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N-Heterocyclic Carbene Palladium Complexes Bearing Carboxylate Ligands and Their Catalytic Activity in the Hydroarylation of Alkynes

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*Summary: The synthesis and reactivity of palladium acetate/trifluoroacetate complexes stabilized by the presence of N-heterocyclic carbene (NHC) ligands are described. The structures and coordination characteristics of both (IPr)Pd(OAc)$_2$ (**1**) and (IPr)Pd(OOCCF$_3$)$_2$(H$_2$O) (**2**) were elucidated by spectroscopic and X-ray diffraction studies. The structure of **1** shows a novel coordination of the anions in a monomeric complex, with one acetate anion acting as a monodentate ligand while the second one coordinates through both oxygens. The NHC ligands in **1** and **2** are stable under acidic conditions. The complexes were used as precatalysts in the hydroarylation of alkynes. Using this simple protocol, a number of arenes react with various alkynes to produce stilbenes.*

Introduction

N-heterocyclic carbene have proven to be excellent supporting ligands in numerous transition-metal-mediated reactions.[1] Their ability to strongly coordinate to the metal center[2] allows for the formation of stable metal species facilitating catalyst design efforts. Despite the great interest in palladium N-heterocyclic carbene (NHC) complexes as catalysts or catalyst precursors, very little has been reported on such complexes bearing ligands such as acetate and trifluoroacetate.[3] We wish to report here the synthesis of novel palladium mononuclear complexes bearing acetate or trifluoroacetate groups and the carbene *N*,*N′*-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr). The initial catalytic activity of these species in the hydroarylation of alkynes is presented.

It is known that palladium/tertiary phosphine/acetate complexes lack stability, due to a propensity to oxidize the supporting phosphine ligand via an intramolecular process. Triphenylphosphine is a classical example where the reaction of Pd(OAc)$_2$ and excess PPh$_3$ leads to Pd(PPh)$_4$ and O=PPh$_3$.[4] In contrast, the imidazolium salts are efficient precursors for NHC-stabilized palladium complexes. Two equivalents of the imidazolium salt can react with 1 equiv of Pd(OAc)$_2$ to form (NHC)$_2$PdX$_2$ complexes, where X is the imidazolium salt anion.[1a,3,5] The reaction chemistry may involve the acetate anion acting as a base to deprotonate the imidazolium salt, leading to the free carbene that then coordinates to the metal center. This reaction scheme is limited in almost all cases to metal to imidazolium salt precursor ratios of 1:2 and leads to the absence of acetate ligand in the final product.

Results and Discussion

Sigman recently reported the synthesis of (NHC)Pd(OAc)$_2$·H$_2$O by reaction of [(NHC)PdCl$_2$]$_2$ with Ag(OAc) in CH$_2$Cl$_2$.[3b] We have used a different approach and have achieved the synthesis and isolation of (NHC)Pd complexes bearing acetate type ligands without the need for expensive silver additives. Our first synthetic attempts were based on a simple scheme involving reaction of the NHC with commercially purchased Pd(OAc)$_2$ in toluene. These reactions repeatedly failed, leading to an unidentified mixture of products. Upon closer examination of the resulting product mixture, ^{1}H NMR spectroscopy revealed the presence of a resonance at 11 ppm, characteristic of an imidazolium salt. This is probably due to slow decomposition of the palladium acetate in air and concomitant elimination of acetic acid, which can generate the aforementioned salt upon interaction with the NHC. After careful purification of Pd(OAc)$_2$ by recrystallization from benzene, we were able to carry out our initial reaction scheme using IPr in toluene at room temperature. The product **1** precipitated from the reaction medium as analytically pure microcrystals in 77% yield. Addition of hexanes to the toluene solution increased the yield to 85%. Crystals suitable for X-ray diffraction study were grown from hexanes/CH$_2$Cl$_2$ mixtures. When strictly anhydrous conditions were used to carry out the reaction and crystallization, the X-ray structure of **1**[6] revealed a distorted-square-planar geometry around the metal center. One acetate anion acts as a monodentate ligand, and the second one coordinates through both oxygens (Figure 1), stabilizing a 16-electron configuration around

