Formation of a Vinyliminium Palladium Complex by C−C Coupling in Vinylcarbene Palladium Aryl Complexes

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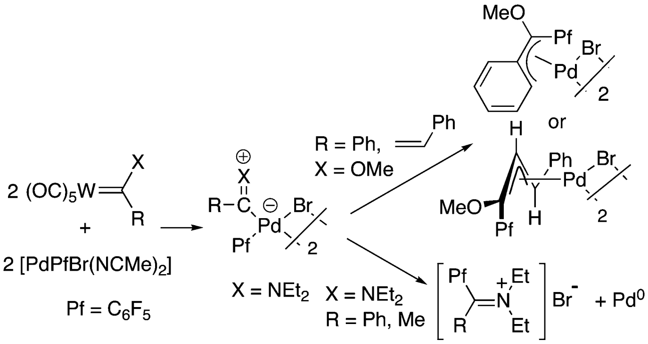
Pentafluorophenyl palladium complexes **3** and **5** bearing a vinylcarbene ligand slowly decompose on heating by migratory insertion to give Pd(0) and the vinyliminium salts ($Et_2N{=}C(C_6F_5)CH{=}CHPh)X$ ($X = Br, BF_4$). However, the presence of triphenylphosphine in complex **4** stabilizes **7**, a compound with a C=C Pd-bound vinyliminium moiety, where there is a strong preference for the C=C versus the C=N coordination.

Introduction

Many organic transformations of unsaturated amines and imines involve the formation of iminium cations as intermediates.[1] The hydrolysis of vinylic amines and the acid-catalyzed Manich reaction are common examples.[2] Iminium salts, either previously prepared or synthesized "in situ", are used as powerful electrophiles in a variety of transformations.[2,3] Metal-catalyzed reactions, such as the enantioselective isomerization of allylamines to enamines developed by Noyori et al., are also believed to occur via an intermediate complex with a metal-coordinated iminium fragment.[4,5] Several examples of formation of iminium salts by C−C coupling of an N-substituted carbene and an organometallic group on palladium have been reported in the past few years. Most of the examples reported so far involve N-heterocyclic carbenes, and the products are imidazolium salts.[6−8] We have reported the formation of iminium salts by coupling of monoaminocarbenes and a pentafluorophenyl group bound to palladium.[9] These iminium salts are formally the product of a reductive elimination reaction in the complex, although a migratory insertion route can be envisioned based on the reactions of related alkoxycarbenes, where alkyl palladium derivatives (stabilized as η^3-allylic or η^3-benzylic moieties) are formed as a result of a migratory insertion process (Scheme 1).[9]

Scheme 1. C−C Coupling in Aryl Palladium Carbene Complexes



We report here the formation of a vinyliminium cation by coupling of a vinylcarbene ligand and a pentafluorophenyl group in a palladium complex. The iminium compound remains C=C coordinated to palladium when a suitable auxiliary ligand is used. The coordination preferences and behavior of the vinyliminium ligand are analyzed in detail.

Results

The syntheses of palladium vinylic carbene complexes are depicted in Scheme 2. Complex **3** was prepared from complex **2** by transmetalation with the corresponding tungsten carbene **1**, as previously reported by us for the preparation of other monoamino carbene palladium complexes.[9,10] The transfer of carbene fragments from group 6 metal complexes has been also used in the synthesis of other transition metal carbene complexes.[11] Addition of triphenylphosphine to **3** gave complex **4**. Both compounds were isolated as yellow (**3**) or orange (**4**) solids.

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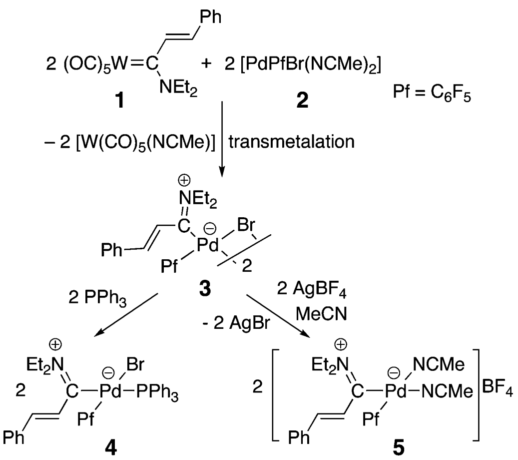
10.1021/om051028s CCC: $33.50

Scheme 2. Synthesis of Complexes 3−5



Removal of the bromo ligand of **3** using $AgBF_4$ in acetonitrile gave **5**, which was characterized and used in solution. The three complexes show a ^{13}C NMR resonance in the range typical for a carbene carbon bound to the metal (215−228 ppm).

