Synthesis of Chiral (Diaminocarbene)Pd(allyl)Cl Complexes

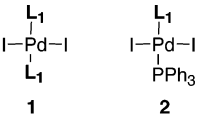
Sylvain Roland,* Max Audouin, and Pierre Mangeney

Laboratoire de Chimie Organique, UMR 7611 CNRS, Université Pierre et Marie Curie, 4 Place Jussieu, Tour 44-45, 75252 Paris Cedex 05, France

Received February 4, 2004

Summary: Palladium(II)-allyl complexes bearing one chiral diaminocarbene ligand have been synthesized from the corresponding silver(I) complexes. The activation of these precatalysts by nucleophiles allowed the in situ generation of Pd(0) species, which are active in the Mizoroki−Heck reaction.

N-Heterocyclic carbenes (NHC) have recently emerged as an important family of ligands with strong σ-donor electronic properties.[1] In contrast to the widely used phosphines complexes, most of the complexes formed with these ligands are stable toward heat, air, and moisture. Indeed, *N*-heterocyclic carbenes are tightly bound to the metal, thereby avoiding decomposition pathway or deposition of free (and inactive) metal under catalytic conditions. Herrmann et al. reported for the first time in 1995 the use of palladium(II) NHC complexes in the Heck reaction.[2] This group postulated that the Pd(II) species, a stable catalyst precursor, might be activated into Pd(0) for the coupling to occur. Since then, carbene complexes of Pd(II) or Pd(0) have been widely used as catalysts or catalyst precursors for many reactions.[1] Several groups have recently reported syntheses of chiral NHC complexes of palladium.[3] However, to our knowledge, only two examples of asymmetric catalysis, giving good selectivities, were reported the literature. Hartwig et al. in 2001 reached 76% ee in intramolecular α-arylation of amides.[4] In 2003, Douthwaite et al. also reported ee up to 92% in the allylic alkylation reaction.[5] We wish to report here the synthesis of new palladium-allyl complexes having one chiral diaminocarbene ligand. The preparation of silver(I) and palladium(II) complexes and an X-ray crystal structure of a palladium(II) complex are presented. The behavior of these palladium-allyl complexes in solution is also discussed.



1 **2**

Diaminocarbene ligands:

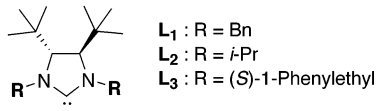


Figure 1.

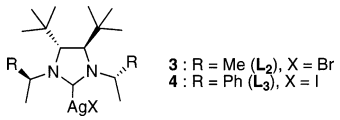


Figure 2.

We recently described the syntheses of the chiral Pd(II) bis-diaminocarbene complex **1** and mixed diaminocarbene-phosphine complex **2** (Figure 1).[6] Their activity in the Heck reaction was studied. We demonstrated that the reduction of such Pd(II) precatalysts into Pd(0) is the limiting step in this coupling reaction. The in situ activation of these complexes allowed Heck reactions at 40 °C instead of 120 °C (without activation).

In a more recent work, we focused on the synthesis of chiral Pd(II) bis-diaminocarbene complexes or mixed diaminocarbene-phosphine complexes having more hindered ligands such as $\mathbf{L_2}$ or $\mathbf{L_3}$ (Figure 1). In these two diaminocarbenes, both nitrogen atoms bear a trisubstituted sp^3 carbon instead of the initial benzyl groups on $\mathbf{L_1}$.

To explore the preparation of such complexes, the silver diaminocarbenes **3** and **4** were synthesized (Figure 2).

Compound **3** was obtained in two steps from the imidazoline **5** (Scheme 1).[7] The reaction of **5** with 2-bromopropane (4 equiv) in the presence of K_2CO_3 and in refluxing acetonitrile gave the imidazolinium salt **6** in 77% yield, after precipitation in AcOEt. The Ag(I) carbene **3** was obtained quantitatively by treatment of **6** with Ag_2O (0.5 equiv).[8] The synthesis of the silver carbene **4** was already reported by our group.[9]

* Corresponding author. Tel: +33 1 44275567. Fax: +33 1 44277567. E-mail: sroland@ccr.jussieu.fr.

(1) (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (b) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2001**, *46*, 181. (c) Bourrissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (d) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

(2) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371.