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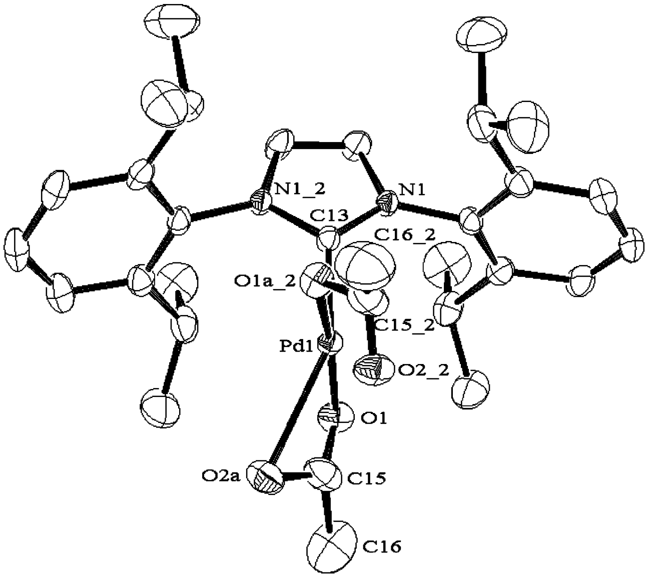


Figure 1. ORTEP drawing of **1**. Hydrogens are removed for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(13) = 1.950(3), Pd(1)−O(1a) = 2.005(4); O(1a)−Pd(1)−O(1) = 170.28(16), C(13)−Pd(1)−O(2a) = 147.11(12).

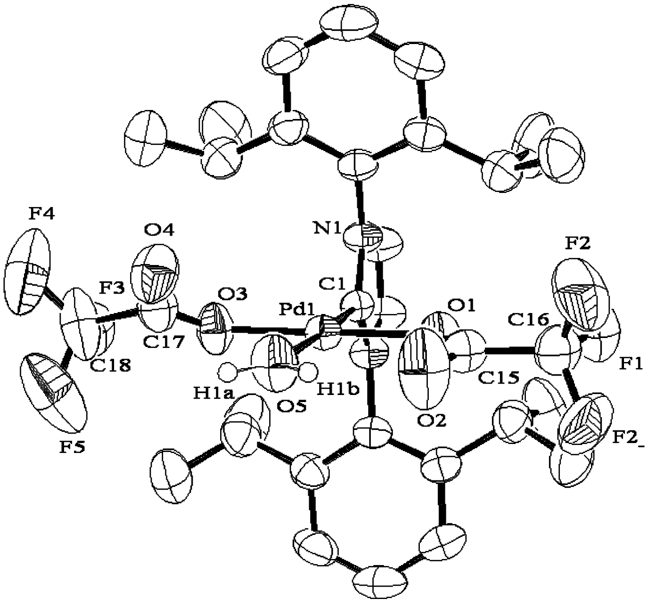
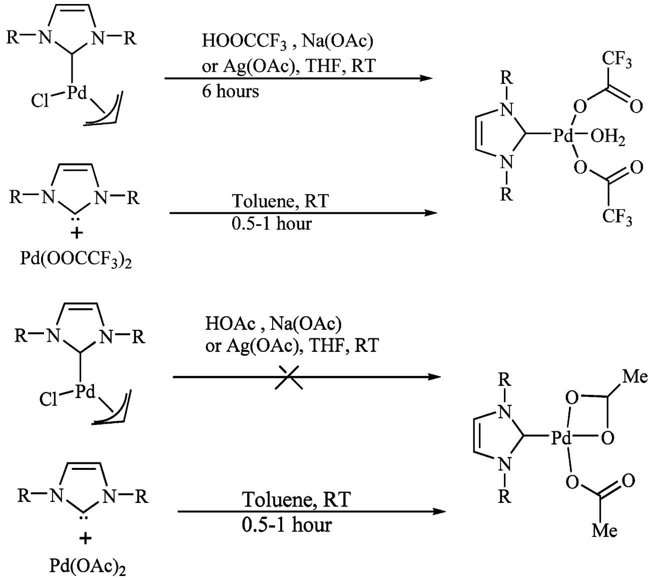


Figure 2. ORTEP drawing of **2**. The thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (deg): Pd(1)−O(1) = 2.0423(9); Pd(1)−O(3) = 2.0077(10); Pd(1)−C(1) = 1.9533(1); O(2)−H(1b) = 1.855; C(1)−Pd(1)−O(5) = 175.74(4); O(1)−Pd(1)−O(3) = 176.73(4).

