ORGANOMETALLICS

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Cyclometalated 2-Phenylimidazole Palladium Carbene Complexes in the Catalytic Suzuki−Miyaura Cross-Coupling Reaction

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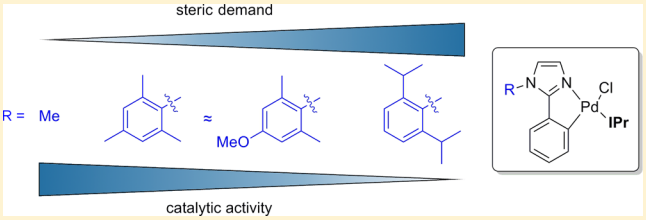
Supporting Information

ABSTRACT: We present the syntheses of 12 cyclometalated palladium C^N 2-phenylimidazole carbene complexes with different *N*-1 groups as well as different substituents at the C-2 phenyl group of the cyclometalating imidazole. We investigated the influence of these substituents by comparing the catalytic performance of the complexes in the Suzuki−Miyaura cross-coupling reaction of aryl chlorides. We can show a strong dependence between the steric demand of the *N*-1 substituent of the cyclometalating imidazole and the catalytic activity in the cross-coupling reaction. The most active complex shows a wide substrate scope, where several aryl as well as benzyl chlorides could be coupled with different boronic acids in excellent yields using very low catalyst concentrations of 0.05 mol %.



INTRODUCTION

Palladium-catalyzed cross-coupling reactions are one of the most important carbon−carbon bond-forming processes.[1−6] Nowadays, the Suzuki−Miyaura cross-coupling reaction has become a standard tool in natural product syntheses.[7] Although there are some ligand-free systems that allow for the coupling of aryl chlorides,[8−11] the development of new ligands led to an improvement of the catalytic activity, and due to the introduction of tertiary alkyl phosphane[12−14] or sterically demanding *N*-heterocyclic carbene (NHC) ligands,[15−20] even the reaction of aryl chlorides under mild reaction conditions could be accomplished in high yields.

Not only can the development of new ligands lead to improvements but also the design of new precatalyst structures can increase the catalytic activity as they initiate the formation of the catalytically active species in the cross-coupling reaction. It is often reported in the literature that a palladium source and the phosphane or the imidazolium salt (as carbene precursor) were added to the reaction mixture and an in situ formation of a Pd(0)-L complex was postulated. However, it is unlikely that a quantitative in situ complex formation occurs in a short reaction time, which leads to a waste of palladium source and ligand. In many cases, it was found that defined palladium complexes show a better activity than similar in situ systems.[16,21,22]

Several air-stable (NHC)-palladium(II) precatalysts have been reported in the literature. (NHC)-palladium(II) complexes with ligands (e.g., 3-chloropyridine[23] and 1-methylimidazole[24,25]) and complexes with acetylacetonate[26] or allyl counterions,[27,28] as well as others,[29−32] show high catalytic activities in various cross-coupling reactions.[21,33,34] Most important for the design of the palladium(II) precatalyst structures is a fast Pd(0)-L formation under the cross-coupling conditions. For example, the higher activity of (NHC)-palladium cinnamyl complexes compared to the corresponding allyl complexes was explained by a faster Pd(0)-L formation in the case of the cinnamyl complexes.[35]

Another promising class of air-stable palladium(II) precatalysts are NHC- or phosphane-ligated palladacycles. (NHC)- or phosphane-palladium complexes with cyclometalating ligands, such as *N*,*N*-dimethyl-2-aminobiphenyl,[36,37] *N*,*N*-dimethylbenzylamine,[38] 2-aminobiphenyl,[39,40] and others, have been reported.[41−44] The fast activation process for these types of precatalysts is proposed to occur via a reductive elimination of the cyclometalating ligand, resulting in the release of the catalytically active monoligated Pd(0) species.

Herein, we report our results on (NHC)-palladium complexes with cyclometalating 2-phenyl-imidazoles. They are of general interest as these ligands allow for the modification of the *N*-1 substituent as well as different substituents at the C-2 phenyl ring and the investigation of steric and electronic effects on the catalytic activity.

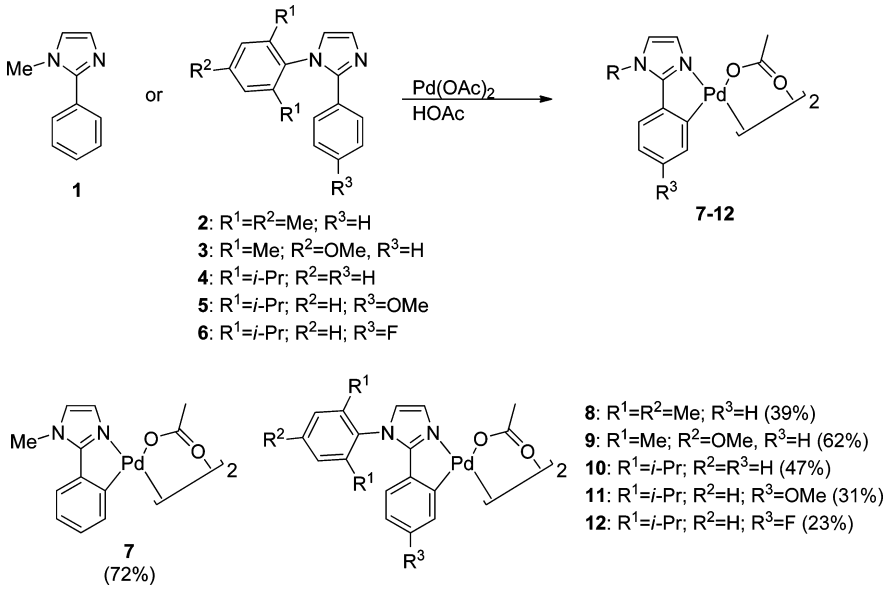
RESULTS AND DISCUSSION

Synthesis and Characterization. The treatment of imidazoles **1**−**6** with palladium(II) acetate in glacial acetic acid afforded the dimeric palladacycles **7**−**12** (Scheme 1). The imidazoles **2**−**6** were synthesized according to a recently reported method.[45] We confirmed the formation of all reported complexes by standard techniques like ^{1}H and ^{13}C NMR spectroscopy as well as elemental analysis. In the case of **10**, we could determine the solid-state structure that contains two additional dichloromethane molecules per formula unit [**10**·2(CH_2Cl_2)] (Figure 1).

Received: April 24, 2014
Published: July 23, 2014

   dx.doi.org/10.1021/om5004336 | *Organometallics* 2014, 33, 3966−3976

Scheme 1. Syntheses of the μ-Acetato Palladium Dimers 7−12



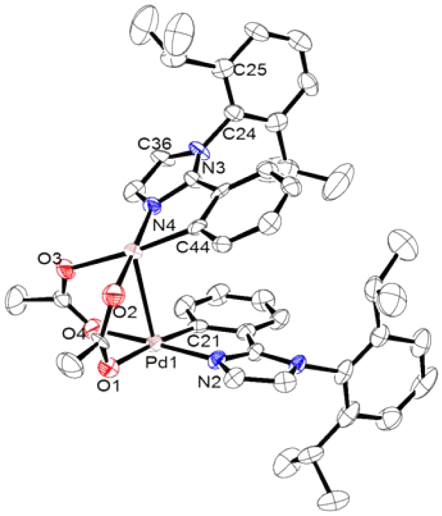


Figure 1. ORTEP drawing of complex [**10**·2(CH_2Cl_2)]. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and the solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−N(2) 1.976(5), Pd(1)−C(21) 1.966(7), Pd(1)−O(1) 2.131(5), Pd(1)−O(4) 2.045(6), Pd(1)−Pd(2) 2.822(1); C(21)−Pd(1)−N(2) 81.6(3), N(2)−Pd(1)−O(1) 94.1(2), N(2)−Pd(1)−Pd(2) 100.3(2).

The palladium atoms in the solid-state structure of **10** are coordinated in a square-planar fashion, bidentate by one cyclometalated carbon atom and one nitrogen atom of the imidazole and monodentate by one oxygen atom of both acetate ions. We found palladium−carbon distances of 1.966(7) Å [Pd(1)−C(21)] and palladium−nitrogen distances of 1.976(5) Å [Pd(1)−N(2)]. The trans effect of the carbon atoms resulted in longer palladium−oxygen bonds [2.131(5) Å for Pd(1)−O(1)] trans to the carbon atoms compared to the palladium−oxygen bonds [2.045(6) Å for Pd(1)−O(4)] trans to the nitrogen atoms. Because of the bridging acetate ions, the palladium atoms are in close proximity with a Pd−Pd distance of 2.822(1) Å. The complex forms a U-shaped geometry in which the angle between the planes of the two palladacycles is 35°. The dihedral angle between the diisopropylphenyl groups and the cyclometalated ring is found to be 86(1)° [C(25)−C(24)−N(3)−C(36)].

We then added a well-known and readily available NHC ligand, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**IPr**), 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (**IMes**), or 1,3-bis(4-methylphenyl)imidazol-2-ylidene (**ITol**). Treatment of the dimeric palladacycles **7**−**12** with the free *N*-heterocyclic carbene or its corresponding imidazolium salt led to the air- and moisture-stable, monomeric complexes **13**−**21**. When chloride ions are present in the reaction mixture—either by addition of potassium chloride or by using the imidazolium chloride—the chloro complexes **13**−**18** (Scheme 2) are formed in yields of 12%−62%, whereas, in the absence of chloride ions, the acetato complexes **19**−**21** could be isolated in yields of 33%−44% (Scheme 3). With the exception of **13b**, all complexes show excellent solubility in various solvents, such as dichloromethane, tetrahydrofuran, or acetone. Surprisingly, **13b** is only poorly soluble in these solvents at room temperature, which might be caused by a higher degree of organization in the solid state.