Complex **4** was further characterized by single-crystal X-ray diffraction (Figure 1). The carbene ligand lies almost perpendicular to the Pd coordination plane (the dihedral angle between the N1−C1−C2 and Pd1−Br1−P1−C1−C21 planes is 82.6°) and shows a trans configuration of the conjugated double bond. The pentafluorophenyl group is slightly tilted, this ring and the Pd coordination plane making a 75.5° dihedral angle. The phosphine ligand is trans to the carbene moiety. The C−N distance corresponds to a double bond, whereas the Pd−C(carbene) distance suggests a single one, as expected for a Fischer type late transition metal carbene, and as depicted throughout this paper for complexes **3**−**5**. NMR spectra show that the same structure is kept in solution. The large value of $^{3}J_{C-P}$ for the carbene carbon (147.3 Hz) confirms a trans arrangement of the carbene and phosphine ligands. Restricted rotation of the C_6F_5 group is revealed by the nonequivalence of both F_{ortho} (and both F_{meta}) atoms.

In solution, **3** is a mixture of two isomers, out of four possible coordination arrangements.[12] Complex **5** shows a cis stereochemistry with two separate ^1H NMR signals for the two nonequivalent acetonitrile ligands.

Complexes **3**−**5** undergo very slow decomposition in solution as a result of carbene−pentafluorophenyl coupling. Weeks are needed for complete decomposition at room temperature in $CDCl_3$, so experiments were also carried out at 50 °C in the same solvent. Complexes **3** and **5** give Pd(0) and the iminium salt **6**,[13] but for complex **4** the formation of a Pd(0) complex **7** is observed (Scheme 3). A minor decomposition route for **4** produces some $[PdBr(C_6F_5)(PPh_3)_2]$. Complex **7** can be kept in the air at room temperature for long periods, both as a solid and in solution.

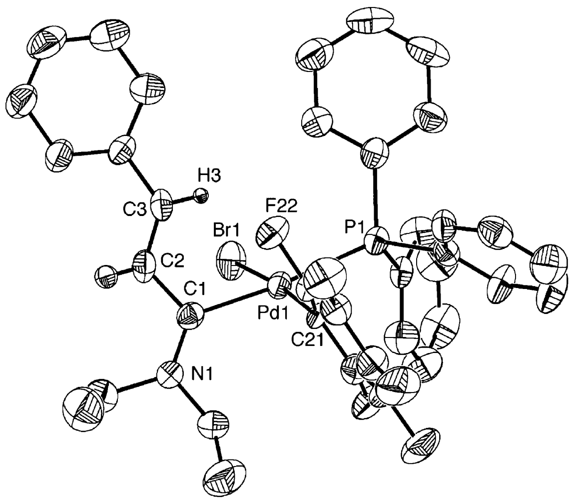
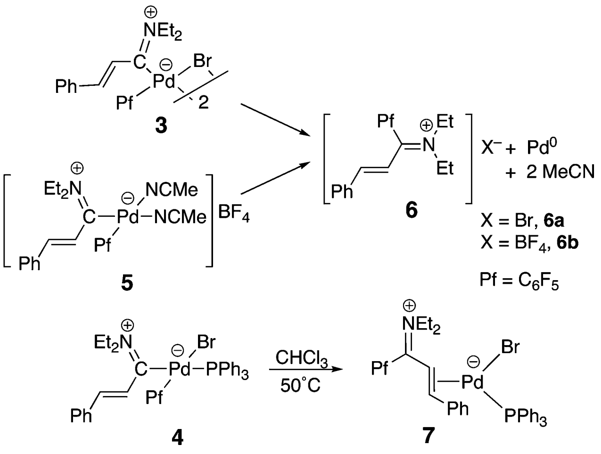


Figure 1. X-ray structure of complex **4**. Selected bond lengths (Å): Pd1−C1, 2.025(6); Pd1−C21, 2.031(6); Pd1−Br1, 2.4844(16); Pd1−P1, 2.324(2); C1−C2, 1.467(9); C1−N1, 1.300(8); C2−C3, 1.330(10).

