by palladium complexes containing bidentate phosphine and nitrogen ligands.<sup>3–11</sup> Recent work, in our<sup>12</sup> and

other laboratories,<sup>13–15</sup> has shown that polyketone formation is accomplished by an alternating insertion of carbon monoxide and alkenes into palladium–carbon bonds. By using model palladium systems containing the bidentate nitrogen ligand bis(arylimino)acenaphthene (Ar-BIAN), we were able to synthesize and also characterize some key intermediates of the copolymerization process.<sup>12</sup> Brookhart *et al.* also characterized key intermediates in in-situ systems. They were able to determine thermodynamic parameters of these reactions at low temperature.<sup>14,15</sup>

It has been generally accepted that the unsaturated fragment and the hydrocarbyl group should be *cis* in the reacting complex<sup>16–18</sup> and that the hydrocarbyl

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<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, January 15, 1997.

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group migrates to the unsaturated ligand rather than *vice versa*.<sup>19,20</sup>

The insertion of alkenes into the palladium–acyl bond, the rate-determining step of the polyketone synthesis, has been scarcely investigated.<sup>12,13,15,21–24</sup> Recently, we have shown that allene insertion into Pd–acyl bonds of complexes containing not only bidentate but also terdentate nitrogen ligands can be achieved quantitatively and with relatively high rates;<sup>25</sup> hitherto allene insertions into Pd–C bonds only had been carried out with complexes containing phosphine ligands.<sup>26–32</sup> This route gives easy excess to highly substituted  $\eta^3$ -allyl–Pd complexes, which are hard to obtain via conventional routes. Additionally, cooligomerization of CO and allenes using a palladium complex containing the Ar-BIAN ligand has been demonstrated to be possible, analogous to the cooligomerization of CO and norbornadiene.<sup>33</sup> To obtain more insight into the mechanism of the allene insertion reaction, we will present in this article a kinetic study on allene insertions into the Pd–R bond of  $(\widehat{N}N)Pd(R)X$  complexes in which  $\widehat{N}N$  are bidentate nitrogen ligands and R represents the acyl and methyl groups.

## Experimental Section

**Material and Apparatus.** All manipulations were carried out in an atmosphere of purified, dry nitrogen using standard Schlenk techniques. Solvents were dried and stored under nitrogen. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker AMX 300 and DRX 300 (300.13 and 75.48 MHz, respectively). Elemental analyses were carried out by Dornis u. Kolbe Mikroanalytisches Laboratorium, Mühlheim a.d. Ruhr, Germany, and at the Inorganic Chemistry Department of the J. H. van't Hoff Institute, University of Amsterdam.

Propadiene was purchased from Air Products, while 1,2-heptadiene,<sup>34</sup> (*cis,cis*-1,5-cyclooctadiene)Pd(Me)Cl,<sup>35</sup> [Pd( $\eta^3$ -

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$C_3H_5Cl)_2$ ,<sup>36</sup> (8-(2-pyridyl)quinoline)Pd(R)Cl,<sup>37</sup> (bis(*p*-anisylimino)acenaphthene)Pd(C(O)Me)Cl,<sup>12</sup> (bis(*p*-anisylimino)acenaphthene)Pd(C(O)Ph)Cl,<sup>38</sup> (2-(*N*-2-propane-carbaldimino)pyridine)Pd(C(O)Me)Cl,<sup>39</sup> 1,4-di-*i*-Pr-1,4-diaza-1,3-butadiene,<sup>40</sup> and 1,4-di-*p*-An-1,4-diaza-1,3-butadiene<sup>40</sup> were synthesized according to previously reported procedures.

**Synthesis of {8-(2-Pyridyl)quinoline}(methyl)bromopalladium(II), (8-PQ)Pd(Me)Br (2).** (8-PQ)Pd(Me)Cl (100 mg; 0.27 mmol) and KBr (164 mg; 1.4 mmol) were dissolved in a mixture of dichloromethane (60 mL) and acetone (40 mL) and stirred for 2 h. The solvent was evaporated, and the residue was washed twice with dichloromethane. The volume of the solvent was concentrated and hexane (30 mL) was added providing a yellow crystalline material, which was collected by centrifugation. Yield: 90% (101 mg; 0.25 mmol).

<sup>1</sup>H NMR data (300 MHz, CDCl<sub>3</sub>;  $\delta$ ) (numbering scheme presented in Figure 1): 9.54 (dd, <sup>3</sup>*J* = 4.2 Hz, <sup>4</sup>*J* = 1.7 Hz, 1H, H2), 7.51 (dd, <sup>3</sup>*J* = 8.2 Hz, <sup>3</sup>*J* = 4.2 Hz, 1H, H3), 8.34 (dd, <sup>3</sup>*J* = 8.2 Hz, <sup>4</sup>*J* = 1.8 Hz, 1H, H4), 8.04 (dd, <sup>3</sup>*J* = 8.2 Hz, <sup>4</sup>*J* = 1.5 Hz, 1H, H5), 7.74 (t, <sup>3</sup>*J* = 7.6 Hz, 1H, H6), 8.10 (dd, <sup>3</sup>*J* = 8.2 Hz, <sup>4</sup>*J* = 1.5 Hz, 1H, H7), 7.62 (d, <sup>3</sup>*J* = 7.3 Hz, 1H, H8), 7.97 (dt, <sup>3</sup>*J* = 7.8 Hz, <sup>4</sup>*J* = 1.6 Hz, 1H, H9), 7.47 (m, 1H, H10), 8.85 (dd, <sup>3</sup>*J* = 5.1 Hz, <sup>3</sup>*J* = 3.7 Hz, 1H, H11), 1.04 (s, 3H, Pd–CH<sub>3</sub>).

<sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>;  $\delta$ ): 157.7 (C2), 122.5 (C3), 139.1 (C4), 131.9 (C5), 127.4 (C6), 132.9 (C7), 127.9 (C8), 139.0 (C9), 124.8 (C10), 152.3 (C11), 156.0 (C12), 135.0 (C13), 144.4 (C14), 129.1 (C15), –1.4 (Pd–CH<sub>3</sub>).

Anal. Found (calcd for C<sub>15</sub>H<sub>13</sub>BrN<sub>2</sub>Pd): C, 44.09 (44.20); H, 3.28 (3.22); N, 6.79 (6.87).

**Synthesis of (R-1,4-diazabutadiene)(methyl)chloropalladium(II), (R-DAB)Pd(Me)Cl (R = *i*-Pr, R = *p*-An).** (COD)Pd(Me)Cl (100 mg) and the appropriate amount of ligand (1.1 equiv) were dissolved in toluene (20 mL). The red suspension, which was formed after 15 min, was centrifuged and washed twice with diethyl ether (20 mL) to yield a red powder (95%).

<sup>1</sup>H NMR data (300 MHz, CDCl<sub>3</sub>;  $\delta$ ): R = *i*-Pr, 8.17 (s, 1H, H<sub>imine</sub>), 8.05 (s, 1H, H<sub>imine</sub>), 4.31 (sept, <sup>3</sup>*J* = 6.4, 1H, CH<sub>1Pr</sub>), 4.21 (sept, <sup>3</sup>*J* = 6.4, 1H, CH<sub>1Pr</sub>), 1.40 (d, <sup>3</sup>*J* = 6.4, 6H, CH<sub>3iPr</sub>), 1.35 (d, <sup>3</sup>*J* = 6.4, 6H, CH<sub>3iPr</sub>), 1.00 (s, 3H, Pd–CH<sub>3</sub>); R = *p*-An, 8.26 (s, 1H, H<sub>imine</sub>), 8.21 (s, 1H, H<sub>imine</sub>), 7.74 (d, <sup>3</sup>*J* = 8.8 Hz, 2H, H<sub>meta</sub>), 7.13 (d, <sup>3</sup>*J* = 8.8 Hz, 2H, H<sub>ortho</sub>), 6.95 (d, <sup>3</sup>*J* = 8.8 Hz, 4H, H<sub>meta</sub>), 3.85 (s, 6H, OCH<sub>3</sub>), 1.07 (s, 3H, Pd–CH<sub>3</sub>).

<sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>;  $\delta$ ): R = *i*-Pr, 160.0 (C<sub>imine</sub>), 155.2 (C<sub>imine</sub>), 58.9 (CH<sub>1Pr</sub>), 56.4 (CH<sub>1Pr</sub>), 22.5 (CH<sub>3iPr</sub>), 22.1 (CH<sub>3iPr</sub>), –0.2 (Pd–CH<sub>3</sub>); R = *p*-An, 161.3 (C<sub>imine</sub>), 151.8 (C<sub>imine</sub>), 139.5, 124.8, 123.0, 113.2, 113.0 (Ph<sub>anisyl</sub>), 54.5 (OCH<sub>3</sub>), 4.4 (Pd–CH<sub>3</sub>).

Anal. R = *i*-Pr, found (calcd for C<sub>9</sub>H<sub>19</sub>ClN<sub>2</sub>Pd): C, 36.31 (36.38); H, 6.41 (6.45); N, 9.20 (9.42). R = *p*-An, found (calcd for C<sub>19</sub>H<sub>19</sub>ClN<sub>2</sub>O<sub>2</sub>Pd): C, 47.94 (48.02); H, 4.52 (4.51); N, 6.56 (6.59).

**Synthesis of (R-1,4-diazabutadiene)(acetyl)chloropalladium(II), (R-DAB)Pd(C(O)Me)Cl (R = *i*-Pr (8), R = *p*-An (9)).** CO was bubbled through a solution of (R-DAB)Pd(Me)Cl (100 mg) in dichloromethane (20 mL) for 5 min after which the solution was filtered. The volume of the solution was concentrated to 5 mL, and diethyl ether was added. The crystalline material (85% yield) was collected by centrifugation.

<sup>1</sup>H NMR data (300 MHz, CDCl<sub>3</sub>;  $\delta$ ): **8**, 7.96 (br, 2H, H<sub>imine</sub>), 4.10 (br, 2H, CH<sub>1Pr</sub>), 1.36 (br, 12H, CH<sub>3iPr</sub>), 2.62 (s, 3H, Pd–

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C(O)CH<sub>3</sub>); **9**, 8.22 (s, 2H, H<sub>imine</sub>), 7.48 (br, 4H, H<sub>ortho</sub>), 6.86 (d, <sup>3</sup>J = 8.9 Hz, 4H, H<sub>meta</sub>), 3.83, (s, 6H, OCH<sub>3</sub>), 2.36 (s, 3H, Pd–C(O)CH<sub>3</sub>).

<sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>; δ): **8**, 58.8 (CH<sub>IPr</sub>), 34.7 (CH<sub>3IPr</sub>), 21.2 (C(O)CH<sub>3</sub>), 225.1 (C(O)CH<sub>3</sub>), C<sub>imine</sub> not observed; **9**, 139.5, 125.6, 113.3 (Ph<sub>anisyl</sub>), 54.4 (OCH<sub>3</sub>), C<sub>imine</sub> and acetyl not observed.

Anal. **8**, found (calcd for C<sub>10</sub>H<sub>19</sub>ClN<sub>2</sub>OPd): C, 36.79 (36.94); H, 5.75 (5.89); N, 8.60 (8.62). **9**, found (calcd for C<sub>18</sub>H<sub>19</sub>ClN<sub>2</sub>O<sub>3</sub>Pd): C, 47.44 (47.70); H, 4.18 (4.23); N, 6.14 (6.18).

**General Procedure for the Synthesis of Allyl Complexes (N<sup>−</sup>N)Pd(η<sup>3</sup>-allyl)X (X = Cl, Br).** To a solution of (N<sup>−</sup>N)Pd(R)X (X = Cl, Br) (0.28 mmol) in dichloromethane (20 mL) was added the allene either by a microsyringe or by bubbling the allene through the solution from a lecture bottle. After the solution was stirred for about 30 min, the solvent was removed in vacuo and the product could be isolated in virtually quantitative yield.

<sup>1</sup>H NMR data (300 MHz, CDCl<sub>3</sub>; δ) are as follows. **6b** (numbering scheme presented in Figure 1): acenaphthene, 7.98 (d, <sup>3</sup>J = 8.3 Hz, 2H, H<sub>3</sub>), 7.48 (t, <sup>3</sup>J = 7.8 Hz, 2H, H<sub>2</sub>), 7.23 (t, <sup>3</sup>J = 7.8 Hz, 2H, H<sub>1</sub>); *p*-anisyl, 7.03 (d, <sup>3</sup>J = 8.8 Hz, 4H, H<sub>meta</sub>), 7.40 (d, <sup>3</sup>J = 8.8 Hz, 4H, H<sub>ortho</sub>), 3.90 (s, 6H, OCH<sub>3</sub>); allyl, 4.82 (t, <sup>3</sup>J = 7.2 Hz, 1H, H<sub>anti</sub>), H<sub>syn</sub> and H<sub>anti</sub> not observed; *n*-butyl, 0.71 (t, <sup>3</sup>J = 7.1 Hz, 3H, CH<sub>3</sub>), 1.04 (q, <sup>3</sup>J = 7.1 Hz, 2H, CH<sub>2</sub>), 1.24 (br, 2H, CH<sub>2</sub>), 1.42 (br, 2H, CH<sub>2</sub>), 2.16 (s, 3H, C(O)CH<sub>3</sub>). **7b**: acenaphthene, 7.98 (d, <sup>3</sup>J = 8.0 Hz, 2H, H<sub>3</sub>), 7.57 (t, <sup>3</sup>J = 8.2 Hz, 2H, H<sub>2</sub>), 7.17 (t, <sup>3</sup>J = 7.3 Hz, 2H, H<sub>1</sub>), 6.99 (m, 6H, H<sub>meta</sub>, H<sub>C(O)Ph</sub>), 7.41 (m, 7H, H<sub>ortho</sub>, H<sub>C(O)Ph</sub>), 3.89 (s, 6H, OCH<sub>3</sub>); allyl, 4.82 (t, <sup>3</sup>J = 7.2 Hz, 1H, H<sub>anti</sub>), 3.90 (br, 1H, H<sub>syn</sub>), 3.51 (br, 1H, H<sub>anti</sub>); *n*-butyl, 0.68 (t, <sup>3</sup>J = 7.1 Hz, 3H, CH<sub>3</sub>), 0.90 (br, 2H, CH<sub>2</sub>), 1.06 (br, 2H, CH<sub>2</sub>), 1.26 (br, 2H, CH<sub>2</sub>). **9b**: DAB, 8.62 (br, 2H, H<sub>imine</sub>); *p*-anisyl, 7.46 (d, <sup>3</sup>J = 8.3 Hz, H<sub>ortho</sub>), 6.94 (d, <sup>3</sup>J = 8.3 Hz, H<sub>meta</sub>), 3.84 (s, 6H, OCH<sub>3</sub>); allyl: 5.17 (br, 1H, H<sub>anti</sub>), 3.35 (br, 1H, H<sub>syn</sub>), 3.30 (br, 1H, H<sub>anti</sub>); *n*-butyl, 0.81 (t, <sup>3</sup>J = 7.1 Hz, 3H, CH<sub>3</sub>), 1.26 (br, 2H, CH<sub>2</sub>), 1.40 (br, 2H, CH<sub>2</sub>), 1.60 (br, 2H, CH<sub>2</sub>), 2.36 (s, 3H, C(O)CH<sub>3</sub>).

<sup>13</sup>C-NMR (75.48 MHz, CDCl<sub>3</sub>; δ) are as follows. **6b**: *p*-An-BIAN, 163.6, 159.0, 143.2, 131.8, 130.8, 128.6, 128.5, 124.9, 122.0, 115.5, 56.3 (OCH<sub>3</sub>); allyl, CH, CH<sub>2</sub>, and C<sub>central</sub> not observed, 25.7 (C(O)CH<sub>3</sub>), 195.1 (C(O)CH<sub>3</sub>); *n*-butyl, 32.9, 30.5, 22.8 (CH<sub>2</sub>), 14.4 (CH<sub>3</sub>). **7b**: *p*-An-BIAN, 164.2, 158.6, 142.4, 130.8, 130.3, 129.5, 128.7, 122.7, 121.9, 56.0 (OCH<sub>3</sub>); allyl, CH, CH<sub>2</sub>, and C<sub>central</sub> not observed, 141.0, 128.6, 124.7 (C(O)C<sub>6</sub>H<sub>5</sub>), 194.0 (C(O)C<sub>6</sub>H<sub>5</sub>); *n*-butyl, 32.7, 31.1, 22.7 (CH<sub>2</sub>), 14.3 (CH<sub>3</sub>). **9b**: DAB, 158.2 (C<sub>imine</sub>); *p*-anisyl, 160.1, 142.6, 123.4, 114.4, 55.4 (OCH<sub>3</sub>); allyl, CH and CH<sub>2</sub> not observed, 118.1 (C<sub>central</sub>), 25.7 (C(O)CH<sub>3</sub>), 194.8 (C(O)CH<sub>3</sub>); *n*-butyl, 31.9, 29.9, 21.9 (CH<sub>2</sub>), 13.4 (CH<sub>3</sub>).

Anal. **1a**, found (calcd for C<sub>18</sub>H<sub>17</sub>ClN<sub>2</sub>Pd): C, 53.63 (53.62); H, 4.29 (4.25); N, 6.98 (6.95). **1b**, found (calcd for C<sub>22</sub>H<sub>25</sub>ClN<sub>2</sub>Pd): C, 57.36 (57.53); H, 5.42 (5.49); N, 6.01 (6.10). **2a**, found (calcd for C<sub>18</sub>H<sub>17</sub>BrN<sub>2</sub>Pd): C, 48.76 (48.29); H, 3.88 (3.83); N, 6.10 (6.25). **6b**, found (calcd for C<sub>35</sub>H<sub>35</sub>ClN<sub>2</sub>O<sub>3</sub>Pd·CH<sub>2</sub>Cl<sub>2</sub>): C, 57.63 (57.01); H, 5.01 (4.92); N, 4.24 (3.69).

FABMS (*m/e*) data are as follows. **1b**, found (calcd for C<sub>22</sub>H<sub>25</sub>ClN<sub>2</sub>OPd – Cl): 423 (423). **2b**, found (calcd for C<sub>22</sub>H<sub>25</sub>BrN<sub>2</sub>OPd – Br): 423 (423). **3a**, found (calcd for C<sub>19</sub>H<sub>17</sub>ClN<sub>2</sub>OPd – Cl): 395 (395). **3b**, found (calcd for C<sub>23</sub>H<sub>25</sub>ClN<sub>2</sub>OPd – Cl): 451 (452). **4a**, found (calcd for C<sub>24</sub>H<sub>19</sub>ClN<sub>2</sub>OPd – Cl): 457 (457). **5a**, found (calcd for C<sub>21</sub>H<sub>21</sub>ClN<sub>2</sub>OPd – Cl): 423 (423). **8b**, found (calcd for C<sub>17</sub>H<sub>31</sub>ClN<sub>2</sub>OPd – Cl): 385 (385).

MALDIMS (*m/e*) data are as follows. **7b**, found (calcd for C<sub>40</sub>H<sub>37</sub>ClN<sub>2</sub>O<sub>3</sub>Pd – Cl): 700 (700).

Compound **9b** could not be characterized by FD-, FAB- or MALDIMS measurements due to fast fragmentations during the measurements.

**Synthesis of [(8-(2-pyridyl)quinoline)(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)palladium(II)]OTf, [(8-PQ)Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)](OTf) (**12**).** [Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>-Cl)<sub>2</sub> (100 mg; 0.27 mmol), 8-PQ (62 mg; 0.30 mmol), and NaOTf (244 mg; 1.37) were dissolved in dichloromethane (20 mL) and stirred for 1 h. The suspension was filtered and the solvent

**Table 1. Crystal Data and Details of the Structure Determination of (8-PQ)Pd{(1-3-η)-2-methylpropenyl}Cl (**1a**)**

empirical formula		Crystal Data	
fweight		C <sub>18</sub> H <sub>17</sub> ClN <sub>2</sub> Pd	
cryst system		403.22	
space group		triclinic	
<i>a</i> – <i>c</i> , Å		P $\bar{1}$ (No. 2)	
$\alpha$ – $\gamma$ , deg		9.2427(13), 11.211(2), 15.966(8)	
<i>V</i> , Å <sup>3</sup>		88.19(3), 88.76(3), 89.728(12)	
<i>D</i> <sub>calc</sub> , g·cm <sup>−3</sup>		1653.2(9)	
<i>Z</i>		1.620	
<i>F</i> (000)		4	
$\mu$ , cm <sup>−1</sup>		808	
cryst size, mm		12.8 (Mo K $\alpha$ )	
		0.08 × 0.20 × 0.30	
		Data Collection	
<i>T</i> , K		150	
$\theta$ <sub>min</sub> , $\theta$ <sub>max</sub> , deg		1.3, 27.5	
wavelength, Å		0.710 73 (Mo K $\alpha$ ) (graphite monochr)	
scan type; scan, deg		$\omega/2\theta$ , 0.84 + 0.35 tan $\theta$	
ref reflns		221, 225, 132	
data set		−12 to 12, −14 to 14, −13 to 20	
tot., uniq data, <i>R</i> (int)		9113, 7582, 0.0382	
obsd data [ <i>I</i> > 2.0 $\sigma$ ( <i>I</i> )]		5495	
		Refinement	
<i>N</i> <sub>ref</sub> , <i>N</i> <sub>param</sub>		7574, 399	
<i>R</i> , w <i>R</i> , <i>S</i>		0.0732, 0.1682, 1.14	
$(\Delta/\sigma)$ <sub>max</sub>		0.001	
min and max $\rho$ , e Å <sup>−3</sup>		−1.21, 1.59	

$$^a w = 1/[\sigma^2(F_o^2) + (0.0202P)^2 + 24.296P], P = (F_o^2 + 2F_c^2)/3.$$

evaporated under vacuo. The solid was washed twice with ether yielding 130 mg (0.26 mmol, 95%) of product.