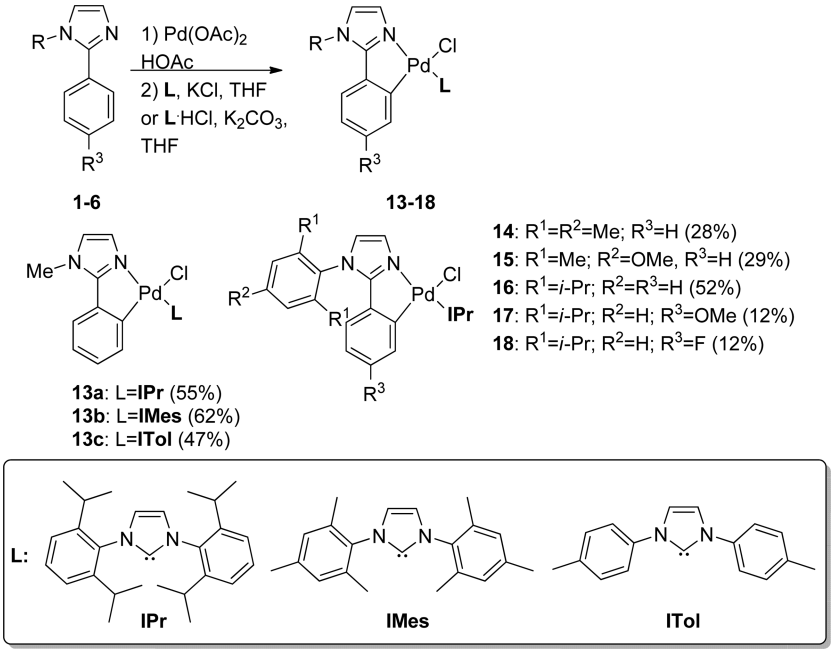
We were also able to determine the solid-state structure of complex **13a** (Figure 2). The palladium atom is coordinated by the cyclometalated phenylimidazole, a chloride ion, and the carbene carbon atom trans to the nitrogen atom of the imidazole with a palladium−carbene carbon distance of 1.989(3) Å [Pd(1)−C(11)]. Compared to the palladium−carbon and palladium−nitrogen bonds in the solid state of the dimeric palladacycle **10**, the corresponding bonds in the solid-state structure of **13a** are slightly longer with a palladium−carbon bond length of 2.008(4) Å [Pd(1)−C(10)] and a palladium−nitrogen bond length of 2.053(3) Å [Pd(1)−N(2)]. The dihedral angle between the central five-membered ring of the **IPr** ligand and the plane of the cyclometalated ligand is found to be 68.4(3)° [N(3)−C(11)−Pd(1)−C(l1)].

For the synthesis of the acetato complexes, we used the isolated dimers (**7**, **9**, and **10**) and purified the products by recrystallization (Scheme 3).

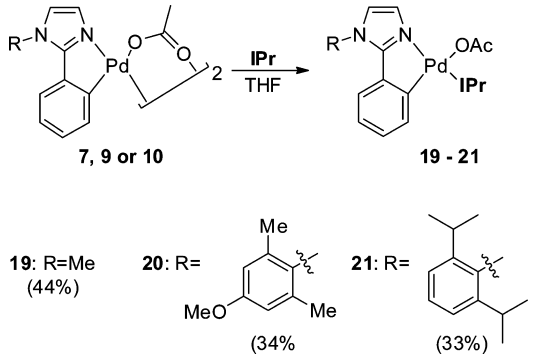
The solid-state structure of complex **21** (Figure 3) shows the carbene ligand in a similar orientation as observed in the structure of **13a**. It is located trans to the nitrogen atom with a

dx.doi.org/10.1021/om5004336 | *Organometallics* 2014, 33, 3966−3976

Scheme 2. Syntheses of the Chloro Complexes 13−18



Scheme 3. Syntheses of the Acetato Complexes 19−21



palladium−carbene carbon distance of 1.991(4) Å [Pd(1)−C(22)]. Compared to the solid-state structure of **10**, one finds longer palladium−carbon [2.010(4) Å for Pd(1)−C(21)] and palladium−nitrogen bonds [2.058(3) Å for Pd(1)−N(2)] in the solid-state structure of **21**.

To check whether cationic species of this type are stable, we prepared an acetonitrile ligated complex from the chloro complex **13a** with silver tetrafluoroborate in a dichloromethane acetonitrile mixture (Scheme 4). The complex could be synthesized in a high yield and is air-stable.

Catalytic Studies. To investigate the catalytic activity of the synthesized complexes, we evaluated the reaction conditions for the Suzuki−Miyaura cross-coupling reaction using the test reaction of 4-chlorotoluene and phenylboronic acid with 1 mol % of complex **13a** within a reaction time of 1 h (Table 1). Initially, we ran the reaction in air with Cs_2CO_3 in different solvents (entries 1−6) and found that the reaction only took place in methanol, ethanol, and isopropanol. When *tert*-butanol, dioxane, or toluene was used, no product formation could be observed. When ethanol and methanol were used as solvents, good yields of 66% were obtained (entries 1 and 2), whereas, in isopropanol, only a low yield of 10% was observed. While varying the base (entries 7−10), we found that the strong bases

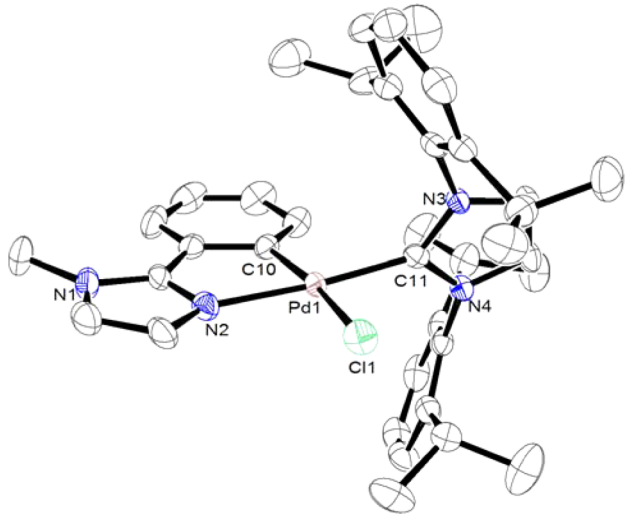


Figure 2. ORTEP drawing of complex **13a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−N(2) 2.053(3), Pd(1)−C(10) 2.008(4), Pd(1)−C(11) 1.989(3), Pd(1)−Cl(1) 2.383(1); N(2)−Pd(1)−C(10) 80.6(1), C(10)−Pd(1)−C(11) 97.1(1).

K_3PO_4 and KO*t*-Bu (entries 9 and 10) were superior, leading to quantitative yields within 1 h. With the solvent/base combination ethanol/K_3PO_4, we obtained quantitative yields also at lower reaction temperatures (entries 11−13). When the reaction was run at a temperature of 60 °C (entry 11), a quantitative yield was obtained within 1 h, whereas lower reaction temperatures required longer reaction times. At a temperature of 40 °C, it took 4 h to reach the same yield (entry 12) and 24 h at room temperature (entry 13). Therefore, even under mild reaction conditions, precatalyst **13a** allows for excellent yields with the inexpensive and environmentally friendly solvent/base combination ethanol/K_3PO_4.

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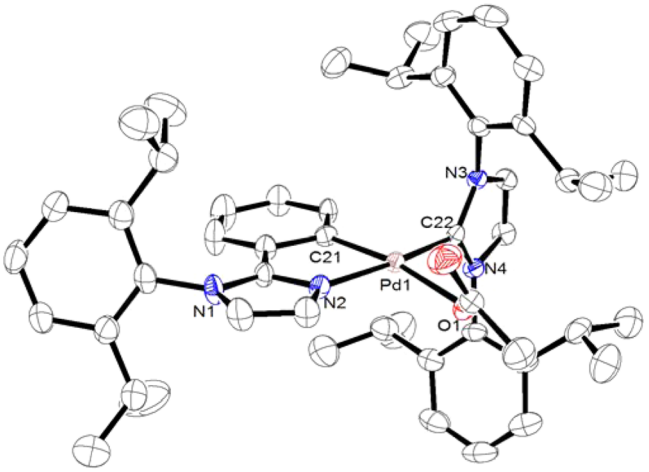


Figure 3. ORTEP drawing of complex **21**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−N(2) 2.058(3), Pd(1)−C(21) 2.010(4), Pd(1)−C(22) 1.991(4), Pd(1)−O(1) 2.115(3); N(2)−Pd(1)−C(21) 80.7(1), C(21)−Pd(1)−C(22) 91.3(2).