(3) (a) Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber.* **1996**, *129*, 1483. (b) Herrmann, W. A.; Goossen, L. J.; Spiegler, M. *Organometallics* **1998**, *17*, 2162. (c) Clyne, D. S.; Jin, J.; Genest, E.; Gallucci, J. C.; RajanBabu, T. V. *Org. Lett.* **2000**, *2*, 1125. (d) Tulloch, A. A. D.; Danopoulos, A. A.; Tizzard, G. J.; Colles, S. J.; Hursthouse, M. B.; Hay-Motherwell, R. S.; Motherwell, W. B. *Chem. Commun.* **2001**, 1270. (e) Enders, D.; Gielen, H. *J. Organomet. Chem.* **2001**, *617−618*, 70. (f) Herrmann, W. A.; Böhm, V. P. W.; Gstöttmayr, C. W. K.; Grosche, M.; Reisinger, C.-P.; Weskamp, T. *J. Organomet. Chem.* **2001**, *617−618*, 616. (g) Perry, M. C.; Cui, X.; Burgess, K. *Tetrahedron: Asymmetry* **2002**, *13*, 1969. (h) Bonnet, L. G.; Douthwaite, R. E.; Hodgson, R. *Organometallics* **2003**, *22*, 4384.

(4) Lee, S.; Hartwig, J. F. *J. Org. Chem.* **2001**, *66*, 3402.

(5) Bonnet, L. G.; Douthwaite, R. E. *Organometallics* **2003**, *22*, 4187.

(6) Pytkowicz, J.; Roland, S.; Mangeney, P.; Meyer, G.; Jutand, A. *J. Organomet. Chem.* **2003**, *678*/1-2, 166−179.

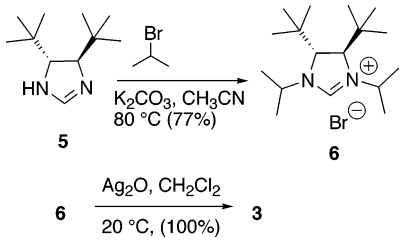
(7) Alexakis, A.; Aujard, I.; Pytkowicz, J.; Roland, S.; Mangeney, P. *J. Chem. Soc., Perkin Trans. 1* **2001**, 949.

(8) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.

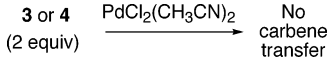
(9) Pytkowicz, J.; Roland, S.; Mangeney, P. *J. Organomet. Chem.* **2001**, *631*, 157.

10.1021/om040013b CCC: $27.50
Publication on Web 05/08/2004

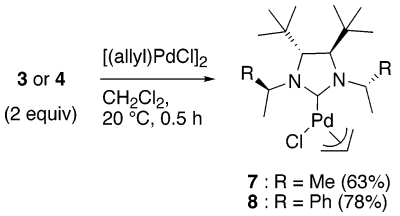
Scheme 1



Scheme 2



Scheme 3



Starting from **3** or **4**, the methods described by the groups of Enders[3e] and Herrmann,[3f] which were efficient for the obtention of **1** and **2**,[6] did not allow the synthesis of bis-diaminocarbene or mixed diaminocarbene-phosphine complexes. For example, the reaction of these silver diaminocarbenes (2 equiv) with $PdCl_2(CH_3CN)_2$ gave neither a trace of the expected Pd(II) bis-carbene complexes nor a trace of complexes having only one carbene ligand, even in refluxing CH_2Cl_2 or CH_3CN (Scheme 2). Therefore, it seems that ligands $\mathbf{L_2}$ and $\mathbf{L_3}$ cannot be transferred onto the palladium, contrary to $\mathbf{L_1}$.

These first observations led us to explore the synthesis of palladium-allyl complexes with these chiral hindered carbene ligands. Nolan et al. recently reported the preparation of achiral diaminocarbene palladium-allyl complexes and demonstrated that they could be activated into Pd(0) by nucleophiles such as *t*-BuOK. These complexes were used by this group in aryl amination reactions, Suzuki couplings, or ketone α-arylations.[10] Moreover, such complexes generated from silver(I) diaminocarbenes and [(allyl)PdCl]$_2$ were used by Douthwaite in the asymmetric allylic alkylation reaction.[5]