Anal. Found (calcd for C<sub>18</sub>H<sub>15</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>SPd): C, 43.43 (42.99); H, 3.46 (3.01); N, 5.60 (5.57).

**General Procedure for the Synthesis of Allyl Complexes (N<sup>−</sup>N)Pd(η<sup>3</sup>-allyl)X (X = BF<sub>4</sub>, OTf).** After insertion of the allene as described above, an excess of NaX (X = BF<sub>4</sub>, OTf) was added to a solution of the complex in dichloromethane (20 mL). After 2 h the suspension was filtered and the solvent was removed in vacuo providing the product isolated in yields up to 95%.

<sup>1</sup>H NMR data (300 MHz, CDCl<sub>3</sub>; δ) are as follows. **15**: *i*-Pr-DAB, 8.52 (s, 2H, H<sub>imine</sub>), 4.06 (sept, <sup>3</sup>J = 6.3 Hz, 2H, CH<sub>IPr</sub>), 1.35 (t, <sup>3</sup>J = 6.1 Hz, 6H, CH<sub>3IPr</sub>); allyl, 5.70 (t, <sup>3</sup>J = 7.0 Hz, 1H, H<sub>syn</sub>), 4.65 (s, 1H, H<sub>anti</sub>), 3.56 (s, 1H, H<sub>anti</sub>), 2.42 (s, 3H, C(O)CH<sub>3</sub>); *n*-butyl, 1.92 (m, 2H, CH<sub>2</sub>), 1.57 (m, 2H, CH<sub>2</sub>), 0.91 (m, 3H, CH<sub>3</sub>). **16** (numbering scheme presented in Figure 1): *i*-Pr-PyCa, 9.00 (s, 1H, H<sub>imine</sub>), 8.97 (d, <sup>3</sup>J = 5.7, 1H, H<sub>2</sub>), 7.82 (t, <sup>3</sup>J = 5.7 Hz, 1H, H<sub>3</sub>), 8.16 (t, 7.8, 1H, H<sub>4</sub>), 8.25 (d, <sup>3</sup>J = 7.7, 1H, H<sub>5</sub>), 1.36, 1.32 (d, <sup>3</sup>J = 6.1 Hz, 6H, CH<sub>3IPr</sub>), 4.16 (sept, <sup>3</sup>J = 6.1, 1H, CH<sub>IPr</sub>); allyl, 5.75 (br, 1H, H<sub>syn</sub>), 4.72 (br, 1H, H<sub>anti</sub>), 3.46 (br, 1H, H<sub>anti</sub>), 2.46 (s, 3H, C(O)CH<sub>3</sub>); *n*-butyl, 1.90 (m, 2H, CH<sub>2</sub>), 1.60 (m, 2H, CH<sub>2</sub>), 0.88 (t, <sup>3</sup>J = 7.3 Hz, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR data (75.48 MHz, CDCl<sub>3</sub>; δ) are as follows. **15**: *i*-Pr-DAB: 165.1 (C<sub>imine</sub>), 63.6 (CH<sub>IPr</sub>), 23.1 (CH<sub>3IPr</sub>); allyl, 55.0 (CH<sub>2</sub>), 116.6 (C<sub>central</sub>), 85.3 (CH), 26.3 (C(O)CH<sub>3</sub>), 193.9 (C(O)CH<sub>3</sub>); *n*-butyl: 32.9, 30.8, 22.3 (CH<sub>2</sub>), 13.9 (CH<sub>3</sub>). **16**: *i*-Pr-PyCa, 166.0 (C<sub>imine</sub>), 152.5, 140.3, 128.9, 128.2 (C<sub>pyridyl</sub>), 61.9 (CH<sub>IPr</sub>), 22.3 (CH<sub>3IPr</sub>); allyl, CH<sub>2</sub>, CH and C<sub>central</sub> not observed, 22.3 (C(O)CH<sub>3</sub>), 193.7 (C(O)CH<sub>3</sub>); *n*-butyl, 31.6, 29.6, 21.2 (CH<sub>2</sub>), 12.6 (CH<sub>3</sub>).

Anal. **14**, found (calcd for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>BF<sub>4</sub>Pd): C, 47.30 (47.56); H, 3.94 (3.77); N, 6.05 (6.16).

FABMS (*m/e*) data are as follows. **13**, found (calcd for C<sub>19</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub>F<sub>3</sub>SPd – CF<sub>3</sub>SO<sub>3</sub>): 367 (367). **15**, found (calcd for C<sub>18</sub>H<sub>31</sub>F<sub>3</sub>N<sub>2</sub>O<sub>4</sub>SPd – CF<sub>3</sub>SO<sub>3</sub>): 386 (385). **16**, found (calcd for C<sub>19</sub>H<sub>27</sub>F<sub>3</sub>N<sub>2</sub>O<sub>4</sub>SPd – CF<sub>3</sub>SO<sub>3</sub>): 394 (393).

**Crystal Structure Determination of 1a.** Numerical data on the structure determination have been collected in Table 1. X-ray data were collected for a yellowish crystal glued on top of a glass fiber and transferred into a cold nitrogen stream

of an Enraf-Nonius Cad4T diffractometer on a rotating anode. The intensity data were corrected for absorption with the program DIFABS.<sup>41</sup> The structure was solved by standard Patterson and Fourier methods (SHELXS86<sup>42</sup>) and refined on  $F^2$  with SHELXL-93.<sup>43</sup> Hydrogen atoms were introduced at calculated positions and were refined riding on their carrier atom with isotropic displacement parameters related to  $U(\text{eq})$  of the atom they are attached to. Geometrical calculations and the ORTEP illustration were done with PLATON.<sup>44</sup>

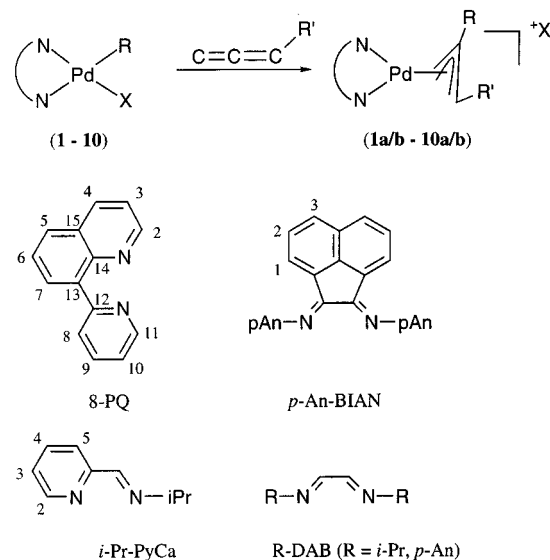
**Kinetic Measurements.** The reaction rates were obtained spectrophotometrically by repetitive scanning of the spectrum at that wavelength, at which the difference in absorbance of product and educt was largest. Propadiene or 1,2-heptadiene was added to a prethermostated solution of the palladium complex in the appropriate solvent in a 1 cm quartz cell. The UV spectra were recorded on a Perkin-Elmer Lambda 5 spectrometer, and the solution was thermostated by a MGW Lauda K4R electronic with a temperature accuracy of 0.5 °C.

## Synthetic Results

Allene insertion into the palladium–carbon bond has been studied for complexes  $(\text{N}\text{N})\text{Pd}(\text{R})\text{X}$  in which the bidentate nitrogen ligands are 8-(2-pyridyl)quinoline (8-PQ), bis(*p*-anisylimino)acenaphthene (*p*-An-BIAN), 1,4-di-*i*-Pr-1,4-diaza-1,3-butadiene (*i*-Pr-DAB), 1,4-di-*p*-An-1,4-diaza-1,3-butadiene (*p*-An-DAB), and 2-(*N*-2-propanecarbaldimino)pyridine (*i*-Pr-PyCa) as shown in Figure 1.

The complexes (8-PQ)Pd(Me)Cl (**1**), (8-PQ)Pd(Me)Br (**2**), and (8-PQ)Pd(C(O)Me)Cl (**3**) reacted with propadiene and 1,2-heptadiene yielding the  $\eta^3$ -allyl complexes **1a–3a** and **1b–3b**, respectively. The complexes (8-PQ)Pd(C(O)Ph)Cl (**4**) and (8-PQ)Pd(C(O)*i*-Pr)Cl (**5**) have been used in the reaction with propadiene resulting in the complexes **4a** and **5a**, respectively, while several uncharacterizable products have been obtained besides the  $\eta^3$ -allyl product upon reaction of 1,2-heptadiene with the complexes **4** and **5**. The reaction of the complexes (*p*-An-BIAN)Pd(C(O)Me)Cl (**6**), (*p*-An-BIAN)Pd(C(O)Ph)Cl (**7**), (*i*-Pr-DAB)Pd(C(O)Me)Cl (**8**), (*p*-An-DAB)Pd(C(O)Me)Cl (**9**), and (*i*-Pr-PyCa)Pd(C(O)Me)Cl (**10**) with 1,2-heptadiene led to the products **6b–10b**, respectively. All insertions have been carried out with neutral complexes, while for those containing Bipy, halide abstraction by a silver salt was required.<sup>25</sup> For complexes containing the ligand 8-PQ insertion of highly substituted allenes like 3-methyl-1,2-butadiene resulted in the formation of several uncharacterizable side products in addition to the desired  $\eta^3$ -allyl product. Insertions of propadiene and 1,2-heptadiene could be carried out in solvents like  $\text{CH}_2\text{Cl}_2$  and THF and in more polar solvents like  $\text{CH}_3\text{CN}$ . The products, of which the ones with R = H are mostly crystalline and the ones with R = *n*-Bu are mostly oils, are stable in solution for days except for complex **10b** which decomposes within a few hours. The  $\eta^3$ -allyl complexes containing the ligands 8-PQ, *i*-Pr-DAB, and *i*-Pr-PyCa are pale yellow, while the complexes containing the ligands *p*-An-BIAN and *p*-An-DAB are red.