Scheme 4. Synthesis of Complex 22

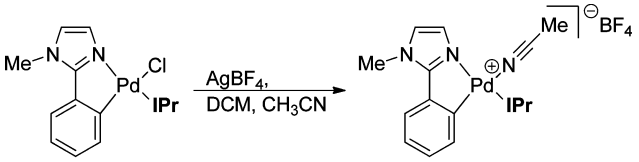
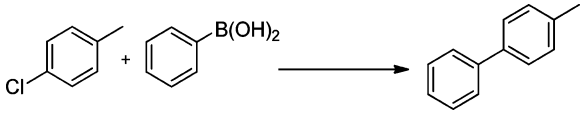


Table 1. Different Reaction Conditions for the Suzuki−Miyaura Coupling with Complex 13a[a]

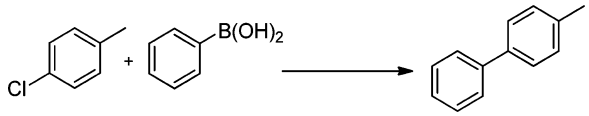


entry	solvent	base	T [°C]	yield[b] [%]
1	MeOH	Cs_2CO_3	80	66
2	EtOH	Cs_2CO_3	80	66
3	*i*-PrOH	Cs_2CO_3	80	10
4	*t*-BuOH	Cs_2CO_3	80	0
5	toluene	Cs_2CO_3	80	0
6	dioxane	Cs_2CO_3	80	0
7	EtOH	K_2CO_3	80	50
8	EtOH	Na_2CO_3	80	0
9	EtOH	K_3PO_4	80	100
10	EtOH	KO*t*-Bu	80	100
11	EtOH	K_3PO_4	60	100
12	EtOH	K_3PO_4	40	100[c]
13	EtOH	K_3PO_4	RT	100[d]
14	EtOH	K_3PO_4	60	100[e]

[a]Reaction conditions: 4-chlorotoluene (1 mmol), phenylboronic acid (1.5 mmol), base (2 mmol), **13a** (1 mol %), solvent (3 mL), air atmosphere, 1 h. Yield determined by GC−MS with dodecane as internal standard; average of two runs. [b]Yields determined by GC−MS with dodecane as internal standard; average of two runs. [c]The reaction time was 4 h. [d]The reaction time was 24 h. [e]The reaction was run with 1.1 equiv of phenylboronic acid.

We then investigated the necessary catalyst loading and reduced the amount of precatalyst **13a** in the cross-coupling reaction (Table 2). We found that, in air, the amount of

Table 2. Evaluation of the Catalyst Loading[a]



entry	mol %	atmosphere	yield[b] [%]
1	1	air	100
2	0.5	air	100
3	0.2	air	97
4	0.1	air	47
5	0.2	argon	100
6	0.1	argon	100
7	0.05	argon	100
8	0.01	argon	63
9	0.01	argon	80[c]

[a]Reaction conditions: 4-chlorotoluene (1 mmol), phenylboronic acid (1.1 mmol), K_3PO_4 (2 mmol), **13a**, ethanol (3 mL), 1 h, 60 °C. [b]Yields determined by GC−MS with dodecane as internal standard; average of two runs. [c]Reaction was run for 24 h.

precatalyst **13a** could be reduced to 0.2 mol % while still leading to an excellent yield of 97% (entry 3). When we further reduced the catalyst concentration of **13a**, only a yield of 47% could be obtained (entry 4), and even with longer reaction times, no significantly higher yield could be obtained.

When the cross-coupling reactions were performed under argon, the precatalyst concentration could be reduced even further (entries 5−9) while still leading to quantitative yields with precatalyst concentrations of 0.05 mol % (entry 7). For 0.01 mol % of **13a**, the yield decreased to 63% after a reaction time of 1 h (entry 8), but when the reaction time was extended to 24 h, a yield of 80% was obtained (entry 9).

Activity Differences of Complexes 13−22. We used these optimized reaction conditions to compare the catalytic activity of complexes **13**−**21**. We ran the cross-coupling reaction of 4-chlorotoluene and phenylboronic acid with 0.2 mol % precatalyst and determined the conversion of 4-chlorotoluene after different reaction times. The comparison for the chloro complexes **13**−**18** is shown in Figure 4.

After a short induction period of 10 min, complexes **13a** and **13b** showed similar initial reaction rates. However, whereas 4-chlorotoluene was fully converted within only 25 min by **13a**, the reaction rate in the case of complex **13b** slowed down significantly after 30 min, and the complex reached only a maximum conversion of 80%, even after 4 h. The catalytic activity of the formed **IMes**-Pd(0) species seems to be similar, but it decomposes prior to reaching full conversion. For the even smaller **ITol** ligand in **13c**, we did not observe any conversion, but fast palladium-black formation, probably due to the decomposition of the corresponding Pd(0) species.

Complexes **14** and **15** also showed high catalytic activities, with nearly the same reaction rates compared to **13a**, but longer induction periods of 25 min. Both catalysts then reached full conversion after approximately 60 min. The complexes with diisopropylphenyl groups at the cyclometalating imidazole ligand (**16**−**18**) are only moderately active. We observed long induction periods of 30 min and more for these precatalysts and only moderate reaction rates afterward. All cross-coupling

dx.doi.org/10.1021/om5004336 | *Organometallics* 2014, 33, 3966−3976

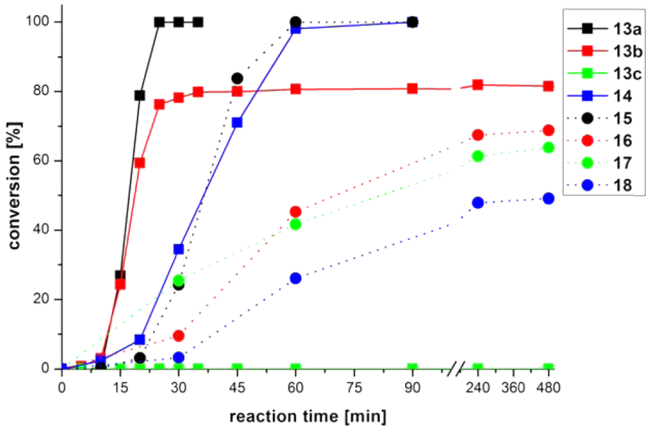


Figure 4. Comparison of the catalytic activity of complexes **13**–**18**. Reaction conditions: 4-chlorotoluene (2 mmol), phenylboronic acid (2.2 mmol), K_3PO_4 (4 mmol), [Pd] (0.2 mol %), ethanol (6 mL), 60 °C, dodecane as internal standard, argon. Conversions are averages of two runs.

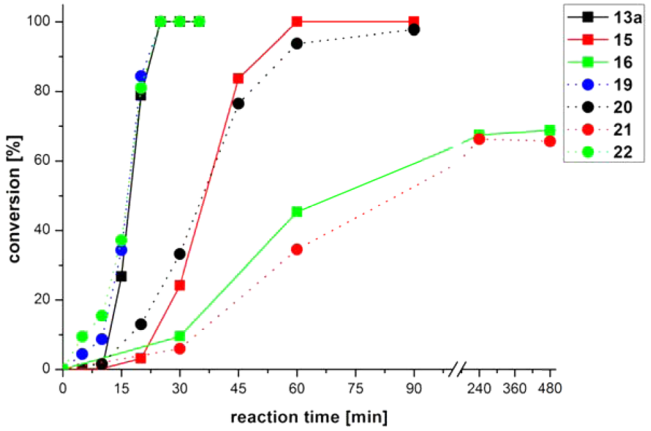


Figure 5. Comparison of the catalytic activity of complexes **13a**, **15**, **16**, and **19**–**22**. Reaction conditions: 4-chlorotoluene (2 mmol), phenylboronic acid (2.2 mmol), K_3PO_4 (4 mmol), [Pd] (0.2 mol %), ethanol (6 mL), 60 °C, dodecane as internal standard, argon. Conversions are averages of two runs.

reactions with complexes **16**–**18** led to conversions of 60–70% after a reaction time of 8 h without significant improvement at extended reaction times. Additionally, we tested the corresponding in situ system (0.2 mol % $Pd(OAc)_2$ + 0.2 mol % **IPr**·HCl) under these reaction conditions and found that this system only led to a low conversion of 10% even after an extended reaction time.

The comparison of the reaction rates of **13**–**18** indicates a strong dependence of the catalytic activity from the steric demand of the *N*-1 group of the cyclometalating imidazole. We found that the activity significantly decreases with increasing steric demand. The steric demand of the *N*-1 group seems to be crucial for the activation of the complex. For the complexes with the smallest *N*-1 substituents (**13a** and **13b**), the shortest induction period of 10 min was found; the equally demanding *N*-1 substituents in **14** and **15** needed 25 min, whereas the *N*-1 substituents in **16**–**18** lead to the longest induction periods. Additionally, the comparison of complexes **14** and **15** indicates that there is no influence of the electronic properties of the *N*-1 phenyl group as the mesityl group in **14** led to the same induction period and reaction rate as the 2,6-dimethyl-4-methoxyphenyl group in **15**. This can be explained by the perpendicular arrangement of the *N*-1 phenyl group to the plane of the imidazole ring, which prevents conjugation. Comparing complexes **16**–**18**, we found the effect of the C-2 phenyl substituents at the cyclometalating imidazole ligand to be insignificant. The cross-coupling reactions with complexes **16**–**18** led to nearly the same conversions.

To investigate the influence of the anion of the precatalyst, we also compared the acetato complexes **19**–**21** and the acetonitrile complex **22** with their corresponding chloro complexes (Figure 5). Therefore, we used the acetato complexes with methyl (**19**), 2,6-dimethyl-4-methoxyphenyl (**20**), and 2,6-diisopropylphenyl (**21**) as *N*-1 substituent, whose corresponding chloro complexes showed different levels of activity.

For all acetato complexes, nearly the same catalytic performance was found compared to their corresponding chloro complexes (**13a** vs **19**, **15** vs **20**, and **16** vs **21**). The more weakly bound acetate had no influence on the induction period or the reaction rate afterward. Compared to complexes **13a** and **19**, the acetonitrile complex **22** shows a comparable catalytic performance. Since the investigated precatalysts with different anions showed similar induction periods and reaction rates, an influence of the anion on the activation process can be ruled out.

Activation Process. Some years ago, Nolan et al. proposed an activation mechanism for cyclometalated *N*,*N*-dimethyl-2-aminobiphenyl palladium(II) carbene complexes[36] with a chloride counterion that also seems to be operative in our case. After an anion metathesis, a palladium(II) alkoxide complex is formed, which can undergo a *β*-hydride elimination to generate a palladium(II) hydrido complex. Subsequently, the palladium(II) hydrido complex liberates the catalytically active (NHC)-Pd(0) species by reductive elimination of a C–H bond.