Scheme 1. Synthesis of Complexes 1 and 2



the metal center. To the best of our knowledge, this is the first example of a mononuclear complex having acetate anions mono- as well as dicoordinated to a palladium center.

The molecule sits on a crystallographic 2-fold rotation axis passing through the imidazole ring. The inequivalent nature of the bonding between the acetate ions to the Pd, together with the 2-fold rotation axis, results in a disordered structure with both the Pd and oxygen atoms occupying two equally populated sites.[7] In noncoordinative solvents (C_6D_6), a fluxional behavior of the acetate anions was observed. ^{1}H NMR recorded at room temperature shows broad signals corresponding to the coordinated anions.

The reaction of **1** and acids led to the replacement of the acetate units with the corresponding counteranions. In the case of HCl, a previously reported dimeric complex was identified.[8] In the case of TFA, the new monomeric complex (IPr)Pd($OOCCF_3$)$_2$(H_2O) (**2**) was formed in 92% yield. Complex **2** can also be synthesized (in 86% yield) by reaction of Pd($OOCCF_3$)$_2$ and NHC using a protocol similar to that for the synthesis of **1**.

The ORTEP drawing of **2** reveals a different structure: an almost perfect square-planar coordination around palladium.[9] The fourth metal site, trans to the NHC, is occupied by a water molecule. Trifluoroacetate groups are located trans to each other and are bent toward the water molecule, indicating the formation of hydrogen bonds (H(1b)−O(2) = 1.855 Å). The palladium−carbenic-carbon bond is slightly shorter (1.953 Å) than that found in most Pd/NHC complexes (around 2 Å), as a direct result of the electron-withdrawing properties of the anions (Figure 2).

An alternative synthetic route to **2** involves acidic cleavage of an alkyl palladium group in trifluoroacetic acid (62%) (Scheme 1). Ag(OAc) was added in order to remove the chloride anion. The acidic cleavage of the

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(6) Crystal data for $C_{31}H_{42}N_2O_4Pd$ (**1**): monoclinic crystal system, space group $C2/c$, $a = 22.768(2)$ Å, $b = 8.6694(7)$ Å, $c = 17.6035(16)$ Å, $\alpha = \gamma = 90°$, $\beta = 118.569(3)°$, $V = 3051.6(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.334$ g/cm^3, $F(000) = 1280$, temperature 150(2) K, θ range for data collection from 2.44 to 22.50°, refinement method full-matrix least squares on F^2, GOF = 1.174, final R indices ($I > 2\sigma(I)$) R1 = 0.0318 and wR2 = 0.0733, R indices (all data) R1 = 0.0341 and wR2 = 0.0741.

(7) Refinement of the structure in the primitive cell (triclinic, space group $P\bar{1}$), which does not impose a 2-fold axis on the structure, also yields a disordered structure which does not fit the experimental data significantly better than the structure refined in the higher symmetry (monoclinic, space group $C2/c$) structure.

(8) The [(IPr)PdCl$_2$]$_2$ complex has previously been synthesized and fully characterized: Viciu, M. S.; Kissling, R. M.; Stevens, E. D.; Nolan, S. P. *Org. Lett.* **2002**, *4*, 2229−2231.

(9) Crystal data for $C_{31}H_{38}F_6N_2O_5Pd$ (**2**): orthorhombic crystal system, space group $Pnma$, $a = 9.8267(9)$ Å, $b = 16.9277(15)$ Å, $c = 20.2409(19)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 3366.9(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.458$ g/cm^3, $F(000) = 1512$, temperature 295(2) K, θ range for data collection 1.57 to 27.53°, 22 938 reflections collected, 99.5% completeness to $\theta = 27.53°$, refinement method full-matrix least squares on F^2, goodness of fit on F^2 1.083, final R indices ($I > 2\sigma(I)$) R1 = 0.0279 and wR2 = 0.0681.

palladium–carbon bond without affecting the NHC ligand coordination has been observed previously.[10] Unfortunately, the reaction of (IPr)Pd(allyl)Cl with weaker acids such as HOAc to form **1** does not proceed as expected, even in the presence of Ag(OAc).

