Aryl Palladium Carbene Complexes and Carbene–Aryl Coupling Reactions

Ana C. Albéniz,* Pablo Espinet,* Raúl Manrique, and Alberto Pérez-Mateo[a]

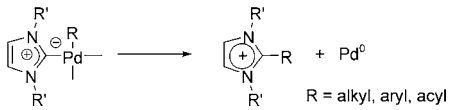
Abstract: Transmetalation of an aminocarbene moiety from $[W(CO)_5\{C(NEt_2)R\}]$ to palladium leads to isolable monoaminocarbene palladium aryl complexes $[\{Pd(\mu\text{-}Br)Pf[C(NEt_2)R]\}_2]$ (R = Me, Ph; Pf = C_6F_5). When $[W(CO)_5\{C(OMe)R\}]$ is used, the corresponding palladium carbenes cannot be isolated since these putative, more electrophilic carbenes undergo a fast migratory insertion process to give alkyl palladium complexes. These complexes could be stabilized in the η^3-allylic form for R = 2-phenylethenyl or in the less stable η^3-benzylic fashion for R = Ph. Hydrolysis products and a pentafluorophenylvinylic methyl ether (when R = Me) were also observed. The monoaminocarbenes slowly decompose through carbene–aryl coupling to produce the corresponding iminium salts and, depending on the reaction conditions, the corresponding hydrolysis products. The electrophilicity of the carbene carbon, which is mainly determined by the nature of the heteroatom group, controls the ease of evolution by carbene–aryl coupling. Accordingly, no carbene–aryl coupling was observed for a diaminocarbene palladium aryl complex.

Keywords: C–C coupling · carbenes · insertion · palladium · transmetalation

Introduction

Diamino ($C(NR'_2)_2$) and N-heterocyclic carbenes are currently used as ligands in palladium-catalyzed transformations.[1,2] Their good donor properties, which are easily modulated by varying the substituents, and the high stability of the palladium complexes formed, due to the reduced electrophilicity of the carbene, provide catalysts that are often superior to their phosphane-based analogues. Many of their catalytic processes presumably involve "[PdR(carbene)$_n$]" intermediates,[3] and understanding the reactivity of these species may be important in order to assess the suitability of a given ligand for a chosen transformation, and to explain how catalyst deactivation occurs. However, only a few examples of reactivity involving the carbene ligand have been reported. Cavell and co-workers have reported the formation of imidazolium salts by decomposition of alkyl, aryl, or acyl palladium complexes bearing N-heterocyclic carbenes [Eq. (1)].[4] Theoretical studies discount an R-migration process and support a concerted reductive elimination mechanism for the decomposition.[4a] The same process has been described for aryl palladium complexes.[5] Recently, Danopoulos, Green, and co-workers observed methyl migration to an N-heterocyclic carbene in the reaction of the free ligand with $[PdMe_2(tmeda)]$ (tmeda = tetramethylethylenediamine), and proposed a migratory insertion mechanism in a palladium carbene intermediate.[6]

In contrast to the numerous very stable palladium–diaminocarbene complexes, those with only one amino group are still rare.[7] Moreover, palladium complexes with carbene ligands of the type CR″(OR′) (R″ = hydrocarbyl),[8] or lacking substituents containing a heteroatom (CR''_2),[9] are elusive species, although they are often proposed as intermediates in various Pd-catalyzed reactions. Thus, the cyclopropanation of alkenes with diazoalkanes,[10] the dimerization of Group 6 metal carbenes,[11] and a change in the regioselectivity of Stille couplings (called *cine*-substitution),[12] are all thought to involve palladium–carbene complexes as intermediates. In this context, we have already communicated the C–C coupling reactions of complexes on "[PdR(carbene)]" intermediates in which the carbene ligand has only one amino or one alkoxy substituent.[13] Herein, we report a



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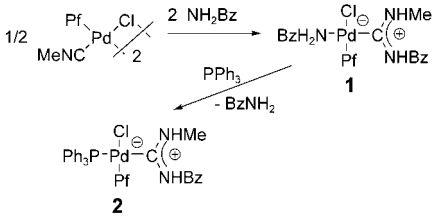
detailed account of this C–C coupling, including the isolation and X-ray structural determination of key products.

Results and Discussion

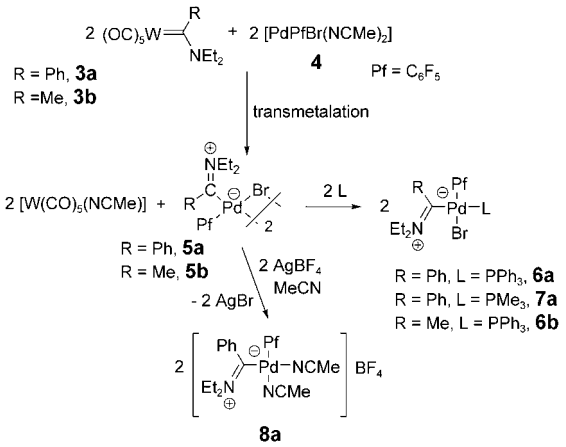
Synthesis and characterization of palladium monoaminocarbene and diaminocarbene complexes: Two diaminocarbene–palladium derivatives were prepared according to Scheme 1.



Scheme 1. Synthesis of palladium diaminocarbene complexes.

Complex **1** was synthesized by nucleophilic attack of an amine on a coordinated isonitrile.[14] The facile displacement of the coordinated amine by triphenylphosphane gave complex **2**.

Monoaminocarbene complexes were obtained by carbene transmetalation from the tungsten–carbene complexes **3a** and **3b** to the (pentafluorophenyl)palladium derivative **4**. This method, which had been previously applied only to the preparation of more stable diaminocarbene complexes,[15] afforded the dimeric palladium monoaminocarbenes **5** (Scheme 2). The by-product $[W(CO)_5(NCMe)]$ was observed in the ^1H NMR and IR spectra of the reaction mixture.[16] Complexes **5** could be isolated as white or yellowish solids in yields of 50–60%. The addition of phosphanes to solutions of **5** gave the monomeric complexes **6a**, **6b**, and **7a**. The cationic derivative **8a** was obtained from complex **5a** and a stoichiometric amount of $AgBF_4$ in CH_3CN.



Scheme 2. Synthesis of aryl palladium carbene complexes **5**–**8**.

The synthetic method could not be extended to the preparation of palladium methoxycarbenes. The reactions of tungsten methoxycarbenes $[W(CO)_5\{C(OMe)R\}]$ (R = Ph, **9a**; R = Me, **9b**; R = CH=CHPh, **9c**) with complex **4** led only to decomposition products. These are discussed later and their analysis suggests that transmetalation does occur, but that the intermediate palladium carbene complexes undergo a fast migratory insertion reaction.

Complexes **1** and **2** exist as mixtures of atropisomers in solution due to restricted rotation about the C(carbene)–N bonds.[17] Up to four stereoisomers are possible for each complex, but NMR signals for only three are observed at room temperature in $CDCl_3$ for **1**, whereas just two of these isomers are apparently observed for complex **2**. Low-temperature spectra of a solution of **2** reveal the presence of the four expected atropisomers, but fast interconversion between some of them leads to two equilibrium signals being observed at room temperature. Complex **8a** has a *cis* stereochemistry according to its ^1H NMR spectrum, two signals being observed for the Me groups of the nitrile ligands.

In $CDCl_3$ solution, complexes **5** exist as mixtures of two isomers, out of the four possible arrangements of the ligands in this dimeric structure (Figure 1). These are tentatively assigned the *syn–trans* and *anti–trans* structures. The 1.3:1 mixtures of *syn* and *anti* isomers can be observed by ^1H NMR spectroscopy at room temperature for both *trans*-**5a** and *trans*-**5b**. These isomers can also be distinguished by ^{19}F and ^{13}C NMR spectroscopy at 253 K in the case of *trans*-**5a**. When complexes **5** are kept in solution for several days, the *syn–cis* and *anti–cis* isomers are slowly formed from their *trans* parents, along with the decomposition products to be discussed later. Both *trans*-**5** and the slowly produced *cis*-**5** are converted into complexes **6** upon addition of a stoichiometric amount of PPh_3.