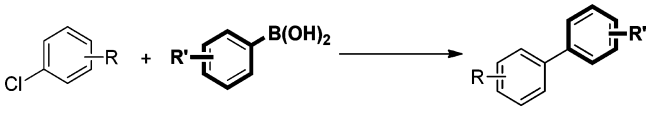
Several of our observations are in agreement with this mechanism. We found that the cross-coupling reaction with precatalyst **13a** only occurs in alcoholic solvents that can undergo a *β*-hydrogen elimination (Table 1). For further validation, we treated complex **13a** in ethanol with an excess of K_3PO_4 at 60 °C and were able to isolate the ligand 1-methyl-2-phenylimidazole in quantitative yield.

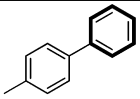
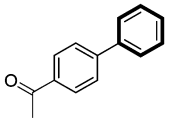
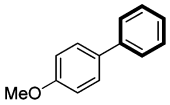
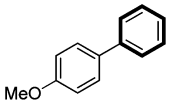
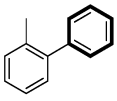
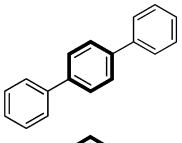
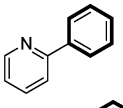
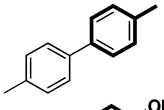
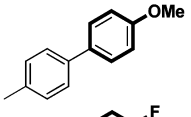
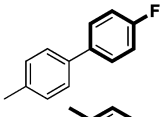
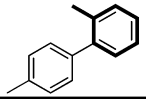
Substrate Scope. As demonstrated before, the catalyst precursor **13a** is highly active even at low catalyst concentrations. We, therefore, tested the scope of precatalyst **13a** in the Suzuki–Miyaura cross-coupling reaction using different *para*- and *ortho*-substituted aryl chlorides and boronic acids at low catalyst concentrations (Table 3). 4-Chlorotoluene as well as 4-chloroacetophenone was coupled with 0.05 mol % of **13a** in nearly quantitative yields (entries 1 and 2), whereas the more challenging 4-chloroanisole (entries 3 and 4) required a higher precatalyst amount and reaction temperature to obtain a high yield. When 1,4-dichlorobenzene (entry 6) was used, both chloro groups were coupled with 2.2 equiv of phenylboronic acid to obtain *para*-terphenyl in quantitative yield without the need to increase the amount of precatalyst. 2-Chloropyridine (entry 7) was converted in high yields, although an increased reaction time of 24 h was required.

The use of different boronic acids led to good to excellent yields (entries 8–11), and we also extended the substrate scope to benzyl chlorides (Table 4). With 0.1 mol % of precatalyst **13a**, we obtained full conversion for most substrates to the corresponding diaryl methanes within 2 h. Neither substituents

dx.doi.org/10.1021/om5004336 | *Organometallics* 2014, 33, 3966–3976

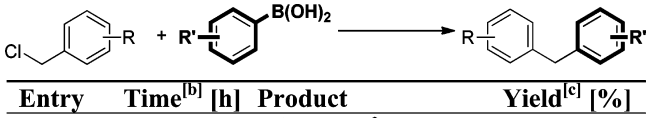
Table 3. Scope of the Suzuki−Miyaura Coupling of Aryl Chlorides with 13a[a,b,c,d,e]

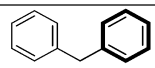
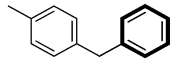
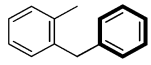
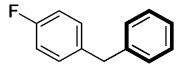
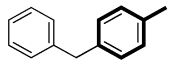
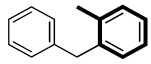
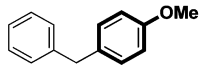
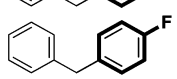
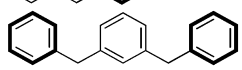
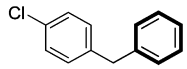
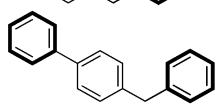
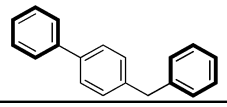


Entry	Time[b] [h]	Product	Yield[c] [%]
1	1		96
2	1		100
3	1		71
4	1		90[d]
5	4		82
6	6		100[e]
7	24		88
8	1		96
9	1		81
10	1		89
11	1		82

[a]Reaction conditions: aryl chloride (1 mmol), phenylboronic acid (1.1 mmol), K_3PO_4 (2 mmol), **13a** (0.05 mol %), ethanol (3 mL), 60 °C, argon. [b]Reaction time was monitored by GC−MS. [c]Isolated yield; average of two runs. [d]Reaction was run with 0.1 mol % of **13a** at 80 °C. [e]Reaction was run with 2.2 equiv of phenylboronic acid and 4 equiv of K_3PO_4.

Table 4. Scope of the Suzuki−Miyaura Coupling of Benzyl Chlorides with 13a[a,b,c,d,e]



Entry	Time[b] [h]	Product	Yield[c] [%]
1	2		96
2	2		100
3			95
4	2		100
5	2		100
6	2		99
7	2		98
8	2		99
9	3		97[d]
10	2		54[e]
			23
11	3		84[d]

[a]Reaction conditions: benzyl chloride (1 mmol), phenylboronic acid (1.1 mmol), K_3PO_4 (2 mmol), **13a** (0.1 mol %), ethanol (3 mL), 60 °C, argon. [b]Reaction time was monitored by GC−MS. [c]Isolated yield; average of two runs. [d]Reaction was run with 2.2 equiv of phenylboronic acid and 4 equiv of K_3PO_4. [e]Reaction was run with 1.0 equiv of phenylboronic acid, resulting in the formation of mono (54%) and doubly coupled (23%) products.

at the benzyl chlorides nor substituents of the boronic acids showed a significant influence on the yield (entries 1−8). We were also able to couple 1,3-bis(chloromethyl)benzene (entry 9) in high yields without the need to increase the amount of precatalyst. For the competition experiment of the cross-coupling of aryl versus benzyl chlorides, we used the substrate 1-chloro-4-(chloromethyl)benzene (entry 10). With 1.0 equiv of phenylboronic acid, we obtained the coupling product of the benzylic group as the main product in 54% yield together with a side product in 23% yield, which turned out to be the product, where both chlorine atoms were coupled, as well as some remaining starting material. We found no product where the aryl chlorine group was coupled exclusively. We can conclude that the coupling of the benzylic chlorine atoms proceeds faster compared to those chlorine atoms bound to the aromatic ring. Toward the end of the reaction, as the concentration of the benzylic chlorine atoms becomes lower, the coupling of the chlorine atoms at the aromatic ring becomes competitive, leading to the observed product mixture. Increasing the amount of boronic acid (entry 11) leads to higher yields (84%) of the product where both chlorine atoms reacted.

CONCLUSION

In conclusion, we report the synthesis of 12 new C^N cyclometalated (NHC)-palladium imidazole complexes. The catalytic activity of these carbene-ligated palladacycles has been investigated in the Suzuki−Miyaura cross-coupling reaction of aryl chlorides with low catalyst concentrations. After induction periods of 10−30 min, most of the precatalysts led to full

dx.doi.org/10.1021/om5004336 | Organometallics 2014, 33, 3966−3976

conversion in short reaction times. We found a strong dependence between the steric demand of the *N*-1 substituent of the cyclometalating imidazole and the catalytic activity. The activity decreases with increasing steric demand, whereas C-2 phenyl substituents of the cyclometalating imidazole ligands as well as the counterion of the precatalyst showed no influence on the catalytic activity. For the most active precatalyst (**13a**), we could show that good yields could be obtained even with very low catalyst concentrations (0.05 mol %) for various aryl and benzyl chlorides substituted with electron-donating as well as electron-withdrawing groups.

EXPERIMENTAL SECTION

General Information. ^{1}H and ^{13}C NMR spectra were referenced internally using the resonances of the solvent (^{1}H: 7.26 and ^{13}C: 77.0 for $CDCl_3$). ^{19}F NMR spectra were referenced externally against (trifluoromethyl)benzene. The chemical shifts (δ) are given in parts per million (ppm), coupling constants J in Hz. Elemental analyses were performed by the microanalytical laboratory of our institute. Melting points are not corrected.

Dry tetrahydrofuran (THF) was obtained from a Braun Solvent Purification System. DCM, isohexane, and ethyl acetate were distilled prior to use. All other chemicals were used as received. Imidazoles **1**[46] and **2**−**6**,[45] 1,3-bis[2,6-diisopropylphenyl]-1*H*-imidazolium chloride (**IPr**·HCl),[47] 1,3-bis[2,4,6-trimethylphenyl]-1*H*-imidazolium chloride (**IMes**·HCl),[48] 1,3-bis[4-methylphenyl]-1*H*-imidazolium chloride (**ITol**·HCl),[49] and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**IPr**)[49] were prepared according to literature procedures.