The reaction of **3** or **4** with [(allyl)PdCl]$_2$ proceeds rapidly in CH_2Cl_2 at 20 °C (Scheme 3). Precipitation of the silver salts (AgBr or AgI) is observable almost immediately (after 1−2 min stirring). The palladium species so formed are stable on silica gel, and the progress of the reaction could be followed by TLC. After 0.5 h, the crude complexes **7** and **8** were isolated by simple filtration of the silver salts and concentration. Purification by silica gel chromatography afforded **7** (63% yield) and **8** (78% yield) as white crystalline solids. These two complexes can be handled in air with no observable degradation. Elemental analyses of **7** and **8** were in complete accordance with the expected structures. Nevertheless, the interpretation of the ^{1}H NMR spectra of such complexes was not obvious. Indeed, **7** and **8** were respectively isolated as a 1:1 and 6:4 mixture of two nonsymmetrical species. In the ^{1}H NMR spectrum of **8**, for example, four signals are visible for the *t*-Bu groups. This indicated that the symmetry of the carbene ligand did not exist anymore and that two species were present. Two sets of signals were also observed for each proton of the allyl fragment. The chemical shifts (^{13}C NMR) of the carbene carbon are very close for the two species. Complex **8** exhibits two signals at 209.41 and 209.28 ppm. The same obervations were made for complex **7**. The two isomers of each complex were not separable by silica gel chromatography.

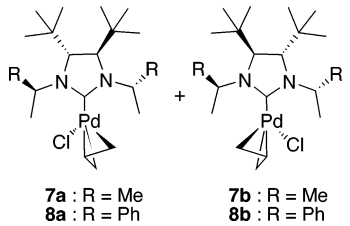


Figure 3. Isomers of the palladium-allyl complexes.

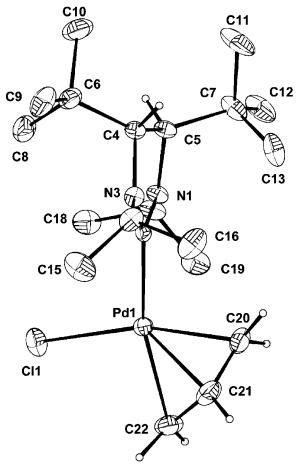


Figure 4. Molecular structure of complex **7a**.

From these results, we postulated that the two species observed for each complex must be two isomers that differ in the position of the allyl group borne by the palladium. The two possible structures, **7a**/**8a** or **7b**/**8b**, are represented in Figure 3. As shown by Nolan et al. in X-ray analysis of similar complexes (with achiral carbene ligands), the bond lengths between the palladium and the three carbons of the allyl moiety are not identical.[10] Therefore, the palladium in such complexes is a stereogenic center and the two species observed for **7** and **8**, which have a chiral ligand, are diastereomeric π-allyl intermediates.

To confirm the structure of these complexes, **7** was crystallized by slow evaporation in Et_2O. An X-ray analysis of a single crystal was performed (Figure 4). The ORTEP of this crystal corresponds to the isomer **7a**. This structure showed a distorted square-planar coordination around the palladium center as well as η^3 coordination of the allyl fragment. The distances between the palladium and the carbon atoms of the allyl are close but not identical (2.123, 2.134, and 2.209 Å). The palladium−chloride bond is perpendicular to the plane of the carbene ligand. Selected bond lengths and angles are presented in Table 1.

We were unable to obtain a ^{1}H NMR spectrum of the single crystal used for the X-ray analysis. Nevertheless,

(10) (a) Viciu, M. S.; Germaneau, R. F.; Navarro-Fernandez, O.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2002**, *21*, 5470. (b) Viciu, M. S.; Germaneau, R. F.; Nolan, S. P. *Org. Lett.* **2003**, *4*, 4053.

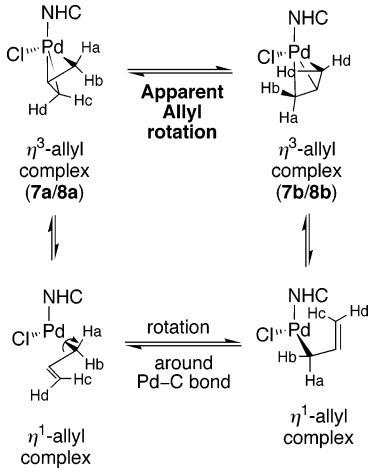
Table 1. Selected List of Bond Lenghts (Å) and Angles (deg) for 7a