Complexes **1** and **2** show a versatile chemistry in acidic media and can be easily used for the synthesis of other catalysts/catalyst precursors by simple anion exchange.

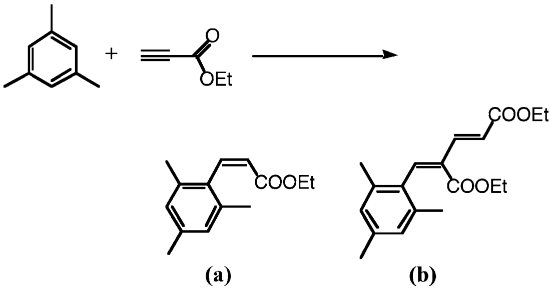
Catalytic Hydroarylation of Alkynes. In a protocol involving palladium acetate as catalyst, Fujiwara has described the reaction of simple arenes with alkynes in TFA to form stilbenes.[11] This reaction displays high atom economy and makes use of inexpensive starting materials (arenes) with no requirement for prefunctionalization. The proposed mechanism for this reaction is believed to involve an electrophilic metalation and $Pd(OOCCF_3)_2$ is regenerated by protonolysis of the Pd–C bond in the last step of the catalytic cycle. The similarity between this step and the generation of **2** from (NHC)Pd(allyl)Cl/Ag(OAc) and TFA encouraged us to investigate the role of **1** and **2** as catalysts in the hydroarylation of alkynes.

We speculated that addition of a NHC ligand to the palladium center might induce a well-defined chemical environment around the metal that might improve the selectivity of the reaction by steric control. The compatibility of the complexes with the reaction conditions (TFA as solvent) should promote the NHC as potentially powerful ligands in palladium chemistry performed under acidic conditions.[12]

The reaction between mesitylene and ethyl propiolate in TFA mediated by 1 mol % **1**, **2**, or [(IPr)Pd(allyl)]Cl/$NaOOCCF_3$ is complete in 18 h at room temperature. Ligandless $Pd(OAc)_2$ led to 57% conversion in 24 h at room temperature. It is interesting to note the poor catalytic activity of $Pd(dba)_2$, which supports the idea of a mechanism based on Pd(II) exclusively.[11]

Changing the NHC ligand has little influence on the rate of the reaction. However, an increase in selectivity toward (a) (Table 1) was observed if sterically demanding ligands such as IPr (IPr = bis(2,6-diisopropylphenyl)imidazol-2-ylidene) are involved. The bulkiness of the ligand prevents the insertion of a second alkyne molecule. Arenes bearing alkyl substituents, alkoxy groups, or halogens are competent substrates. 2-Bromomesitylene is converted to the corresponding product, leaving the C–Br bond unaffected. Arenes bearing alkoxy groups display slower reaction rates compared with their alkyl-substituted counterparts. The reaction of anisole with ethyl propiolate led to ortho-substituted product in 83% yield by NMR; however, the reaction required heating to 60 °C. A possible explanation for this observation is a heteroatom-assisted mechanism in which the oxygen coordinates to the palladium center, limiting the availability of coordination sites for the alkyne insertion. Alkynes having electron-withdrawing groups are also effective, leading in most cases to (*Z*)-arylalkenes (Table 2, entries 3 and 4 form (*E*)-arylalkenes). Both terminal and internal alkynes are tolerated. Internal nonactivated alkynes, such as 4-octyne, require higher temperature and led to a mixture of (*E*)- and (*Z*)-arylalkene.

Table 1. Catalyst Optimization[a]



catalyst	time (h)	conversion (a)/(b) (%)
$Pd(OAc)_2$	24	49/8
$Pd(dba)_2$	24	trace
$(IMes)Pd(OOCCF_3)_2$	18	72/2
2	18	78/0
(IPr)Pd(allyl)CI/NaOAc	18	80/0
1	18	>99/1

[a] Reaction conditions: ArH, 1.5 mmol; ethyl propiolate, 1 mmol; catalyst, 1 mol %; room temperature; TFA, 1 mL.