The complexes have been fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (see Experimental Section

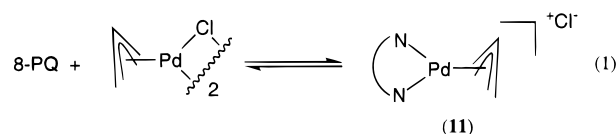


	educt			product	
	N\N	R	X		R'
1:	8-PQ	Me	Cl	<b>1a:</b>	H
				<b>1b:</b>	<i>n</i> -Bu
2:	8-PQ	Me	Br	<b>2a:</b>	H
				<b>2b:</b>	<i>n</i> -Bu
3:	8-PQ	C(O)Me	Cl	<b>3a:</b>	H
				<b>3b:</b>	<i>n</i> -Bu
4:	8-PQ	C(O)Ph	Cl	<b>4a:</b>	H
5:	8-PQ	C(O) <i>i</i> -Pr	Cl	<b>5a:</b>	H
6:	<i>p</i> -An-BIAN	C(O)Me	Cl	<b>6b:</b>	<i>n</i> -Bu
7:	<i>p</i> -An-BIAN	C(O)Ph	Cl	<b>7b:</b>	<i>n</i> -Bu
8:	<i>i</i> -Pr-DAB	C(O)Me	Cl	<b>8b:</b>	<i>n</i> -Bu
9:	<i>p</i> -An-DAB	C(O)Me	Cl	<b>9b:</b>	<i>n</i> -Bu
10:	<i>i</i> -Pr-PyCa	C(O)Me	Cl	<b>10b:</b>	<i>n</i> -Bu

**Figure 1.**

and Tables 2 and S8 (Supporting Information), respectively, for complexes containing the ligand 8-PQ) except for complexes **8b** and **10b** (*vide infra*). The crystalline products gave satisfactory elemental analyses, while the oily products could only be characterized satisfactorily by FAB and MALDI mass spectrometry.

To assign the chemical shifts of the *syn* and *anti* protons in the <sup>1</sup>H NMR spectrum of the  $\eta^3$ -allyl complexes we have synthesized the complexes (8-PQ)Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Cl (**11**) by reaction of the bidentate nitrogen ligand 8-PQ with [Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> (see eq 1). Only in this instance, the ligand dissociates upon washing with ether regenerating the starting compounds according to the equilibrium of eq 1.



The equilibrium is shifted to the right by substitution of the chloride by a triflate anion giving the very stable complex [(8-PQ)Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)](OTf) (**12**). The <sup>1</sup>H NMR spectrum of complex **12** (see Table 2) shows the *syn* proton signals at higher ppm value than the *anti* proton signals, as expected,<sup>45–48</sup> although the opposite situation

(41) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(42) Sheldrick, G. M. *SHELXL-86 Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1986.

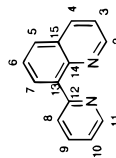
(43) Sheldrick, G. M. *SHELXL-93 Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany 1993.

(44) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

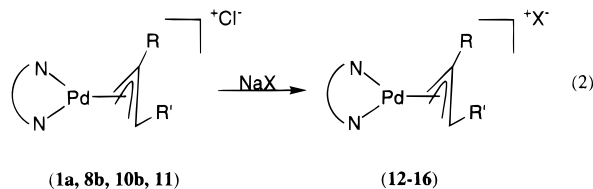
Table 2. <sup>1</sup>H NMR Data (δ) for the Allyl Complexes (8-PQ)Pd(η<sup>3</sup>-allyl)X<sup>a,1</sup>

	H2	H3	H4	H5	H6	H7	H8	H9	H10	H11	H <sub>syn</sub>	H <sub>anti</sub>	R
<b>1a</b>	8.92 (dd) (4.1; 1.5)	7.46 (dd) (8.3; 4.1)	8.25 (dd) (8.3; 1.5)	7.93 (d) (7.8)	7.68 (t) (7.8)	8.43 (d) (7.8)	7.72 (d) (7.8)	7.84 (t) (7.7)	7.42 (t) (5.1)	9.03 (d) (5.1)	3.00 (br)	2.11 (br)	Me, 1.26 (br)
<b>1b</b>	8.95 (dd) (4.1; 1.7)	7.47 (dd) (8.3; 4.1)	8.26 (dd) (8.3; 4.1)	7.95 (d) (7.7)	7.73 (t) (7.7)	b	c	7.85 (s)	7.41 (s)	8.99 (s)	2.95 (br)	d	d
<b>2a</b>	8.95 (dd) (4.2; 1.8)	7.49 (dd) (8.3; 4.2)	8.26 (dd) (8.3; 1.8)	7.95 (dd) (8.2; 1.4)	7.71 (t) (8.2)	8.46 (d) (8.2)	7.76 (d) (7.8)	7.86 (dt) (7.8; 1.7)	7.43 (m)	9.07 (d) (4.9)	3.26 (br)	2.22 (br)	Me, 1.31 (br)
<b>2b</b>	8.97 (d) (4.1)	7.49 (dd) (8.3; 4.1)	8.27 (dd) (8.3; 1.6)	7.96 (d) (7.6)	7.74 (t) (7.6)	b	c	7.86 (t) (7.7)	7.41 (m)	9.00 (br)	3.15 (br)	d	d
<b>3a</b>	8.97 (dd) (4.2; 1.8)	7.50 (dd) (8.3; 4.2)	8.28 (dd) (8.3; 1.8)	7.97 (dd) (8.2; 1.4)	7.68 (dd) (8.2; 7.2)	8.40 (dd) (7.2; 1.4)	7.79 (d) (7.8)	7.90 (dt) (7.8; 1.7)	7.45 (m)	8.92 (d) (4.8)	3.75 (br)	2.16 (br)	Me, 2.08 (br)
<b>3b</b>	8.96 (dd) (4.1; 1.6)	7.51 (dd) (8.3; 4.1)	8.28 (dd) (8.3; 1.6)	7.98 (dd) (7.5; 1.0)	7.68 (t) (7.5)	8.44 (s)	7.81 (s)	7.89 (dt) (7.2; 1.4)	7.44 (t) (7.2)	8.87 (d) (5.2)	4.78 (br)	1.71 (s)	Me, <sup>e</sup> 2.08 (s)
<b>4a</b>	8.69 (d) (4.1)	7.55 (m)	8.21 (dd) (8.1; 1.3)	c	c	8.33 (d) (7.6)	7.81 (d) (7.6)	7.90 (t) (7.6)	7.45 (m)	9.02 (d) (5.2)	3.61 (br)	2.48 (br)	Ph <sup>f</sup>
<b>5a</b>	8.93 (s)	7.54 (dd) (8.1; 4.8)	8.30 (d) (8.3)	7.93 (dd) (7.8)	7.73 (t) (7.8)	8.51 (d) (7.8)	7.94 (s)	7.94 (s)	7.47 (t) (5.4)	9.09 (s)	3.87 (br)	2.11 (br)	i-Pr <sup>g</sup>
<b>12<sup>k</sup></b>	9.22 (d) (4.8)	7.73 (dd) (8.3; 4.8)	8.58 (d) (8.3)	8.15 (d) (8.2)	7.86 (t) (8.2)	8.25 (d) (8.2)	7.84 (d) (7.8)	8.12 (t) (7.8)	7.58 (t) (5.4)	8.96 (d) (5.4)	4.17 (d), <sup>h</sup> 3.89 (d) <sup>h</sup>	3.48 (d), <sup>j</sup> 3.34 (d) <sup>j</sup>	H, 5.90 (m)
<b>13</b>	9.25 (dd) (4.8; 1.6)	7.76 (dd) (8.2; 4.8)	8.60 (dd) (8.2; 1.6)	8.16 (9d) (7.8)	7.85 (t) (7.8)	8.29 (d) (7.8)	7.88 (d) (7.70)	8.13 (dt) (7.7; 1.5)	7.61 (t) (6.6)	8.98 (d) (4.6)	3.94 (br), 3.70 (br)	3.25 (br)	Me, 2.14 (s)
<b>14</b>	9.14 (dd) (4.8; 1.6)	7.69 (dd) (8.3; 4.8)	8.56 (dd) (8.3; 1.6)	8.12 (dd) (7.8; 1.2)	7.78 (t) (7.8)	8.25 (dd) (7.8; 1.2)	7.82 (d) (8.0)	8.07 (dt) (8.0; 1.7)	7.57 (m)	8.93 (dd) (5.4; 1.0)	3.71 (s)	3.08 (s)	Me, 2.02 (s)

<sup>a</sup> Recorded at 300.13 MHz in CDCl<sub>3</sub> at 21 °C with J in parentheses (s = singlet, d = doublet, dd = doublet doublets, t = triplet, m = multiplet, br = broad). <sup>b</sup> Not observed. <sup>c</sup> Obscured by other signals. <sup>d</sup> n-Butyl group. H<sub>anti</sub>, and R group show very broad signals between 0.6–1.5 ppm. <sup>e</sup> n-Butyl: 0.87 (t, <sup>3</sup>J = 7.1 Hz, CH<sub>2</sub>), 1.32, 1.12 (br, CH<sub>2</sub>), 0.76 (t, <sup>3</sup>J = 6.9 Hz, CH<sub>3</sub>). <sup>f</sup> Ph: ortho 7.89 (d, <sup>3</sup>J = 7.6 Hz, 2H), meta 7.40 (t, <sup>3</sup>J = 7.6 Hz, 1H). <sup>g</sup> i-Pr CH 2.93 (sept, <sup>3</sup>J = 6.8 Hz), CH<sub>3</sub> 1.08 (d, <sup>3</sup>J = 6.8 Hz), <sup>h</sup> <sup>3</sup>J = 6.6 Hz, <sup>i</sup> <sup>3</sup>J = 12.4 Hz, <sup>j</sup> <sup>3</sup>J = 6.6 Hz, <sup>k</sup> Measured at 220 K. <sup>1</sup> Numbering as follows:



has been observed as well.<sup>49</sup> By the same method we have synthesized the complexes [(8-PQ)Pd{(1-3- $\eta$ )-2-methyl-propenyl}](OTf) (**13**), [(8-PQ)Pd{(1-3- $\eta$ )-2-methyl-propenyl}](BF<sub>4</sub>) (**14**), [(*i*-Pr-DAB)Pd{(1-3- $\eta$ )-2-acetyl-2-heptenyl}](OTf) (**15**), and [(*i*-Pr-PyCa)Pd{(1-3- $\eta$ )-2-acetyl-2-heptenyl}](OTf) (**16**) (eq 2).

