Synthesis and Reactivity of Four-Membered Azapalladacycles Derived from *N,N*-Dialkyl-2-iodoanilines: Insertion Reactions of Carbenes into the Carbon−Palladium Bond

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Three new four-membered azapalladacycles derived from *N,N*-dialkyl-2-iodoanilines have been synthesized: [Pd(κ^2-$C_6H_4NMe_2$-2)I(PPh_3)] (**4a**), [Pd{κ^2-$C_6H_4N(Me)CH_2Ph$-2}I(PPh_3)] (**4b**), and [Pd{κ^2-$C_6H_4N(Me)Pr$-2}I(PPh_3)] (**4c**). On heating in solution azapalladacycles **4a** and **4c** undergo aryl−aryl interchange between the palladium atom and the phosphine ligand to give the phosphanyl-amine palladium complexes [PdPhI($PNMe_2$)] (**7a**) and [PdPhI{PN(Me)Pr}] (**7c**), respectively. Azapalladacycles **4a**−**c** react with dichlorocarbene to give acyl palladium complexes [Pd{κ^2-$C(O)C_6H_4NMe_2$-2}I(PPh_3)] (**8a**), [Pd{κ^2-$C(O)C_6H_4N(Me)CH_2Ph$-2}I(PPh_3)] (**8b**), and [Pd{κ^2-$C(O)C_6H_4N(Me)Pr$-2}I(PPh_3)] (**8c**), respectively. Smooth insertion of N_2CHCO_2Et into the carbon−palladium bond of azapalladacycles **4a**−**c** results in the formation of the single-insertion products [Pd{κ^2-$CH(CO_2Et)C_6H_4NMe_2$-2}I(PPh_3)] (**9a**), [Pd{κ^2-$CH(CO_2Et)C_6H_4N(Me)CH_2Ph$-2}I($PPh_3$)] (**9b**), and [Pd{$\kappa^2$-$CH(CO_2Et)C_6H_4N(Me)Pr$-2}I($PPh_3$)] (**9c**), respectively. On the other hand, complexes **4a** and **4c** react with N_2CHTMS to give mainly the single-insertion products [Pd{κ^2-$CH(SiMe_3)C_6H_4NMe_2$-2}I(PPh_3)] (**10a**) and [Pd{κ^2-$CH(SiMe_3)C_6H_4N(Me)Pr$-2}I(PPh_3)] (**10c**), respectively, while under similar reaction conditions **4b** affords *N*-benzyl-*N*-methyl-2-[(*Z*)-2-(trimethylsilyl)vinyl]aniline (**11b**) as a consequence of a double-insertion process. Solid state structures of palladium complexes **4b**, **8b**·EtOAc, **9a**, **9b**, and **9c**·Et_2O have been determined by X-ray analysis.

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Introduction

Insertion reactions into the carbon−metal bond constitute one of the fundamental processes of organometallic chemistry.[1] Cyclopalladated complexes, especially those with nitrogen as the donor atom,[2] exhibit high reactivity to undergo insertion of a variety of substrates. Emphasis has been placed on insertion reactions of alkynes,[3] carbon monoxide,[4] and isocyanides.[5,6] In contrast, the insertion of carbenes into palladium(II) complexes has been completely ignored,[7,8] although it is becoming increasingly important to understand the reactivity of these species, due to the growing use of carbene ligands in palladium chemistry[9] as well as the frequency with which palladium carbenes are proposed as intermediates in some Pd-catalyzed reactions.[10]

In the context of our studies on the Pd(0)-catalyzed intramolecular coupling of aryl halides and ketones,[11] we have recently reported the synthesis and X-ray characterization of azapalladacycles **1** and **2**,[12] which constitute the first examples of the family of four-

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(1) (a) Tsuji, J. *Transition Metal Reagents and Catalysts-Innovations in Organic Synthesis*; Wiley: Chichester, 2000. (b) Negishi, E., Ed. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Wiley: New York, 2002; Vols. I and II.

(2) Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917.

(3) (a) Maassarani, F.; Pfeffer, M.; Le Borgne, G.; Wehman, E.; van Koten G. *J. Am. Chem. Soc.* **1984**, *106*, 8002. (b) Maassarani, F.; Pfeffer, M.; Le Borgne, G. *Organometallics* **1987**, *6*, 2029. (c) Maassarani, F.; Pfeffer, M.; van Koten, G. *Organometallics* **1989**, *8*, 871. (d) Ryabov, A. D.; van Eldik, R.; Le Borgne, G.; Pfeffer, M. *Organometallics* **1993**, *12*, 1386. (e) Vicente, J.; Saura-Llamas, I.; Ramírez de Arellano, M. C. *J. Chem. Soc., Dalton Trans.* **1995**, 2529. (f) Vicente, J.; Saura-Llamas, I.; Palin, M. G.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1995**, 2534. (g) Vicente, J.; Abad, J.-A.; Gil-Rubio, J.; Jones, P. G. *Organometallics* **1995**, *14*, 2677. (h) Vicente, J.; Abad, J.-A.; Martínez-Viviente, E.; Ramírez de Arellano, M. C. *Organometallics* **2000**, *19*, 752. (i) Gül, N.; Nelson, J. H.; Willis, A. C.; Rae, A. D. *Organometallics* **2002**, *21*, 2041.

(4) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985; pp 341−400.

(5) Yamamoto, Y.; Yamazaki, H. *Synthesis* **1976**, 750.

(6) For the insertion of isocyanides into the metal−carbon bond of (2-aminoaryl)palladium(II) complexes, see: Vicente, J.; Abad, J.-A.; Frankland, A. D.; López-Serrano, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **2002**, *21*, 272.

(7) The migratory insertion in aryl palladium carbene complexes has recently been described: Albéniz, A. C.; Espinet, P.; Manrique, R.; Pérez-Mateo, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 2363.

(8) For the concerted alkyl-carbene reductive elimination from Pd(II) complexes, see: (a) McGuinness, D. S.; Saendig, N.; Yates, B. F.; Cavell, K. J. *J. Am. Chem. Soc.* **2001**, *123*, 4029. For the concerted aryl-carbene reductive elimination from Pd(II) complexes, see: (b) Marshall, W. J.; Grushin, V. V. *Organometallics* **2003**, *22*, 1591.

(9) For a review, see: Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.

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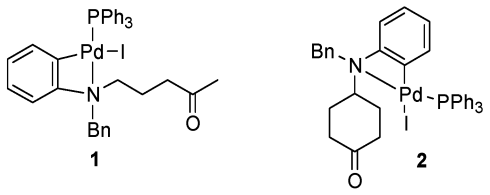
Chart 1. Four-Membered Azapalladacycles



membered azapalladacycles in which the metallacycle is fused with an aromatic ring.[13] We hypothesized that this kind of palladium complex might be of interest in the study of insertion reactions not only for their high reactivity but also because after the insertion the coordination ability of the amino group would give rise to the formation of stable five-membered chelates.

We here report the synthesis of new members of this family of four-membered azapalladacycles and study their thermal behavior and their reactions with carbenes.

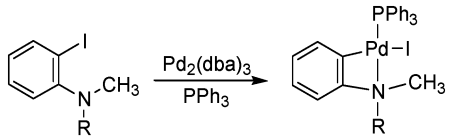
Results and Discussion

Synthesis of Four-Membered Azapalladacycles. We have previously reported the synthesis of the four-membered azapalladacycles **1** and **2** by reacting the corresponding *N*,*N*-dialkyl-2-iodoanilines either with $Pd_2(dba)_3$ in the presence of PPh_3 or with $Pd(PPh_3)_4$.[14] The inferior results of the latter process were attributed to the intermediacy of the corresponding *trans*-bis(triphenylphosphane)palladium(II) complexes, although these intermediates could not be isolated and characterized.[12] To establish the best methodology for the synthesis of the four-membered azapalladacycles, we have studied both procedures starting from iodoanilines **3a**−**c**.

The reaction of 2-iodoanilines **3a**−**c** with $Pd_2(dba)_3$ and PPh_3 (0.55:1 molar ratio) in benzene at room temperature afforded azapalladacycles **4a**−**c** in good yields (Scheme 1). These four-membered azapalladacycles are robust compounds that can be purified by flash chromatography without decomposition.

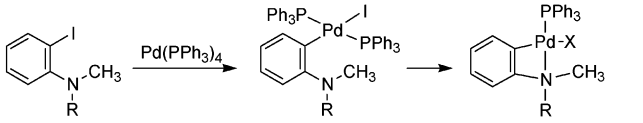
On the other hand, 2-iodoanilines **3a** and **3b** reacted with $Pd(PPh_3)_4$ (1 equiv) to give the *trans*-bis(triphenylphosphane)palladium complexes **5a** and **5b**, respectively (Scheme 2). These quite stable palladium complexes could now be characterized and were partially transformed to the corresponding azapalladacycles. Thus, when **5a** was submitted to flash chromatography (SiO_2, hexane−EtOAc), azapalladacycle **4a** (44%) was obtained, and part of the starting material (25%) was recovered. Under similar treatment, **5b** afforded azapalladacycle **4b** (65%) and hydroxopalladium compound **6** (13%), together with some of the starting material (15%). Finally, on treatment with $Pd(PPh_3)_4$, 2-iodoaniline **3c** afforded a reaction mixture in which the main product was azapalladacycle **4c**, the corresponding bis(triphenylphosphane)palladium complex not being isolated in this case.