Bis[μ-(acetato-κ*O*:κ*O*′)]bis[2-(1-methyl-1*H*-imidazol-2-yl-κN^3)phenyl-κ*C*]dipalladium(II) (7). Complex **7** was prepared similar to a literature procedure.[50] Under argon, imidazole **1** (230 mg, 1.5 mmol) and palladium(II) acetate (300 mg, 1.3 mmol) were dissolved in acetic acid (40 mL) and stirred for 90 min at 110 °C. Subsequently, the solvent was removed in vacuo, and the residue was dissolved in DCM (10 mL) and washed with water (10 mL). The aqueous phase was extracted with DCM (2 × 10 mL), the combined organic layers were dried over Na_2SO_4, and, after filtration, the solvent was removed. Purification by column chromatography on silica gel (chloroform/ethanol 95:5) gave **7** (310 mg, 72%) as a yellow solid containing a mixture of the trans and cis complexes (approximately 7:1). mp 220 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 0.2 H), 2.21 (s, 3 H), 2.30 (s, 0.2 H), 3.51 (s, 3 H), 3.66 (s, 0.4 H), 6.20 (d, J = 1.6 Hz, 1 H), 6.40 (d, J = 1.3 Hz, 0.2 H), 6.42 (d, J = 1.6 Hz, 1 H), 6.51 (d, J = 1.3 Hz, 0.2 H), 6.59 (m, 0.2 H), 6.66 (m, 1.2 H), 6.72 (s, 0.4 H), 6.79 (d, J = 4.4 Hz, 2 H), 6.87 (d, J = 7.6 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.5, 24.6, 34.7, 34.8, 119.4, 119.7, 120.0, 120.1, 122.5, 122.9, 125.4, 125.5, 126.2, 126.7, 132.6, 133.1, 134.0, 134.5, 146.7, 147.1, 152.1, 152.9, 180.3, 181.2, 182.3. Anal. Calcd $C_{24}H_{24}N_4O_4Pd_2$ (645.31): C, 44.67; H, 3.75; N, 8.68. Found: C, 44.64; H, 3.72; N, 8.56.

Bis[μ-(acetato-κ*O*:κ*O*′)]bis[2-(1-(2,4,6-trimethylphenyl)-1*H*-imidazol-2-yl-κN^3)phenyl-κ*C*]dipalladium(II) (8). Imidazole **2** (400 mg, 1.5 mmol) and palladium(II) acetate (342 mg, 1.5 mmol) were dissolved in acetic acid (80 mL) and stirred for 6 h at 50 °C. Subsequently, the solvent was removed, and the residue was dissolved in DCM (10 mL), washed with a Na_2CO_3 solution (5%, 10 mL) and water (10 mL), and dried over Na_2SO_4, and, after filtration, the solvent was removed in vacuo. Recrystallization from acetone/methyl *t*-butyl ether gave **8** (251 mg, 39%) as a colorless solid. mp 183 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (s, 3 H), 1.88 (s, 3 H), 2.29 (s, 3 H), 2.37 (s, 3 H), 5.67 (dd, J = 1.4, 7.5 Hz, 1 H), 6.36 (d, J = 1.6 Hz, 1 H), 6.48 (td, J = 1.3, 7.6 Hz, 1 H), 6.71 (td, J = 1.4, 7.5 Hz, 1 H), 6.81 (d, J = 1.6 Hz, 1 H), 6.88 (br s, 1 H), 6.96 (br s, 1 H), 7.04 (dd, J = 1.1, 7.7 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.2, 17.4, 21.2, 24.4, 118.6, 119.9, 123.3, 126.7, 127.0, 128.9, 129.3, 132.1, 132.2, 134.6, 135.5, 139.6, 147.0, 152.1, 181.0. Anal. Calcd $C_{40}H_{40}N_4O_4Pd_2$ (853.61): C, 56.28; H, 4.72; N, 6.56. Found: C, 56.33; H, 4.75; N, 6.35.

Bis[μ-(acetato-κ*O*:κ*O*′)]bis[2-(1-(2,6-dimethyl-4-methoxyphenyl)-1*H*-imidazol-2-yl-κN^3)phenyl-κ*C*]dipalladium(II) (9). Imidazole **3** (400 mg, 1.4 mmol) and palladium(II) acetate (323 mg, 1.4 mmol) were dissolved in acetic acid (80 mL) and stirred for 6 h at 50 °C. Subsequently, the solvent was removed, and the residue was dissolved in DCM (10 mL), washed with a Na_2CO_3 solution (5%, 10 mL) and water, (10 mL) and dried over Na_2SO_4. After filtration, the solvent was removed in vacuo and the residue was washed with cold acetone (2 × 5 mL) and pentane (2 × 5 mL) to give **9** (396 mg, 62%) as an off-white solid. mp 260 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10 (s, 3 H), 1.88 (s, 3 H), 2.26 (s, 3 H), 3.82 (s, 3 H), 5.66 (dd, J = 1.3, 7.6 Hz, 1 H), 6.34 (d, J = 1.3 Hz, 1 H), 6.46 (td, J = 1.0, 7.41 Hz, 1 H), 6.57 (br s, 1 H), 6.64 (br s, 1 H), 6.69 (td, J = 1.3, 7.6 Hz, 1 H), 6.79 (d, J = 1.6 Hz, 1 H), 7.02 (td, J = 0.6, 7.3 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.5, 17.9, 24.4, 55.4, 113.0, 113.8, 118.9, 119.9, 123.3, 126.6, 127.0, 127.6, 132.2, 134.5, 137.2, 147.0, 152.3, 159.8, 181.0. Anal. Calcd $C_{40}H_{40}N_4O_6Pd_2$ (885.61): C, 54.25; H, 4.55; N, 6.33. Found: C, 54.44; H, 4.80; N, 6.14.

Bis[μ-(acetato-κ*O*:κ*O*′)]bis[2-(1-(2,6-diisopropylphenyl)-1*H*-imidazol-2-yl-κN^3)phenyl-κ*C*]dipalladium(II) (10). Imidazole **4** (400 mg, 1.3 mmol) and palladium(II) acetate (295 mg, 1.3 mmol) were dissolved in acetic acid (80 mL) and stirred for 6 h at 50 °C. Subsequently, the solvent was removed, and the residue was dissolved in DCM (10 mL), washed with a Na_2CO_3 solution (5%, 10 mL) and water, (10 mL) and dried over Na_2SO_4. After filtration, the solvent was removed in vacuo and the residue was dissolved in ethyl acetate (2 mL). Pentane (20 mL) was added to precipitate a solid, which was filtrated. This solid was dissolved in DCM (2 mL), and pentane was added (15 mL). The product was allowed to crystallize at −8 °C overnight and was filtrated afterward to give **10** (286 mg, 47%) as a yellow solid. mp 250 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.51 (br s, 3 H), 0.82−1.06 (m, 9 H), 1.83 (br m, 1 H), 2.29 (m, 4 H), 5.66 (dd, J = 1.4, 7.7 Hz, 1 H), 6.50 (td, J = 1.1, 7.5 Hz, 1 H), 6.60 (d, J = 1.6 Hz, 1 H), 6.68 (td, J = 1.3, 7.6 Hz, 1 H), 6.94 (d, J = 1.6 Hz, 1 H), 7.02 (dd, J = 1.1, 7.7 Hz, 1 H), 7.21 (m, 2 H), 7.46 (t, J = 7.7 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.0, 24.3, 24.6, 28.0, 120.5, 120.8, 123.0, 124.3, 126.0, 126.8, 130.5, 131.9, 132.2, 134.5, 145.9, 146.4, 147.3, 153.4, 181.4. Anal. Calcd $C_{46}H_{52}N_4O_4Pd_2$ (937.77): C, 58.92; H, 5.59; N, 5.97. Found: C, 59.18; H, 5.75; N, 6.22.

Bis[μ-(acetato-κ*O*:κ*O*′)]bis[2-(1-(2,6-diisopropylphenyl)-1*H*-imidazol-2-yl-κN^3)-5-methoxyphenyl-κ*C*]dipalladium(II) (11). Imidazole **5** (400 mg, 1.2 mmol) and palladium(II) acetate (269 mg, 1.2 mmol) were dissolved in acetic acid (80 mL) and stirred for 6 h at 50 °C. Subsequently, the solvent was removed, and the residue was dissolved in DCM (10 mL), washed with a Na_2CO_3 solution (5%, 10 mL) and water, (10 mL) and dried over Na_2SO_4. After filtration, the volume of the solvent was reduced to 2 mL and pentane (20 mL) was added. The solvents were removed in vacuo, and the solid was washed with cold acetone (3 × 3 mL) to give **11** (184 mg, 31%) as a yellow solid. mp 230 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.52 (br s, 3 H), 0.84−1.07 (m, 9 H), 1.86 (m, 1 H), 2.31 (m, 4 H), 3.64 (s, 3 H), 5.58 (d, J = 8.5 Hz, 1 H), 6.08 (dd, J = 2.5, 8.5 Hz, 1 H), 6.57 (d, J = 1.6 Hz, 1 H), 6.59 (d, J = 2.5 Hz, 1 H), 6.90 (d, J = 1.3 Hz, 1 H), 7.21 (br s, 2 H), 7.45 (t, J = 7.7 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.2, 24.3, 24.7, 28.1, 54.6, 109.9, 115.9, 119.6, 121.7, 124.2, 125.4, 127.3, 130.4, 131.8, 146.2, 146.4, 149.5, 153.8, 157.5, 181.6. Anal. Calcd $C_{48}H_{56}N_4O_6Pd_2$ (997.82): C, 57.78; H, 5.66; N, 5.61. Found: C, 57.85; H, 5.60; N, 5.74.