Scheme 3. C−C Coupling in Complexes 3−5



The X-ray crystal structure of **7** reveals a three-coordinated Pd complex with a vinyliminium ligand bound to Pd through the C═C bond (Figure 2). Br and PPh_3 ligands complete the coordination sphere of the metal. The Br−Pd−P angle is very

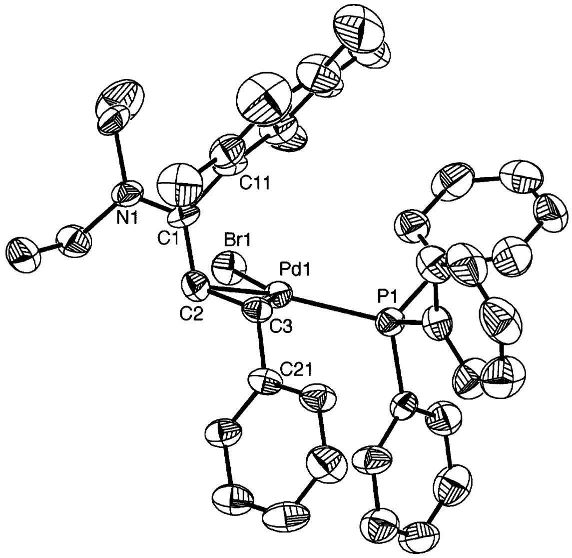


Figure 2. X-ray structure of complex **7**. Selected bond lengths (Å): Pd1−C2, 2.167(13); Pd1−C3, 2.095(12); Pd1−Br1, 2.5456(16); Pd1−P1, 2.278(3); C1−N1, 1.335(13); C1−C2, 1.413(15); C2−C3, 1.416(15).

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[12] The four possible isomers arise from the combination of trans-carbene or cis-carbene arrangements in the dimer and syn (both NEt_2 groups of the carbenes on the same side of the coordination plane) or anti (both NEt_2 groups on opposite sides) alignments. The observed isomers are tentatively assigned the trans-syn and trans-anti configurations. This type of isomerism has been reported and discussed before in refs 9 and 10.

[13] The decomposition of **5** is clean, giving only product **6**. However **3** undergoes, along with the C−C coupling process, isomerization to a new organometallic complex, which we believe is the cis isomer (probably a mixture of anti and syn isomers; see ref 9). *cis*-**3** eventually decomposes to **6** as well. Variable amounts of pentafluorobenzene are also obtained in the decomposition of **3**.

Table 1. Selected ^{1}H and ^{13}C NMR Data (δ) for Compounds 6b, 7, and 8[a]

compound	H^2	H^3	C^1	C^2	C^3
7	5.11	2.81	148	71.7	58.7
8[b]	5.75	4.20		83.4	70.9
6b	7.76	7.25	164.2	117.6	160.3

[a] $CDCl_3$ as solvent; δ referenced to TMS. [b] See text and ref 9.