Bond Lengths	
Pd(1)−C(2)	2.042(3)
Pd(1)−Cl(1)	2.3714(9)
Pd(1)−C(20)	2.123(4)
Pd(1)−C(21)	2.134(4)
Pd(1)−C(22)	2.209(4)
C(20)−C(21)	1.400(5)
C(21)−C(22)	1.392(6)
C(2)−N(1)	1.360(4)
C(2)−N(3)	1.328(4)
Bond Angles	
C(2)−Pd(1)−C(20)	97.80(13)
C(2)−Pd(1)−C(21)	131.18(14)
C(2)−Pd(1)−C(22)	165.25(13)
Cl(1)−Pd(1)−C(2)	98.61(8)
Cl(1)−Pd(1)−C(20)	162.98(11)
Cl(1)−Pd(1)−C(21)	127.85(11)
Cl(1)−Pd(1)−C(22)	95.48(12)
C(20)−C(21)−C(22)	120.0(4)
N(1)−C(2)−N(3)	107.5(2)
Pd(1)−C(2)−N(1)	125.2(2)
Pd(1)−C(2)−N(3)	127.2(2)

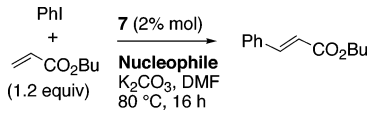
a spectrum realized on all the crystals obtained in Et_2O revealed the presence of **7a** and **7b** in a ratio not significantly different from that obtained from the crude and from the complex purified by chromatography. For these reasons, we could not determine if the palladium center is configurationally stable or if an equilibrium exists in solution between the two diastereomers **7a** and **7b** (or **8a** and **8b**). Nevertheless, π-allyl metal complexes are known to be dynamic systems that are in equilibrium at room temperature. In this case, two processes must be taken into account: *syn*−*anti* isomerization or apparent allyl rotation.[11] Therefore, the Pd(II) species **7a** and **7b** or **8a** and **8b** could be in dynamic conformational exchange in solution, although a single crystal of **7a** was obtained by crystallization. In complexes **7** and **8**, the allyl fragment is not substituted. This implies that the *syn*−*anti* isomerization led to the same diastereomer and cannot be observed. The most obvious conclusion is that the two species observed by NMR for each complex are in a rapid equilibrium through apparent allyl rotation. One of the possible mechanisms proposed for this interconversion, described in Scheme 4, proceeds via $\pi-\sigma-\pi$ isomerization with rotation around the Pd−C bond in the η^1-intermediate. To confirm this hypothesis, we performed complementary NMR experiments on complex **8**. In the ^{1}H NMR spectrum of this species, the signals corresponding to each isomer are separated for nearly all the protons. These signals could be attributed to one or the other isomer by COSY experiment and by comparing the integrations (the ratio of the two isomers is about 6:4). An EXSY experiment performed on this sample clearly demonstrated that the two isomers are in equilibrium during the NMR time scale. Correlation spots between the two diastereomers are visible for all the protons of the allyl moiety but also, for example, for the CH_3 and C*H* of the phenylethyl groups.

(11) (a) Trost, B. M.; Lee, C. In *Asymmetric Allylic Alkylation Reactions*; *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, 2000; pp 593−649. (b) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (c) Pfaltz, A.; Lautens, M. In *Allylic Substitution Reactions*; *Comprehensive Asymmetric Catalysis II*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer-Verlag: Berlin, 1999; pp 833−884.

Scheme 4



Scheme 5



Nucleophile	Conversion
t-BuONa (10% mol)	60%
PPh_3 (5% mol)	75%
MeONa (10% mol)	94%

Complex **7** was tested in the classical Heck coupling of phenyl iodide with butylacrylate (Scheme 5). The ability of several nucleophiles to activate the Pd(II) precatalyst into Pd(0) was compared. The reaction was performed at 80 °C in DMF, in the presence of 2% mol of catalyst and 10−20% mol of activating agent. Under these conditions, the best conversion in (*E*)-butylcinnamate (94%) was obtained with sodium methylate as the nucleophile.

In summary, a synthesis of new chiral diaminocarbene palladium allyl complexes was developed from the corresponding silver(I) diaminocarbenes. This method allowed the preparation of palladium(II) complexes having carbene ligands with bulky nitrogen substituents. By comparison, the synthesis of palladium(II) biscarbene complexes with such ligands was not possible. The activation of these precatalysts by nucleophiles led to catalytic species active in the Heck reaction. NMR and X-ray analysis demonstrated the stereogenic nature of the palladium center, which is not configurationally stable. The potential of these chiral complexes in asymmetric catalysis is under investigation.