Scheme 1. Synthesis of Four-Membered Azapalladacycles 4a−c



3a : R = CH_3 **4a** : R = CH_3
3b : R = CH_2Ph **4b** : R = CH_2Ph
3c : R = Pr **4c** : R = Pr

Scheme 2. Reaction of Iodoanilines 3a and 3b with $Pd(PPh_3)_4$



3a : R = CH_3 **5a** : R = CH_3 **4a** : R = CH_3, X = I
3b : R = CH_2Ph **5b** : R = CH_2Ph **4b** : R = CH_2Ph, X = I
6 : R = CH_2Ph, X = OH

Thus, we can conclude that the reaction of 2-iodoanilines with $Pd_2(dba)_3$ and PPh_3 is a good methodology for the preparation of the four-membered azapalladacycles. Additionally, the results obtained in the reactions of *N*,*N*-dialkyl-2-iodoanilines with $Pd(PPh_3)_4$ confirm the hypotheses[12] we made in our previous work: (i) in these reactions the *trans*-bis(triphenylphosphane)palladium complexes are the intermediates in the formation of the four-membered azapalladacycles; (ii) the steric bulk of the substituents on the nitrogen atom is the main reason for the formation of the four-membered palladacycles. When starting from *N*,*N*-dialkyl-2-haloanilines, the bis(triphenylphosphane)palladium complexes could be obtained only when substituents at the nitrogen were small, otherwise the steric hindrance would force those substituents out of the plane, directing the nonbonding electron pair toward the palladium atom to afford the azapalladacycle, and (iii) the hydroxopalladium species are exclusively formed from the bis(triphenylphosphane)palladium complexes.[15]

Thermal Behavior of Four-Membered Azapalladacycles. The thermal stability of azapalladacycles **4a**−**c** was then studied. It was found that on heating at 110 °C, azapalladacycle **4a** underwent aryl−aryl interchange between the palladium and the phosphine ligand to give the palladium complex **7a** (Scheme 3),

(10) For the mechanism of the palladium-catalyzed cyclopropanation of alkenes by CH_2N_2, see: (a) Rodríguez-García, C.; Oliva, A.; Ortuño, R.-M.; Branchadell, V. *J. Am. Chem. Soc.* **2001**, *123*, 6157. (b) Straub, B. F. *J. Am. Chem. Soc.* **2002**, *124*, 14195. For the Pd-catalyzed dimerization of carbene ligands in group 6 metal-carbene complexes, see: (c) Sierra, M. A.; Mancheño, M. J.; Sáez, E.; del Amo, J. C. *J. Am. Chem. Soc.* **1998**, *120*, 6812. (d) Sierra, M. A.; del Amo, J. C.; Mancheño, M. J.; Gómez-Gallego, M. *J. Am. Chem. Soc.* **2001**, *123*, 851.

(11) (a) Solé, D.; Vallverdú, L.; Bonjoch, J. *Adv. Synth. Catal.* **2001**, *343*, 439. (b) Solé, D.; Vallverdú, L.; Peidró, E.; Bonjoch, J. *Chem. Commun.* **2001**, 1888.

(12) Solé, D.; Vallverdú, L.; Solans, X.; Font-Bardía, M.; Bonjoch, J. *J. Am. Chem. Soc.* **2003**, *125*, 1587.

(13) For other types of four-membered Pd−N−C−C palladacycles, see: (a) Arnek, R.; Zetterberg, K. *Organometallics* **1987**, *6*, 1230. (b) Falvello, L. R.; Forniés, J.; Navarro, R.; Sicilia, V.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1994**, 3143. (c) Agnus, Y.; Gross, M.; Labarelle, M.; Louis, R.; Metz, B. *J. Chem. Soc., Chem. Commun.* **1994**, 939. (d) Henderson, W.; Oliver, A. G.; Rickard, C. E. F.; Baker, L. J. *Inorg. Chim. Acta* **1999**, *292*, 260.

(14) The oxidative addition of 2-iodoaniline to Pd(0) complexes has been described, see: (a) Vicente, J.; Abad, J.-A.; Frankland, A. D.; Ramírez de Arellano, M.-C. *Chem. Commun.* **1997**, 959. (b) Vicente, J.; Abad, J.-A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem. Eur. J.* **1999**, *5*, 3066.

(15) In fact, the hydroxopalladium complexes were not obtained during the purification by flash chromatography of either azapalladacycles **4a**−**c** or **1** and **2**.[12]

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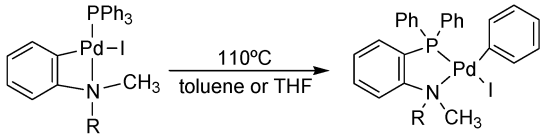
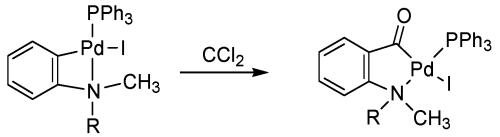
Scheme 3. Thermal Aryl−Aryl Interchange from 4a and 4c



4a : R = CH_3 **7a** : R = CH_3
4c : R = Pr **7c** : R = Pr

Scheme 4. Insertion of Dichlorocarbene into the C−Pd Bond of 4a−c



4a : R = CH_3 **8a** : R = CH_3
4b : R = CH_2Ph **8b** : R = CH_2Ph
4c : R = Pr **8c** : R = Pr

which was obtained as a 10:1 mixture of the *trans*P,I and *cis*P,I isomers. The identity of **7a** was fully confirmed by comparison with an authentic sample prepared by oxidative addition of iodobenzene to $Pd_2(dba)_3$ in the presence of the $PNMe_2$ ligand.[16,17]

The thermal aryl−aryl interchange between the palladium and the phosphine ligand was also observed starting from azapalladacycle **4c**, which under similar treatment afforded **7c** as a 4:1 mixture of the *trans*P,I and *cis*P,I isomers. In contrast, under the same reaction conditions, palladacycle **4b** gave a complex reaction mixture from which no compound could be isolated and characterized.

The interchange between phosphorus-bound aryl moieties and palladium-bound aryl groups in $RPdL_2X$ complexes (L = triarylphosphine, R = aryl) is a known process[18] that has been recently applied in the synthesis of different substituted phosphines.[19]

Insertion of Dichlorocarbene. The synthesis of carboxylic acids by palladium-catalyzed carbonylation of aryl halides with chloroform and aqueous alkali has been described.[20] This catalytic reaction uses dichlorocarbene as a carbon monoxide equivalent and is believed to proceed through palladium carbene complexes. With this precedent in mind, we decided to begin our investigation into the insertion reaction of carbenes by studying the reaction of azapalladacycles **4a−c** with dichlorocarbene.

Dichlorocarbene, generated in situ from chloroform and KO*t*-Bu,[21] smoothly reacted at room temperature with azapalladacycle **4a** to directly give the acyl palladium complex **8a** (Scheme 4). The identity of **8a** was confirmed by comparison with an authentic sample prepared by reaction of **4a** with CO.[22,23] Similarly, complexes **4b** and **4c** reacted with dichlorocarbene to give **8b** and **8c**, respectively.

The formation of acyl palladium complexes **8a−c** can be interpreted assuming that dichlorocarbene, generated from chloroform and KO*t*-Bu, undergoes coordination with the palladium atom of the four-membered azapalladacycle to give a dichlorocarbene complex.[24] Migratory insertion in the latter will afford the corresponding dichloromethylene intermediate, which then hydrolyzes to the acyl palladium complex.[25] The alternative pathway involving the hydrolysis of the dichlorocarbene complex to give the carbonyl complex, followed by the migratory insertion in the latter to the acyl palladium compound, seems to be less likely since, although the carbon−chloride bond in coordinated dichlorocarbene ligands is reactive toward nucleophiles, the hydrolysis is a slow reaction[24] and the insertion processes in the four-membered azapalladacycles are very favorable (vide infra).[26,27]

Insertion of Diazoalkanes. Once we had proved the readiness of four-membered azapalladacycles **4a−c** to undergo insertion reactions, we decided to explore the reactivity of these palladium complexes with diazoalkanes.[28,29] The palladium-catalyzed cyclopropanation of olefins with diazoalkanes is a widely used synthetic methodology.[30] The formation of transient palladium-carbene complex intermediates from the diazoalkane and the palladium catalyst seems to be the rate-determining step of these reactions.[10a,b]

Initially, we focused on the reaction of **4a−c** with diazomethane. However, when treated with an excess of diazomethane, palladium complexes **4a−c** gave complex reaction mixtures from which no compound could be isolated and characterized.

On the contrary, we were gratified to find that **4a** smoothly reacted with ethyl diazoacetate to give the insertion compound **9a**, which was obtained in 56% yield after "flash" chromatography (Scheme 5). Under essentially the same reaction conditions, azapalladacycle

(16) $PNMe_2$ means *N*,*N*-dimethyl-2-(diphenylphosphanyl)aniline.
(17) (a) Crociani, L.; Bandoli, G.; Dolmella, A.; Basato, M.; Corain, B. *Eur. J. Inorg. Chem.* **1998**, 1811. (b) Amatore, C.; Fuxa, A.; Jutand, A. *Chem. Eur. J.* **2000**, *6*, 1474.
(18) (a) Kong, K.-C.; Cheng, C.-H. *J. Am. Chem. Soc.* **1991**, *113*, 6313. (b) Goddson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441.
(19) (a) Kwong, F. Y.; Chan, K. S. *Chem. Commun.* **2000**, 1069. (b) Kwong, F. Y.; Chan, K. S. *Organometallics* **2001**, *20*, 2570. (c) Kwong, F. Y.; Lai, C. W.; Chan, K. S. *Tetrahedron Lett.* **2002**, *43*, 3537.
(20) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 3846.
(21) Doering, W. von E.; Hoffmann, A. K. *J. Am. Chem. Soc.* **1954**, *76*, 6162.
(22) For the insertion of carbon monoxide into the carbon−palladium bond of 2-aminophenylpalladium(II) complexes, see refs 14a,b.
(23) The chloro analogue of **8a** had been prepared previously by reaction of 2-(dimethylamino)benzaldehyde with Li_2PdCl_4, followed by addition of PPh_3, see: Anklin, C. G.; Pregosin, P. S. *J. Organomet. Chem.* **1983**, *243*, 101.
(24) The existence of dichlorocarbene complexes of different transition metals has been unambiguously demonstrated, see for example: (a) Mansuy, D.; Lange, M.; Chottard, J. C.; Bartoli, J. F.; Chevrier, B.; Weiss, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 781. (b) Clark, G. R.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Am. Chem. Soc.* **1980**, *102*, 1206.
(25) As the reaction mixtures were worked up in air, adventitious water could account for the hydrolysis process.
(26) However, if the hydrolysis had taken place, the migratory insertion from the resulting CO complex would be very favorable, from either a pentacoordinated CO complex or a square-planar CO complex with a *cis* arrangement between the aryl and the CO ligands.
(27) The generation of CO by hydrolysis of CCl_2 and the subsequent carbonylation of the azapalladacycles can be completely rejected, because CCl_2 can be efficiently generated from chloroform and 50% NaOH. For a review on the generation of dichlorocarbene and its use in organic synthesis, see: Fedorynski, M. *Chem. Rev.* **2003**, *103*, 1099.
(28) For the formation of metallacarbenes from diazoalkanes, see: Cohen, R.; Rybtchinski, B.; Gandelman, M.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2003**, *125*, 6532.
(29) Recently, a Pd(II) complex of a non-heteroatom-stabilized carbene ligand has been prepared by reaction of di(*p*-tolyl)diazomethane with Trpy-PdOAc, see: Bröring, M.; Brandt, C. D.; Stellwag, S. *Chem. Commun.* **2003**, 2344.
(30) See for example: Markó, I. E.; Kumamoto, T.; Giard, T. *Adv. Synth. Catal.* **2002**, *344*, 1063, and references therein.