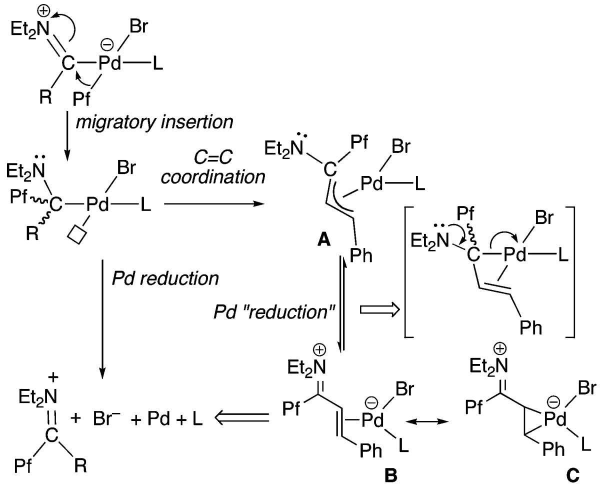
open (109.1°), to compensate the small C−Pd−C angle. This is a feature found in many reported $[Pd^0(olefin)L_2]$ complexes.[14a,d] The triphenylphosphine ligand is trans to C2, and the Pd−C1 nonbonding distance is 2.692 Å (cf. 2.167 and 2.095 Å for Pd−C2 and Pd−C3 bonds). The C1−N1 distance (1.335 Å) is short, consistent with a double bond. The C1−C2 and C2−C3 distances are equal (1.413(15) and 1.416(15) Å) and intermediate between a single and a double bond, a feature also observed in complexes of iron and tungsten with vinyliminium groups coordinated through the C═C bond and also for palladium(0) complexes with coordinated conjugated olefins.[14,15] Similar C−C distances are also found in analogous zwitterionic palladium(0) complexes with alkenylphosphonium ligands.[16] In contrast, the iminium salt **6b** shows the expected short C2−C3 (1.343(7) Å) and long C1−C2 (1.425(7) Å) bond lengths as determined by X-ray crystal structure determination (Supporting Information).

NMR data for **7** reveal that the nature of the vinyliminium moiety is strongly altered upon coordination (Table 1). Complex **7** shows a very large difference in chemical shifts for H^2 and H^3. The chemical shifts for H^2, H^3, and C^1−C^3 are significantly lower than those for the free iminium salt **6b**. These data are closer to the chemical shift differences and ranges obtained for the palladium allylic complex $[Pd(\mu\text{-}Br)(\eta^3\text{-}MeO{-}C(C_6F_5){=}CH{=}CHPh)]_2$ (**8**) (see Scheme 1 and Table 1).[9] As it was observed in the latter allylic complex, slow rotation about the C^1−pentafluorophenyl ring occurs for **7**. Hindered rotation about the C^1−N bond is also observed. Line shape analysis afforded $\Delta G^{\ddagger}_{303} = 66.7 \pm 1.6$ kJ mol^{-1},[17] a lower value than the one found for **6b** (**$\Delta G^{\ddagger}_{396} = 78.1 \pm 0.4$ kJ mol^{-1}**)[18] or for conjugated iminium salts.[19] This easier than expected rotation is noteworthy and is discussed below.

Discussion

The reactivity of vinylaminocarbene palladium complexes shows some features distinct from those of alkyl- or arylaminocarbene complexes and from the analogous alkoxycarbene complexes. For Fischer type vinylaminocarbene complexes, the existence of a C═C bond conjugated to the C−N bond reduces the electrophilicity of the carbene carbon. In fact the chemical shifts for the ^{13}C resonances of C(carbene) in complexes **3**−**5** are consistently lower (ca. 14 ppm) than the values found for the analogous Ph and Me derivatives. Accordingly, **3**−**5** are noticeably more stable and resistant to insertion than similar complexes reported before for R = Ph, Me.[9] The evolution following carbene insertion is also strongly influenced by the vinylic fragment and by the ancillary ligands (Scheme 4). A difference was already reported for methoxycarbene palladium complexes,[9] which undergo C−C coupling, leading to different types of products depending on the R group of the carbene moiety (Scheme 1). For aminocarbenes the insertion leads to an iminium salt and Pd-black, whereas a remarkably stable complex containing the coordinated iminium salt (**7**) is obtained when a vinylic-substituted carbene, in addition to a good ancillary ligand (PPh_3), is used (**4**, Scheme 3). The decompositions of **3** or **5** should lead initially to similar palladium complexes, but, at the temperature used and in the absence of a good stabilizing ligand, these presumed intermediates decompose to the free iminium salt and Pd(0).