Experimental Section

General Comments. All experiments were carried out under argon. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 instrument in $CDCl_3$ as the solvent. Unless otherwise indicated, all chemicals were used as received. Silver(I) oxide 99+% and dimeric allylpalladium chloride were respectively purchased from Acros and Aldrich. (4*R*,5*R*)-1,3-2Bis[(*S*)-1-phenylethyl]-4,5-di-*tert*-butylimidazolin-2-ylidene silver iodide was prepared according to ref 9. Solvents were of analytical grade type and used without special drying or distillation except for the synthesis of the palladium complexes, where dichloromethane was distilled from CaH_2 before use. Flash chromatography was performed on silica gel 60 (0.015−0.040 mm).

(4*R*,5*R*)-1,3-Diisopropyl-4,5-di-*tert*-butylimidazolinium Bromide (6). The reaction was performed under argon

in a screw-cap tube. To a solution of imidazoline **5** (364 mg, 2 mmol) in CH_3CN (4 mL) were added 713 μL (4 mmol) of 2-bromopropane and 553 mg (2 mmol) of K_2CO_3. The mixture was stirred for 72 h at 80 °C, filtered through Celite, and concentrated. To the residue was added 10 mL of AcOEt to triturate the product. The white precipitate formed was washed several times with AcOEt and dried to afford 535 mg (77%) of a white solid. Mp: 295 °C. ^{1}H NMR: δ 10.4 (s, 1H, N−C*H*═N), 3.79 (m, 2H), 3.57 (s, 2H), 1.91 (d, 6H, J = 6.8 Hz), 1.53 (d, 6H, J = 6.6 Hz), 1.03 (s, 18H). ^{13}C NMR: δ 157.43 (N−*C*H═N), 72.34 (*C*H), 53.30 (*C*H), 35.94 (*C*(CH_3)$_3$), 26.11 (C(*C*H_3)$_3$), 24.58 (CH(*C*H_3)$_2$), 22.65 (CH(*C*H_3)$_2$). Anal. Calcd for $C_{17}H_{35}BrN_2$ (MW = 347.38): C, 58.78; H, 10.16; N, 8.06. Found: C, 58.35; H, 10.15; N, 8.40. $[\alpha]^{20}_D$ −117° (*c* 1.1, CH_2Cl_2).

(4*R*,5*R*)-1,3-Diisopropyl-4,5-di-*tert*-butylimidazolin-2-ylidene Silver Bromide (3). To a solution of imidazolinium **6** (514 mg, 1.48 mmol) in CH_2Cl_2 (30 mL) was added 206 mg (0.89 mmol) of Ag_2O. The mixture was stirred at 20 °C for 12 h under argon, filtered through Celite, and concentrated to give 689 mg (>100%) of a beige solid. Mp: 260 °C. ^{1}H NMR: δ 3.61 (m, 2H), 3.20 (s, 2H), 1.79 (d, 6H, J = 6.8 Hz), 1.41 (d, 6H, J = 6.6 Hz), 0.94 (s, 18H). ^{13}C NMR: δ 73.97 (*C*H), 51.47 (*C*H), 35.33 (*C*(CH_3)$_3$), 26.63 (CH(*C*H_3)$_2$), 26.54 (C(*C*H_3)$_3$), 24.31 (CH(*C*H_3)$_2$), the carbene carbon was not observed. $[\alpha]^{20}_D$ −48° (*c* 0.33, CH_2Cl_2). The crude was used without purification in the next step.