Abstract in Spanish: *La transmetalación de un grupo aminocarbeno desde $[W(CO)_5\{C(NEt_2)R\}]$ al paladio lleva al aislamiento de los complejos arílicos de paladio que contienen un grupo monoaminocarbeno $[\{Pd(\mu\text{-}Br)Pf[C(NEt_2)R]\}_2]$ (R = Me, Ph; Pf = C_6F_5). Cuando se usa $[W(CO)_5\{C(OMe)R\}]$ no se pueden aislar los correspondientes carbenos de paladio ya que estos supuestos carbenos, mucho más electrofílicos, sufren un rápido proceso de inserción migratoria para dar complejos alquílicos de paladio. Estos alquilos pueden ser estabilizados como η^3-alilo para R = 2-feniletenilo o como η^3-bencilo, menos estable, para R = Ph. También se observan los productos de hidrólisis y un metil pentafluorofenilvinil éter (si R = Me). Los monoaminocarbenos se descomponen lentamente mediante acoplamiento carbeno–arilo dando las correspondientes sales de iminio y, dependiendo de las condiciones de reacción, los correspondientes productos de hidrólisis. La electrofilia del carbono carbénico, determinada fundamentalmente por la naturaleza del sustituyente con heteroátomo, controla la facilidad de evolución mediante acoplamiento carbeno–arilo. Así, no se observó acoplamiento carbeno–arilo en el caso de un complejo arílico de paladio con un grupo diaminocarbeno.*

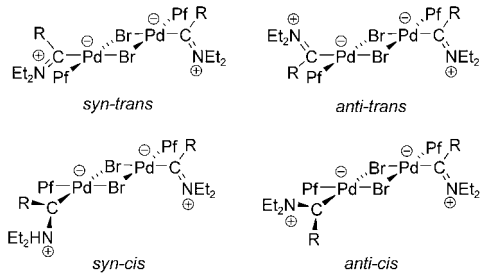


Figure 1. Isomeric structures for complexes **5**.

The $^{1}J_{C,P}$ values for complexes **2**, **6**, and **7** (about 145–156 Hz) support a *trans*-carbene–phosphane arrangement. This isomer is thermodynamically preferred because it avoids a *trans* arrangement of the ligands with the higher *trans* influence. An X-ray crystal structure determination of complex **7a** confirmed this structure (Figure 2). The carbene ligand and the pentafluorophenyl group are in a mutually

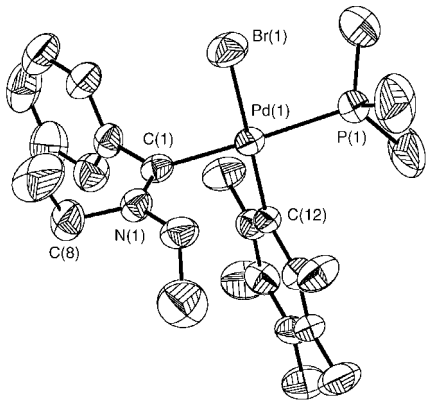


Figure 2. Molecular structure of **7a** (ORTEP plot, hydrogen atoms have been omitted for clarity).

cis arrangement and lie perpendicular to the palladium coordination plane. The C=N bond length is consistent with a double bond, reflecting the important donation of the lone pair of the amino group to the vacant p orbital of the carbene-carbon atom. The Pd(1)–C(1) bond length, which is very similar to the Pd(1)–C(12) bond length, corresponds to a single bond (Table 1).

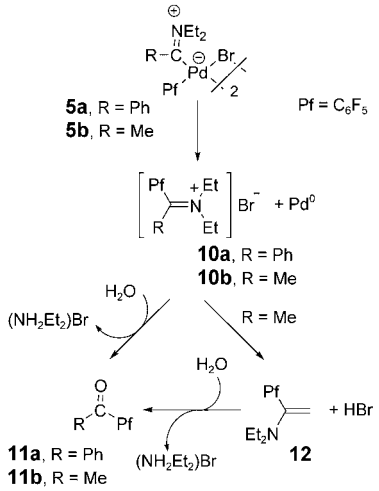
All of the prepared complexes show ^{13}C resonances typical for an sp^2 carbon atom in a carbene moiety bound to palladium. Complexes **1** and **2** display resonances at δ = 190–198 ppm, in the upper portion of the range found for diamino carbene complexes (cf. $[PdX_2\{C(NR)CH{=}CH(NR)\}L]$, δ = 165–195 ppm).[4c] For the monoaminocarbene complexes, the carbene-arbon signal appears in the range δ = 229–244 ppm, halfway between the chemical shifts seen for the diaminocarbene complexes and the only reported example of a methoxycarbene–palladium complex (*trans*-$[Pd\{C(OMe)Me\}(C_6Cl_5)(PPhMe_2)_2]$, δ = 335 ppm).[8b] The shieldings reflect the increase in electron density on the carbene carbon atom (and consequently the decrease in electrophilicity of the coordinated carbene) depending on the electron donation from the substituents (1 OMe < 1 NEt_2 < 2 NR_2). These data, the IR absorption observed between 1572 and 1592 cm^{-1} for ν(C–N), and the C–N distance found in the solid-state structure of **7a** support a larger contribution from the resonance form chosen to depict these Pd complexes in Scheme 2.

Table 1. Selected bond lengths [Å] and angles [°] for complex **7a**.

Pd(1)–C(1)	2.030(5)	C(1)–N(1)	1.291(6)
Pd(1)–C(2)	2.016(5)	C(1)–C(2)	1.498(7)
Pd(1)–Br(1)	2.4743(12)	N(1)–C(8)	1.484(7)
Pd(1)–P(1)	2.3071(19)	N(1)–C(10)	1.479(6)
C(1)-Pd(1)-Br(1)	87.95(14)	Pd(1)-C(1)-N(1)	125.0(4)
P(1)-Pd(1)-Br(1)	90.22(6)	Pd(1)-C(1)-C(2)	117.6(3)
C(1)-Pd(1)-C(12)	90.96(19)	C(1)-N(1)-C(8)	124.3(4)
P(1)-Pd(1)-C(12)	90.94(15)	C(1)-N(1)-C(10)	121.7(5)

Carbene–aryl coupling reactions: The variations in electrophilicity of the coordinated carbene-carbon atom, as revealed by the ^{13}C resonances, are reflected in the reactivities of the molecules. Thus, solutions of the diamino carbene **2** in $CDCl_3$, monitored by NMR spectroscopy for 20 days at room temperature, remain unaltered. A solution of **2** kept at 50 °C for 10 days also remains unchanged. Under the same conditions, the analogous monoaminocarbene **6a** undergoes 33 % decomposition after 10 days, as discussed later. In the extreme case, the reactions of the methoxycarbene tungsten complexes **9a**,**b** with **4** lead only to the decomposition products of the presumed methoxycarbene palladium intermediates, as discussed below (see Scheme 4). A detailed study of these reactions has been carried out.

Decomposition pathways from aminocarbene–palladium complexes: The slow decomposition of the aminocarbene–palladium complexes gives, after several days, organic products resulting from carbene–pentafluorophenyl coupling. The decomposition of complexes **5** affords the three types of products depicted in Scheme 3: the iminium salts **10** along



Scheme 3. Carbene–pentafluorophenyl coupling and hydrolysis reactions for palladium aminocarbene complexes.

with the hydrolysis products **11** and, in the case of R = Me, the vinylic amine **12**. Concomitant *trans*/*cis* isomerization of **5** is also observed (Figure 1), but both isomers decompose to the same organic compounds. Hydrolysis processes affecting **10** (and also **12** in the case of complex **5b**) lead to ketones (**11**) as final decomposition products.

The decomposition of complexes **6** (L = PPh_3) in solution produces only the ketone **11a** in the case of **6a**, or a mixture of **11b** and **12** in the case of **6b**. Kinetic experiments carried out with different starting concentrations of **6a** (and **6b**) indicated that this decomposition is an intramolecular process.

The decomposition of the cationic complex **8a** led cleanly to the iminium salt **10a**, which could be isolated with BF_4^- as the counterion. The X-ray crystal structure of **10a** is shown in Figure 3.