Scheme 4. Reactivity of Vinyl- versus Other R-Aminocarbene Palladium Complexes



An examination of complex **7** reveals how much its formulation as a Pd(0) or as a Pd(II) complex is a formalism. In addition to the olefin-palladium (**B**) and the palladacyclopropane (**C**) resonant forms, a further aminoallylpalladium representation (**A**) needs to be considered (Scheme 4). While forms **B** and **C** explain the solid-state structure (including the long C2−C3 bond length), they cannot explain the ^{1}H NMR behavior in solution, where the Et groups bound to N become equivalent at moderate temperatures. This easy rotation is better understood in the allylic form **A**. Coordination mode **A**, along with the contribution of **C** to the "Pd(II)" form, also accounts for the reluctance of **7** to oxidize and its high stability in the air. Looking at the low-energy separation between the aminoallyl-palladium and the κ^2-*C,C*-vinyliminium-palladium isomers, it is obvious that small changes in this kind of structure can produce a reversal of stability. Thus, for alkoxycarbenes the lesser stability of an oxonium moiety as compared to an iminium moiety results in the stabilization of the alkoxyallylpalladium structure $[Pd(\mu\text{-}Br)\{(\eta^3\text{-}C(C_6F_5)(OMe)CHCHPh\}]_2$ (Scheme 1). An interesting related case was reported by Kurosawa et al. for a family of derivatives prepared by reaction of a Lewis acid with η^2-enone palladium(0) complexes.[20] They found a continuous structure

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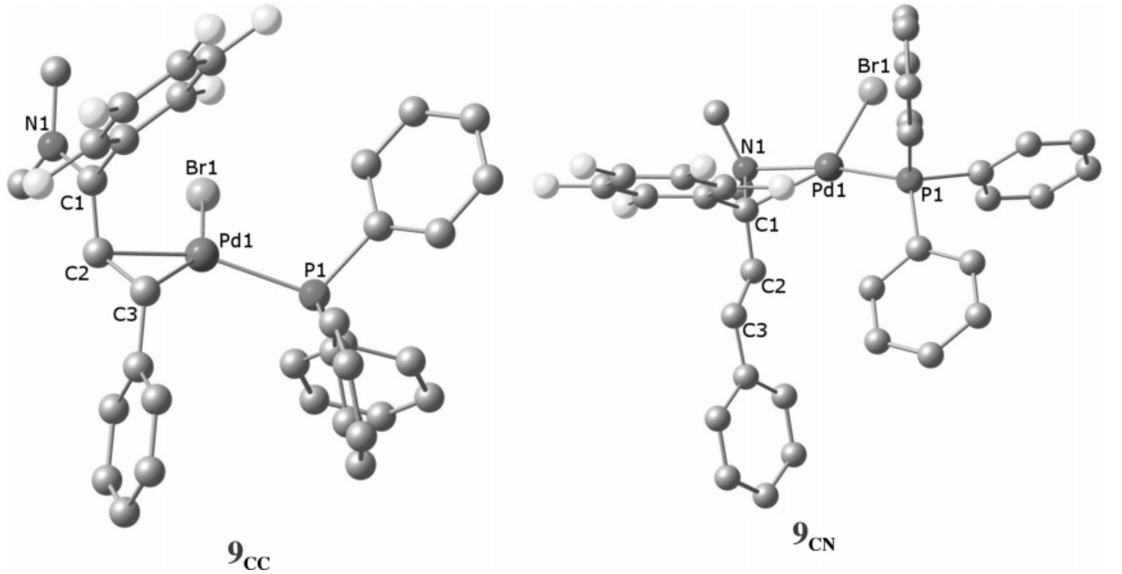
[17] Fast rotation and inversion of nitrogen brings about the equivalence of the three methylene signals (1:1:2 ratio) in one multiplet and the appearance of just one triplet for the methyl groups. Line shape analysis was carried out using gNMR v3.6.5, IvorySoft; Cherwell Scientific Publishing Ltd., Oxford.

[18] This difference in $\Delta G^{\ddagger}$ led to a coalescence temperature difference of 60 °C for the methyl groups of the NEt_2 moiety in **6b** and **7**.