At this point the catalytic cycle and substrate-dependent isomer distribution are poorly understood. For instance, no reaction is observed between mesitylene and **1** in $HOOCCF_3$. This observation may hint at a different step than electrophilic metalation as the initial step of the catalytic cycle.[11] Catalyst **1** is simply converted to **2** by anion exchange with the acid under these conditions. Furthermore, using neutral solvents instead of TFA or TFA/1,2-dichloroethane as reaction medium completely inhibits hydroarylation but promotes a very fast dimerization of alkynes. In THF, the reaction of mesitylene and phenylacetyene leads to the corresponding acetylene dimer and unreacted arene[13] in 30 min at room temperature.

Conclusions

The NHC/Pd/acetate type complexes described here show complex coordination behavior and versatile chemistry. The NHC supporting ligands are unaffected by the harsh acidic conditions. The complexes can be used as precursors for further catalyst development by simple anion exchange in the presence of various acids. They have proven to be pertinent catalysts in the functionalization of simple arenes, extending the range of reactions mediated by NHC/Pd complexes. Further studies aimed at understanding the mechanism of the hydroarylation of alkynes reaction under acidic conditions and dimerization of alkynes are ongoing in our laboratory.

Experimental Section

General Considerations. Arenes and alkynes were used as received with no further purification (Aldrich). TFA (99%;

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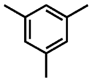
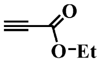
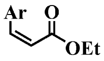
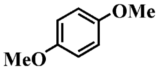
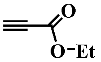
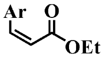
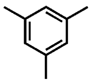
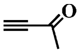
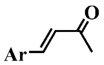
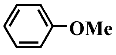
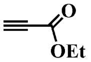
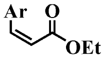
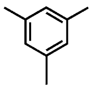
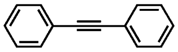
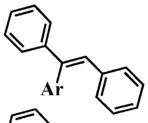
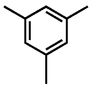
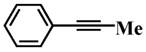
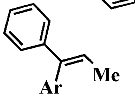
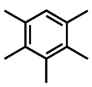
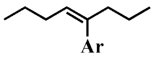
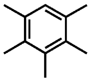
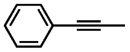
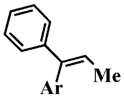
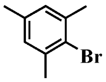
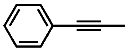
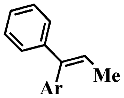
(10) Protonolysis of Pd–C bonds in NHC/palladium complexes: Jensen, D. R.; Sigman, M. S. *Org. Lett.* **2003**, *5*, 63–65.

(11) (a) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633–639. (b) Jia, C.; Lu, W.; Oyamada, J.; Kitamura, T.; Matsuda, K.; Irie, M.; Fujiwara, Y *J. Am. Chem. Soc.* **2000**, *122*, 7252–7263. (c) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, *287*, 1992–1995.

(12) NHC/Pd complexes were successfully used in the oxidation of methane to methanol in TFA: Muehlhofer, M.; Strassner, T.; Herrmann, W. A. *Angew.* Chem., Int. Ed. Engl. **2002**, *41*, 1745–1747.

(13) Similar dimerizations were reported for $Pd(OAc)_2$/tertiary phosphine systems: (a) Trost, B. M.; Chan, C.; Ruhter, G. *J. Am. Chem. Soc.* **1987**, *109*, 3486-3487. (b) Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Ruhter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698–708.

Table 2. (NHC)Pd(OAc)$_2$-Catalyzed Hydroarylation of Alkynes[a]

Arene	Alkyne	Product	Time (h)	Temp (°C)	Yield (%)
			18[b] 24 2	rt[b] rt 60	100[b] 78 100 (82)[c]
			48 4	rt 60	49 82 (68)
			18 1	rt 60	100 100 (91)
			1	60	83 *(ortho)* *(69)*
			6	rt	96[b] (94)
			2	rt	98[b] (95)
			6	60	72 (65)
			6	rt	88 (84)
			6	rt	78[b](70)

[a] Reaction conditions: (IPr)Pd(OOCCF$_3$)$_2$, 1 mol %; TFA, 1 mL; arene, 1.5 mmol; alkyne, 1 mmol. [b] (IPr)Pd(OAc)$_2$ 1 mol %. [c] Isolated yields are reported in parentheses.