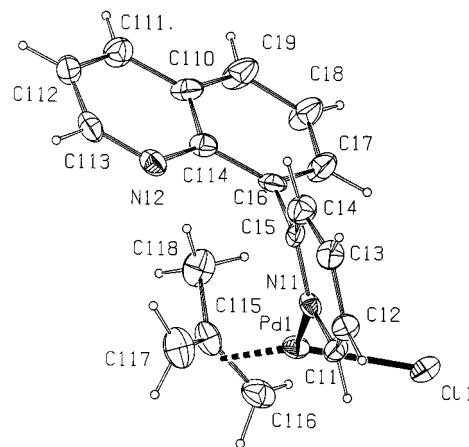


	N^N	R	R'	X <sup>-</sup>
12:	8-PQ	H	H	OTf
13:	8-PQ	Me	H	OTf
14:	8-PQ	Me	H	BF <sub>4</sub>
15:	<i>i</i> -Pr-DAB	C(O)Me	<i>n</i> -Bu	OTf
16:	<i>i</i> -Pr-PyCa	C(O)Me	<i>n</i> -Bu	OTf

Several (R-DAB)Pd( $\eta^3$ -allyl)Cl and (R-PyCa)Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Cl complexes analogous to complex **8b**, **9b**, and **10b** have been described by Crociani et al.,<sup>46,47,50</sup> who demonstrated the existence of equilibria between complexes like [Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> and uncoordinated nitrogen ligand (eq 1) and the formation of [PdCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>(R-DAB)] complexes in which R-DAB acts as a bridging ligand. The <sup>1</sup>H NMR spectra of complex **8b** and **10b** show very broad signals for both the bidentate nitrogen ligand and allyl protons which made interpretation of the spectra difficult even at low temperatures (185 K). Complexes **15** and **16**, however, were easily characterized with <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (see Experimental Section), and it was shown that the *n*-butyl group is positioned on the *syn* position of the allyl group.

**X-ray Structure of Complex 1a.** An X-ray structure determination has been carried out for complex **1a** (see Figure 2). In the crystal cell of the space group *P* $\bar{1}$  two crystallographic independent molecules of **1a** have crystallized of which two different sets of atomic distances and angles appear, probably due to crystal packing effects. Most corresponding atomic distances and angles of the two sets fall within the standard deviation, while some of the dihedral angles between several least-squares planes are different. In Figure 2 only one of the two components containing Pd(1) is displayed.

Interestingly, the nitrogen ligand 8-PQ is coordinated as a monodentate, while the quinoyl group is dissociated and bent away from the metal center. Both the  $\eta^3$ -allyl ligand and the chloride are coordinated to palladium. Monodentate coordination of the ligand 8-PQ has been observed before in the complexes (8-PQ)M(PET<sub>3</sub>)Cl<sub>2</sub> (M = Pd, Pt).<sup>37</sup> For two other  $\eta^3$ -allyl



**Figure 2.** ORTEP plot at the 50% probability level for complex (8-PQ)Pd{(1-3- $\eta$ )-2-methylpropenyl}Cl (**1a**).

**Table 3.** Selected Bond Distances (Å) and Bond Angles (deg) for Complex (8-PQ)Pd{(1-3- $\eta$ )-2-methylpropenyl}Cl (**1a**) (with Esd's in Parentheses)

Bond Distances			
Pd(1)–Cl(1)	2.367(2)	Pd(1)–C(117)	2.098(10)
Pd(1)–N(11)	2.115(7)	C(115)–C(116)	1.392(14)
Pd(1)–C(115)	2.113(10)	C(115)–C(117)	1.408(15)
Pd(1)–C(116)	2.086(10)	C(115)–C(118)	1.501(14)
Bond Angles			
Cl(1)–Pd(1)–N(11)	92.22(18)	N(11)–Pd(1)–C(116)	167.6(3)
Cl(1)–Pd(1)–C(115)	131.9(3)	N(11)–Pd(1)–C(117)	100.1(3)
Cl(1)–Pd(1)–C(116)	99.1(3)	C(115)–Pd(1)–C(116)	38.7(4)
Cl(1)–Pd(1)–C(117)	166.2(3)	C(115)–Pd(1)–C(117)	39.1(4)
N(11)–Pd(1)–C(115)	132.9(3)	C(116)–Pd(1)–C(117)	68.1(4)

complexes (2,9-dimethyl-1,10-phenanthroline)Pd{(1-3- $\eta$ )-3-methyl-2-butenyl}Cl<sup>51</sup> and (*p*-An-BIAN)Pd{(1-3- $\eta$ )-2-acetyl-3-methyl-2-butenyl}Cl<sup>33</sup> containing very rigid bidentate nitrogen ligands also one nitrogen is dissociated from the palladium and positioned at the apical position above the coordination plane.<sup>33,51</sup>

Selected bond lengths and angles of the non-hydrogen atoms of **1a** have been collected in Table 3. The Pd(1)–N(11) distance of 2.115(7) Å is comparable to the ones measured for both the cationic complex [(Bipy)Pd{(1-3- $\eta$ )-2-benzyl-propenyl}](BF<sub>4</sub>)<sup>25</sup> and the neutral complexes (2,9-dimethyl-1,10-phenanthroline)Pd{(1-3- $\eta$ )-3-methyl-2-butenyl}Cl<sup>51</sup> and (*p*-An-BIAN)Pd{(1-3- $\eta$ )-2-acetyl-3-methyl-2-butenyl}Cl.<sup>33</sup> The Pd(1)–C(11) distance of 2.367(2) Å appears rather short as compared to the analogous distances in the above mentioned neutral complexes, which are 2.405(3) and 2.451(3) Å, respectively. The allyl fragment is symmetrically bonded to palladium with Pd(1)–C(116) = 2.086(10) Å and Pd(1)–C(117) = 2.098(10) Å. The geometries of both complexes containing the rigid bidentate nitrogen ligands have been described as distorted square pyramidal,<sup>33,51</sup> while complex **1a** may be characterized as square planar.

**(8-PQ)Pd( $\eta^3$ -allyl) Complexes in Solution.** The <sup>1</sup>H NMR data of the complexes **1a**, **2a**, and **3a** at 294 K in CDCl<sub>3</sub>, compiled in Table 2, show a relatively low-field shift of proton H7 as compared to proton H4. This shift has been observed before for the complexes (8-PQ)M(PET<sub>3</sub>)Cl<sub>2</sub> (M = Pd, Pt),<sup>37</sup> which is due to the short

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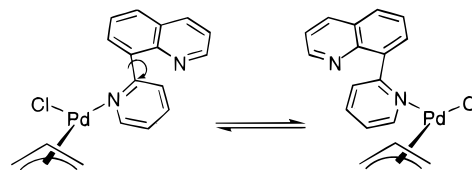
distance between the proton H7 and the metal center when the ligand is coordinated in a monodentate fashion.<sup>52–55</sup> Hence, analogous to the solid structure of **1a**, in the nonpolar solvent CDCl<sub>3</sub> the ligand 8-PQ is very likely coordinated in a monodentate fashion. The signals for protons H7 and H4 show a shift to upper and lower field, respectively, upon addition of the polar solvent CD<sub>3</sub>CN to a solution of complexes **1a**, **2a**, and **3a** in CDCl<sub>3</sub> resulting in values for the chemical shifts of these protons comparable to those of complexes **13** and **14** containing a bidentate 8-PQ. These observations strongly indicate that the ligand 8-PQ coordinates as a bidentate when these complexes are dissolved in polar solvents such as CH<sub>3</sub>CN.

This is corroborated by conductivity measurements, which show that complexes **1a**, **2a**, and **3a** just as **14** behave as electrolytes in CH<sub>3</sub>CN (19.9, 22.8, 16.1, and 76.6 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, respectively, at 294 K), whereas in a solvent with a low dielectric constant like CH<sub>2</sub>Cl<sub>2</sub> the values are 1.6, 1.5, 1.5, and 20.6 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, respectively. The low values for the first three complexes dissolved in CH<sub>2</sub>Cl<sub>2</sub> indicate the presence of neutral species, while the high value for complex **14** is indicative of ionic species. The relatively low values for the first three complexes dissolved in CH<sub>3</sub>CN as compared to complex **14** might be caused by the existence of contact ion pairs.

Unambiguous proof for the coordination mode of the ligand 8-PQ has been obtained from <sup>1</sup>H 2D-NOESY and NOE-difference measurements, which have shown their value in characterizing (N,N)Pd(η<sup>3</sup>-allyl) complexes in solution.<sup>45,56</sup> The expected bidentate coordination of the ligand 8-PQ in complex **14** can clearly be deduced from these <sup>1</sup>H 2D-NOESY measurements, which show a clear NOE between the *ortho* protons of the pyridyl and quinolyl rings and the *syn* protons of the η<sup>3</sup>-allyl. A <sup>1</sup>H 2D-NOESY measurement of complex **1a** could not be carried out in CD<sub>3</sub>CN because of its low solubility. NOE-difference experiments, however, with irradiation on the *syn* protons showed a significant NOE on the *ortho* protons of both the pyridyl and quinolyl group, indicating a bidentate coordination of the nitrogen ligand in CD<sub>3</sub>CN. In the case of CDCl<sub>3</sub> as solvent no NOE's have been observed suggesting a monodentate coordination of the ligand 8-PQ.

**Fluxional Behavior of Allyl Complexes.** Since the palladium η<sup>3</sup>-allyl complexes are highly fluxional, it appeared worthwhile to carry out variable-temperature NMR spectroscopy on these complexes.