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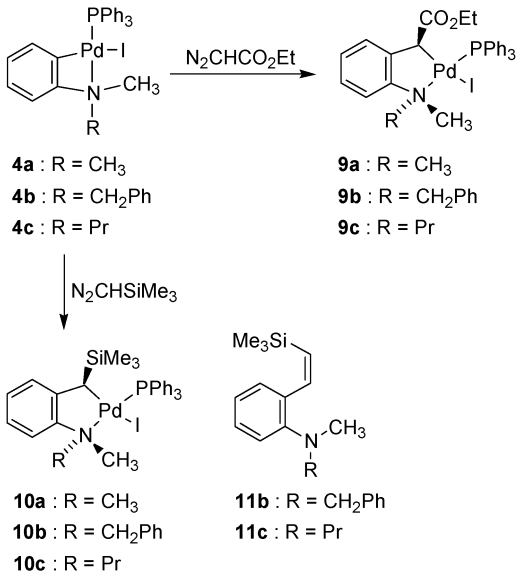
Scheme 5. Insertion Reactions of Diazoalkanes into the C−Pd Bond of 4a−c[a]



[a] Compounds **9** and **10** are racemic. The scheme depicts only one of the enantiomers.

4b afforded a reaction mixture from which the insertion compound **9b** could be isolated in 51% yield. The *syn* relationship between the CO_2Et group and the *N*-methyl substituent in **9b** was confirmed by the X-ray diffraction study of a single crystal. A second compound was also formed in the reaction of **4b** with ethyl diazoacetate. Although this minor compound could not be isolated in a pure form and fully characterized, the signals in the ^1H and ^{13}C NMR spectra suggested that it may be a double-insertion product (vide infra) rather than a diastereomer of **9b**. On the other hand, azapalladacycle **4c** slowly reacted with ethyl diazoacetate to stereoselectively afford the insertion product **9c**, which also shows, as confirmed by X-ray analysis, a *syn* relationship between the CO_2Et group and the *N*-methyl substituent.

With these results in hand, attention was next devoted to the reaction of the four-membered azapalladacycles with trimethylsilyldiazomethane.[31] When complexes **4a−c** were treated with Me_3SiCHN_2 in benzene at room temperature, different reaction behavior was observed (Scheme 5). Thus, **4a** reacted with Me_3SiCHN_2 (1:3.3 molar ratio) to afford **10a** in nearly quantitative yield,[32] while, under the same conditions, **4b** gave alkene **11b** instead of the expected insertion product. The use of equimolecular amounts of azapalladacycle **4b** and Me_3SiCHN_2 resulted in a complex reaction mixture, the major product again being alkene **11b**, which was isolated in 30% yield. On successive chromatographic purifications, a fraction enriched with a second compound was obtained. Although this new compound could not be isolated as a pure substance, it was assigned as the monomolecular insertion azapalladacycle **10b** on the basis of its NMR data.[33]

On the other hand, when complex **4c** was treated with Me_3SiCHN_2 (1:3.3 molar ratio), palladium complex **10c** was obtained in 57% yield after flash chromatography, together with trace amounts of alkene **11c**. The relative configuration of azapalladacycle **10c** was established by means of NOESY experiments, which allowed the *syn* relationship between the *N*-methyl substituent and the Me_3Si group to be determined. The NOESY experiment on **10c** showed an off-diagonal cross-peak connecting the *N*-methyl protons (δ 3.35, d, J = 2.7 Hz) with the Me_3Si grouping (δ, −0.27, s), thus indicating that these substituents are *syn*-related. The NOESY spectrum also showed off-diagonal cross-peaks connecting the methyl protons of the *N*-propyl group (δ 0.84, t, J = 7.2 Hz) with the PPh_3 protons (δ 7.42, m, and δ 7.79, m) and one of the methylene protons (δ 2.50, m) with the PPh_3 protons (δ 7.79, m), thus indicating the spatial proximity between the *N*-propyl substituent and the PPh_3 group.

The insertion of carbenes derived from diazoalkanes into the Pd−C bond of the four-membered azapalladacycles constitutes a new strategy to synthesize azapalladacycles with a palladated stereogenic carbon, which until now had only been obtained by either direct palladation of a prochiral ligand[34] or transmetalation of lithiated tertiary amines to chloropalladium complexes.[32]

The stereoselective formation of alkene **11b** in the reaction of **4b** with excess Me_3SiCHN_2 could be rationalized as outlined in Scheme 6. The insertion of a first molecule of Me_3SiCHN_2 into the Pd−C bond of azapalladacycle **4b** will afford **10b**. Although this palladium complex has not been fully characterized, it is most likely that in **10b** the bulky Me_3Si group and the *N*-methyl substituent present a *syn* relationship, as occurs in complex **10c** (vide supra). In this context, it should be noted that in the five-membered azapalladacycles **9b**, **9c**, **10b**, and **10c** the more sterically demanding substituent at the nitrogen atom (Bn or Pr) and the substituent at the palladated carbon (CO_2Et or Me_3Si) are always *anti* located. The high stereoselectivity in the formation of these azapalladacycles is probably the result of the steric control exerted by the more bulky *N*-substituent in the insertion of the carbene in the four-membered azapalladacycles.

The high tendency of **10b** to undergo insertion of a second molecule of carbene is probably a consequence of its steric hindrance. So, it is reasonable to assume that the distortion of the square-planar geometry of the palladium atom in this very congested palladium intermediate takes place in the same direction as in **9b**, forcing the bulky PPh_3 ligand and the benzyl group close together (vide infra). Pd−N bond dissociation in **10b** will relieve the steric crowding and give rise to a coordinatively unsaturated intermediate, which could therefore react with a second molecule of Me_3SiCHN_2 to give a palladium carbene complex.[35] Migratory insertion in the latter would afford a six-membered azapalladacycle.[36] For steric reasons, the *anti* relationship between the two

(31) For the use of Me_3SiCHN_2 in palladium-catalyzed cyclopropanation reactions, see: Aoyama, T.; Iwamoto, Y.; Nishigaki, S.; Shioiri, T. *Chem. Pharm. Bull.* **1989**, *37*, 253.

(32) For an alternative synthesis of palladacycles with the monoanionic $CH(SiMe_3)C_6H_4NMe_2$-2, see: (a) Maassarani, F.; Pfeffer, M.; Le Borgne, G.; Jastrzebski, J. T. B. H.; van Koten, G. *Organometallics* **1987**, *6*, 1111. (b) See also refs 3a and 3c.

(33) Significant signals: ^1H NMR ($CDCl_3$, 200 MHz) δ 5.31 (d, J = 12.8 Hz, 1H), 4.48 (dd, J = 12.8 and 5.5 Hz, 1H), 3.54 (d, J = 2.8 Hz, 3H), 2.87 (d, J = 6.2 Hz, 1H).

(34) See for example: (a) Sokolov, V. I.; Sorokina, T. A.; Troitskaya, L. L.; Solovieva, L. I.; Reutov, O. A. *J. Organomet. Chem.* **1972**, *36*, 389. (b) Yoneda, A.; Hakushi, T.; Newkome, G. R.; Fronczek, F. R. *Organometallics* **1994**, *13*, 4912. (c) Portscheller, J. L.; Malinakova, H. C. *Org. Lett.* **2002**, *4*, 3679, and references therein.

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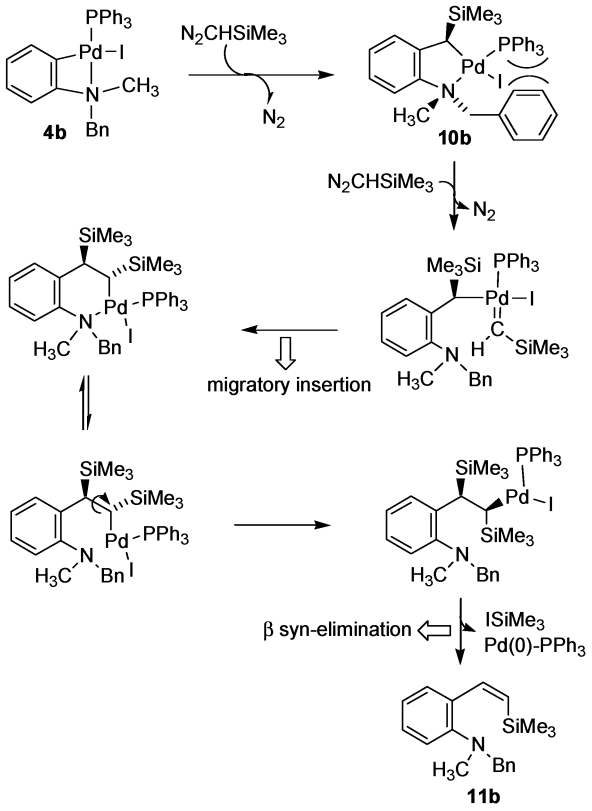
Scheme 6. Proposed Reaction Path for the Formation of 11b



Me_3Si groups will be the most accessible one in this insertion process. Finally, Pd−N bond dissociation and *β syn*-elimination of Me_3SiI and Pd(0)[37] would give alkene **11b** with high stereoselectivity.

X-ray Crystal Structures. The molecular structures of complexes **4b**, **8b**·EtOAc, **9a**, **9b**, and **9c**·Et_2O have been determined by X-ray diffraction studies and are shown in Figures 1−5, respectively.

Although in the five palladium complexes the Pd is linked to the same atoms (I, P, C, and N), there are significant differences between the structure of the four-membered azapalladacycle **4b** and those of the five-membered azapalladacycles **8b**, **9a**, **9b**, and **9c**. The four-membered metallacycle of **4b** is planar, and both the I and P atoms are deviated to the same side from the mean plane 0.156(1) Å [0.110(1) Å in the second molecule] and 0.098(2) Å [0.074(2) Å in the second molecule], respectively. This deviation causes the palladium atom to be outside of the plane defined by the four ligands. The planarity of the four-membered ring causes the length of the Pd−ligand bonds to be shorter in **4b** than in the five-membered azapalladacycles **8b**, **9a**, **9b**, and **9c**.

The five-membered metallacycles in **8b**, **9a**, **9b**, and **9c** have an envelope form with the Pd being the out-of-plane atom. In similar five-membered azapalladacycles both the planar[6,14b] and envelope form on nitrogen[32a] and palladium[14a] have been described, the latter being observed when bulky ligands are bonded to the palladium atom. All the five-membered azapalladacycles show somewhat tetragonally distorted square-planar coordination around the palladium atom, the largest deviation to the mean plane being in the C atom [deviation of 0.166(3) Å in **8b**, 0.193(6) Å in **9a**, 0.318(3) Å in **9b**, and 0.326(10) Å in **9c**].