Bis[μ-(acetato-κ*O*:κ*O*′)]bis[2-(1-(2,6-diisopropylphenyl)-1*H*-imidazol-2-yl-κN^3)-5-fluorophenyl-κ*C*]dipalladium(II) (12). Imidazole **6** (396 mg, 1.2 mmol) and palladium(II) acetate (276 mg, 1.2 mmol) were dissolved in acetic acid (80 mL) and stirred for 6 h at 50 °C. Subsequently, the solvent was removed, the residue was dissolved in DCM (10 mL), washed with a Na_2CO_3 solution (5%, 10 mL) and water (10 mL), and dried over Na_2SO_4, and, after filtration, the solvent was removed in vacuo. Purification by column chromatography on silica gel (dichloromethane/ethanol 98:2) gave **12** (136 mg, 23%) as a yellow solid. mp 200 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.53 (br s, 3 H), 0.90 (d, J = 3.8 Hz, 3 H), 1.01 (m, 6 H), 1.85 (br s, 1 H), 2.28 (m, 4 H), 5.65 (dd, J = 5.4, 8.2 Hz, 1 H), 6.24 (td, J = 2.5, 8.7 Hz, 1 H), 6.64 (d, J = 1.6 Hz, 1 H), 6.71 (dd, J = 2.7, 9.0 Hz, 1 H), 6.92 (d, J = 1.6 Hz, 1 H), 7.24 (m, 2 H), 7.47 (t, J = 7.7 Hz, 1 H). ^{13}C NMR

dx.doi.org/10.1021/om5004336 | *Organometallics* 2014, 33, 3966−3976

(125 MHz, $CDCl_3$) δ 22.9, 23.2, 24.3, 24.7, 28.1, 109.8 (d, $^2J_{C,F}$ = 23.0 Hz), 119.0 (d, $^2J_{C,F}$ = 19.4 Hz), 120.6, 121.6 (d, $^3J_{C,F}$ = 8.5 Hz), 124.2, 124.5, 125.7, 130.7, 130.8, 131.5, 145.9, 146.4, 150.3, 152.7, 160.2 (d, $^1J_{C,F}$ = 253.1 Hz), 182.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ −111.6. Anal. Calcd $C_{46}H_{50}F_2N_4O_4Pd_2$ (973.75): C, 56.74; H, 5.18; N, 5.75. Found: C, 56.54; H, 5.09; N, 5.69.

***SP*-4-4-[1,3-Bis[2,6-diisopropylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene]chloro[2-(1-methyl-1*H*-imidazol-2-yl-κN^3)-phenyl-κC]palladium(II) (13a).** Under argon, imidazole **1** (271 mg, 1.7 mmol) and palladium(II) acetate (385 mg, 1.7 mmol) were dissolved in acetic acid (40 mL) and stirred for 90 min at 110 °C. Subsequently, the solvent was removed in vacuo, and the residue was dissolved in DCM (10 mL) and washed with water (10 mL). The aqueous phase was extracted with DCM (2 × 10 mL), and the combined organic layers were dried over Na_2SO_4. After filtration, the solvent was removed in vacuo. Under argon, **IPr** (666 mg, 1.7 mmol), KCl (800 mg, 10.7 mmol), and dry THF (10 mL) were added. The mixture was stirred for 1 day at room temperature, followed by filtration and the removal of the solvent in vacuo. Purification by column chromatography on silica gel (chloroform/ethyl acetate 9:1) gave **13a** (643 mg, 55%) as a colorless solid. mp 270 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78 (d, J = 6.6 Hz, 6 H), 1.02 (d, J = 6.9 Hz, 6 H), 1.18 (d, J = 6.9 Hz, 6 H), 1.49 (d, J = 6.3 Hz, 6 H), 3.30 (m, 4 H), 3.61 (s, 3 H), 6.27 (d, J = 1.3 Hz, 1 H), 6.71 (d, J = 7.6 Hz, 1 H), 6.80 (td, J = 7.4, 1.3 Hz, 1 H), 6.89 (td, J = 7.6, 0.9 Hz, 1 H), 7.07 (dd, J = 7.9, 1.3 Hz, 1 H), 7.16 (dd, J = 1.4, 7.7 Hz, 2 H), 7.16 (d, J = 1.6 Hz, 1 H), 7.23 (s, 2 H), 7.29 (dd, J = 7.6, 1.3 Hz, 2 H), 7.36 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.1, 23.2, 26.1, 26.5, 28.4, 29.0, 35.3, 120.5, 121.0, 122.6, 124.0, 124.2, 124.8, 125.3, 127.3, 129.8, 136.0, 137.6, 137.8, 145.0, 147.8, 152.1, 152.6, 180.1. Anal. Calcd $C_{37}H_{45}ClN_4Pd$ (687.65): C, 64.63; H, 6.60; N, 8.15. Found: C, 64.83; H, 6.79; N, 8.20.

***SP*-4-4-[1,3-Bis[2,4,6-trimethylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene]chloro[2-(1-methyl-1*H*-imidazol-2-yl-κN^3)-phenyl-κC]palladium(II) (13b).** Under argon, imidazole **1** (100 mg, 0.6 mmol) and palladium(II) acetate (129 mg, 0.6 mmol) were dissolved in acetic acid (20 mL) and stirred for 1 h at 110 °C. Subsequently, the solvent was removed in vacuo, and the residue was dissolved in DCM (5 mL) and washed with water (5 mL). The aqueous phase was extracted with DCM (2 × 5 mL), and the combined organic layers were dried over Na_2SO_4. After filtration, the solvent was removed in vacuo. Under argon, **IMes**·HCl (196 mg, 0.6 mmol), potassium carbonate (397 mg, 2.9 mmol), and dry THF (5 mL) were added and stirred at 60 °C overnight. Subsequently, the reaction mixture was cooled to 0 °C, and the solid was filtered and washed with cold THF (0 °C, 2 × 5 mL). The solid was extracted with hot chloroform (60 °C, 8 × 10 mL), and the solvent of the filtrate was removed in vacuo. Purification by column chromatography on silica gel (dichloromethane/ethyl acetate 9:1) gave **13b** (213 mg, 62%) as a colorless solid. mp 294 °C (dec.). ^{1}H NMR (500 MHz, DMSO−D_6) δ 2.15 (s, 6 H), 2.23 (s, 6 H), 2.30 (s, 6 H), 3.85 (s, 3 H), 6.64 (d, J = 7.6 Hz, 1 H), 6.83 (t, J = 7.6 Hz, 1 H), 6.86 (s, 2 H), 6.94 (m, 4 H), 7.07 (s, 1 H), 7.30 (d, J = 7.6 Hz, 1 H), 7.66 (s, 2 H). ^{13}C NMR (125 MHz, DMSO−D_6) δ 19.6, 20.0, 20.9, 35.4, 122.3, 122.4, 123.9, 124.5, 124.9, 126.6, 129.1, 129.5, 134.3, 136.6, 137.3, 137.4, 138.1, 140.2, 150.8, 152.4, 176.2. Anal. Calcd $C_{31}H_{33}ClN_4Pd$ (602.14): C, 61.70; H, 5.51; N, 9.28. Found: C, 61.77; H, 5.52; N, 9.13.

***SP*-4-4-[1,3-Bis[4-methylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene]chloro[2-(1-methyl-1*H*-imidazol-2-yl-κN^3)phenyl-κC]-palladium(II) (13c).** Under argon, imidazole **1** (100 mg, 0.6 mmol) and palladium(II) acetate (129 mg, 0.6 mmol) were dissolved in acetic acid (20 mL) and stirred for 1 h at 110 °C. Subsequently, the solvent was removed in vacuo, and the residue was dissolved in DCM (5 mL) and washed with water (5 mL). The aqueous phase was extracted with DCM (2 × 5 mL), and the combined organic layers were dried over Na_2SO_4. After filtration, the solvent was removed in vacuo. Under argon, **ITol**·HCl (164 mg, 0.6 mmol), potassium carbonate (397 mg, 2.9 mmol), and dry THF (5 mL) were added and stirred at 60 °C overnight. Subsequently, the reaction mixture was filtered, and the solvent was removed in vacuo. Purification by column chromatography on silica gel (dichloromethane/ethyl acetate 5:1) gave **13c** (147 mg, 47%) as a colorless solid. mp 269 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.29 (s, 6 H), 3.67 (s, 3 H), 6.08 (dd, J = 1.3 Hz, 7.6 Hz, 1 H), 6.53 (d, J = 1.3 Hz, 1 H), 6.72 (td, J = 1.3 Hz, 7.6 Hz, 1 H), 6.82 (td, J = 1.1, 7.5 Hz, 1 H), 7.06 (dd, J = 1.4, 7.7 Hz, 1 H), 7.19 (d, J = 8.5 Hz, 4 H), 7.26 (d, J = 1.6 Hz, 1 H), 7.38 (s, 2 H), 7.96 (d, J = 8.5 Hz, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 35.2, 120.9, 121.5, 122.7, 123.0, 125.3, 125.7, 127.8, 129.7, 136.5, 137.2, 137.89, 137.92, 151.9, 152.6, 174.8. Anal. Calcd $C_{27}H_{25}ClN_4Pd$ (547.39): C, 59.24; H, 4.60; N, 10.24. Found: C, 59.35; H, 4.48; N, 10.19.