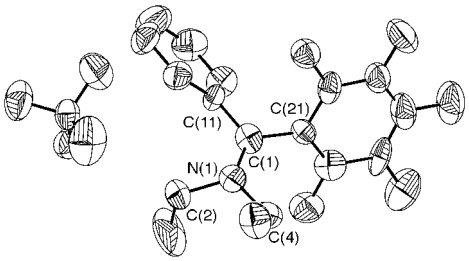
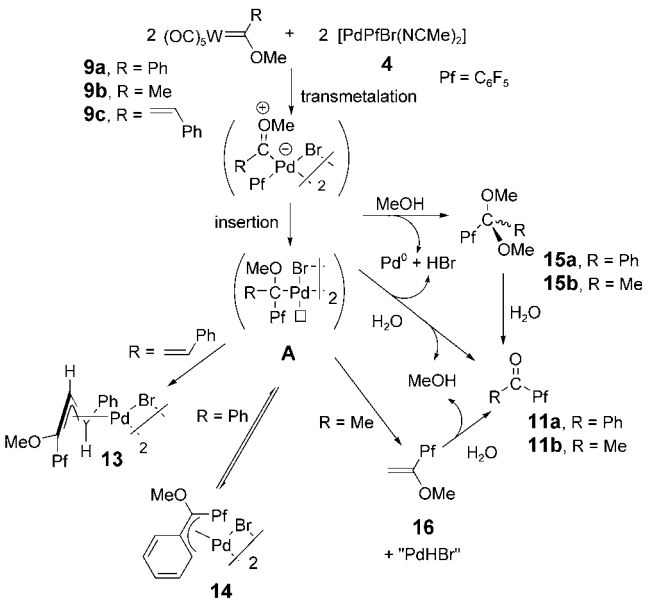


Figure 3. Molecular structure of **10a**-BF_4 (ORTEP plot, hydrogen atoms have been omitted for clarity). Selected distances [Å] and angles [°]: C(1)–N(1) 1.305(10), C(1)–C(11) 1.515(12), C(1)–C(21) 1.484(11); C(11)-C(1)-C(21) 116.1(7), N(1)-C(1)-C(11) 122.6(7), N(1)-C(1)-C(21) 121.2(9), C(1)-N(1)-C(2) 122.6(8), C(1)-N(1)-C(4) 122.8(7).

The iminium salts **10** are the products of a formal reductive elimination from the aminocarbene–pentafluorophenyl–palladium complexes. Hydrolysis of **10** produces the ketones **11**, and deprotonation of **10b** yields the vinylic amine **12**. The actual distribution of these products depends on the reaction conditions (particularly on the amounts of water and base present), which affect the stability of **10**. Deliberate addition of water increases the rate of disappearance of **10a** by hydrolysis. The auxiliary ligands liberated in the decomposition processes (Br^- or PPh_3) can act as bases in $CDCl_3$ solution, and hence they influence the ratio of **10** to hydrolysis and deprotonation products (e.g., **10a** and **11a** are produced from **5a**; **11a** from **6a**; and just **10a** from **8a**).[18]

Decomposition pathways from presumed alkoxycarbene–palladium complexes: The reactions of the methoxycarbene tungsten complexes **9a**,**b** with **4** give the products shown in Scheme 4. They are the result of migratory insertion in the putative palladium–carbene complexes analogous to **5a**,**b**, followed by evolution of the alkyl palladium complex **A** thus generated (Scheme 4). The possible competition of a Pd-catalyzed carbene dimerization was not observed.[11]

The intermediate **A** can be trapped in the form of a η^3-allyl complex, **13**, when the carbene substituent is 2-phenylethenyl. Complex **13** is moderately stable in solution and



Scheme 4. Transmetalation, migratory insertion, and hydrolysis reactions in palladium methoxycarbene complexes.

can be isolated and fully characterized. Its X-ray crystal structure is shown in Figure 4 top, and selected distances and angles are collected in Table 2. The molecule is a bromo-bridged dimeric species with the two allyl ligands having a mutually *cis* C(2) arrangement and a *trans* C(1) arrangement (Figure 4, bottom). The allyl ligand has an *anti*-pentafluorophenyl *syn*-OMe configuration at C1 and a *syn* arrangement at C(3). The Pd–C(allyl) bond lengths are similar to the distances found for other substituted palladium allyls.[19] Bent halide bridges are common for dimeric *cis*-allyl palladium complexes.[20] This bending places the Pd atoms quite close to each other (3.0608 Å).

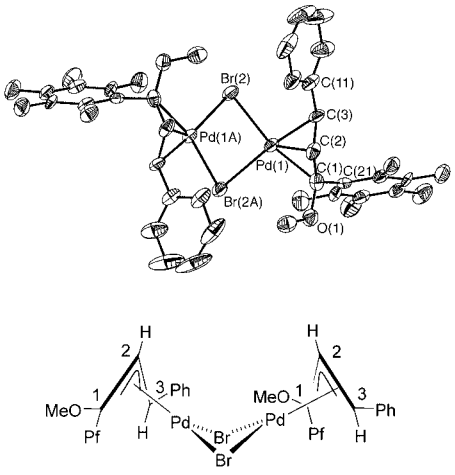


Figure 4. Molecular structure of **13**: top: ORTEP plot of the molecule (hydrogen atoms have been omitted for clarity); bottom: drawing showing the coordination sphere of the palladium atoms and the bridge geometry.

Table 2. Selected bond lengths [Å] and angles [°] for complex **13**.

Pd(1)–C(1)	2.190(11)	C(1)–C(2)	1.413(14)
Pd(1)–C(2)	2.093(11)	C(2)–C(3)	1.426(15)
Pd(1)–C(3)	2.127(11)	C(1)–O(1)	1.379(12)
Pd(1)–Br(2)	2.5347(14)	C(1)–C(21)	1.483(14)
Pd(1)–Br(2A)	2.5522(16)	C(3)–C(11)	1.445(14)
Pd(1)–Pd(1A)	3.0608(17)		
Br(2)-Pd(1)-Br(2A)	87.75(6)	C(1)-C(2)-C(3)	116.1(11)
C(1)-Pd(1)-C(3)	67.8(4)	O(1)-C(1)-C(21)	105.9(9)
C(1)-Pd(1)-Br(2A)	103.7(3)	O(1)-C(1)-Pd(1)	121.0(7)
C(3)-Pd(1)-Br(2)	101.5(3)	C(21)-C(1)-Pd(1)	110.0(8)
		C(11)-C(3)-Pd(1)	119.9(8)

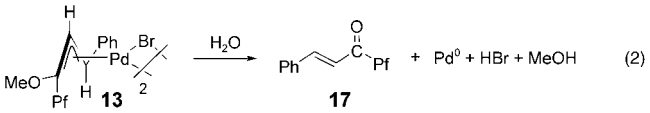
In $CDCl_3$ solution at room temperature, complex **13** apparently exists as a mixture of two isomers in a 1.2:1 ratio, but at 213 K four isomers are clearly seen, which correspond to the four possible arrangements of a substituted allyl in a dimer (combinations of *cis*- and *trans*-allyl groups with *cis* and *trans* C1 arrangements). As the temperature is increased, fast exchange occurs among some of the isomers to give the signals observed at room temperature. The exchange must occur by bridge cleavage and recombination, as studied previously for other dimeric allylic derivatives.[21] The structure of the allyl moiety is retained in solution and no *syn–anti* exchange is observed. Hindered rotation is observed for the Pf group in an *anti* sterically congested position, and two distinct F_{ortho} signals are observed in the ^{19}F NMR spectrum even at 323 K, indicating a high barrier for the rotation process.

For R = Ph (Scheme 4), the η^3-benzylic complex **14** is formed, which is unstable in solution but can be isolated as a yellowish solid. It was identified on the basis of its NMR spectra. Its ^1H NMR spectrum shows a characteristic high field shift for the aromatic proton involved in the η^3 Pd-bound benzylic moiety (δ = 5.55 ppm).[22] The ^{19}F NMR spectrum of **14** is similar to that of **13**, showing two broad signals for the two nonequivalent F_{ortho} atoms due to restricted rotation of the Pf group, and chemical shifts (δ = −135.9 and −127.5 ppm) consistent with an *anti* stereochemistry for the Pf group bound to C(1). Besides **14**, decomposition products **15a** and **11a** were observed in the reaction mixture. These are the result of methoxide attack on **A** (or on **14** in the case of the benzylic derivative) and hydrolysis of **A** (or **14**) as well as of **15a**.[23] Eventually, the final product of the reaction is in all cases the ketone **11a**.

For R = Me, no intermediate alkyl complex was observed, but fast β-H elimination from this putative complex can account for the formation of the vinylic ether **16**, observed in the reaction mixture along with the methanolysis and hydrolysis products **15b** and **11b**. Compounds **16** and **15b** are also susceptible to hydrolysis to the fluorinated acetophenone **11b**.