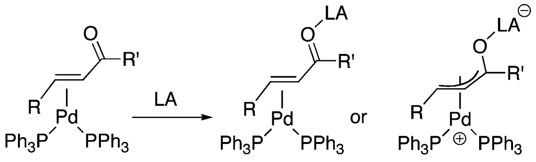
[19] Merényi, R. in ref 3, p 83.



$\mathbf{9}_{\mathbf{CC}}$ $\mathbf{9}_{\mathbf{CN}}$

Figure 3. Geometries of structures $\mathbf{9}_{\mathbf{CC}}$ and $\mathbf{9}_{\mathbf{CN}}$.

variation from η^2-olefin to η^3-allyl type depending on the enone and acid used (eq 1). The Pd−C1 distances found ranged from 2.41 to 2.96 Å (cf. 2.692 Å for **7**).[21]



(1)

The structure and behavior found for complex **7** shows that coordination to a C═C(olefin) bond is preferred over coordination to a C═N(iminium) bond. Both coordination isomers, modeling NEt_2 by NMe_2, were studied using DFT calculations. The optimized geometry for the C═C bound isomer ($\mathbf{9}_{\text{CC}}$, Figure 3) matches the solid-state structure of **7**, with calculated distances Pd1−C1 2.739 Å; Pd1−C2, 2.215 Å; and Pd1−C3, 2.139 Å. The C═N bound isomer ($\mathbf{9}_{\text{CN}}$, Figure 3), not detected experimentally, shows a longer C−N bond length (1.438 Å) than $\mathbf{9}_{\text{CC}}$ (1.350 Å) or complex **7** (1.335(13) Å). Stronger π-back-donation from Pd to the π-antibonding orbitals of the iminium C═N bond accounts for this lengthening and gives $\mathbf{9}_{\text{CN}}$ a higher Pd(II) palladacycle character. The structure $\mathbf{9}_{\text{CC}}$ is 7.3 kcal/mol more stable than the C═N bound isomer $\mathbf{9}_{\text{CN}}$ (Figure 3). Taking this energy difference and assuming that the entropy variation in the interconversion between both structures should be small (in nonpolar media), a simple calculation for the equilibrium $\mathbf{9}_{\text{CN}} \rightleftharpoons \mathbf{9}_{\text{CC}}$ affords $K_{298} = 2.2 \times 10^5$. This leaves the C═C bound iminium Pd complex as the only detectable structure by NMR spectroscopy.

Although examples of simple iminium complexes coordinated by the C═N bond have been reported for other transition metals,[22] Fe and W vinyliminium complexes also coordinate through the C═C bond,[15] suggesting that this coordination mode is preferred. In contrast, a vinyliminium complex coordinated by the iminium C═N bond rather than by the C═C bond is proposed as an intermediate in Noyori's Rh-catalyzed isomerization of allylamines to enamines.[4] We are currently examining the viability of C═C bound vinyliminium intermediates in the Rh system.

In conclusion, both κ^2-*C,C*-vinyliminium and aminoallyl forms are close in energy and contribute to an accurate description of the structure and properties observed for the palladium complex **7**. A nonobserved κ^2-*C,N*-vinyliminium coordination is higher in energy than the observed κ^2-*C,C* form.

Experimental Section

General Procedures. All manipulations were carried out using Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use. Compounds **1**[23] and **2**[24] were prepared using literature methods. Percentages of products in the reactions mixtures were determined by integration of ^{19}F NMR signals. Full spectroscopic and analytical data for the compounds can be found in the Supporting Information.

***trans*-$[\mathbf{Pd}(\boldsymbol{\mu}\textbf{-Br})(\mathbf{C_6F_5})\{\mathbf{C}(\mathbf{NEt_2})\mathbf{CH{=}CHPh}\}]_2$ (3).**[12] To a solution of **1** (0.2500 g, 0.489 mmol) in CH_2Cl_2 (20 mL) was added **2** (0.2130 g, 0.489 mmol). The mixture was stirred for 30 min. The dark solution was then filtered through activated carbon and Celite and evaporated to dryness. Et_2O (10 mL) was added to the residue, and the solution was kept at −20 °C for 12 h. A yellow solid crystallized, which was filtered, washed with pentane (10 × 5 mL), and vacuum-dried (yield 0.1623 g; 61%). *trans*-**3** is a mixture of syn and anti isomers (**3**, **3′**) in solution in a 1 (**3**):1.6 (**3′**) ratio.[12]