At 180 K in CD<sub>2</sub>Cl<sub>2</sub> the <sup>1</sup>H NMR spectrum of complex **14** shows four broad singlets for the *syn* and *anti* protons. In the temperature range from 200 to 250 K in CDCl<sub>3</sub>, however, one *syn* and one *anti* proton signal of the allyl group are broadened, while the other two are relatively sharp. This observation might be explained by a rapid on–off movement of the BF<sub>4</sub> anion in the temperature range from 200 to 250 K giving rise



**Figure 3.**

to a *syn/anti* exchange for two of the four allyl protons occurring via a η<sup>3</sup>–η<sup>1</sup>–η<sup>3</sup> mechanism.<sup>57</sup> That the great majority of the BF<sub>4</sub> anions are not coordinated to palladium in the initial state is judged from the appearance of only one signal in the <sup>19</sup>F NMR at –153.0 ppm in the temperature range from 220 to 293 K, which is indicative of a noncoordinating BF<sub>4</sub> anion.<sup>58,59</sup> The <sup>1</sup>H NMR spectrum at 293 K shows one sharp signal for the *syn* and one sharp signal for the *anti* protons, indicating a fast *syn/syn* and *anti/anti* proton exchange on the NMR time scale of the allyl moiety, while all the signals for the ligand 8-PQ are sharp in the temperature range from 220 to 293 K. This *syn/syn* and *anti/anti* exchange might occur via a monodentate 8-PQ ligand forming a three-coordinate T-shaped intermediate,<sup>56,60</sup> subsequent isomerization, and re-association of the nitrogen atom.

The influence of the anion on the fluxional behavior in the cationic complexes is clearly demonstrated by replacing the BF<sub>4</sub> by an OTf anion. The <sup>1</sup>H NMR spectra of the complex **13** in the temperature range from 220 to 270 K shows four identical signals for the allyl protons. Coalescence of the two *syn* protons and coalescence of the two *anti* protons is reached at 295 K indicating a fast *syn/syn* and *anti/anti* exchange, while at 323 K one signal for the *syn* and one signal for the *anti* protons can be observed. The VT NMR spectra of complex **12** exhibit the same characteristics as those of complex **13**. The <sup>1</sup>H NMR spectrum at 220 K of complex **12** reveals four doublets for the *syn* and *anti* protons, which clearly shows that the *syn* protons are found at higher ppm value (4.17 and 3.89 ppm) than the *anti* protons (3.48 and 3.34 ppm). Coalescence of the two *syn* and the two *anti* protons is reached at the same temperature as for complex **13**.

The situation for the halide complexes **1a–5a** and **1b–3b** is quite different since the ligand 8-PQ coordinates as a monodentate in CDCl<sub>3</sub> (*vide supra*). At 180 K the <sup>1</sup>H NMR spectra of the complexes **1a–5a** exhibit separate signals for the four *syn* and *anti* protons analogous to complexes **13** and **14**. At 293 K in CDCl<sub>3</sub> as well as in CD<sub>3</sub>CN one broadened singlet for the *syn* and one broadened singlet for the *anti* protons of the allyl moiety is observed, indicating a *syn/syn* and *anti/anti* exchange of the allyl protons. Besides the *syn/syn* and *anti/anti* exchange probably via a T-shaped intermediate (*vide supra*), the quinoline nitrogen might temporarily coordinate to the palladium complex enabling Berry pseudorotations. The *syn/syn* and *anti/anti* exchange at 293 K is, however, only feasible not only when the Cl and pyridyl group of the nitrogen ligand

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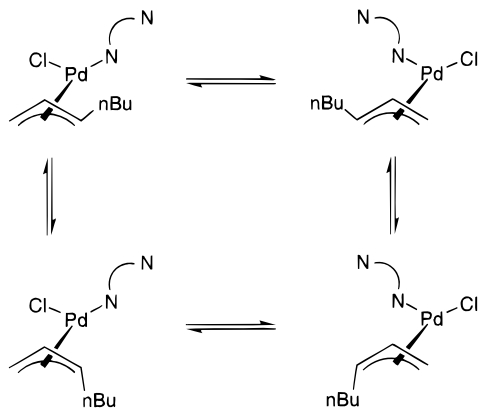
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**Figure 4.**

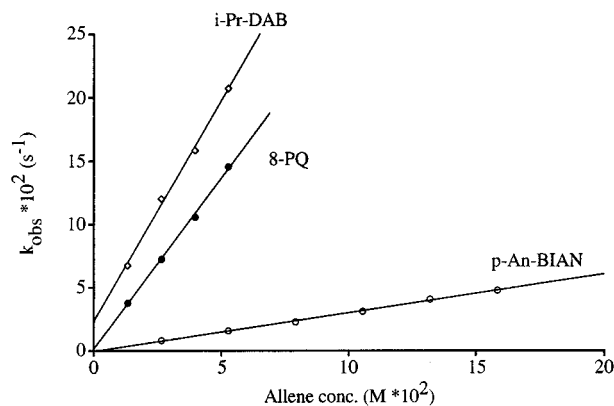
interchange coordination sites but when simultaneously a fast rotation on the NMR time scale around the C–C bond between the quinolyl and pyridyl group occurs (see Figure 3).

Since the rate of the exchange process is not dependent on the concentration of the complex, direct reactions between complexes do not occur.

Interestingly, the signals for H7, H8, and H11 of the 8-PQ ligand of the complexes **1a**, **2a**, and **3a** are broad in the  $^1\text{H}$  NMR spectra at 220 K, whereas they sharpen upon raising the temperature to 240 K and broaden again at 293 K. The same effect can be observed for the signal of the methyl group on the 2-position of the allyl. This might be rationalized by the rotation around the C–C bond between the quinolyl and pyridyl group (see Figure 3). At 220 K the *syn/syn* and *anti/anti* exchange is slow on the NMR time scale, whereas the rotation of the quinolyl group around the pyridyl–quinolyl axis is still in the intermediate exchange causing broad signals for H7, H9, and H11.

The spectra of the complexes **1b–3b** are much more complicated than the spectra of the complexes **1a–3a** since several isomers can be expected in solution, which differ with respect to the position of the *n*-Bu group (*syn* or *anti*) and the position of the pyridyl group (*cis* or *trans*) to the most substituted carbon of the allyl moiety (see Figure 4). Similar phenomena have been observed before for  $\eta^3$ -allyl–Pd complexes containing dissymmetric  $\text{N}^{\wedge}\text{S}$  and  $\text{N}^{\wedge}\text{N}$  ligands.<sup>61</sup>

The characterization and properties of several (Ar-BIAN)Pd( $\eta^3$ -allyl)Cl complexes have been described before,<sup>33</sup> and an X-ray structure analysis of one of these complexes showed also a monodentate coordination of the very rigid bidentate nitrogen ligand Ar-BIAN. Complex **6b**, which exhibited a comparable fluxional behavior to other (Ar-BIAN)Pd( $\eta^3$ -allyl)Cl complexes,<sup>33</sup> occurs in two isomeric forms, one with the *n*-Bu group positioned *anti* (20%) and one with the *n*-Bu group positioned *syn* (80%) on the allyl moiety. The ratio for complex **7** is 50% *syn* and 50% *anti*. The  $^1\text{H}$  NMR spectrum at 294 K revealed both halves of the BIAN ligand to be magnetically equivalent on the NMR time scale indicating a fast *syn/syn* and *anti/anti* exchange of the allyl group (*vide supra*), which could also be observed for complexes **9** and **15**.

**Figure 5.** Dependence of the pseudo-first-order rate constants  $k_{\text{obs}}$  on the 1,2-heptadiene concentration for the reaction of the complexes  $(\text{N}^{\wedge}\text{N})\text{Pd}(\text{C}(\text{O})\text{Me})\text{Cl}$  in  $\text{CH}_2\text{Cl}_2$  at 288 K with 1,2-heptadiene ( $[\text{Pd}] = 1.38 \text{ mM}$ ).

### Kinetic Results

The kinetics of the allene insertion were studied by UV–vis spectrometry, from which the rates were obtained by monitoring the absorption in the range of 360–620 nm as a function of time. All reactions were carried out with a large excess (at least 10-fold) of allene compared to metal complex, *i.e.* under pseudo-first-order conditions. The conversion of the starting complexes is 100% under these conditions, and in all cases isosbestic points were obtained. The conversion of the starting complexes could also be studied by  $^1\text{H}$  NMR, which did not show the occurrence of any intermediate in the temperature range from 220 to 293 K.

All reactions were found to be first order in concentration of the metal complex for both the insertion of propadiene and 1,2-heptadiene for at least 6 half-life times. The pseudo-first-order rate constants  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) (calculated from the slope of the plots of  $\ln\{(A_t - A_\infty)/A_0 - A_\infty\}$  vs time), obtained for the reactions with 1,2-heptadiene, give straight lines when plotted against the concentration of the allene with a zero intercept in most cases except for complex  $(p\text{-An-BIAN})\text{Pd}(\text{C}(\text{O})\text{Ph})\text{Cl}$  (**7**) (see Table 4) and  $(i\text{-Pr-DAB})\text{Pd}(\text{C}(\text{O})\text{Me})\text{Cl}$  (**8**) (see Figure 5). The usual rate equation  $k_{\text{obs}} = k_1 + k_2[\text{allene}]$  is obeyed, while a distinct value for  $k_1$  can be measured for reactions of 1,2-heptadiene with **7** and **8**. The  $k_1$  and  $k_2$  values for the different complexes have been collected in Table 4. The  $k_1$  value is very small relative to  $k_2[\text{allene}]$  for the complexes containing the ligands 8-PQ and complex  $(p\text{-An-BIAN})\text{Pd}(\text{C}(\text{O})\text{Me})\text{Cl}$  (**6**). The zero intercept obtained for complex **6** containing the *p*-An-BIAN ligand is unexpected, since kinetic measurements carried out for the reaction of norbornadiene with complex **6** showed a relatively large  $k_1$  of  $(2.5 \pm 0.5) \times 10^{-3} \text{ s}^{-1}$  ( $k_2 = (3.81 \pm 0.21) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ ) at 288 K.<sup>38</sup>

The activation parameters were obtained from an Eyring plot for the reactions of the complexes **1–3** and **6–8** with 1,2-heptadiene (Table 4). The activation parameters for the allene-independent  $k_1$  pathway found for the reaction of complex **7** and **8** with 1,2-heptadiene could not be calculated properly, since the standard deviations are large.