Along with the hydrolysis or methanolysis of intermediate **A** (or of **14**), an alternative route to compounds **11** and **15** might involve a nucleophilic attack on the putative initial palladium carbene complex, which would be very electrophilic, and subsequent reductive elimination (Scheme 4). Although we have no indication that this mechanism is operating, it cannot be ruled out.

It should be noted that complex **13** undergoes a similar hydrolysis process since it eventually decomposes to the ketone Pf(CO)CH=CHPh (**17**) when kept in $CDCl_3$ solution for 11 days [Eq. (2)].



The expression "migratory reductive elimination" has been coined to describe reactions in which the mechanism for C–C bond formation in the transition state is a migration of one of the groups to the other hydrocarbyl moiety, rather than a concerted weakening of both Pd–C bonds. It has been proposed in theoretical work on the reductive elimination of vinylpalladium derivatives[24] and silylene- and germylene–methylpalladium complexes,[25] and has found experimental support in certain methyl–aryl couplings, as well as in aryl–X (X = SR, OR, NR_2) reductive eliminations in palladium complexes.[26] The mechanism operating in the decomposition of the methoxy- and monoaminocarbenes of palladium must pertain to this type, although the products formed are formally the result of a migratory insertion (CR″(OR′)) or a reductive elimination (CR″(NR'_2)). The stability of the iminium salts formed in the decomposition of the monoaminocarbenes is possibly responsible for driving the reaction to these products, whereas the formation of oxonium derivatives is not a favored route.

Conclusion

The results described herein clearly indicate that the electrophilicity of the carbene-carbon atom in these systems controls the ease of C–C coupling. This reaction can be described as a result of the interaction of the electron density of the pentafluorophenyl group with the electrophilic carbene-carbon atom. The carbene substituents modulate the electron density on the carbene-carbon atom, and the migratory insertion rates observed ($C(NR'_2)_2$ < CR″(NR'_2) < CR″(OR′)) follow the opposite trend of electron-donating properties of the heteroatom-containing groups ($C(NR'_2)_2$ > CR″(NR'_2) > CR″(OR′)). The hydrocarbyl substituents have less influence on the carbene electrophilicity. The arrangement of the phenyl ring in complex **7a** (perpendicular to the plane formed by C(2)–C(1)—N(1), Figure 2) and the rotation of the phenyl group about the C(2)–C(1) bond observed in solution for complexes **a** suggest that electron delocalization from this substituent to the carbene carbon is negligible. Thus, the small differences in reactivity found for the R groups arise mainly from inductive effects. Irrespective of the R group (Me or Ph), complexes **5** (and **6**) decompose over a period of days, as compared with the extremely reactive undetected methoxycarbenes or the totally unreactive diamino derivatives.

The reactivity observed with the electron-poor pentafluorophenyl group is thought to be a slow model for other aryls. Pentafluorophenyl monoaminocarbenes of palladium are just stable enough to be characterized, but are sufficiently reactive for their evolution by C–C coupling to be observed. More nucleophilic aryls bound to palladium are expected to react similarly but faster.

Experimental Section

All manipulations were carried out using Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Bruker AC-300 and ARX-300 spectrometers. Chemical shifts (in δ units, ppm) were referenced to TMS for ^{1}H and ^{13}C, to $CFCl_3$ for ^{19}F, and to H_3PO_4 for ^{31}P. The spectral data were recorded at 293 K unless otherwise noted. IR spectra were recorded on a Perkin Elmer FT-1720X spectrophotometer. C, H, and N elemental analyses were performed on a Perkin-Elmer 240 microanalyzer. Complex **4**,[21b] and the tungsten carbenes **3a**, **3b**,[27] **9a**, **9b**,[28] and **9c**,[29] were prepared according to literature methods.

[PdClPf{C(NHMe)(NHBz)}(NH$_2$Bz)] (Pf = C$_6$F$_5$, 1): The complex was prepared following a similar method to that described elsewhere.[14a] $BzNH_2$ (0.124 mL, 1.14 mmol) was added to a stirred suspension of $[\{Pd(\mu\text{-}Cl)Pf(CNMe)\}_2]$[30] (0.200 g, 0.286 mmol) in CH_2Cl_2 (20 mL). After 9 h, concentration to dryness and addition of Et_2O (3 mL) and *n*-pentane (10 mL) afforded a colorless oil, which was stirred for 12 h. Complex **1** was obtained as a white solid, which was collected by filtration, washed with *n*-pentane (2×5 mL), and dried in air. Yield: 90% (0.290 g). Three atropisomers deriving from hindered rotation about both C(carbene)–N bonds were found in solution at room temperature (10:6:1 ratio). Isomer 1: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.09 (m, 10H; Ph), 6.63 (m, 1H; *H*NCH$_2$Ph), 5.61 (m, 1H; *H*NCH$_3$), 4.29 (d, J = 5.6 Hz, 2H; HNC*H*$_2$Ph), 3.73 (m, 2H; PdNH$_2$C*H*$_2$), 3.51 (d, J = 4.6 Hz, 3H; HNC*H*$_3$), 2.50 ppm (m, 2H; PdN*H*$_2$CH$_2$); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −162.5 (m, 2F; *m*-Pf), −159.9 (t, 1F; *p*-Pf), −118.1 ppm (m, 2F; *o*-Pf). Isomer 2: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.09 (m, 10H; Ph), 6.44 (m, 1H; *H*NCH$_3$), 5.58 (m, 1H; *H*NCH$_2$Ph), 5.34 (d, J = 5.1 Hz, 2H; HNC*H*$_2$Ph), 3.73 (m, 2H; PdNH$_2$C*H*$_2$), 2.78 (d, J = 4.6 Hz, 3H; HNC*H*$_3$), 2.50 ppm (m, 2H; PdN*H*$_2$CH$_2$); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −162.5 (m, 2F; *m*-Pf), −159.9 (t, 1F; *p*-Pf), −118.4 ppm (m, 2F; *o*-Pf). Isomer 3: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.09 (m, 10H; Ph), 6.40* (m, 1H; *H*NCH$_2$Ph), 6.28 (m, 1H; *H*NCH$_3$), 5.21 (m, 2H; HNC*H*$_2$Ph), 3.73 (m, 2H; PdNH$_2$C*H*$_2$), 3.51* (3H; HNC*H*$_3$), 2.50 ppm (m, 2H; PdN*H*$_2$CH$_2$); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −162.9 (m, 2F; *m*-Pf), −160.4 (t, 1F; *p*-Pf), −117.3 ppm (m, 2F; *o*-Pf); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ = 190.92, 190.13 ppm (isomers 1 and 2, Pd–C$_{carbene}$); IR (Nujol): $\tilde{\nu}$ = 1594, 1552 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{22}H_{21}ClF_5N_3Pd$: C 46.82, H 3.75, N 7.45; found: C 46.86, H 3.71, N 7.34.

*Signal overlapped with signals of the other isomers.

[PdClPf{C(NHMe)(NHBz)}PPh$_3$] (Pf = C$_6$F$_5$, 2): PPh_3 (0.0861 g, 0.328 mmol) was added to a stirred suspension of **1** (0.1250 g, 0.222 mmol) in CH_2Cl_2 (6 mL). After 2 h, complete evaporation of the solvent and treatment of the residue with *n*-hexane afforded **2** as a white solid, which was collected by filtration, washed with *n*-hexane (2×5 mL), and dried in air. Yield: 87% (0.1394 g). Two atropisomers deriving from hindered rotation about both C(carbene)–N bonds were found in solution at room temperature (1.25:1 ratio). Isomer 1: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.54 (m, 6H; PPh$_3$), 7.45–7.26 (m, 14H; PPh$_3$/Ph), 6.70 (m, 1H; *H*NCH$_2$Ph), 5.72 (m, 1H; *H*NMe), 4.30 (d, J = 5.0 Hz, 2H; HNC*H*$_2$Ph), 3.56 ppm (d, J = 4.4 Hz, 3H; HNC*H*$_3$); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −163.5 (m, 2F; *m*-Pf), −162.4 (t, 1F; *p*-Pf), −117.4 ppm (m, 2F; *o*-Pf); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ = 21.30 ppm. Isomer 2: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.54 (m, 6H; PPh$_3$), 7.45–7.26 (m, 14H; PPh$_3$/Ph), 6.49 (m, 1H; *H*NMe), 5.72 (m, 1H; *H*NCH$_2$Ph), 5.36 (d, J = 5.2 Hz, 2H; HNC*H*$_2$Ph), 2.77 ppm (d, J = 4.9 Hz, 3H; HNC*H*$_3$); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −163.4 (m, 2F; *m*-Pf), −162.3 (t, 1F; *p*-Pf), −117.8 ppm (m, 2F; *o*-Pf); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ = 21.69 ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ = 198.5, 198.4 ppm (d, $^2J_{P,C}$ = 147, 156 Hz; isomers 1 and 2, Pd–C$_{carbene}$); IR (Nujol): $\tilde{\nu}$ = 1577 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{33}H_{27}ClF_5N_2PPd$: C 55.09, H 3.78, N 3.89; found: C 55.28, H 3.90, N 3.67.