Aldrich) was used as received. Pd(OAc)$_2$ was received from Johnson Matthey and recrystallized from C$_6$H$_6$. Flash chromatography was performed on silica gel 60 (320−400 mesh) with hexanes/THF mixtures. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 300, 400, or 500 MHz spectrometer at room temperature. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., and dried prior to use. Elemental analyses were performed at Desert Analysis, Tucson, AZ. The imidazolium salt 1,3-bis(2,6-diisopropylphenyl)-imidazolium chloride (IPr·HCl)[14] was prepared on the basis of synthetic methods previously reported. Product isolation and characterization are described in the Supporting Information.

Synthesis of (IPr)Pd(OAc)(κ^2-OAc) (1). Pd(OAc)$_2$ (224.4 mg, 1 mmol) recrystallized from benzene was suspended in toluene, and IPr (388 mg, 1 mmol) was added. The mixture was stirred at room temperature for 1 h. The product crystallized from the mixture as yellow crystals. The solvent was evaporated in vacuo almost to dryness, and dry hexane was added. The product was collected by filtration as a microcrystalline material and washed with 20 mL of dry hexane. Yield: 85% (520 mg, 0.85 mmol). Crystals suitable for diffraction study were grown from CH$_2$Cl$_2$/hexanes solutions. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): 7.64 (t, J = 8 Hz, 2H), 7.46 (d, J = 8 Hz, 4H), 7.18(s, 2H), 2.64 (heptet, J = 6 Hz, 4H), 1.64 (s, 6H), 1.33 (d, J = 7.2 Hz, 12H), 1.10 (d, J = 7.2 Hz, 12H) ppm. ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): 22.95, 23.80, 26.23, 29.08, 124,78, 126.24, 131.22, 134.94, 147.03, 173.8 ppm. Anal. Calcd for C$_{31}$H$_{42}$N$_2$O$_4$-Pd (**1**): C,60.68; H, 6.85, N, 4.57. Found: C, 60.61; H, 7.01; N, 4.48.

Synthesis of (IPr)Pd(OOCCF$_3$)$_2$ (H$_2$O) (2). Pd(OOCCF$_3$)$_2$ (156.7 mg, 0.5 mmol) recrystallized from benzene was suspended in toluene, and IPr (194 mg, 0.5 mmol) was added. The mixture was stirred at room temperature for 1 h. The product crystallized from the mixture as yellow crystals. The solvent was evaporated under vacuum almost to dryness, and hexane was added. The product was filtered out as an off-yellow powder and washed with three 20 mL portions of hexanes. Yield: 86% (309 mg, 0.43 mmol). Crystals suitable for diffraction study were grown from CH$_2$Cl$_2$/hexanes solutions. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): 7.66 (t, J = 8 Hz, 2H), 7.48 (d, J = 7.6 Hz, 4H), 7.24 (s, 2H), 2.66 (heptet, J = 6.8 Hz, 4H), 1.28 (d, J = 6.8 Hz, 12H), 1.08 (d, J = 6.8 Hz, 12H) ppm. ^{13}C NMR (125 MHz, CD$_2$Cl$_2$): 23.93, 25.05, 27.35, 29.99, 125,96, 127.77, 131.22, 133.77, 147.99, 173.2 ppm. Anal. Calcd for C$_{31}$H$_{38}$F$_6$N$_2$O$_5$Pd (**2**): C, 50.34; H, 5.14, N, 3.79. Found: C, 51.01; H, 5.25; N, 3.81.

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Supporting Information Available: Text giving experimental details for the synthesis of nucleophilic carbene/palladium complexes **1** and **2**, catalysis protocol, and product isolation and tables giving crystallographic data for **1** and **2**; crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Method adapted from: Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 9889−9890.