**Influence of R Group and X Ligand.** The reaction rate is strongly influenced by the R group attached to the palladium atom in the reaction of  $(8\text{-PQ})\text{Pd}(\text{R})\text{Cl}$  with propadiene; the reaction rate increases in the

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**Table 4. Rate Constants and the Enthalpy and Entropy of Activation for the Reaction of (N<sup>∧</sup>N)Pd(R)X (1–3, 6–8) with 1,2-Heptadiene (with Esd's in Parentheses)<sup>a</sup>**

compd	solvent	T (K)	10 <sup>2</sup> k <sub>1</sub> (s <sup>-1</sup> )	k <sub>2</sub> (M <sup>-1</sup> s <sup>-1</sup> )	ΔH <sup>‡</sup> (kJ/mol)	ΔS <sup>‡</sup> (J/K·mol)
(8-PQ)Pd(Me)Cl ( <b>1</b> )	CH <sub>2</sub> Cl <sub>2</sub>	303.0		0.21(1)		
		298.0		0.146(6)		
		293.0		0.082(3)	74(3)	-11(9)
		288.0		0.045(2)		
		285.0		0.033(2)		
	THF	293.0		0.065(2)		
	CH <sub>3</sub> CN	293.0		0.133(3)		
(8-PQ)Pd(Me)Br ( <b>2</b> )	CH <sub>2</sub> Cl <sub>2</sub>	303.0		0.388(2)		
		298.0		0.240(7)		
		293.0		0.185(5)	58(3)	-62(11)
		288.0		0.113(2)		
		283.0		0.068(1)		
(8-PQ)Pd(C(O)Me)Cl ( <b>3</b> )	CH <sub>2</sub> Cl <sub>2</sub>	294.0		3.6(1)		
		288.0		2.8(1)		
		283.0		1.86(1)	41(3)	-94(11)
		278.0		1.28(4)		
		273.0		0.99(3)		
(p-An-BIAN)Pd(C(O)Me)Cl ( <b>6</b> )	CH <sub>2</sub> Cl <sub>2</sub>	295.0		0.47(4)		
		288.0		0.305(7)	39.9(9)	-116(3)
		283.0		0.23(1)		
		278.0		0.162(2)		
(p-An-BIAN)Pd(C(O)Ph)Cl ( <b>7</b> )	CH <sub>2</sub> Cl <sub>2</sub>	305.0	0.09(3)	0.032(3)		
		300.0	0.10(4)	0.024(2)	37(3)	-154(9)
		295.0	0.05(1)	0.0173(7)		
		290.0	0.02(1)	0.0148(8)		
		288.0	2.4(5)	3.5(1)		
(i-Pr-DAB)Pd(C(O)Me)Cl ( <b>8</b> )	CH <sub>2</sub> Cl <sub>2</sub>	283.0	0.8(5)	2.9(1)	33(4)	-121(13)
		278.0	0.7(5)	2.0(1)		
		274.0	0.3(2)	1.70(5)		

<sup>a</sup> [Pd] = 1.38 mM.**Table 5. Rate Constants for Propadiene Insertions into (8-PQ)Pd(R)Cl in CH<sub>2</sub>Cl<sub>2</sub> at 293 K ([Pd] = 1.38 mM, [Propadiene] = 75.8 mM)**

R	k <sub>obs</sub> (s <sup>-1</sup> )	R	k <sub>obs</sub> (s <sup>-1</sup> )
Me ( <b>1</b> )	0.039(1)	C(O) <i>i</i> -Pr ( <b>4</b> )	0.079(1)
C(O)Me ( <b>3</b> )	0.222(4)	C(O)Ph ( <b>5</b> )	0.029(1)

sequence C(O)Ph < Me < C(O)*i*-Pr < C(O)Me (Table 5). These measurements have been carried out with propadiene since the reaction of 1,2-heptadiene with the complexes **4** (R = C(O)Ph) and **5** (R = C(O)*i*-Pr) resulted in the formation of uncharacterized side products. In analogy with this, the k<sub>2</sub> for the reaction of complex (*p*-An-BIAN)Pd(C(O)Ph)Cl (**7**) with 1,2-heptadiene is almost 30 times smaller than the value of k<sub>2</sub> for the reaction of complex (*p*-An-BIAN)Pd(C(O)Me)Cl (**6**) with 1,2-heptadiene at 295 K.

Kinetic measurements carried out for the reaction of 1,2-heptadiene with complex **1** (X = Cl<sup>-</sup>) and complex **2** (X = Br<sup>-</sup>) resulted in a value of k<sub>2</sub> for complex **2** that is about twice as high as that for complex **1** (see Table 4).

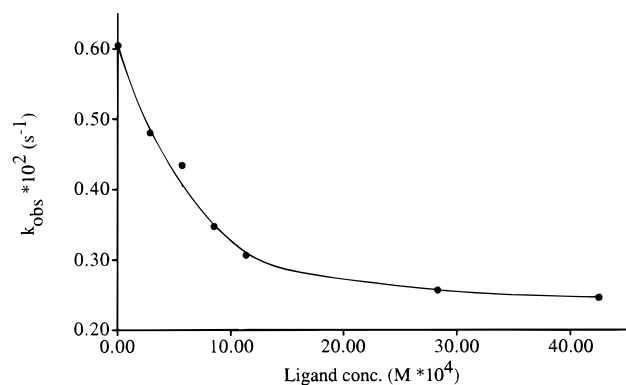
**Influence of the Solvent.** The rate of the insertion of 1,2-heptadiene into the Pd–Me bond of the complex **1** increases with increasing polarity of the solvent in the range THF < CH<sub>2</sub>Cl<sub>2</sub> << CH<sub>3</sub>CN (see Table 4). The difference in the values of k<sub>2</sub> between the reaction in THF and CH<sub>2</sub>Cl<sub>2</sub> is not very large (0.065 ± 0.002 M<sup>-1</sup> s<sup>-1</sup>, and 0.082 ± 0.003 M<sup>-1</sup> s<sup>-1</sup> respectively) while the difference between the value of k<sub>2</sub> in CH<sub>3</sub>CN (0.133 ± 0.003 M<sup>-1</sup> s<sup>-1</sup>) and those in THF and CH<sub>2</sub>Cl<sub>2</sub> is more pronounced.

**Influence of the Bidentate Nitrogen Ligand.** The rate of the allene insertion appears to be strongly influenced by the bidentate nitrogen ligand coordinated to the metal center. The value for k<sub>2</sub>, determined at 288 K for the reaction of 1,2-heptadiene with the

complexes (N<sup>∧</sup>N)Pd(C(O)Me)Cl, decreases in the order N<sup>∧</sup>N = *p*-An-DAB > *i*-Pr-DAB > 8-PQ >> *p*-An-BIAN (see Figure 5 and Table 4). Proper kinetic data for complex **8** could only be obtained at lower temperatures, since at temperatures above 288 K the reaction is too fast to be measured. The reaction of complex **9**, (*p*-An-DAB)Pd(C(O)Me)Cl, with 1,2-heptadiene appeared to be too fast to be measured with the method used. However, it could be estimated that the reaction is about four times faster than the reaction of **8** with 1,2-heptadiene. Unfortunately, the kinetic results for complex **10** could not be used, since at the later stages of the reaction the isobesticity is lost. This may be caused by the instability of the product **10b** (*vide supra*).

**Influence of Excess Free Bidentate Nitrogen Ligand and Free Halide.** The influence of excess nitrogen ligand on the k<sub>obs</sub> has been studied for complexes (8-PQ)Pd(Me)Cl (**1**), (8-PQ)Pd(C(O)Me)Cl (**3**), (*i*-Pr-DAB)Pd(C(O)Me)Cl (**8**), and (*p*-An-BIAN)Pd(C(O)Me)Cl (**6**). Addition of ligand to the first three complexes led to a decrease of the reaction rate while in the case of (*p*-An-BIAN)Pd(C(O)Me)Cl the reaction rate is independent of the ligand concentration. The latter result is analogous to results obtained for the reaction of norbornadiene with **6**.<sup>38</sup> A typical example of the mentioned retardation of the reaction, in this case the reaction of complex **1** with 1,2-heptadiene, is shown in Figure 6.

The influence of additional Cl<sup>-</sup> and Br<sup>-</sup> has been measured for complexes **1–3**, **6**, and **8**. To keep the ionic strength constant throughout the experiment, the total ion concentration was compensated by addition of NEt<sub>4</sub>OTf. An unexpected, small (30%) increase of the reaction rate has been observed upon addition of 4 equiv of Cl<sup>-</sup> with respect to complex **1** in reaction with 1,2-heptadiene in CH<sub>2</sub>Cl<sub>2</sub>, while a large (ca. 100%) increase



**Figure 6.** Effect of the concentration of additional 8-PQ on the pseudo-first-order rate constant  $k_{\text{obs}}$  of the reaction of 1,2-heptadiene with **1** in  $\text{CH}_2\text{Cl}_2$  at 293 K ( $[\text{Pd}] = 1.38 \text{ mM}$ ,  $[1,2\text{-heptadiene}] = 77.6 \text{ mM}$ ).

of  $k_{\text{obs}}$  has been observed upon addition of 2 equiv of  $\text{Br}^-$  with respect to complex **2** in reaction with 1,2-heptadiene and upon addition of 2 equiv of  $\text{Cl}^-$  with respect to complex **8** in reaction with 1,2-heptadiene. The rate enhancement is peculiar and, as far as we know, has never been observed before for insertions of unsaturated hydrocarbons into palladium carbon bonds, since usually retardation or no influence is observed.<sup>62–65</sup> The rates of complexes **3** and **6** were not affected by addition of extra  $\text{Cl}^-$  in analogy to the kinetic measurements carried out for norbornadiene insertions.<sup>38</sup>

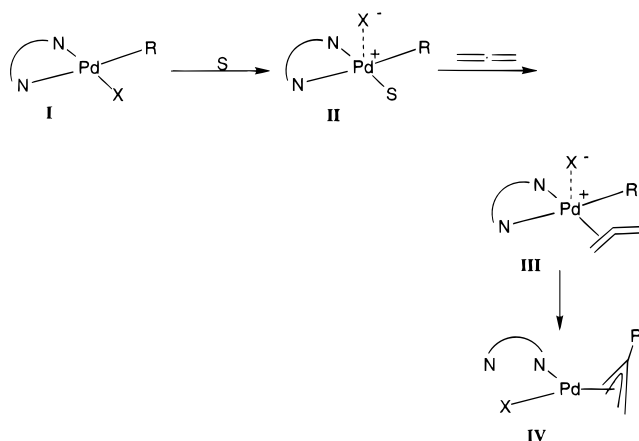
### Discussion

The reactions of the allenes propadiene and 1,2-heptadiene with the complexes  $(\text{N}^-\text{N})\text{Pd}(\text{R})\text{X}$  leading to  $\eta^3\text{-allyl-Pd}$  complexes appeared to be quantitative and relatively fast especially for complex **9**. An interesting feature is that coordinatively saturated, neutral halide complexes can be used. The ligand 8-PQ has the possibility to coordinate both in a monodentate and in a bidentate fashion in the complexes **1a–5a** and **1b–3b** depending on the solvent;  $\text{CHCl}_3$  promotes a monodentate bonding of 8-PQ resulting in neutral complexes, while the polar solvent  $\text{CH}_3\text{CN}$  favors bidentate coordination leading to ionic complexes.