***trans*-[{Pd(μ-Br)Pf[CPh(NEt$_2$)]}$_2$] (Pf = C$_6$F$_5$, *trans*-5a)**: Complex **4** (0.3000 g, 0.689 mmol) was added to a solution of **3a** (0.3342 g, 0.689 mmol) in MeCN (15 mL) at room temperature. After 18 h, the solvent was evaporated and the residue was extracted with $CHCl_3$. The resulting solution was filtered through activated charcoal and then concentrated to a small volume (ca. 2 mL). Addition of Et_2O (10 mL) and cooling to −20°C afforded **5a** as a yellow solid, which was collected by filtration, washed with cold *n*-hexane (4×4 mL), and dried in air. Yield: 58% (0.204 g). *trans*-**5a** exists as a mixture of *syn* and *anti* isomers (**5a**, **5a′**) in solution in a 1.3(**5a**):1(**5a′**) ratio. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.5–7.2 (m, 3H; *m*-, *p*-Ph, **5a/5a′**), 6.77 (m, 2H; *o*-Ph, **5a/5a′**), 5.23 (m, J = 13.3, 7.4 Hz, 1H; C*H*H, **5a′**), 5.11 (m, J = 14.5, 7.2 Hz, 2H; CH$_2$, **5a**), 5.09 (m, 1H; CH*H*, **5a′**), 3.53 (m, J = 14.4, 7.2 Hz, 1H; C*H′*H, **5a/5a′**), 3.40 (m, 1H; CH*H′*, **5a′**), 3.38 (m, 1H; CH*H′*, **5a**), 1.55 (t, J = 7.4 Hz, 3H; CH$_3$, **5a′**), 1.50 (t, J = 7.2 Hz, 3H; CH$_3$, **5a**), 1.02 (t, J = 7.2 Hz, 3H; CH′$_3$, **5a′**), 1.01 ppm (t, J = 7.2 Hz, 3H; CH′$_3$, **5a**); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −163.8 (m, 2F; *m*-Pf, **5a/5a′**), −160.6 (t, 1F; *p*-Pf, **5a/5a′**), −117.4 ppm (m, 2F; *o*-Pf, **5a/5a′**); ^{19}F NMR (282 MHz, $CDCl_3$, 253 K): δ = −164.0 (m, 1F; *m*-Pf, **5a′**), −163.8 (m, 1F; *m*-Pf, **5a**), −162.6 (m, 1F; *m*-Pf, **5a**), −162.3 (m, 1F; *m*-Pf, **5a′**), −160.1 (t, 1F; *p*-Pf, **5a**), −160.0 (t, 1F; *p*-Pf, **5a′**), −117.9 (m, 1F; *o*-Pf, **5a′**), −117.5 (m, 2F; *o*-Pf, **5a**), −117.1 ppm (m, 1F; *o*-Pf, **5a′**); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 253 K): δ = 229.2 (s; Pd–C, **5a′**), 228.9 (s; Pd–C, **5a**), 146.7 (m, $^1J_{C,F}$ = 228.9 Hz; *o*-Pf, **5a/5a′**), 141.1 (s; *i*-Ph, **5a**), 140.9 (*i*-Ph, **5a′**), 139.7–113.0 (*i*-, *m*-, *p*-Pf, **5a/5a′**), 128.6 (*m*-Ph, **5a/5a′**), 128.4 (s; *p*-Ph, **5a/5a′**), 122.1 (brs; *o*-Ph, **5a/5a′**), 57.6 (s; CH$_2$, **5a/5a′**), 46.9 (s; C′H$_2$, **5a/5a′**), 13.8 (s; CH$_3$, **5a/5a′**), 12.5 ppm (s; C′H$_3$, **5a/5a′**); IR (Nujol): $\tilde{\nu}$ = 1601, 1580 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{34}H_{30}Br_2F_{10}N_2Pd_2$: C 39.68, H 2.94, N 2.72; found: C 39.47, H 2.90, N 2.62.

***trans*-[{Pd(μ-Br)Pf[CMe(NEt$_2$)]}$_2$] (Pf = C$_6$F$_5$, *trans*-5b)**: Complex **4** (0.4107 g, 0.943 mmol) was added to a solution of **3b** (0.3990 g, 0.943 mmol) in CH_2Cl_2 (5 mL) at room temperature. After 5 h, the solution was filtered through activated charcoal and then concentrated to a small volume (ca. 3 mL). Addition of Et_2O (8 mL) and cooling to −20°C afforded **5b** as a pale-gray solid, which was collected by filtration, washed with cold *n*-hexane (2×5 mL), and dried in air. Yield: 50% (0.2137 g). *trans*-**5b** is a mixture of *syn* (**5b**) and *anti* (**5b′**) isomers in solution in a 1:0.7 ratio). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.90 (m, 1H; C*H*H, **5b/5b′**), 4.75 (m, J = 13.6, 7.2 Hz, 1H; CH*H*, **5b**), 4.69 (m, J = 12.9, 7.2 Hz, 1H; CH*H*, **5b′**), 3.54 (m, J = 18.3, 7.3 Hz, 2H; CH$_2$, **5b/5b′**), 2.74 (s, 3H; C(NR$_2$)C*H*$_3$, **5b′**), 2.73 (s, 3H; C(NR$_2$)C*H*$_3$, **5b**), 1.39 (t, J = 7.2 Hz, 3H; CH$_3$, **5b/5b′**), 1.11 ppm (t, J = 7.3 Hz, 3H; CH$_3$, **5b/5b′**); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −163.5 (m, 2F; *m*-Pf), −160.6 (t, 1F; *p*-Pf), −116.6 ppm (m, 2F; *o*-Pf); IR (Nujol): $\tilde{\nu}$ = 1592 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{24}H_{26}Br_2F_{10}N_2Pd_2$: C 31.85, H 2.90, N 3.10; found: C 32.03, H 2.53, N 3.11.

[PdBrPf{CPh(NEt$_2$)}(PPh$_3$)] (Pf = C$_6$F$_5$, 6a): PPh_3 (0.0380 g, 0.145 mmol) was added to a solution of **5a** (0.0700 g, 0.068 mmol) in CH_2Cl_2 (8 mL). After stirring for 1 h at room temperature, the solvent was completely evaporated and the brown residue was crystallized from *n*-hexane at −20°C to afford a pale-orange solid. Yield: 69% (0.073 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.45 (m, 6H; PPh$_3$), 7.35–7.20 (m, 12H; PPh$_3$/Ph), 6.95 (m, 2H; *o*-Ph), 4.92 (q, J = 7.3 Hz, 2H; CH$_2$), 3.61 (m, J = 13.3, 7.3 Hz, 1H; C*H′*H), 3.42 (m, J = 13.3, 7.3 Hz, 1H; CH*H′*), 1.63 (t, J = 7.3 Hz, 3H; CH$_3$), 1.12 ppm (t, J = 7.3 Hz, 3H; CH′$_3$); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −164.6 (m, 1F; *m*-Pf), −163.2 (m, 1F; *m*-Pf), −162.4 (t, 1F; *p*-Pf), −117.2 (m, 1F; *o*-Pf), −116.4 ppm (m, 1F; *o*-Pf); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ = 21.73 ppm (d, $^4J_{F,P}$ = 7.15 Hz); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 263 K): δ = 241.6 (d, $^2J_{C,P}$ =

142.4 Hz; Pd–C), 145.1 (m, $^1J_{C,F}$ = 222.5 Hz; *o*-Pf), 141.8 (s; *i*-Ph), 139.0–120.0 (*i*-, *m*-, *p*-Pf), 134.1 (d, $^2J_{C,P}$ = 11.6 Hz; *o*-PPh_3), 130.6 (d, $^1J_{C,P}$ = 41.9 Hz; *i*-PPh_3), 130.0 (s; *p*-PPh_3), 128.2 (s; *m*-Ph), 127.7 (d, $^3J_{C,P}$ = 9.7 Hz; *m*-PPh_3), 127.6 (s; *p*-Ph), 122.3 (s; *o*-Ph), 57.3 (s; CH_2), 46.3 (d, $^4J_{C,P}$ = 6.0 Hz; C′H_2), 13.6 (s; CH_3), 12.5 ppm (s; C′H_3); IR (Nujol): $\tilde{\nu}$ = 1600, 1583 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{35}H_{30}BrF_5NPPd$: C 54.11, H 3.89, N 1.80; found: C 54.44, H 3.99, N 1.99.