In complexes **9a**−**c** the I and PPh_3 ligands are in equatorial positions, the bulky CO_2Et group and the *syn*-related *N*-methyl substituent are in axial positions,[38]

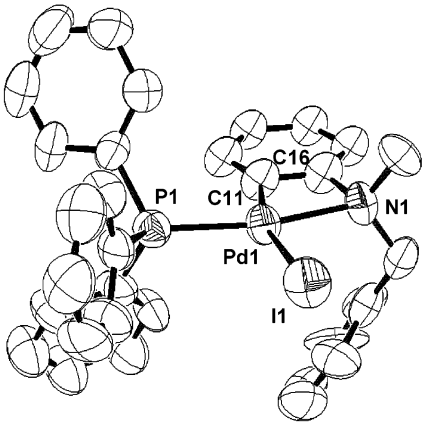


Figure 1. Molecular structure of **4b** (ORTEP view). H atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg], [values for the second molecule]: Pd(1)−C(11) = 1.961(9), [1.974(9)]; Pd(1)−N(1) = 2.127(7), [2.090(7)]; Pd(1)−P(1) = 2.162(3), [2.170(2)]; Pd(1)−I(1) = 2.5883(10), [2.5941(9)]; C(11)−Pd(1)−N(1) = 67.8(3), [68.3(3)]; C(11)−Pd(1)−P(1) = 96.2(3), [97.8(3)]; N(1)−Pd(1)−I(1) = 96.2(2), [95.01(19)]; P(1)−Pd(1)−I(1) = 99.65(7), [98.88(7)]; C(16)−N(1)−Pd(1) = 85.5(5), [87.7(5)]; C(11)−C(16)−N(1) = 109.3(8), [107.9(8)]; C(16)−C(11)−Pd(1) = 97.3(7), [96.0(7)].

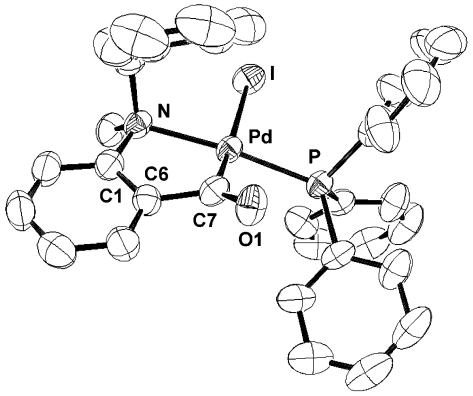


Figure 2. Molecular structure of **8b**·$0.5CH_3CO_2CH_2CH_3$ (ORTEP view). H atoms and solvent are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Pd−C(7) = 1.976(2), Pd−N = 2.1752(19), Pd−P = 2.2503(6), Pd−I = 2.7509(3), C(7)−Pd−N = 82.72(8), C(7)−Pd−P = 91.80(7), N−Pd−I = 94.67(5), P−Pd−I = 91.444(17), C(1)−N−Pd = 106.32(13), C(6)−C(1)−N = 117.3(2), C(1)−C(6)−C(7) = 118.2(2), C(6)−C(7)−Pd = 110.45(16).

(35) Additionally, the higher nucleophilicity of $TMSCHN_2$ than of ethyl diazoacetate (Bug, T.; Hartnagel, M.; Schlierf, C.; Mayr, H. *Chem. Eur. J.* **2003**, *9*, 4068) agrees with the experimental fact that the former has a higher tendency to give the double-insertion product than the latter, as can be seen when comparing the reactions of **4b** with $TMSCHN_2$ and $N_2CHCOOEt$.

(36) As the reaction is carried out in the presence of an excess of diazoalkane, the formation of disubstituted alkenes that could be inserted into the Pd−C bond of the four-membered palladacycle to give the six-membered palladacycle cannot be definitively ruled out.

(37) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1989**, *54*, 1773.

(38) The axial position for bulky groups in related complexes has been previously described. Maassarani, F.; Pfeffer, M.; Spek, A. L.; Schreurs, A. M. M.; van Koten, G. *J. Am. Chem. Soc.* **1986**, *108*, 4222. See also ref 32a.

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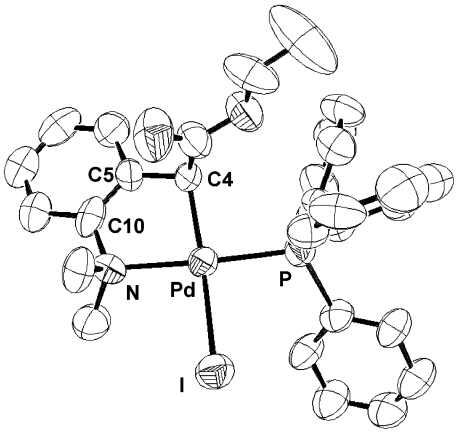

Figure 3. Molecular structure of **9a** (ORTEP view). H atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Pd−C(4) = 2.058(6), Pd−N = 2.150(5), Pd−P = 2.2491(16), Pd−I = 2.6910(7), C(4)−Pd−N = 83.8(2), C(4)−Pd−P = 91.93(17), N−Pd−I = 92.98(14), P−Pd−I = 92.33(5), C(10)−N−Pd = 106.3(3), C(5)−C(4)−Pd = 106.9(4), C(10)−C(5)−C(4) = 121.2(6), C(5)−C(10)−N = 117.7(5).

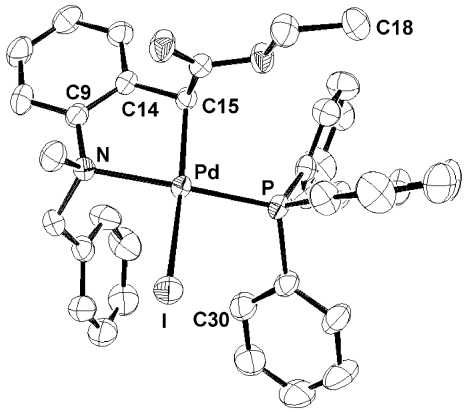

Figure 4. Molecular structure of **9b** (ORTEP view). H atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Pd−C(15) = 2.075(3), Pd−N = 2.178(2), Pd−P = 2.2601(8), Pd−I = 2.6765(3), C(15)−Pd−N = 82.83(10), C(15)−Pd−P = 94.55(8), N−Pd−I = 93.59(7), P−Pd−I = 92.32(2), C(9)−N−Pd = 107.73(18), C(14)−C(9)−N = 117.0(3), C(9)−C(14)−C(15) = 120.8(3), C(14)−C(15)−Pd = 107.86(19).

and the remaining *N*-alkyl substituent (CH_3 in **9a**, CH_2-Ph in **9b**, and Pr in **9c**) is in the bisector site of the envelope.

As can be deduced from the pronounced tetragonal distortion of the square-planar geometry, azapalladacycles **9b** and **9c** are highly stressed structures. In fact, in compound **9b** a short intramolecular distance is observed between the $COOCH_2CH_3$ group and one of the phenyl groups of PPh_3 [C(18)−H(18B)···C(19)··· C(24) ring, distance of H(18B) to the aromatic centroid = 2.596 Å]. The distance between the same groups is markedly longer (3.135 Å) in the less stressed azapalladacycle **9a**. Additionally, a short distance is also observed in compound **9b** between another phenyl group of the PPh_3 ligand and the *N*-Bn group [C(30)−H(30)··· C(1)···C(6) ring, distance of H(30) to the aromatic centroid = 2.735 Å].

In summary, we have studied the insertion reactions into the carbon−palladium bond in the four-membered azapalladacycles derived from *N*,*N*-dialkyl-2-iodoanilines. The insertion of dichlorocarbene afforded acyl palladium complexes, while the insertion of diazoalkanes gave rise to a new synthetic entry to five-membered azapalladacycles with a palladated stereogenic carbon. Further investigation will be conducted both to gain deeper insight into the reaction of carbenes with the azapalladacycles and to study the insertion of other substrates into the carbon−palladium bond of these complexes.

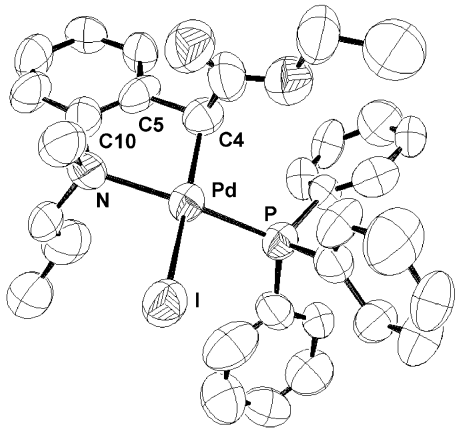

Figure 5. Molecular structure of **9c**·Et_2O (ORTEP view). H atoms and solvent are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Pd−C(4) = 2.046(10), Pd−N = 2.180(8), Pd−P = 2.225(3), Pd−I = 2.6682(11), C(4)−Pd−N = 84.6(4), C(4)−Pd−P = 94.3(3), N−Pd−I = 92.8(2), P−Pd−I = 91.86(7), C(5)−C(4)−Pd = 105.3(8), C(10)−C(5)−C(4) = 124.0(11), C(5)−C(10)−N = 114.4(10), C(10)−N−Pd = 107.2(6).

Experimental Section

General Information. All reactions were performed under an argon atmosphere using dry solvents. THF was distilled under nitrogen from sodium benzophenone ketyl. Benzene, toluene, dichloromethane, and acetonitrile were dried over CaH_2 and distilled under nitrogen. Other solvents were used as received. Chemicals were used as received from Acros ($NaBH(OAc)_3$, $Pd(PPh_3)_4$), Aldrich (benzyl bromide, 2-iodoaniline, propionaldehyde, $Pd_2(dba)_3$, N_2CHCO_2Et, N_2CHTMS), and Fluka (iodomethane, PPh_3, KO*t*-Bu). 2-Iodo-*N*-methylaniline[39] and 2-iodo-*N*,*N*-dimethylaniline[40] were prepared according to literature procedures. Nuclear magnetic resonance spectra were recorded in $CDCl_3$. Chemical shifts are given in parts per million (ppm) relative to Me_4Si for ^1H and ^{13}C NMR and relative to 85% H_3PO_4 for ^{31}P NMR. Only noteworthy IR absorptions are listed. Melting points were determined in a capillary tube and are uncorrected. Chromatography refers to flash chromatography and was carried out on SiO_2 (silica gel 60, 230−400 mesh ASTM).