***SP*-4-4-[1,3-Bis[2,6-diisopropylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene]chloro[2-(1-(2,4,6-trimethylphenyl)-1*H*-imidazol-2-yl-κN^3)phenyl-κC]palladium(II) (14).** Imidazole **2** (100 mg, 0.4 mmol) and palladium(II) acetate (86 mg, 0.4 mmol) were dissolved in acetic acid (20 mL) and stirred for 6 h at 50 °C. Subsequently, the solvent was removed, and the residue was dissolved in DCM (5 mL), washed with a Na_2CO_3 solution (5%, 5 mL) and water (5 mL), and dried over Na_2SO_4. After filtration, the solvent was removed in vacuo. Under argon, **IPr** (148 mg, 0.4 mmol), KCl (150 mg, 2.0 mmol), and dry THF (5 mL) were added. The mixture was stirred for 1 day at room temperature, followed by a filtration and the removal of the solvent in vacuo. Purification by column chromatography on silica gel (dichloromethane/ethyl acetate 30:1) gave **14** (84 mg, 28%) as a colorless solid. 298 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.72 (d, J = 6.6 Hz, 6 H), 1.04 (d, J = 6.9 Hz, 6 H), 1.15 (d, J = 6.9 Hz, 6 H), 1.53 (d, J = 6.6 Hz, 6 H), 1.84 (s, 6 H), 2.36 (s, 3 H), 3.31 (m, 4 H), 5.94 (dd, J = 1.3, 7.9 Hz, 1 H), 6.49 (d, J = 1.6 Hz, 1 H), 6.56 (td, J = 1.1, 7.5 Hz, 1 H), 6.65 (d, J = 6.6 Hz, 1 H), 6.71 (td, J = 1.3, 7.3 Hz, 1 H) 6.96 (s, 2 H), 7.17 (dd, J = 1.6, 7.6 Hz, 2 H), 7.22 (s, 2 H), 7.33 (dd, J = 1.3, 7.9 Hz, 2 H), 7.40 (t, J = 7.6 Hz, 2 H), 7.49 (d, J = 1.6 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.5, 21.1, 22.8, 23.2, 26.0, 26.6, 28.4, 29.0, 118.7, 120.2, 122.7, 124.0, 124.3, 124.9, 127.1, 127.5, 129.3, 129.8, 133.0, 135.4, 136.1, 137.2, 137.5, 139.3, 145.1, 147.8, 152.2, 180.1. Anal. Calcd $C_{45}H_{53}ClN_4Pd$ (790.30): C, 68.26; H, 6.75; N, 7.08. Found: C, 68.43; H, 6.93; N, 6.94.

***SP*-4-4-[1,3-Bis[2,6-diisopropylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene]chloro[2-(1-(2,6-dimethyl-4-methoxyphenyl)-1*H*-imidazol-2-yl-κN^3)phenyl-κC]palladium(II) (15).** The synthesis of **15** was carried out as described above for **14** starting from imidazole **3** (100 mg, 0.4 mmol) and palladium(II) acetate (81 mg, 0.4 mmol). Purification by column chromatography on silica gel (dichloromethane/ethyl acetate 50:1) gave **15** (83 mg, 29%) as a colorless solid. mp 305 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.72 (d, J = 6.6 Hz, 6 H), 1.03 (d, J = 6.9 Hz, 6 H), 1.15 (d, J = 6.9 Hz, 6 H), 1.53 (d, J = 6.6 Hz, 6 H), 1.85 (s, 6 H), 3.31 (m, 4 H), 3.84 (s, 3 H), 5.95 (dd, J = 1.4, 7.7 Hz, 1 H), 6.48 (d, J = 1.6 Hz, 1 H), 6.57 (td, J = 1.1, 7.5 Hz, 1 H), 6.66 (m, 3 H), 6.71 (td, J = 1.3, 7.6 Hz, 1 H), 7.17 (dd, J = 1.4, 7.7 Hz, 2 H), 7.22 (s, 2 H), 7.33 (dd, J = 1.6, 7.6 Hz, 2 H), 7.40 (t, J = 7.6 Hz, 2 H), 7.48 (d, J = 1.6 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.9, 22.8, 23.2, 26.0, 26.6, 28.4, 29.0, 55.4, 113.6, 118.9, 120.2, 122.8, 124.0, 124.3, 124.9, 127.1, 127.5, 128.5, 129.8, 136.1, 137.1, 137.2, 137.5, 145.1, 147.8, 152.2, 152.4, 159.6, 180.1. Anal. Calcd $C_{45}H_{53}ClN_4OPd$ (806.29): C, 66.91; H, 6.61; N, 6.94. Found: C, 67.02; H, 6.54; N, 6.88.

***SP*-4-4-[1,3-Bis[2,6-diisopropylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene]chloro[2-(1-(2,6-diisopropylphenyl)-1*H*-imidazol-2-yl-κN^3)phenyl-κC]palladium(II) (16).** The synthesis of **16** was carried out as described above for **14** starting from imidazole **4** (100 mg, 0.3 mmol) and palladium(II) acetate (74 mg, 0.3 mmol). Purification by column chromatography on silica gel (dichloromethane/ethyl acetate 20:1) gave **16** (143 mg, 52%) as a colorless solid. mp 290 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.65 (d, J = 6.6 Hz, 6 H), 0.86 (d, J = 6.9 Hz, 6 H), 1.03 (dd, J = 1.6, 6.9 Hz, 12 H), 1.14 (d, J = 6.6 Hz, 6 H), 1.54 (d, J = 6.6 Hz, 6 H), 2.37 (spt, J = 6.8 Hz, 2 H), 3.24 (spt, J = 6.7 Hz, 2 H), 3.34 (spt, J = 6.6 Hz, 2 H), 5.84 (dd, J = 1.3, 7.6 Hz, 1 H), 6.51 (dd, J = 0.9, 7.6 Hz, 1 H), 6.53 (d, J = 1.6 Hz, 1 H), 6.62 (d, J = 6.9 Hz, 1 H), 6.68 (td, J = 1.3, 7.6 Hz, 1 H), 7.18 (dd, J = 1.4, 7.7 Hz, 2 H), 7.22 (s, 2 H), 7.26 (d, J = 7.9 Hz, 2 H), 7.34 (dd, J = 1.4, 7.7 Hz, 2 H), 7.41 (t, J = 7.6 Hz, 2 H), 7.47 (d, J = 7.9 Hz, 1 H), 7.49 (d, J = 1.3 Hz, 1 H). ^{13}C NMR (125 MHz,

dx.doi.org/10.1021/om5004336 | *Organometallics* 2014, 33, 3966−3976

$CDCl_3$) δ 22.8, 23.0, 23.2, 24.5, 25.9, 26.6, 27.9, 28.4, 29.0, 120.2, 121.4, 122.4, 124.1, 124.3, 125.1, 126.8, 127.4, 129.8, 130.2, 132.7, 136.1, 136.9, 137.6, 145.2, 146.2, 147.8, 152.3, 153.1, 180.2. Anal. Calcd $C_{48}H_{59}ClN_4Pd$ (832.36): C, 69.14; H, 7.13; N, 6.72. Found: C, 68.87; H, 7.12; N, 6.58.

***SP*-4-4-[1,3-Bis[2,6-diisopropylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene]chloro[2-(1-(2,6-diisopropylphenyl)-1*H*-imidazol-2-yl-κN^3)-5-methoxyphenyl-κC]palladium(II) (17).** The synthesis of **17** was carried out as described above for **14** starting from imidazole **5** (100 mg, 0.3 mmol) and palladium(II) acetate (67 mg, 0.3 mmol). Purification by column chromatography on silica gel (dichloromethane/ethyl acetate 70:1) gave **17** (32 mg, 12%) as a light yellow solid. 295 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.60 (d, J = 6.6 Hz, 6 H), 0.85 (d, J = 6.6 Hz, 6 H), 1.02 (d, J = 6.9 Hz, 6 H), 1.03 (d, J = 6.6 Hz, 6 H), 1.16 (d, J = 6.6 Hz, 6 H), 1.53 (d, J = 6.3 Hz, 6 H), 2.38 (spt, J = 6.9 Hz, 2 H), 3.17 (spt, J = 6.6 Hz, 2 H), 3.38 (spt, J = 6.6 Hz, 2 H), 3.63 (s, 3 H), 5.78 (d, J = 8.5 Hz, 1 H), 6.06 (dd, J = 2.5, 8.5 Hz, 1 H), 6.14 (d, J = 2.5 Hz, 1 H), 6.49 (d, J = 1.6 Hz, 1 H), 7.19 (dd, J = 1.4, 7.7 Hz, 2 H), 7.23 (s, 2 H), 7.25 (d, J = 7.9 Hz, 2 H), 7.33 (dd, J = 1.4, 7.7 Hz, 2 H), 7.42 (t, J = 7.6 Hz, 2 Hz), 7.43 (d, J = 1.6 Hz, 1 H), 7.47 (t, J = 7.6 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.4, 23.0, 23.1, 24.5, 25.9, 26.7, 27.9, 28.4, 29.0, 54.4, 105.8, 119.5, 122.1, 124.2, 124.3, 125.28, 125.33, 126.3, 129.9, 130.08, 130.14, 132.7, 136.1, 145.3, 146.4, 147.9, 153.2, 153.4, 157.6, 180.3. Anal. Calcd $C_{49}H_{61}ClN_4OPd$ (862.36): C, 68.12; H, 7.12; N, 6.49. Found: C, 67.99; H, 7.20; N, 6.28.

***SP*-4-4-[1,3-Bis[2,6-diisopropylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene]chloro[2-(1-(2,6-diisopropylphenyl)-1*H*-imidazol-2-yl-κN^3)-5-fluorophenyl-κC]palladium(II) (18).** The synthesis of **18** was carried out as described above for **14** starting from imidazole **6** (100 mg, 0.3 mmol) and palladium(II) acetate (71 mg, 0.3 mmol). Purification by column chromatography on silica gel (dichloromethane/ethyl acetate 70:1) gave **18** (33 mg, 12%) as a colorless solid. mp 290 °C (dec.) ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.68 (d, J = 6.6 Hz, 6 H), 0.85 (d, J = 6.9 Hz, 6 H), 1.03 (d, J = 6.9 Hz, 6 H), 1.04 (d, J = 6.9 Hz, 6 H), 1.18 (d, J = 6.9 Hz, 6 H), 1.53 (d, J = 6.3 Hz, 6 H), 2.34 (spt, J = 6.8 Hz, 2 H), 3.24 (m, 4 H), 5.82 (dd, J = 5.8, 8.7 Hz, 1 H), 6.25 (td, J = 2.5, 8.7 Hz, 1 H), 6.31 (dd, J = 2.5, 9.8 Hz, 1 H), 6.54 (d, J = 1.6 Hz, 1 H), 7.20 (dd, J = 1.4, 7.7 Hz, 2 H), 7.24 (s, 2 H) 7.25 (d, 2 H, partial overlapping with solvent peak), 7.34 (dd, J = 1.4, 7.7 Hz, 2 H), 7.43 (t, J = 7.6 Hz, 2 H), 7.48 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.3, 23.0, 23.1, 24.5, 26.0, 26.6, 27.9, 28.5, 29.0, 108.9 (d, $^2J_{C,F}$ = 23.0 Hz), 120.2, 122.2 (d, $^3J_{C,F}$ = 8.4 Hz), 124.2, 124.3, 124.36 (d, $^2J_{C,F}$ = 18.2 Hz), 124.40, 125.4, 126.6, 130.0, 130.4, 132.3, 133.22, 133.24, 135.9, 145.2, 146.2, 147.8, 152.4, 155.3, 155.3, 160.6 (d, $^1J_{C,F}$ = 250.7 Hz), 178.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ −113.4. Anal. Calcd $C_{48}H_{58}ClFN_4Pd$ (851.87): C, 67.68; H, 6.86; N, 6.58. Found: C, 67.38; H, 6.93; N, 6.28.