[PdBrPf{CMe(NEt$_2$)}(PPh$_3$)] (Pf = C$_6$F$_5$, 6b): This complex was prepared following the same procedure as described for **6a**, but allowing 12 minutes of reaction time. Yield: 54%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65–7.50 (m, 6H; PPh_3), 7.45–7.20 (m, 9H; PPh_3), 4.61 (m, *J* = 13.5, 7.2 Hz, 1H; C*H*H), 4.55 (m, *J* = 13.6, 7.2 Hz, 1H; CH*H*), 3.56 (m, *J* = 18.5, 7.3 Hz, 2H; CH_2), 2.78 (d, $^4J_{H,P}$ = 4.1 Hz, 3H; C(NR_2)CH_3), 1.41 (t, *J* = 7.2 Hz, 3H; CH_3), 1.16 ppm (t, *J* = 7.3 Hz, 3H; CH′$_3$); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −163.7 (m, 1F; *m*-Pf), −163.3 (m, 1F; *m*-Pf), −162.4 (t, 1F; *p*-Pf), −117.5 (m, 1F; *o*-Pf), −115.0 ppm (m, 1F; *o*-Pf); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ = 21.12 ppm (s); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 263 K): δ = 240.8 (d, $^2J_{C,P}$ = 148.4 Hz; Pd–C), 145.3 (m, $^1J_{C,F}$ = 224.7 Hz; *o*-Pf), 140.0–118.0 (*i*-, *m*-, *p*-Pf), 134.1 (d, $^2J_{C,P}$ = 11.7 Hz; *o*-PPh_3), 130.7 (d, $^1J_{C,P}$ = 41.2 Hz; *i*-PPh_3), 130.0 (s; *p*-PPh_3), 128.0 (d, $^3J_{C,P}$ = 10.0 Hz; *m*-PPh_3), 58.1 (s; CH_2), 44.7 (d, $^4J_{C,P}$ = 6.8 Hz; C′H_2), 29.6 (s; C(NR_2)CH_3), 12.9 (s; CH_3), 12.4 ppm (s; C′H_3); IR (Nujol): $\tilde{\nu}$ = 1590 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{30}H_{28}BrF_5NPPd$: C 50.41, H 3.95, N 1.96; found: C 50.38, H 3.78, N 2.20.

[PdBrPf{CPh(NEt$_2$)}(PMe$_3$)] (Pf = C$_6$F$_5$, 7a): This complex was prepared following the same procedure as described for the preparation of **6a**, but using a 1M solution of PMe_3 in THF. Yield: 50%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4–7.2 (m, 3H; *m*-, *p*-Ph), 6.80 (m, 2H; *o*-Ph), 4.75 (q, *J* = 7.2 Hz, 2H; CH_2), 3.51 (m, *J* = 13.4, 7.2 Hz, 1H; C*H*′H), 3.37 (m, *J* = 13.6, 7.2 Hz, 1H; CH*H*′), 1.54 (t, 3H, *J* = 7.2 Hz; CH_3), 1.19 (d, $^2J_{H,P}$ = 9.6 Hz, 9H; PCH_3), 1.08 ppm (t, *J* = 7.2 Hz, 3H; CH′$_3$); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −163.8 (m, 1F; *m*-Pf), −162.9 (m, 1F; *m*-Pf), −160.8 (t, 1F; *p*-Pf), −116.5 ppm (m, 2F; *o*-Pf); ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ = −17.34 ppm (d, $^4J_{F,P}$ = 7.9 Hz); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 253 K): δ = 244.3 (d, $^2J_{C,P}$ = 151.3 Hz; Pd–C), 145.8 (m, $^1J_{C,F}$ = 225.4 Hz; *o*-Pf), 142.1 (s; *i*-Ph), 138.0–133.0 (*m*-, *p*-Pf), 128.2 (s; *m*-Ph), 127.2 (s; *p*-Ph), 121.6 (s; *o*-Ph), 117.8 (m; *i*-Pf), 56.9 (s; CH_2), 46.0 (d, $^4J_{C,P}$ = 6.7 Hz; C′H_2), 14.3 (d, $^1J_{C,P}$ = 28.1 Hz; PCH_3), 13.2 (s; CH_3), 12.2 ppm (s; C′H_3); IR (Nujol): $\tilde{\nu}$ = 1572 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{20}H_{24}BrF_5NPPd$: C 40.67, H 4.10, N 2.37; found: C 40.35, H 3.79, N 2.32.

[PdPf{CPh(NEt$_2$)}(NCMe)$_2$]BF$_4$ (Pf = C$_6$F$_5$, 8a): $AgBF_4$ (0.0382 g, 0.196 mmol) was added to a solution of **5a** (0.0995 g, 0.097 mmol) in MeCN (9 mL). The mixture was stirred for 45 minutes, protected from light, and then it was filtered through activated charcoal and $MgSO_4$. The filtrate was concentrated to dryness and the resulting residue was crystallized from *n*-hexane to afford **8a** as a white solid. Yield: 32% (0.00368 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37 (m, 3H; *m*-, *p*-Ph), 6.64 (m, 2H; *o*-Ph), 5.17 (m, 1H; C*H*H), 4.80 (m, 1H; CH*H*), 3.60 (m, 2H; CH′$_2$), 2.54 (s, 3H; $NCCH_3$), 2.24 (s, 3H; NCCH′$_3$), 1.62 (t, *J* = 7.0 Hz; CH_3), 1.11 ppm (t, *J* = 7.0 Hz; CH′$_3$); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −162.4 (m, 2F; *m*-Pf), −158.2 (t, 1F; *p*-Pf), −152.5 (s, 4F; BF_4), −119.1 ppm (m, 2F; *o*-Pf); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 253 K): δ = 220.6 (s; Pd–C), 147.4 (m, $^1J_{C,F}$ = 221.7 Hz; *o*-Pf), 141.4 (*i*-Ph), 138.9 (m, $^1J_{C,F}$ = 237.5 Hz; *p*-Pf), 136.8 (m, $^1J_{C,F}$ = 248.8 Hz; *m*-Pf), 129.60 (s; *m*-, *p*-Ph), 122.8 (s; *o*-Ph), 109.4 (t, $^2J_{C,F}$ = 48.5 Hz; *i*-Pf), 58.7 (s; CH_2), 49.1 (s; C′H_2), 13.8 (s; CH_3), 12.8 ppm (s; C′H_3); elemental analysis calcd (%) for $C_{21}H_{21}BF_9N_3Pd$: C 41.79, H 3.51, N 6.96; found: C 41.72, H 3.29, N 7.07; IR (Nujol): $\tilde{\nu}$ = 1609, 1594 cm^{-1} (C=N).

Decomposition of the monoaminocarbene–palladium complexes: Solutions of 0.01–0.02 mmol of complexes *trans*-**5a**, *trans*-**5b**, **6a**, **6b**, and **8a** in $CDCl_3$ (0.6 mL) were prepared in 5 mm NMR tubes under nitrogen at room temperature. The solutions were then monitored by ^{1}H and ^{19}F NMR spectroscopy over a period of days, and when the decomposition was complete, the resulting products were identified and separated by preparative TLC. Details of partial decompositions are given below. All the products led eventually to the ketones **11a** or **11b** when kept in solution for long periods of time.

Decomposition of *trans*-5a: The composition of the solution after four days was: *trans*-**5** (55%), *cis*-**5a** (14%), **10a**·Br (14%), **11a** (12%).