$[\mathbf{PdBr}(\mathbf{C_6F_5})\{\mathbf{C}(\mathbf{NEt_2})\mathbf{CH{=}CHPh}\}(\mathbf{PPh_3})]$ (4). PPh_3 (0.0728 g, 0.278 mmol) was added to a solution of **3** (0.150 g, 0.139 mmol) in CH_2Cl_2 (15 mL). The orange solution was stirred for 35 min and evaporated to dryness. *n*-Hexane (10 mL) was added to the residue, and **4** was obtained as a light orange solid, which was filtered, washed with *n*-hexane (3 × 5 mL), and air-dried (yield 0.1607 g, 72%).

$[\mathbf{Pd}(\mathbf{C_6F_5})\{\mathbf{C}(\mathbf{NEt_2})\mathbf{CH{=}CHPh}\}(\mathbf{NCMe})_2]\mathbf{BF_4}$ (5). Complex **3** (0.0106 g, 0.010 mmol) was added to a solution of AgBF_4 (0.0038

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g, 0.020 mmol) in NCMe (5 mL). The mixture was stirred for 30 min protected from light. The resulting suspension was filtered through Celite and evaporated to dryness. Complex **5** was obtained as a yellowish oil and characterized spectroscopically.

Decomposition of the Palladium Carbene Complexes 3 and 5. An NMR tube was charged with *trans*-**3** (0.0080 g, 0.113 mmol) and $CDCl_3$ (0.6 mL). The solution was kept at 50 °C for 12 h. ^{19}F and ^1H NMR spectra showed the formation of **6a** (41%), C_6F_5H (11%), *cis*-**3** (19%), and unreacted *trans*-**3** (14%) as main products.

Decomposition of **5** was carried out in the same way, and **6b** was obtained (75% after 6 days at 50 °C).

[PdBr{Et$_2$N=C(C$_6$F$_5$)(CH=CHPh)}(PPh$_3$)] (7). A solution of **4** (0.0700 g, 0.065 mmol) in $CHCl_3$ was kept at 50 °C for 24 h. After this time the solution was a mixture of unreacted **4** (52%), **7** (36%), and $[PdBr(C_6F_5)(PPh_3)_2]$ (10%),[25] as major products. The orange solution was evaporated to dryness, and the residue was chromatographed in a silica column using Et_2O as eluent. **7** was separated as an orange band. The solution was evaporated to ca. 0.5 mL, and **7** crystallized by addition of *n*-hexane (isolated yield 0.0168 g, 24%).

X-Ray Crystal Structure Determinations. Crystals for X-ray analysis were obtained by slow evaporation of a solution of **4** (or **7**) in a mixture of CH_2Cl_2/*n*-hexane at room temperature or by cooling a $CHCl_3$ solution of **6b** at −20 °C. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer. Reflections were collected, intensities were integrated, and the structure was solved by direct methods procedure.[26]

Computational Methods. Complexes $\mathbf{9}_{CC}$ and $\mathbf{9}_{CN}$ with C=C and C=N iminium coordination have been calculated using a model where the NEt_2 has been substituted by NMe_2. The calculations were performed using JAGUAR 5.5.[27] The LACVP* basis set describes the Pd, P, and Br atoms with an effective core potential and a double-ζ valence basis set with polarization functions.[27,28] The C, N, and F atoms of the iminium group were described by the 6-31G* basis set, and the rest of the C and H atoms were described by the 6-31G basis set.

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Supporting Information Available: Full spectroscopic and analytical data for compounds, and details for the determination of X-ray crystal structures and C−N rotation barriers for **7** and **6b**. CIF files for X-ray crystal structures of **4**, **6b**, and **7**. Coordinates for the optimized calculated geometries of $\mathbf{9}_{CC}$ and $\mathbf{9}_{CN}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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