(4*R*,5*R*)-1,3-Diisopropyl-4,5-di-*tert*-butylimidazolin-2-ylidene Palladium(allyl) Chloride (7). To a mixture of silver carbene **3** (87 mg, 0.19 mmol) and $[Pd(allyl)Cl]_2$ (35 mg, 0.096 mmol) was added under argon 4 mL of dried CH_2Cl_2. The mixture was stirred at 20 °C for 0.5 h, filtered through Celite to remove the silver salts, and concentrated. Purification by flash chromatography (Et_2O/pentane, 8:2) afforded 54 mg (63%) of a white crystalline solid. The complex was isolated as a 1:1 mixture of two isomers. Mp: 181 °C. ^{1}H NMR (mixture of the two nonsymmetrical complexes, the signals could not be assigned to either isomer): δ 5.35−5.24 (m, 2H, C*H*═CH_2), 4.24 (dd, 1H, J = 7.3 and 2.5 Hz, *H* allyl), 4.20 (dd, 1H, J = 7.6 and 2.5 Hz, *H* allyl), 3.92−3.78 (m, 3H, C*H*(CH_3)$_2$), 3.67 (m, 1H, J = 6.8 Hz, C*H*(CH_3)$_2$), 3.46 (d, 1H, J = 6.3 Hz, *H* allyl), 3.38−3.31 (m, 3H, *H* allyl), 3.22 (d, 1H, J = 2.5 Hz, C*H*-^{t}Bu), 3.19 (s, 2H, C*H*-^{t}Bu), 3.13 (d, 1H, J = 2.5 Hz, C*H*-^{t}Bu), 2.33 (d, 1H, J = 11.9 Hz, *H* allyl), 2.28 (d, 1H, J = 11.4 Hz, *H* allyl), 2.10 (d, 3H, J = 7.1 Hz, CH(CH_3)$_2$), 1.85 (d, 3H, J = 7.1 Hz), 1.83 (d, 3H, J = 7.1 Hz), 1.68 (d, 3H, J = 6.6 Hz), 1.57 (d, 3H, J = 6.8 Hz), 1.53 (d, 3H, J = 6.6 Hz), 1.33 (d, 3H, J = 6.6 Hz), 1.23 (d, 3H, J = 6.8 Hz), 1.01 (s, 9H, ^{t}Bu), 1.00 (s, 9H), 0.94 (s, 18H). ^{13}C NMR: δ 204.52, 203.81 (*C* carbene), 113.68, 113.25 (*C*H═CH_2), 73.43, 73.27, 73.06, 72.87, 72.29, 71.67, 52.86, 52.47, 52.30, 52.13, 51.44, 48.99, 35.77, 35.59, 35.50; 35.34 (*C*(CH_3)$_3$), 27.02, 26.95 (C(*C*H_3)$_3$), 26.90, 26.76, 25.53, 25.12, 24.27, 24.00, 22.85 (CH(*C*H_3)$_2$). Anal. Calcd for $C_{20}H_{39}N_2$PdCl (MW = 449.41): C, 53.45; H, 8.75; N, 6.23. Found: C, 53.60; H, 8.88; N, 6.04.