***cis*-5a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.14 (3H; Ph), 6.85 (m, 2H; Ph), 5.10* (m, 2H; CH_2), 3.50* (m, 2H; CH′$_2$), 1.50 (t, 3H; CH_3), 1.09 ppm (t, 3H; CH′$_3$); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −165.0 (m, 2F; *m*-Pf), −162.8 (t, 1F; *p*-Pf), −116.6 ppm (m, 2F; *o*-Pf).

*Signal overlaps with signals of the *trans* isomers.

10a-Br:[31] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90–7.50 (5H; Ph), 4.67 (q, *J* = 7.3 Hz, 2H; CH_2), 4.58 (q, *J* = 7.3 Hz, 2H; CH′$_2$), 1.70 (t, *J* = 7.3 Hz, 3H; CH_3), 1.45 ppm (t, *J* = 7.3 Hz, 3H; CH′$_3$); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −155.4 (m, 2F; *m*-Pf), −142.1 (t, 1F; *p*-Pf), −135.3 ppm (m, 2F; *o*-Pf); ^{13}C{^{1}H} NMR (75.4 MHz, CD_3CN): δ = 172.9 (s; =C), 149.0–132.0 (*o*-, *m*-, *p*-Pf), 135.7 (s; *p*-Ph), 131.7 (s; *i*-Ph), 130.7 (s; *o*-Ph), 129.9 (s; *m*-Ph), 109.3 (t, *J* = 15.9 Hz; *i*-Pf), 55.0 (s; CH_2), 53.8 (s; C′H_2), 13.9 (s; CH_3), 13.6 ppm (s; C′H_3).

11a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (m, 2H; *o*-Ph), 7.70 (m, 1H; *p*-Ph), 7.54 ppm (m, 2H; *m*-Ph); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −160.3 (m, 2F; *m*-Pf), −150.9 (t, 1F; *p*-Pf), −140.3 ppm (m, 2F; *o*-Pf); MS (70 eV): *m*/*z* (%): 272 (22) [M^+], 195 (15) [$PfCO^+$], 167 (48) [Pf^+], 117 (100), 77 (74) [Ph^+], 51 (61).

Decomposition of *trans*-5b: The composition of the solution after four days was: *trans*-**5b** (26%), *cis*-**5b** (17%), **10b**-Br (23%), **12** (19%), **11b** (15%).

***cis*-5b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.05 (m, 1H; C*H*H), 4.78* (m, 1H; CH*H*), 3.65* (2H; CH′$_2$), 2.65 (s, 3H; C(NR_2)CH_3), 1.52* (3H; CH_3), 1.20* ppm (3H; CH′$_3$); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −164.8 (m, 2F; *m*-Pf), −162.3 (t, 1F, *p*-Pf), −117.1 ppm (m, 2F, *o*-Pf).

*Signal overlaps with signals of other compounds.

10b-Br: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.85* (2H; CH_2), 4.23 (q, 2H; CH′$_2$), 3.27 (s, 3H; C(NR_2)CH_3), 1.71 (t, *J* = 7.3 Hz, 3H; CH_3), 1.61* ppm (3H; CH′$_3$); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −155.1 (m, 2F; *m*-Pf), −143.9 (t, 1F; *p*-Pf), −136.2 ppm (m, 2F; *o*-Pf).

*Signal overlaps with signals of other compounds.

11b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.62 ppm (s, 3H; CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −160.5 (m, 2F; *m*-Pf), −149.4 (t, 1F; *p*-Pf), −141.2 ppm (m, 2F; *o*-Pf); MS (70 eV): *m*/*z* (%): 210 (43) [M^+], 195 (100) [$PfCO^+$], 167 (40) [Pf^+], 117 (24), 43 (30).

12: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.19 (d, *J* = 0.8 Hz, 1H; =C*H*H), 3.85 (d, *J* = 0.8 Hz, 1H; =CH*H*), 3.00 (q, *J* = 7.1 Hz, 4H; CH_2), 1.06 ppm (t, *J* = 7.1 Hz, 6H; CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −162.7 (m, 2F; *m*-Pf), −155.7 (t, 1F, *p*-Pf), −141.6 ppm (m, 2F, *o*-Pf); MS (70 eV): *m*/*z* (%): 265 (73) [M^+], 250 (100) [M^+−Me], 236 (84), 193 (94) [$PfCCH_2^+$], 181 (26), 143 (47), 58 (50).

Synthesis of 10a-BF$_4$:[31] A solution of **8a** (0.1600 g, 0.265 mmol) in $CHCl_3$ was stirred for six days at room temperature. The yellow solution slowly became a dark suspension. After this time, the mixture was filtered through activated charcoal and the filtrate was concentrated to dryness. The residue was triturated with *n*-hexane to afford a yellowish solid, which was collected by filtration, washed with *n*-hexane, and dried in vacuo. Yield: 0.0604 g (55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80–7.50 (m, 5H; Ph), 4.42 (q, *J* = 7.3 Hz, 2H; CH_3), 4.29 (q, *J* = 7.2 Hz; CH′$_2$), 1.61 (t, *J* = 7.3 Hz, 3H; CH_3), 1.43 ppm (t, *J* = 7.2 Hz, 3H; CH′$_3$); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −156.4 (m, 2F; *m*-Pf), −153.5 (s, 4F; BF_4), −142.8 (tt, *J* = 21.5 Hz, 5.1 Hz, 1F; *p*-Pf), −136.1 ppm (m, 2F; *o*-Pf); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ = 173.3 (s; =C), 148.0–137.0 (*o*-, *m*-, *p*-Pf), 135.9 (s; *p*-Ph), 131.9 (s; *i*-Ph), 130.8 (s; *o*-Ph), 129.9 (s; *m*-Ph), 109.4 (t, $^2J_{C,F}$ = 16.2 Hz; *i*-Pf), 54.8 (s; CH_2), 53.7 (s, C′H_2), 13.9 (s; CH_3), 13.4 ppm (s, C′H_3); IR (Nujol): $\tilde{\nu}$ = 1598 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{17}H_{15}BF_9N$: C 49.19, H 3.64, N 3.37; found: C 48.98, H 3.54, N 3.27.

[{Pd(μ-Br)[(η^3-C(Pf)(OMe)CHCHPh]}$_2$] (Pf = C$_6$F$_5$, 13): The palladium complex **4** (0.1930 g, 0.444 mmol) was added to a solution of **9c** (0.2088 g, 0.444 mmol) in CH_2Cl_2 (20 mL) in a flask immersed in a cold bath at −25°C. After stirring for 25 min at low temperature, the flask was taken

out of the cold bath and was left to stand until the mixture reached room temperature. The solution was then filtered through activated charcoal and the filtrate was concentrated to dryness. The residue was triturated with *n*-hexane, collected by filtration, washed with *n*-hexane (10×3 mL), and dried in air. Yield: 64% (0.1421 g). Complex **13** was found to be a mixture of isomers (**13**, **13′**) in solution in a 1.2(**13**):1(**13′**) ratio (see text). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.15 (m, 5H; Ph, **13**/**13′**), 5.76 (d, J = 11.5 Hz, 1H; H^2, **13**), 5.74 (d, J = 11.5 Hz, 1H; H^2, **13′**), 4.21 (d, J = 11.5 Hz, 1H; H^3, **13**), 4.19 (d, J = 11.5 Hz, 1H; H^3, **13′**), 3.83 (s, 3H; OCH_3, **13′**), 3.79 ppm (br s, 3H; OCH_3, **13**); ^{19}F NMR (282 MHz, $CDCl_3$): −161.0 (br m, 2F; *m*-Pf, **13**/**13′**), −151.5 (t, 1F; *p*-Pf, **13**), −151.4 (t, 1F; *p*-Pf, **13′**), −136.0 (m, 1F; *o*-Pf, **13**/**13′**), −128.0 ppm (m, 1F; *o*-Pf, **13**/**13′**); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 273 K): 147.0–130.0 (*o*-, *m*-, *p*-Pf, **13**/**13′**), 136.5 (s; *i*-Ph, **13**/**13′**), 129.0 (s; *m*-Ph, **13**/**13′**), 128.5 (s; *p*-Ph, **13**/**13′**), 128.1 (s; *o*-Ph, **13**/**13′**), 114.6 (s; C^1(OMe)Pf, **13**/**13′**), 110.8 (m; *i*-Pf, **13**/**13′**), 84.0 (s; C^2H, **13**), 83.4 (s; C^2H, **13′**), 70.9 (s; C^3HPh, **13**), 70.8 (s; C^3HPh, **13′**), 57.3 ppm (s; OCH_3, **13**/**13′**); elemental analysis calcd (%) for $C_{32}H_{20}Br_2F_{10}O_2Pd_2$: C 38.47, H 2.02; found: C 38.94, H 2.07.