***N*-Benzyl-2-iodo-*N*-methylaniline (3b).** To a solution of 2-iodo-*N*-methylaniline (0.7 g, 3.0 mmol) in acetonitrile (50 mL) were added benzyl bromide (1.43 mL, 12.0 mmol), K_2CO_3 (3.32 g, 24.0 mmol), and LiI (150 mg), and the mixture was heated at reflux for 24 h. The solvent was evaporated, and the residue was partitioned between CH_2Cl_2 and water. The organic extracts were dried and concentrated, and the residue was purified by chromatography (SiO_2, from hexane to 1:1 hexane−EtOAc) to give aniline **3b** as an oil. Yield: 865 mg,

(39) Larock, R. C.; Yum, E. K.; Refvik, M. D. *J. Org. Chem.* **1998**, *63*, 7652.
(40) Bunnett, J. F.; Mitchel, E.; Galli, C. *Tetrahedron* **1985**, *41*, 4119−4132.

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89%. IR (film) 1580, 1470, 1452 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.61 (s, 3H), 4.11 (s, 2H), 6.79 (ddd, J = 7.8, 7.5, and 1.8 Hz, 1H), 7.08 (dd, J = 7.8 and 1.5 Hz, 1H), 7.20−7.35 (m, 4H), 7.45 (m, 2H), 7.87 (dd, J = 7.8 and 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 41.6 (CH_3), 61.1 (CH_2), 98.5 (C), 122.2 (CH), 125.4 (CH), 127.0 (CH), 128.1 (CH), 128.6 (CH), 128.9 (CH), 138.1 (C), 140.0 (CH), 153.9 (C). HRMS: calcd for $C_{14}H_{14}IN$ 323.0171, found 323.0171.

2-Iodo-*N*-methyl-*N*-propylaniline (3c). To a solution of 2-iodoaniline (760 mg, 3.46 mmol) and propionaldehyde (0.3 mL, 4.17 mmol) in CH_2Cl_2 (50 mL) were added acetic acid (0.6 mL, 10.48 mmol) and $NaBH(OAc)_3$ (1.75 g, 8.26 mmol). After stirring at room temperature for 12 h, the mixture was poured into saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were dried and concentrated. Chromatography (SiO_2, from hexane to 95:5 hexane−EtOAc) of the residue afforded 2-iodo-*N*-propylaniline (768 mg, 85%). To a solution of 2-iodo-*N*-propylaniline (768 mg, 2.94 mmol) in acetonitrile (40 mL) were added K_2CO_3 (1.22 g, 8.82 mmol) and iodomethane (3.66 mL, 58.8 mmol). After stirring at 50 °C for 24 h, the solvent was evaporated and the residue was partitioned between CH_2Cl_2 and water. The organic extracts were washed with water, dried, and concentrated. Chromatography (SiO_2, from hexane to 9:1 hexane−EtOAc) of the residue afforded 2-iodo-*N*-methyl-*N*-propylaniline (**3c**) as an oil. Yield: 685 mg, 85%. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.91 (t, J = 7.2 Hz, 3H), 1.55 (tq, J = 7.5 and 7.2 Hz, 2H), 2.89 (t, J = 7.5 Hz, 2H), 2.69 (s, 3H), 6.77 (ddd, J = 7.8, 7.2, and 1.5 Hz, 1H), 7.08 (dd, J = 8.1 and 1.5 Hz, 1H), 7.29 (ddd, J = 8.1, 7.2, and 1.5 Hz, 1H), 7.84 (dd, J = 7.8 and 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 11.7 (CH_3), 20.7 (CH_2), 42.5 (CH_3), 58.5 (CH_2), 99.1 (C), 121.9 (CH), 125.1 (CH), 128.8 (CH), 139.9 (CH), 154.4 (C).

[Pd(κ^2-$C_6H_4NMe_2$-2)I(PPh_3)] (4a). To a solution of *N*,*N*-dimethyl-2-iodoaniline (**3a**, 0.3 g, 1.21 mmol) in benzene (10 mL) were added $Pd_2(dba)_3$ (0.66 g, 0.72 mmol) and PPh_3 (0.32 g, 1.22 mmol). The reddish reaction mixture was stirred at room temperature for 3 days. The solvent was evaporated, and the solid residue was purified by "flash" chromatography (SiO_2). Elution with hexane−EtOAc (3:2) afforded pure azapalladacycle **4a** as an orange solid which was crystallized from dichloromethane. Yield: 558 mg, 75%. Mp: 94−95 °C dec. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.11 (d, $J(^1H-^{31}P)$ = 3.3 Hz, 6H), 5.86 (dd, J = 7.5 and 1 Hz, 1H), 6.65 (dd, J = 7.8 and 7.5 Hz, 1H), 6.87 (dd, J = 7.8 and 0.9 Hz, 1H), 7.03 (td, J = 7.8 and 1.5 Hz, 1H), 7.35−7.50 (m, 9H), 7.68−7.77 (m, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 50.8 (s, CH_3), 118.3 (s, CH), 124.6 (d, $J(^{13}C-^{31}P)$ = 9.1 Hz, C), 125.1 (s, CH), 125.2 (d, $J(^{13}C-^{31}P)$ = 3 Hz, CH), 128.0 (d, $J(^{13}C-^{31}P)$ = 11.1 Hz, CH PPh_3), 128.7 (d, $J(^{13}C-^{31}P)$ = 7.1 Hz, CH), 130.7 (s, CH PPh_3), 131.5 (d, $J(^{13}C-^{31}P)$ = 52.2 Hz, C PPh_3), 134.8 (d, $J(^{13}C-^{31}P)$ = 12.2 Hz, CH PPh_3), 165.4 (s, C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 39.3. HRMS (FAB): m/z 488.0759 ($[M - I]^+$, 488.0780 calcd for $C_{26}H_{25}NPPd$). Anal. Calcd for $C_{26}H_{25}INPPd$ (615.78)·CH_2Cl_2: C, 46.28; H, 3.88; N, 2.00. Found: C, 46.28; H, 3.70; N, 1.97.

[Pd{κ^2-$C_6H_4N(Me)CH_2Ph$-2}I(PPh_3)] (4b). Operating as in the preparation of **4a**, starting from **3b** (150 mg, 0.46 mmol), $Pd_2(dba)_3$ (240 mg, 0.26 mmol), and PPh_3 (125 mg, 0.47 mmol), azapalladacycle **4b** was obtained after chromatography (SiO_2, from hexane to CH_2Cl_2). Yield: 290 mg, 91%. Azapalladacycle **4b** was crystallized from hexane−EtOAc. Mp: 108−109 °C dec. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.33 (d, $J(^1H-^{31}P)$ = 2.7 Hz, 3H), 4.04 (dd, $J(^1H-^1H)$ = 11.7 and $J(^1H-^{31}P)$ = 9 Hz, 1H), 4.54 (d, J = 11.7 Hz, 1H), 5.62 (d, J = 7.2 Hz, 1H), 6.50 (ddt, J = 7.5, 7.2, and 1 Hz, 1H), 6.94 (dd, J = 7.8 and 1.2 Hz, 1H), 7.01 (ddd, J = 7.8, 7.2, and 1.2 Hz, 1H), 7.20−7.50 (m, 18H), 7.61 (dd, J = 7 and 1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 50.4 (s, CH_3), 64.1 (s, CH_2), 119.7 (s, CH), 124.6 (s, CH), 125.1 (d, $J(^{13}C-^{31}P)$ = 3 Hz, CH), 126.0 (d, $J(^{13}C-^{31}P)$ = 11.6 Hz, C), 127.7 (s, CH), 127.8 (s, CH), 127.9 (d, $J(^{13}C-^{31}P)$ = 10.9 Hz, CH PPh_3), 128.4 (d, $J(^{13}C-^{31}P)$ = 8.2 Hz, CH), 130.6 (s, CH), 131.6 (d, $J(^{13}C-^{31}P)$ = 52.2 Hz, C PPh_3), 132.6 (s, CH), 134.8 (d, $J(^{13}C-^{31}P)$ = 12.1 Hz, CH PPh_3), 135.3 (s, C), 160.9 (d, $J(^{13}C-^{31}P)$ = 2 Hz, C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 39.3. Anal. Calcd for $C_{32}H_{29}INPPd$: C, 55.55; H, 4.22; N, 2.02. Found: C, 55.63; H, 4.32; N, 2.01.

[Pd{κ^2-$C_6H_4N(Me)Pr$-2}I(PPh_3)] (4c). Operating as in the preparation of **4a**, starting from **3c** (154 mg, 0.56 mmol), $Pd_2(dba)_3$ (280 mg, 0.30 mmol), and PPh_3 (145 mg, 0.55 mmol), azapalladacycle **4c** was obtained after chromatography (SiO_2, from hexane to CH_2Cl_2). Yield: 342 mg, 95%. Mp: 169−170 °C dec. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.92 (t, J = 7.2 Hz, 3H), 1.49 (m, 1H), 2.54 (m, 1H), 2.91 (ddd, J = 11.4, 9.9, and 4.2 Hz, 1H), 3.16 (d, $J(^1H-^{31}P)$ = 3 Hz, 3H), 3.30 (td, J = 11.7 and 4.5 Hz, 1H), 5.87 (dd, J = 7.5 and 0.9 Hz, 1H), 6.62 (t, J = 7.5 Hz, 1H), 6.83 (dd, J = 7.5 and 0.9 Hz, 1H), 7.02 (td, J = 7.5 and 1.2 Hz, 1H), 7.33−7.49 (m, 9H), 7.65−7.76 (m, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 11.5 (s, CH_3), 22.5 (s, CH_2), 51.1 (s, CH_3), 62.1 (s, CH_2), 118.7 (s, CH), 125.0 (s, CH), 125.2 (s, CH), 126.0 (d, $J(^{13}C-^{31}P)$ = 10.4 Hz, C), 128.0 (d, $J(^{13}C-^{31}P)$ = 10.9 Hz, CH PPh_3), 128.5 (d, $J(^{13}C-^{31}P)$ = 8.2 Hz, CH), 130.7 (d, $J(^{13}C-^{31}P)$ = 2.2 Hz, CH PPh_3), 131.7 (d, $J(^{13}C-^{31}P)$ = 52.2 Hz, C PPh_3), 134.9 (d, $J(^{13}C-^{31}P)$ = 12.2 Hz, CH PPh_3), 162.3 (d, $J(^{13}C-^{31}P)$ = 4.4 Hz, C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 38.6. HRMS (FAB): m/z 516.1072 ($[M - I]^+$, 516.1064 calcd for $C_{28}H_{29}NPPd$). Anal. Calcd for $C_{28}H_{29}INPPd$ (643.84): C, 52.23; H, 4.54; N, 2.18. Found: C, 52.48; H, 4.52; N, 1.66.