(4*R*,5*R*)-1,3-Bis[(*S*)-1-phenylethyl]-4,5-di-*tert*-butylimidazolin-2-ylidene Palladium(allyl) Chloride (8). To a mixture of silver carbene **4** (131 mg, 0.21 mmol) and $[Pd(allyl)Cl]_2$ (37 mg, 0.1 mmol) was added under argon 4 mL of dried CH_2Cl_2. The mixture was stirred at 20 °C for 0.5 h, filtered through Celite to remove the silver salts, and concentrated. Purification by flash chromatography (Et_2O/pentane, 8:2) afforded 90 mg (78%) of a white crystalline solid. The complex was isolated as a 6:4 mixture of two isomers. Mp: 169 °C. ^{1}H NMR (mixture of the two nonsymmetrical complexes), major isomer: δ 7.62−7.55 (m, 4H), 7.37−7.2 (m, 6H), 5.49 (q, 1H, J = 7.3 Hz), 5.10 (q, 1H, J = 7.3 Hz), 4.59 (m, 1H, C*H*(CH_2) allyl), 4.01 (dd, 1H, J = 7.6 and 2.5 Hz, C*H*(H) allyl), 3.40 (d, 1H, J = 2.5 Hz, C*H*-^{t}Bu), 3.36 (d, 1H, J = 2.5 Hz, C*H*-^{t}Bu), 3.19 (d, 1H, J = 6.3 Hz, C*H*(H) allyl), 3.11 (d, 1H, J = 13.2 Hz, C*H*(H) allyl), 2.42 (d, 3H, J = 7.3 Hz), 1.85 (d, 3H, J = 7.3 Hz), 1.60 (d, 1H, J = 11.6 Hz, C*H*(H) allyl), 0.88 (s, 9H), 0.75 (s, 9H); minor isomer: δ 7.74 (d, 2H, J = 7.3 Hz), 7.46 (d, 2H, J = 7.1 Hz), 7.35−7.21 (m, 6H), 5.62 (q, 1H, J = 7.3 Hz), 5.12 (m, 1H, C*H*(CH_2) allyl), 5.01 (q, 1H, J = 7.1 Hz), 4.14 (dd, 1H, J = 7.3 and 2.5 Hz, C*H*(H) allyl), 3.47 (d, 1H, J = 2.5 Hz, C*H*-^{t}Bu), 3.42 (d, 1H, J = 2.5 Hz, C*H*-^{t}Bu), 2.93 (d, 1H, J = 13.4 Hz, C*H*(H) allyl), 2.86 (d, 1H, J = 6.3 Hz, C*H*(H) allyl), 2.22 (d, 3H, J = 7.3 Hz), 2.04 (d, 3H, J = 7.3 Hz), 1.65 (d, 1H, J = 11.9 Hz, C*H*(H) allyl), 0.85 (s, 9H), 0.79 (s, 9H). ^{13}C NMR (both isomers): δ 209.41, 209.28 (*C* carbene), 143.02, 142.95, 142.26, 141.85 (*Cq* arom), 128.75, 128.42, 128.23, 128.15, 128.06, 127.78, 127.76, 127.34, 127.15 (*C*H arom), 114.07, 113.77 (*C*H═CH_2), 73.83, 73.76, 72.74, 71.62, 69.97, 69.80, 60.37, 60.15, 59.27, 58.75, 51.69, 51.19, 35.54, 35.37, 35.03; 34.93 (*C*(CH_3)$_3$), 27.75, 27.67, 27.50, 27.42 (C(*C*H_3)$_3$), 22.69, 21.88, 21.67, 21.19 (CH-*C*H_3). Anal. Calcd for $C_{30}H_{43}N_2$PdCl (MW = 573.55): C, 62.82; H, 7.56; N, 4.88. Found: C, 62.65; H, 7.66; N, 4.69.

Table 2. Crystal Structure Information for 7a

formula	$C_{20}H_{39}ClN_2Pd$
color	colorless
cryst class	monoclinic
space group	$P2_1$
Flack parameter	0.06(3)
unit cell params	
a (Å)	9.0266(12)
b (Å)	9.0113(5)
c (Å)	13.7577(15)
α	90°
β	91.41(1)°
γ	90°
volume, *Z*	1118.7(2) Å^3, 2
radiation type	Mo Kα
wavelength (Å)	0.710 730
density	1.33
M (g mol^{-1})	449.40
μ (mm^{-1})	0.953
temperature (K)	295
size (mm)	0.2 × 0.21 × 0.45
shape	stick
diffractometer type	Nonius KAPPACCD
no. of reflns measd	7611
no. of indep reflns	3678
R_{int}	0.05

X-ray Structural Determination of 7. Colorless crystals suitable for X-ray diffraction analysis were obtained by slow evaporation at 20 °C of a solution of **7** in Et_2O. Under these conditions, we could not determine if the two isomers **7a** and **7b** crystallized both alike or if the crystals as a whole corresponded to only one isomer. A single crystal of approximate dimensions 0.20 × 0.21 × 0.45 mm was used for the analysis. This crystal corresponds to the isomer **7a**. A summary of crystallographic data for **7a** is given in Table 2.

Typical Procedure for the Mizoroki−Heck Reaction. To a solution of the Pd(II) complex (0.02 mmol) in DMF (2 mL) were added the activating agent (as indicated in Scheme 5), PhI (112 μL, 1 mmol), K_2CO_3 (1.5 mmol), and butyl acrylate (173 μL, 1.2 mmol). Dodecane (230 μL, 1 mmol) can be added as an internal reference for GC. The mixture was degassed under vacuum, then stirred under argon at the indicated temperature. After cooling, the solution was diluted with Et_2O (10 mL) and washed with water (4 × 2 mL). The solution was analyzed by GC.

Acknowledgment. We thank C. Guyard-Duhayon (Centre de Résolution de Structures, Laboratoire de Chimie Inorganique et Matériaux Moléculaires, Université P. et M. Curie) for X-ray structures.

Supporting Information Available: X-ray structural data for **7a** are presented. This material is available free of charge via the Internet at http://pubs.acs.org.

OM040013B