Decomposition of 13: A solution of **13** (0.008 g, 0.008 mmol) in $CDCl_3$ (0.6 mL) was monitored by ^{1}H and ^{19}F NMR spectroscopy. After 11 days at room temperature, complete decomposition to the ketone PfC(O)(CH=CHPh) (**17**) was observed. Ketone **17** could be separated by preparative TLC using a mixture of *n*-hexane/CH_2Cl_2 (1:1) (R_f = 0.3). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.40 (m, 5H; Ph), 7.48 (m, J = 16.0 Hz, 1H; H^3), 7.04 ppm (m, J = 16.0 Hz, 1H; H^2); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −160.3 (m, 2F; *m*-Pf), −150.6 (t, 1F; *p*-Pf), −140.9 ppm (m, 2F; *o*-Pf).

[{Pd(μ-Br)[η^3-PhC(Pf)(OMe)]}$_2$] (Pf = C_6F_5, 14): Complex **4** (0.1082 g, 0.248 mmol) was added to a stirred red solution of **9a** (0.1103 g, 0.248 mmol) in THF (10 mL). The reaction mixture immediately turned dark and it was stirred under N_2 at room temperature for 40 min. Activated charcoal was then added and the suspension was filtered. The filtrate was cooled to −20°C and concentrated to dryness. Addition of Et_2O (3 mL) to the residue afforded a yellowish solid, which was collected by filtration, washed with cold *n*-hexane, and dried in vacuo. Yield: 32% (0.038 g). ^{1}H NMR (300 MHz, $CDCl_3$, 263 K): δ = 8.15–7.30 (m, 4H; Ph), 5.55 (m, 1H; *benz*-η^3-Ph), 3.51 ppm (m, 3H; OCH_3); ^{19}F NMR (282 MHz, $CDCl_3$, 263 K): δ = −160.6 (m, 2F; *m*-Pf), −150.5 (t, 1F; *p*-Pf), −135.9 (br m, 1F; *o*-Pf), −127.5 ppm (br m, 1F; *o*-Pf).

Complete decomposition of **14** in $CDCl_3$ was observed after 12 h at room temperature and gave a mixture of PfC(OMe)$_2$Ph (**15a**) and Pf(CO)Ph (**11a**). A similar mixture of pentafluorophenyl-containing products (**14**, **15a**, **11a**) is observed when complex **4** and the tungsten carbene **9a** are mixed in $CDCl_3$ solution at room temperature.

15a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (m, 2H; Ph), 7.46 (m, 1H; Ph), 7.34 (m, 2H; Ph), 3.23 ppm (s, 6H; OCH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −162.5 (m, 2F; *m*-Pf), −155.0 (t, 1F; *p*-Pf), −139.4 ppm (m, 2F; *o*-Pf); MS (70 eV): *m*/*z* (%): 287 (48) [M^+−OMe], 195 (47) [$PfCO^+$], 167 (59) [Pf^+], 117 (44), 77 (100) [Ph^+], 74 (10), 51 (47).

Reaction of [W(CO)$_5${C(OMe)Me}] (9b) and 4: Complex **4** (0.0376 g, 0.086 mmol) was added to a solution of **9b** (0.0330 g, 0.086 mmol) in $CDCl_3$ (0.6 mL). The mixture turned dark, and after 5 h at room temperature the ^{19}F NMR spectrum showed the disappearance of **4** and the presence of a mixture of **16**, **15b**, and **11b** in solution.

15b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.26 (s, 6H; OCH_3), 1.67 ppm (s, 3H; CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −162.7 (m, 2F; *m*-Pf), −155.5 (t, 1F; *p*-Pf), −140.7 ppm (m, 2F; *o*-Pf); MS (70 eV): *m*/*z* (%): 241 (23) [M^+−Me], 225 (69) [M^+−OMe], 195 (70), 194 (39) [$CMePf^+$], 167 (48) [Pf^+], 117 (58), 84 (100), 43 (69).

16: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.64 (d, J = 3.3 Hz, 1H; =C*H*H), 4.40 (d, J = 3.3 Hz, 1H; =CH*H*), 3.71 ppm (s, 3H; OCH_3); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −162.5 (m, 2F; *m*-Pf), −154.8 (t, 1F; *p*-Pf), −141.2 ppm (m, 2F; *o*-Pf); MS (70 eV): *m*/*z* (%): 224 (69) [M^+], 195 (21), 194 (100), 193 (40), 181 (91) [CH_2Pf^+], 167 (11) [Pf^+], 161 (38), 143 (51), 117 (38), 93 (24).

Crystal structure determinations: Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent from a solution of **7a** in CH_2Cl_2 at room temperature, by cooling a solution of **10a**-BF_4 in a mixture of CH_2Cl_2/Et_2O at −20°C, or by slow evaporation of the solvent from a solution of **13** in a mixture of CH_2Cl_2/*n*-hexane. Each crystal was mounted on the tip of a glass fiber. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo-K_α radiation (λ = 0.71073 Å). Intensities were integrated and the structures were solved by direct methods.[32] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters.

7a: Monoclinic $P2(1)/c$: a = 9.168(6), b = 19.028(12), c = 13.969(9) Å; β = 102.235(13)°; V = 2382(3) Å^3; formula unit: $C_{20}H_{24}BrF_5NPPd$ with Z = 5; formula weight = 590.68; calculated density = 2.059 g cm^{-3}; F(000) = 1460; $\mu(Mo_{K\alpha})$ = 3.211 mm^{-1}. A total of 9864 reflections were collected (1.84° < θ < 21.69°). Full-matrix least-squares refinement (on F^2) based on 2921 independent reflections converged with 267 variable parameters and no restraints. $R1$ = 0.0316, for $F^2 > 2\sigma(F^2)$; $wR2$ = 0.0749.[33] GoF (F^2) = 0.937. $\Delta\rho_{max}$ = 0.669, $\Delta\rho_{min}$ = −0.336 e Å^3.

10a-BF_4: Monoclinic $P2(1)/c$: a = 8.737(12), b = 14.604(19), c = 15.47(2) Å; β = 99.42(2)°; V = 1947(4) Å^3; formula unit: $C_{17}H_{15}BF_9N$ with Z = 4; formula weight = 415.11; calculated density = 1.416 g cm^{-3}; F(000) = 840; $\mu(Mo_{K\alpha})$ = 0.143 mm^{-1}. 8288 reflections were collected (1.93° < θ < 23.25°). Full-matrix least-squares refinement (on F^2) based on 2784 independent reflections converged with 255 variable parameters and no restraints. $R1$ = 0.0996, for $F^2 > 2\sigma(F^2)$; $wR2$ = 0.2788.[33] GoF (F^2) = 0.952. $\Delta\rho_{max}$ = 0.302, $\Delta\rho_{min}$ = −0.285 e Å^3.

13: Monoclinic $C2/c$: a = 25.073(5), b = 11.506(3), c = 12.449(3) Å; 90°, β = 114.073(4)°; V = 3279.1(12) Å^3; formula unit: $C_{32}H_{20}Br_2F_{10}O_2Pd_2$ with Z = 4; formula weight = 999.10; calculated density = 2.024 g cm^{-3}; F(000) = 1920; $\mu(Mo_{K\alpha})$ = 3.621 mm^{-1}. 7567 reflections were collected (1.78° < θ < 23.32°). Full-matrix least-squares refinement (on F^2) based on 2630 independent reflections converged with 218 variable parameters and no restraints. $R1$ = 0.0482, for $F^2 > 2\sigma(F^2)$; $wR2$ = 0.0831.[33] GoF (F^2) = 0.942. $\Delta\rho_{max}$ = 0.571, $\Delta\rho_{min}$ = −0.506 e Å^3.

CCDC-178512, CCDC-246145, and CCDC-246146 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

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[33] $R1 = \Sigma(||F_0|-|F_c||)/\Sigma|F_0|)$; $wR2 = [\Sigma[w(F_0^2-F_c^2)^2/\Sigma[w(|F_0^2|)^2]]^{1/2}$.

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