***trans*-[Pd($C_6H_4NMe_2$-2)I(PPh_3)$_2$] (5a).** To a solution of *N*,*N*-dimethyl-2-iodoaniline (**3a**, 100 mg, 0.40 mmol) in benzene (10 mL) was added $Pd(PPh_3)_4$ (470 mg, 0.40 mmol). After stirring at room temperature for 24 h, the solvent was evaporated and the palladium complex **5a** was precipitated from Et_2O as a yellow solid. Yield: 300 mg, 85%. ^1H NMR ($CDCl_3$, 300 MHz, −10 °C): δ 2.58 (s, 6H), 5.91 (d, J = 7.8 Hz, 1H), 6.05 (t, J = 7.5 Hz, 1H), 6.51 (t, J = 7.5 Hz, 1H), 6.91 (m, 1H), 7.20−7.60 (m, 30H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 44.8 (s, CH_3), 118.3 (s, CH), 119.8 (s, CH), 123.6 (s, CH), 127.5 (s, CH PPh_3), 129.5 (s, CH PPh_3), 130.1 (s, CH), 132.5 (t, $J(^{13}C-^{31}P)$ = 20 Hz, C PPh_3), 134.8 (s, CH PPh_3), 150.0 (s, C), 155.1 (s, C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 19.5.

***trans*-[Pd{$C_6H_4N(Me)CH_2Ph$-2}I(PPh_3)$_2$] (5b).** Operating as in the preparation of **5a**, starting from **3b** (100 mg, 0.31 mmol) and $Pd(PPh_3)_4$ (355 mg, 0.31 mmol), palladium complex **5b** was obtained. Yield: 297 mg, quantitative. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.36 (s, 3H), 4.15 (s, 2H), 6.10 (m, 2H), 6.59 (t, J = 7.5 Hz, 1H), 6.99 (m, 1H), 7.20−7.80 (m, 35H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 39.2 (s, CH_3), 60.5 (s, CH_2), 119.1 (s, CH), 119.7 (s, CH), 123.5 (s, CH), 126.2 (s, CH), 127.2 (br, CH PPh_3), 127.6 (s, CH), 127.9 (s, CH), 129.3 (s, CH PPh_3), 131.6 (s, CH), 131.9 (t, $J(^{13}C-^{31}P)$ = 22.6 Hz, C PPh_3), 134.6 (br, CH PPh_3), 137.1 (s, C), 147.3 (s, C), 154.9 (s, C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 18.1.

"Flash" Chromatography of Palladium Complex 5a. The palladium complex **5a** (150 mg, 0.17 mmol) was submitted to "flash" chromatography (SiO_2, from hexane to 1:1 hexane−EtOAc) to give **5a** (38 mg, 25%) and azapalladacycle **4a** (46 mg, 44%).

"Flash" Chromatography of Palladium Complex 5b. The palladium complex **5b** (200 mg, 0.21 mmol) was submitted to "flash" chromatography (SiO_2, from hexane to 1:1 hexane−EtOAc) to give **5b** (30 mg, 15%), azapalladacycle **4b** (92 mg, 63%), and hydroxopalladium complex **6** (16 mg, 13%).

[Pd{κ^2-$C_6H_4N(Me)CH_2Ph$-2}OH(PPh_3)] (6). ^1H NMR ($CDCl_3$, 300 MHz): δ 3.29 (d, $J(^1H-^{31}P)$ = 3 Hz, 3H), 4.01 (dd, $J(^1H-^1H)$ = 11.4 and $J(^1H-^{31}P)$ = 8.4 Hz, 1H), 4.52 (d, J = 11.4 Hz, 1H), 5.53 (d, J = 7.8 Hz, 1H), 6.48 (m, 1H), 6.93−7.04 (m, 2H), 7.20−7.46 (m, 18H), 7.55−7.75 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 49.0 (s, CH_3), 63.2 (s, CH_2), 118.9 (s, CH), 124.5 (s, CH), 125.1 (s, CH), 127.8 (s, CH), 127.9 (s, CH), 128.0 (d, $J(^{13}C-^{31}P)$ = 11.6 Hz, CH PPh_3), 129.5 (d, $J(^{13}C-$

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^{31}P) = 7.6 Hz, CH), 130.5 (d, J(^{13}C−^{31}P) = 51.1 Hz, C PPh$_3$), 130.6 (s, CH), 132.6 (s, CH), 134.8 (d, J(^{13}C−^{31}P) = 12.6 Hz, CH PPh$_3$), 135.5 (s, C), 160.5 (s, C), one C not observed. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 35.7.

[PdPhI(PNMe$_2$)] (7a).[16] A solution of azapalladacycle **4a** (20 mg, 0.032 mmol) in THF (5 mL) was stirred at 110 °C in a sealed tube for 36 h. The solvent was evaporated, and the residue was purified by flash chromatography (SiO_2, CH_2Cl_2) to give palladium complex **7a** as an 10:1 mixture of the *trans*P,I and *cis*P,I isomers. Yield: 11 mg, 55%. *trans*P,I isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.40 (s, 6H), 6.64−6.74 (m, 3H), 6.94 (m, 2H), 7.28−7.39 (m, 10H), 7.42−7.48 (m, 2H), 7.59 (tt, J = 8.4 and 1.2 Hz, 1H), 7.69 (dd, J = 8.4 and 4.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 53.8 (s, CH_3), 122.5 (s, CH), 123.0 (d, J(^{13}C−^{31}P) = 10 Hz, CH), 126.6 (d, J(^{13}C−^{31}P) = 1.5 Hz, CH), 128.4 (d, J(^{13}C−^{31}P) = 6.1 Hz, CH), 128.7 (d, J(^{13}C−^{31}P) = 10.7 Hz, CH), 129.1 (d, J(^{13}C−^{31}P) = 53.7 Hz, C), 130.9 (d, J(^{13}C−^{31}P) = 3.1 Hz, CH), 131.1 (d, J(^{13}C−^{31}P) = 46.5 Hz, C), 133.2 (d, J(^{13}C−^{31}P) = 12.3 Hz, CH), 133.3 (d, J(^{13}C−^{31}P) = 1.5 Hz, CH), 134.4 (s, CH), 137.7 (d, J(^{13}C−^{31}P) = 4.6 Hz, CH), 138.7 (s, C), 159.5 (d, J(^{13}C−^{31}P) = 18.4 Hz, C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 23.7. *cis*P,I isomer: ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 36.5.

[PdPhI{PN(Me)Pr}] (7c).[41] A solution of azapalladacycle **4c** (25 mg, 0.039 mmol) in toluene (10 mL) was stirred at 110 °C in a sealed tube for 24 h. The solvent was evaporated, and the residue was purified by flash chromatography (SiO_2, from hexane to 1:1 hexane−EtOAc). Elution with hexane−EtOAc (4:1) afforded azapalladacycle **7c**-*trans*P,I. Yield: 8 mg, 32%. Elution with hexane−EtOAc (3:2) afforded azapalladacycle **7c**-*cis*P,I. Yield: 2 mg, 8%. *trans*P,I isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.91 (t, J = 7.2 Hz, 3H), 1.03 (m, 1H), 2.42 (m, 1H), 3.19 (td, J = 11.6 and 4 Hz, 1H), 3.33 (s, 3H), 4.40 (td, J = 11.6 and 4.8 Hz, 1H), 6.65−6.74 (m, 3H), 6.94 (m, 2H), 7.07−7.13 (m, 2H), 7.27−7.49 (m, 10H), 7.57−7.68 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 11.2 (s, CH_3), 21.7 (s, CH_2), 54.1 (s, CH_3), 64.9 (s, CH_2), 122.4 (s, CH), 122.9 (d, J(^{13}C−^{31}P) = 10 Hz, CH), 126.7 (s, CH), 128.4 (d, J(^{13}C−^{31}P) = 6.1 Hz, CH), 128.5 (d, J(^{13}C−^{31}P) = 10.8 Hz, CH), 128.8 (d, J(^{13}C−^{31}P) = 11.5 Hz, CH), 129.9 (d, J(^{13}C−^{31}P) = 53 Hz, C), 130.7 (d, J(^{13}C−^{31}P) = 3 Hz, CH), 131.0 (d, J(^{13}C−^{31}P) = 3 Hz, CH), 133.0 (d, J(^{13}C−^{31}P) = 12.2 Hz, CH), 133.1 (d, J(^{13}C−^{31}P) = 50 Hz, C), 133.4 (d, J(^{13}C−^{31}P) = 1.5 Hz, CH), 133.4 (d, J(^{13}C−^{31}P) = 12.3 Hz, CH), 134.4 (s, CH), 137.7 (d, J(^{13}C−^{31}P) = 4.5 Hz, CH), 139.3 (d, J(^{13}C−^{31}P) = 2.3 Hz, C), 157.3 (d, J(^{13}C−^{31}P) = 18.4 Hz, C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 27.3. MS(FAB): m/z 1161 [2M$^+$ + 2 − I], 1084 [2M$^+$ + 2 − I − C_6H_5], 566 [M$^+$ − C_6H_5], 516 [M$^+$ − I], 439 [M$^+$ − I − C_6H_5]. *cis*P,I isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.87 (t, J = 7.2 Hz, 3H), 0.98 (m, 1H), 2.45 (m, 1H), 3.31 (td, J = 12 and 4.4 Hz, 1H), 3.57 (s, 3H), 4.83 (td, J = 12 and 4.8 Hz, 1H), 7.31 (m, 1H), 7.38 (m, 1H), 7.41−7.49 (m, 6H), 7.50−7.57 (m, 3H), 7.61−7.70 (m, 3H), 7.75−7.85 (m, 5H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 10.8 (s, CH_3), 21.9 (s, CH_2), 57.1 (s, CH_3), 67.8 (s, CH_2), 122.2 (d, J(^{13}C−^{31}P) = 12.3 Hz, CH), 128.7 (d, J(^{13}C−^{31}P) = 11.6 Hz, CH), 128.8 (d, J(^{13}C−^{31}P) = 12.2 Hz, CH), 129.7 (d, J(^{13}C−^{31}P) = 5.3 Hz, CH), 130.3 (d, J(^{13}C−^{31}P) = 59 Hz, C), 131.8−132.1 (several CH), 134.0−134.5 (several CH), 157.9 (d, J(^{13}C−^{31}P) = 17.6 Hz, C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 40.6. MS(FAB): m/z 566 [M$^+$ − C_6H_5], 439 [M$^+$ − I − C_6H_5].