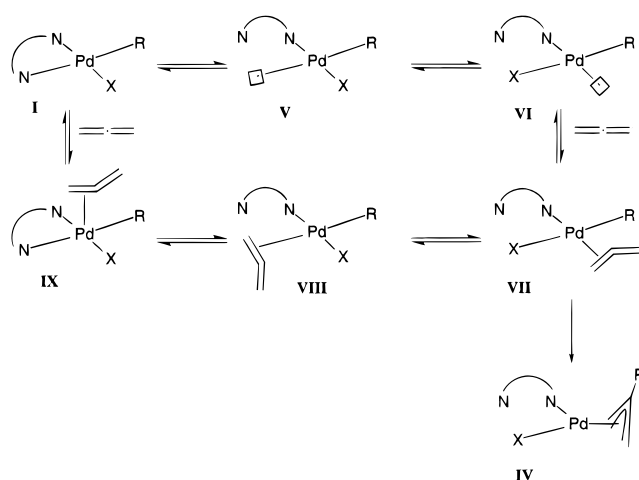
The kinetic measurements show that the allene insertion occurs via an allene-independent  $k_1$  pathway and an allene-dependent  $k_2$  pathway. The  $k_1$  value is very small relative to  $k_2[\text{allene}]$  for the complexes **1–3** and **6**. The allene-independent pathway is important in the case of complexes **7** and **8**, but large errors in the values for  $k_1$  prevented a detailed analysis of this pathway.

**Allene-Independent  $k_1$  Pathway.** We propose that the allene-independent  $k_1$  pathway proceeds via a rate-determining associative substitution of the halide by the solvent from starting complex **I** resulting in intermediate **II** (see Scheme 1). It is likely that a contact ion pair is formed when the reaction is carried out in the moderately polar solvent dichloromethane.

### Scheme 1. Possible Route for the Allene-Independent $k_1$ Pathway



### Scheme 2. Possible Routes for the Allene-Dependent $k_2$ Pathway



The substitution of the halide by the solvent must be the rate-determining step ensuring the reaction to be first order in concentration of palladium and independent of the allene concentration. A fast substitution of the solvent by the allene leads to intermediate **III**, whereafter migration of the R group to the central carbon of the pre-coordinated allene results in product **IV**.

A detailed analysis of the solvento pathway was feasible for reactions with norbornadiene.<sup>38</sup> Since the pathway is independent of the concentration of substrate, we might assume that the mechanism for the reactions with allenes and norbornadiene are identical, at least for the reactions with complexes containing Ar-BIAN.

**Allene-Dependent  $k_2$  Pathway.** Since the  $k_2$  path is dependent on the allene concentration, association of allene at a vacant site of palladium is rate-determining or occurs prior to the rate-determining step. A vacant site may be created by dissociation of one of the nitrogen donor atoms of the bidentate nitrogen ligand thereby forming intermediate **V** (Scheme 2). We previously have suggested that the CO insertion into the Pd–C bond of complexes containing bidentate nitrogen ligands may follow such a route, as derived from the work of Natile

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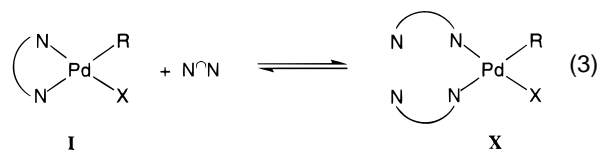
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*et al.*<sup>66–68</sup> and other groups,<sup>51,69,70</sup> who found that even with very rigid bidentate nitrogen ligands (partial) dissociation of one nitrogen donor may occur. Moreover, work done in our and other laboratories has shown that dissociation of one nitrogen donor in the complexes (2,2'-bipyrimidine)Pd(C(=NR)Me)Cl<sup>71</sup> and (2,2'-bipyrimidine)-Pd( $\eta^3$ -allyl)BF<sub>4</sub><sup>60</sup> occurs in solution.

Dissociation of the nitrogen donor *trans* to the R group would be favored because of the higher *trans* influence of the R group compared to halides.<sup>72</sup> The three-coordinate species (intermediate **V**) formed then isomerizes to the more stable T-shaped intermediate **VI** having the R group and the halide in a *trans* position, which has also been proposed by Natile *et al.*<sup>67</sup> Subsequent to allene coordination (intermediate **VII**) migration of the R group now occurs resulting in product **IV**.

An indication for the formation of intermediate **V** may be provided by the observed retardation of the allene insertion upon addition of extra ligand to the reaction of 1,2-heptadiene with the complexes **1**, **3**, and **8**, as allene and free ligand will compete for the vacant site. A mechanism involving a five-coordinate intermediate **IX** in which the allene coordinates at the apical position of the metal center in the initial step might also be retarded by excess nitrogen ligand, as the nitrogen ligand might then be in competition with allene. Since coordination of a nitrogen donor on the apical position of a metal center is relatively difficult, this cannot lead to such a large retardation, and therefore, we prefer a mechanism via intermediate **V**. Additionally, we have strong indications that coordination of two ligands in a monodentate fashion to the metal as shown in eq 3 is possible.



In the temperature region between 185 and 240 K the <sup>1</sup>H NMR spectrum of a mixture of complex **1** and free 8-PQ ligand in CD<sub>2</sub>Cl<sub>2</sub> shows the formation of a new complex, which is most likely a complex **X** as shown in eq 3 containing two 8-PQ ligands coordinated in a monodentate fashion. Analogous to the X-ray structure of **1a** and (8-PQ)Pd(PEt<sub>3</sub>)Cl<sub>2</sub><sup>37</sup> we suppose that the pyridyl group is coordinated to the palladium and that the quinolyl group is bent away from the metal atom. Structures containing Ar-BIAN ligands analogous to structure **X** have never been observed,<sup>38</sup> which is in agreement with the observation that free Ar-BIAN has no influence on the insertion rate of complex **6** and **7**.

Therefore we propose that the mechanism of the allene-dependent pathway for complexes **6** and **7** is

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different than for complexes containing more flexible ligands and proceeds identically to the mechanism proposed for the reaction with norbornadiene.<sup>38</sup> The insertion occurs via an initial allene association (intermediate **IX**) followed by either a halide or nitrogen dissociation and subsequent migration of the R group to the pre-coordinated allene.

A mechanism involving an ionic intermediate and Pd–X breaking is not feasible since the difference in rate between reactions in the moderately polar solvent CH<sub>2</sub>Cl<sub>2</sub> and polar solvent CH<sub>3</sub>CN and between reactions of **1** and **2** (X = Cl<sup>–</sup> and Br<sup>–</sup>, respectively) with 1,2-heptadiene is not very large.

The strong dependence of the reaction rate on the migrating R group strongly indicates that the migration of the R group to the pre-coordinated allene is the rate-determining step in the mechanism. The dependence of the rate of the allene insertion into the Pd–C bond of the acyl complexes (8-PQ)Pd(C(O)R)Cl on the migrating R group can be rationalized both by steric and electronic effects. The migration of the C(O)Me group is faster than of the C(O)*i*-Pr group for steric reasons. The latter group is expected to have more or less the same steric properties as the C(O)Ph group, but the C(O)*i*-Pr– group migrates faster because it is more basic. This trend has been found in experimental and theoretical work concerning CO insertions into metal–carbon bonds.<sup>73–76</sup> In analogy with the results obtained for complexes containing the ligand 8-PQ, complexes containing the ligand *p*-An-BIAN show the same trend, as complex **7** reacts almost 30 times more slowly with 1,2-heptadiene at 295 K than complex **6**.

The observed differences between the migration rate of the Me group and the C(O)Me group are in accord with results of theoretical calculations.<sup>77</sup>

The determination of the activation parameters for the allene dependent *k*<sub>2</sub> path resulted in negative  $\Delta S$  values for all complexes except for complex **1**. Since the proposed mechanism contains several pre-equilibria, it is difficult to rationalize the values in detail, but a negative  $\Delta S$  is in support of association of allene to the metal center in those pre-equilibria.

The *k*<sub>obs</sub> appeared to be strongly influenced by the bidentate nitrogen ligand. The fastest reaction has been found for complex **9** ( $\widehat{N-N} = p$ -An-DAB) followed by complex **8** ( $\widehat{N-N} = i$ -Pr-DAB). A nitrogen atom carrying an electron-withdrawing group such as *p*-anisyl is more prone to dissociation from the metal center, thereby readily creating a vacant site, than a nitrogen atom carrying an electron-donating group such as *i*-Pr. The difference in the reaction rate between complex **6** ( $\widehat{N-N} = p$ -An-BIAN) and **9**, of which the latter reacts 50 times faster than the former, seems to originate from the flexibility rather than from the electronic properties of the ligand. One may imagine that the equilibrium between intermediate **I** and **V** in Scheme 2 will be shifted more to the right using a flexible ligand such as *p*-An-DAB, *i*-Pr-DAB, and also 8-PQ as compared to systems containing a rigid ligand such as *p*-An-BIAN.

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Another explanation for the relatively slow reaction of complex **6** might be a mechanism involving a five coordinate intermediate **IX** for complexes containing rigid bidentate nitrogen ligands as has also been proposed for reaction of complex **6** with NBD.<sup>38</sup>

An unprecedented result is the small but distinct enhancement of the reaction upon addition of Cl<sup>-</sup> or Br<sup>-</sup> to the reaction mixture of complexes **1**, **2**, and **8**. We may only speculate about the origin of this effect, but we can say that the importance of anions in insertion reactions is indicated, which is, however, not very well understood as yet.<sup>4,5,63-65,78</sup>

**Acknowledgment.** Prof. Dr. E. Drent and Dr. W. P. Mul (Koninklijke/Shell-Laboratorium, Amsterdam)

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are acknowledged for their helpful discussions, and Shell Research BV is thanked for financial support. This work was supported in part (N.V. and A.L.S.) by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO). We thank J.-M. Ernsting for NMR spectroscopy assistance and R. H. Fokkens and J. W. H. Peeters for mass spectroscopy.

**Supporting Information Available:** Further details of the structure determinations, including tables of X-ray parameters, atomic coordinates, bond lengths and angles, and thermal parameters for **1a**, tables of NMR data, and tables of the measured  $k_{\text{obs}}$ 's for all the kinetic reactions (15 pages). Ordering information is given on any current masthead page.

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