[Pd{κ^2-C(O)C$_6$H$_4$NMe$_2$-2}I(PPh$_3$)] (8a). KO*t*-Bu (1.6 mmol, 1.6 mL of 1 M solution in *tert*-butyl alcohol) was added to $CHCl_3$ (10 mL). After 5 min at room temperature, a solution of palladacycle **4a** (49 mg, 0.08 mmol) in $CHCl_3$ (5 mL) was added dropwise. The mixture was stirred at room temperature for 5 h under argon, and the solvent was evaporated. Chromatography (SiO_2, from hexane to 1:1 hexane−EtOAc) of the residue afforded palladacycle **8a**. Yield: 37 mg, 72%. Mp: 86−87 °C. IR (film): 1666, 1479, 1435 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.58 (d, J(^{1}H−^{31}P) = 1.8 Hz, 6H), 7.23 (t, J = 7.5 Hz, 1H), 7.29−7.45 (m, 10H), 7.58 (ddd, J = 8.1, 7.5, and 1.5 Hz, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.70−7.80 (m, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 54.3 (s, CH_3), 120.4 (d, J(^{13}C−^{31}P) = 2.8 Hz, CH), 125.4 (s, CH), 127.9 (d, J(^{13}C−^{31}P) = 11 Hz, CH PPh$_3$), 128.5 (s, CH), 130.1 (d, J(^{13}C−^{31}P) = 2.2 Hz, CH PPh$_3$), 132.5 (d, J(^{13}C−^{31}P) = 50.1 Hz, C PPh$_3$), 134.1 (s, CH), 134.7 (d, J(^{13}C−^{31}P) = 12.1 Hz, CH PPh$_3$), 140.8 (d, J(^{13}C−^{31}P) = 9.9 Hz, C), 156.7 (d, J(^{13}C−^{31}P) = 2.5 Hz, C), 209.8 (d, J(^{13}C−^{31}P) = 14.3 Hz, C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 40.0. Anal. Calcd for $C_{27}H_{25}INOPPd$ (643.78): C, 50.37; H, 3.91; N, 2.18. Found: C, 50.25; H, 4.13; N, 2.03.

[Pd{κ^2-C(O)C$_6$H$_4$N(Me)CH$_2$Ph-2}I(PPh$_3$)] (8b). Operating as in the preparation of **8a**, starting from **4b** (27 mg, 0.04 mmol), azapalladacycle **8b** was obtained after chromatography (SiO_2, from hexane to 1:1 hexane−EtOAc). Yield: 18 mg, 64%. Azapalladacycle **8b** was crystallized from EtOAc. Mp: 140−142 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.92 (d, J(^{1}H−^{31}P) = 1.8 Hz, 3H), 4.08 (dd, J = 11.7 Hz and J(^{1}H−^{31}P) = 6 Hz, 1H), 5.56 (d, J = 11.7 Hz, 1H), 6.98−7.09 (m, 3H), 7.15−7.22 (m, 2H), 7.28−7.43 (m, 12H), 7.55−7.67 (m, 6H), 7.80 (d, J = 8.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 53.5 (s, CH_3), 67.4 (s, CH_2), 121.5 (d, J(^{13}C−^{31}P) = 2.5 Hz, CH), 124.9 (s, CH), 127.8 (d, J(^{13}C−^{31}P) = 10.4 Hz, CH PPh$_3$), 127.9 (s, CH), 128.4 (s, CH), 128.6 (s, CH), 130.0 (d, J(^{13}C−^{31}P) = 2.2 Hz, CH PPh$_3$), 131.5 (s, CH), 132.5 (d, J(^{13}C−^{31}P) = 49.5 Hz, C PPh$_3$), 133.7 (s, CH), 134.5 (s, C), 134.7 (d, J(^{13}C−^{31}P) = 11.6 Hz, CH PPh$_3$), 142.9 (d, J(^{13}C−^{31}P) = 9.9 Hz, C), 153.3 (d, J(^{13}C−^{31}P) = 1.5 Hz, C), 207.6 (d, J(^{13}C−^{31}P) = 14 Hz, C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 38.6.

[Pd{κ^2-C(O)C$_6$H$_4$N(Me)Pr-2}I(PPh$_3$)] (8c). Operating as in the preparation of **8a**, starting from **4c** (32 mg, 0.05 mmol) and stirring the reaction mixture at room temperature for 41 h, azapalladacycle **8c** was obtained after chromatography (SiO_2, from hexane to 1:1 hexane−EtOAc). Yield: 23 mg, 69%. Azapalladacycle **8b** was crystallized from dichloromethane. IR (film): 1665, 1435, 1095 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.90 (t, J = 7.2 Hz, 3H), 1.09 (m, 1H), 2.34 (m, 1H), 3.08 (m, 1H), 3.61 (d, J = 1.5 Hz, 3H), 4.51 (td, J = 12 and 4.5 Hz, 1H), 7.23 (m, 1H), 7.31−7.45 (m, 9H), 7.58−7.61 (m, 2H), 7.68−7.77 (m, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 11.1 (s, CH_3), 22.2 (s, CH_2), 54.2 (s, CH_3), 65.6 (s, CH_2), 120.6 (d, J(^{13}C−^{31}P) = 3 Hz, CH), 125.2 (s, CH), 127.9 (d, J(^{13}C−^{31}P) = 11.1 Hz, CH PPh$_3$), 128.5 (s, CH), 130.1 (d, J(^{13}C−^{31}P) = 2 Hz, CH PPh$_3$), 132.7 (d, J(^{13}C−^{31}P) = 49.7 Hz, C PPh$_3$), 134.3 (s, CH), 134.7 (d, J(^{13}C−^{31}P) = 11.6 Hz, CH PPh$_3$), 142.7 (d, J(^{13}C−^{31}P) = 9.7 Hz, C), 154.4 (d, J(^{13}C−^{31}P) = 3 Hz, C), 209.4 (d, J(^{13}C−^{31}P) = 14.2 Hz, C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 43.2. Anal. Calcd for $C_{29}H_{29}INOPPd$ (671.85)·3/4CH_2Cl_2: C, 48.58; H, 4.18; N, 1.90. Found: C, 48.18; H, 4.21; N, 1.77.

[Pd{κ^2-CH(CO$_2$Et)C$_6$H$_4$NMe$_2$-2}I(PPh$_3$)] (9a). To a solution of azapalladacycle **4a** (30 mg, 0.05 mmol) in benzene (10 mL) was added ethyl diazoacetate (0.55 mmol, 1.1 mL of 0.5 M solution in benzene). The mixture was stirred at room temperature for 24 h under argon, and the solvent was evaporated. Chromatography (SiO_2, from hexane to 4:1 hexane−EtOAc) of the residue afforded palladacycle **9a**, which was crystallized from Et_2O−EtOAc. Yield: 20 mg, 56%. Mp: 187−188 °C. IR (film): 1681, 1436, 1146 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, J = 7.2 Hz, 3H), 3.42 (d, J(^{1}H−^{31}P) = 5.7 Hz, 3H), 3.42 (masked, 1H), 3.55 (s, 3H), 3.65 (dq, J = 10.8 and 7.2 Hz, 1H), 4.01 (dq, J = 10.8 and 7.2 Hz, 1H), 6.75 (dd, J = 7.5 and 1.2 Hz, 1H), 7.05 (td, J = 7.5 and 1.2 Hz, 1H), 7.21 (ddd, J = 8.1, 7.5, and 1.2 Hz, 1H), 7.35 (dd, J = 8.1 and 1.2 Hz, 1H), 7.37−7.50 (m, 9H), 7.77−7.88 (m, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 13.9 (s, CH_3), 51.6 (s, CH), 52.1 (s, CH_3), 55.7 (s, CH_3), 59.9 (s, CH_2), 121.5 (s, CH), 127.4 (s, CH), 127.5 (s, CH), 127.8 (d, J(^{13}C−^{31}P) = 10.6 Hz, CH PPh$_3$), 129.0 (s, CH), 130.5 (s, CH), 132.2 (d, J(^{13}C−^{31}P) = 52.2 Hz, C PPh$_3$),

(41) PN(Me)Pr means *N*-methyl-*N*-propyl-2-(diphenylphosphanyl)-aniline.

Table 1. Selected Crystallographic Data of Complexes 4b, 8b·EtOAc, 9a, 9b, and 9c·Et_2O

	4b	**8b**·0.5EtOAc	**9a**	**9b**	**9c**·Et_2O
formula	$C_{32}H_{29}INPPd$	$C_{35}H_{33}INO_2PPd$	$C_{30}H_{31}INO_2PPd$	$C_{36}H_{35}INO_2PPd$	$C_{36}H_{45}INO_3PPd$
fw	691.85	763.90	701.83	777.92	804.00
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$Pbca$
a, Å	10.4880(10)	9.5280(10)	11.9350(10)	16.9770(10)	20.3370(10)
b, Å	13.6220(10)	26.6000(10)	14.3460(10)	10.1480(10)	14.7750(10)
c, Å	19.1130(10)	12.8330(10)	16.9290(10)	21.7403(8)	23.6080(10)
α, deg	100.81(2)	90	90	90	90
β, deg	91.99(2)	101.9260(10)	92.27(2)	121.688(3)	90
γ, deg	97.95(2)	90	90	90	90
V, Å^3	2651.2(3)	3182.3(4)	2896.3(4)	3187.1(4)	7093.7(7)
Z	4	4	4	4	8
D_{calcd}, Mg/m^3	1.733	1.594	1.610	1.621	1.506
F(000)	1368	1520	1392	1552	3248
cryst size, mm	0.2 × 0.1 × 0.1	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
θ range, deg	1.09−25.00	1.79−31.55	2.05−28.92	1.89−31.59	2.42−31.74
no. of reflns collected	7042	27 490	10 477	20 290	24 044
no. of indep reflns (R_{int})	6992 (0.0642)	9233 (0.0454)	4698 (0.0429)	8363 (0.0219)	8028 (0.0905)
R1 ($I > 2\sigma(I)$)	0.0472	0.0321	0.0645	0.0338	0.0760
wR2 ($I > 2\sigma(I)$)	0.1121	0.0790	0.2142	0.0917	0.1550
goodness of fit on F^2	1.017	1.109	1.179	1.221	0.872

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135.3 (d, J(^{13}C−^{31}P) = 11 Hz, CH PPh_3), 141.1 (s, C), 155.6 (s, C), 174.2 (s, C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 31.2. Anal. Calcd for $C_{30}H_{31}INO_2PPd$: C, 51.34; H, 4.45; N, 2.00. Found: C, 51.43; H, 4.42; N, 1.90.

[Pd{κ^2-CH(CO_2Et)C_6H_4N(Me)CH_2Ph-2}I(PPh_3)] (9b). Operating as in the preparation of **9a**, starting from **4b** (36 mg, 0.05 mmol) and stirring the reaction mixture at room temperature for 36 h, azapalladacycle **9b** was obtained after chromatography (SiO_2, from hexane to 4:1 hexane−EtOAc). Yield: 20 mg, 51%. Azapalladacycle **9b** was crystallized from Et_2O−EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.73 (t, J = 7.2 Hz, 3H), 3.15 (d, J(^{1}H−^{31}P) = 6 Hz, 1H), 3.45 (dq, J = 10.8 and 7.2 Hz, 1H), 3.72 (d, J(^{1}H−^{31}P) = 2.8 Hz, 3H), 3.83 (dq, J = 10.8 and 7.2 Hz, 1H), 4.53 (dd, J(^{1}H−^{1}H) = 13.2 and J(^{1}H−^{31}P) = 7.6 Hz, 1H), 5.45 (d, J = 13.2 Hz, 1H), 6.70 (dd, J = 7.5 and 1.2 Hz, 1H), 7.07 (td, J = 7.5 and 1.2 Hz, 1H), 7.14−7.50 (m, 15H), 7.56−7.64 (m, 5H), 7.83−7.89 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 13.7 (s, CH_3), 51.2 (s, CH), 52.7 (d, J(^{13}C−^{31}P) = 3.1 Hz, CH_3), 59.8 (s, CH_2), 67.4 (d, J(^{13}C−^{31}P) = 1.5 Hz, CH_2), 122.5 (s, CH), 127.6 (s, CH), 127.7 (s, CH), 127.8 (d, J(^{13}C−^{31}P) = 10.8 Hz, CH PPh_3), 127.9 (s, CH), 129.1 (s, CH), 130.3 (d, J(^{13}C−^{31}P) = 2.2 Hz, CH PPh_3), 130.9 (s, CH), 131.9 (d, J(^{13}C−^{31}P) = 51.4 Hz, C PPh_3), 132.9 (s, CH), 135.1 (d, J(^{13}C−^{31}P) = 10.7 Hz, CH PPh_3), 135.8 (s, C), 143.4 (s, C), 153.0 (d, J(^{13}C−^{31}P) = 2.3 Hz, C), 174.7 (s, C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 33.3.

[Pd{κ^2-CH(CO_2Et)C_6H_4N(Me)Pr-2}I(PPh_3)] (9c). Operating as in the preparation of **9a**, starting from **4c** (35 mg, 0.05 mmol) and stirring the reaction mixture at room temperature for 72 h, azapalladacycle **9c** was obtained after chromatography (SiO_2, from hexane to 4:1 hexane−EtOAc). Yield: 13 mg, 33%. Azapalladacycle **9c** was crystallized from Et_2O−EtOAc. Mp: 156−158 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.84 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.2 Hz, 3H), 1.25 (m, 1H), 2.61 (m, 1H), 3.22 (m, 1H), 3.43 (d, J(^{1}H−^{31}P) = 2.7 Hz, 3H), 3.43 (masked, 1H), 3.60 (dq, J = 10.8 and 7.2 Hz, 1H), 3.98 (dq, J = 10.8 and 7.2 Hz, 1H), 4.41 (td, J = 11.7 and 3.9 Hz, 1H), 6.76 (d, J = 7.5 Hz, 1H), 7.03 (td, J = 7.5 and 1.2 Hz, 1H), 7.21 (td, J = 7.5 and 1.2 Hz, 1H), 7.26 (d, J = 7.5 Hz, 1H), 7.36−7.50 (m, 9H), 7.77−7.87 (m, 6H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 10.9 (s, CH_3), 13.9 (s, CH_3), 21.7 (s, CH_2), 50.9 (s, CH), 51.8 (d, J(^{13}C−^{31}P) = 2.3 Hz, CH_3), 59.9 (s, CH_2), 66.9 (d, J(^{13}C−^{31}P) = 2.3 Hz, CH_2), 121.3 (s, CH), 127.3 (s, CH), 127.7 (s, CH), 127.9 (d, J(^{13}C−^{31}P) = 10.8 Hz, CH PPh_3), 129.0 (s, CH), 130.4 (d, J(^{13}C−^{31}P) = 2.3 Hz, CH PPh_3), 132.3 (d, J(^{13}C−^{31}P) = 52.1 Hz, C PPh_3), 135.3 (d, J(^{13}C−^{31}P) = 10.8 Hz, CH PPh_3), 142.8 (s, C), 152.9 (d, J(^{13}C−^{31}P) = 3 Hz, C), 174.5 (s, C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 33.1.

[Pd{κ^2-CH($SiMe_3$)C_6H_4NMe_2-2}I(PPh_3)] (10a). To a solution of azapalladacycle **4a** (25 mg, 0.04 mmol) in benzene (10 mL) was added trimethylsilyl diazomethane (0.13 mmol, 65 μL of 2 M solution in hexane). The mixture was stirred at room temperature for 24 h under argon, and the solvent was evaporated. Chromatography (SiO_2, from hexane to 1:1 hexane−EtOAc) of the residue afforded palladacycle **10a**. Yield: 26 mg, 95%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ −0.22 (s, 9H), 2.72 (d, J(^{1}H−^{31}P) = 6.6 Hz, 1H), 3.37 (d, J(^{1}H−^{31}P) = 3.3 Hz, 3H), 3.50 (d, J(^{1}H−^{31}P) = 1.5 Hz, 3H), 6.65 (dd, J = 7.5 and 1.2 Hz, 1H), 6.98 (td, J = 7.5 and 1.2 Hz, 1H), 7.07 (td, J = 7.5 and 1.2 Hz, 1H), 7.27 (d, J = 7.5 Hz, 1H), 7.35−7.548 (m, 9H), 7.75−7.84 (m, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 1.52 (s, CH_3), 1.54 (s, CH_3), 50.4 (d, J(^{13}C−^{31}P) = 2.6 Hz, CH_3), 51.4 (s, CH), 57.4 (s, CH_3), 121.5 (s, CH), 124.7 (s, CH), 127.0 (s, CH), 127.4 (s, CH), 127.9 (d, J(^{13}C−^{31}P) = 10.6 Hz, CH PPh_3), 130.4 (d, J(^{13}C−^{31}P) = 2.6 Hz, CH PPh_3), 132.4 (d, J(^{13}C−^{31}P) = 48.7 Hz, C PPh_3), 135.3 (d, J(^{13}C−^{31}P) = 10.6 Hz, CH PPh_3), 148.5 (s, C), 152.3 (s, C).^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 35.2.

[Pd{κ^2-CH($SiMe_3$)C_6H_4N(Me)Pr-2}I(PPh_3)] (10c). Operating as in the preparation of **10a**, starting from **4c** (25 mg, 0.039 mmol), azapalladacycle **10c** was obtained after chromatography (SiO_2, from hexane to 1:1 hexane−EtOAc). Yield: 16 mg, 57%. Azapalladacycle **10c** was crystallized from Et_2O−EtOAc. ^{1}H NMR ($CDCl_3$, 300 MHz): δ −0.27 (s, 9H), 0.84 (t, J = 7.2 Hz, 3H), 0.95 (m, 1H), 2.50 (m, 1H), 2.84 (d, J(^{1}H−^{31}P) = 6.3 Hz, 1H), 3.04 (m, 1H), 3.35 (d, J(^{1}H−^{31}P) = 2.7 Hz, 3H), 4.43 (td, J = 11.7 and 3.9 Hz, 1H), 6.65 (d, J = 7.5 Hz, 1H), 6.95 (td, J = 7.5 and 1.2 Hz, 1H), 7.05 (td, J = 7.5 and 1.2 Hz, 1H), 7.16 (d, J = 7.5 Hz, 1H), 7.35−7.49 (m, 9H), 7.73−7.84 (m, 6H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 1.62 (s, CH_3), 11.3 (s, CH_3), 21.1 (s, CH_2), 50.2 (s, CH_3), 50.7 (s, CH), 68.5 (s, CH_2), 121.3 (s, CH), 125.0 (s, CH), 126.8 (s, CH), 126.9 (s, CH), 127.9 (d, J(^{13}C−^{31}P) = 10.3 Hz, CH PPh_3), 130.3 (d, J(^{13}C−^{31}P) = 2.4 Hz, CH PPh_3), 132.4 (d, J(^{13}C−^{31}P) = 47.9 Hz, C PPh_3), 135.5 (d, J(^{13}C−^{31}P) = 10.9 Hz, CH PPh_3), 149.5 (s, C), 150.9 (s, C). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 33.0. Anal. Calcd for $C_{32}H_{39}INPPdSi$ (730.04)·2Et_2O: C, 54.70; H, 6.77; N, 1.59. Found: C, 54.89; H, 6.51; N, 1.75.

***N*-Benzyl-*N*-methyl-2-[(*Z*)-2-(trimethylsilyl)vinyl]aniline (11b).** Operating as in the preparation of **10a**, starting from **4b** (25 mg, 0.036 mmol), **11b** was obtained after chromatography (SiO_2, from hexane to 1:1 hexane−EtOAc). Yield: 8 mg, 73%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.05 (s, 9H), 2.62 (s, 3H), 4.14 (s, 2H), 5.82 (d, J = 15 Hz, 1H), 6.98 (d, J = 8.1 Hz, 1H), 7.00 (m, 1H), 7.20−7.40 (m, 7H), 7.60 (d, J = 15 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 0.3 (CH_3), 40.2 (CH_3),

60.4 (CH_2), 118.6 (CH), 121.4 (CH), 126.9 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 130.2 (CH), 130.3 (CH), 134.1 (C), 138.7 (C), 146.0 (CH), 151.2 (CH). HRMS (FAB): *m*/*z* 295.1756 (M^+, 295.1764 calcd for $C_{19}H_{25}NSi$).

Crystallography. Intensities were collected with a MAR345 diffractometer with an image plate detector, and cell parameters were determined from all measured intensities. The structures were solved by direct methods, using the SHELXS-97 computer program, and refined by full-matrix least-squares method with the SHELXL97 computer program.[42] Crystal data for complexes **4b**, **8b**·0.5EtOAc, **9a**, **9b**, and **9c**·Et_2O are listed in Table 1, and their ORTEP plots are shown in Figures 1−5, respectively (H atoms and solvents are omitted for clarity). Other crystallographic data are deposited as Supporting Information.

(42) Sheldrick, G. M. *SHELXL97*, computer program for the determination of crystal structure; University of Göttingen: Germany, 1997.

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Supporting Information Available: Crystallographic data of **4b**, **8b**·EtOAc, **9a**, **9b**, and **9c**·Et_2O are given in PDF and CIF formats. ^1H and ^{13}C NMR spectra for compounds **4a**−**c**, **5a**,**b**, **6**, **7a**,**c**, **8a**−**c**, **9a**−**c**, and **10a**,**c** are also provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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