***SP*-4-4-Acetato[1,3-bis[2,6-diisopropylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene][2-(1-methyl-1*H*-imidazol-2-yl-κN^3)-phenyl-κC]palladium(II) (19).** Under argon, complex **7** (100 mg, 0.2 mmol) and **IPr** (120 mg, 0.3 mmol) were dissolved in dry THF (5 mL) and stirred for 1 day at 40 °C. Subsequently, the solvent was removed in vacuo, and the residue was washed with diethyl ether (3 × 3 mL) and recrystallized from dichloromethane/diethyl ether to give **19** (98 mg, 44%) as a colorless solid. mp 205 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82 (d, J = 6.6 Hz, 6 H), 1.00 (d, J = 6.9 Hz, 6 H), 1.22 (d, J = 6.9 Hz, 6 H), 1.37 (s, 3 H), 1.45 (d, J = 6.6 Hz, 6 H), 2.95 (spt, J = 6.6 Hz, 2 H), 3.30 (spt, J = 6.7 Hz, 2 H), 3.67 (s, 3 H), 6.41 (d, J = 1.3 Hz, 1 H), 6.58 (d, J = 7.6 Hz, 1 H), 6.77 (m, 2 H), 6.88 (t, J = 7.6 Hz, 1 H), 7.07 (dd, J = 1.3, 7.6 Hz, 1 H), 7.18 (dd, J = 1.4, 7.7 Hz, 2 H), 7.25 (s, 2 H), 7.33 (dd, J = 1.6, 7.9 Hz, 2 H), 7.39 (t, J = 7.9 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.7, 23.3, 26.1, 26.3, 26.5, 28.4, 28.8, 35.2, 121.1, 121.3, 122.7, 124.2, 124.4, 124.7, 125.6, 127.4, 129.9, 135.7, 137.6, 138.0, 144.9, 147.7, 148.9, 152.2, 178.4, 179.6. Anal. Calcd $C_{39}H_{48}N_4O_2Pd$ (711.24): C, 65.86; H, 6.80; N, 7.88. Found: C, 66.15; H, 7.03; N, 7.88.

***SP*-4-4-Acetato[1,3-bis[2,6-diisopropylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene][2-(1-(2,6-dimethyl-4-methoxyphenyl)-1*H*-imidazol-2-yl-κN^3)phenyl-κC]palladium(II) (20).** Under argon, complex **9** (100 mg, 0.1 mmol) and **IPr** (88 mg, 0.2 mmol) were dissolved in dry THF (5 mL) and stirred for 1 day at 40 °C. Subsequently, the solvent was removed in vacuo, and the residue was washed with diethyl ether (3 × 3 mL) and recrystallized from dichloromethane/diethyl ether to give **20** (64 mg, 34%) as a colorless solid. mp 141 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.76 (d, J = 6.6 Hz, 6 H), 1.01 (d, J = 6.9 Hz, 6 H), 1.19 (d, J = 6.9 Hz, 6 H), 1.48 (d, J = 6.3 Hz, 6 H), 1.53 (s, 3 H), 1.83 (s, 6 H), 2.99 (spt, J = 6.7 Hz, 2 H), 3.27 (spt, J = 6.9 Hz, 2 H), 3.83 (s, 3 H), 5.93 (dd, J = 1.4, 7.7 Hz, 1 H), 6.48 (d, J = 1.6 Hz, 1 H), 6.50 (d, J = 7.6 Hz, 1 H), 6.54 (td, J = 0.9, 7.6 Hz, 1 H), 6.67 (m, 3 H), 7.04 (d, J = 1.6 Hz, 1 H), 7.19 (dd, J = 1.6, 7.6 Hz, 2 H), 7.25 (s, 2 H), 7.35 (dd, J = 1.6, 7.9 Hz, 2 H), 7.41 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.9, 22.6, 23.1, 26.0, 26.2, 26.5, 28.5, 28.9, 55.4, 113.7, 119.5, 120.5, 122.8, 124.2, 124.4, 124.8, 127.5, 127.6, 128.4, 129.9, 135.7, 137.1, 137.3, 137.6, 145.0, 147.6, 148.8, 152.2, 159.6, 178.2, 179.5. Anal. Calcd $C_{47}H_{56}N_4O_3Pd$ (831.39): C, 67.90; H, 6.79; N, 6.74. Found: C, 67.80; H, 6.98; N, 6.67.

***SP*-4-4-Acetato[1,3-bis[2,6-diisopropylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene][2-(1-(2,6-diisopropylphenyl)-1*H*-imidazol-2-yl-κN^3)phenyl-κC]palladium(II) (21).** Under argon, complex **10** (100 mg, 0.1 mmol) and **IPr** (83 mg, 0.2 mmol) were dissolved in dry THF (5 mL) and stirred for 1 day at 40 °C. Subsequently, the solvent was removed in vacuo, and the residue was washed with diethyl ether (3 × 3 mL) and recrystallized from diethyl ether to give **21** (60 mg, 33%) as a colorless solid. mp 248 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.69 (d, J = 6.6 Hz, 6 H), 0.85 (d, J = 6.6 Hz, 6 H), 1.00 (d, J = 6.6 Hz, 6 H), 1.02 (d, J = 6.9 Hz, 6 H), 1.18 (d, J = 6.9 Hz, 6 H), 1.49 (d, J = 6.6 Hz, 6 H), 1.63 (s, 3 H), 2.35 (spt, J = 6.9 Hz, 2 H), 2.97 (spt, J = 6.7 Hz, 2 H), 3.26 (spt, J = 6.6 Hz, 2 H), 5.83 (dd, J = 1.4, 7.7 Hz, 1 H), 6.46 (d, J = 7.6 Hz, 1 H), 6.49 (td, J = 0.9, 7.6 Hz, 1 H), 6.52 (d, J = 1.6 Hz, 1 H), 6.63 (td, J = 1.4, 7.5 Hz, 1 H), 7.05 (d, J = 1.3 Hz, 1 H) 7.20 (dd, J = 1.4, 7.7 Hz, 2 H), 7.25 (m, 4 H), 7.36 (dd, J = 1.6, 7.6 Hz, 2 H), 7.43 (t, J = 7.6 Hz, 2 H), 7.46 (t, J = 7.9 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.6, 23.01, 23.04, 24.6, 25.96, 26.04, 26.5, 27.9, 28.4, 28.9, 120.7, 121.6, 122.4, 124.31, 124.33, 124.4, 125.0, 127.3, 127.6, 130.0, 130.3, 132.6, 135.8, 137.1, 137.7, 145.1, 146.2, 147.5, 148.9, 152.8, 178.0, 179.7. Anal. Calcd $C_{50}H_{62}N_4O_2Pd$ (857.49): C, 70.04; H, 7.29; N, 6.53. Found: C, 69.67; H, 7.55; N, 6.53.

***SP*-4-3-Acetonitrile[1,3-bis[2,6-diisopropylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene][2-(1-(2,6-diisopropylphenyl)-1*H*-imidazol-2-yl-κN^3)phenyl-κC]palladium(II) Tetrafluoroborate (22).** Complex **13a** (50 mg, 0.07 mmol) and silver tetrafluoroborate (15 mg, 0.08 mmol) were dissolved in DCM (4.5 mL) and acetonitrile (0.5 mL) and stirred at room temperature overnight. The reaction mixture was filtered through Celite, the solvent was reduced to 1 mL, and diethyl ether (10 mL) was added, resulting in the precipitation of an off-white solid. The solvent was removed with a pipet. Purification by column chromatography on silica gel (dichloromethane/acetonitrile 9:1) gave **22** (52 mg, 91%) as a colorless solid. mp 130 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.73−1.43 (m, 24 H), 2.35 (br. s., 3 H), 2.76 (br. s., 2 H), 3.15 (br. s., 2 H), 3.75 (s, 3 H), 6.47 (d, J = 6.9 Hz, 1 H), 6.82 (m, 3 H), 6.99 (t, J = 7.4 Hz, 1 H), 7.14 (d, J = 6.9 Hz, 1 H), 7.26−7.34 (m, 4 H), 7.36 (s, 2 H), 7.47 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.57 (b), 23.0 (b), 26.4 (b), 28.7 (b), 28.9 (b), 35.3, 122.0, 122.9 (b), 122.9, 124.0 (b), 124.5 (b), 125.1 (b), 125.4 (b), 128.1, 130.7, 134.7, 137.2, 145.3 (b), 145.8 (b), 152.3 (*C*), 176.74 (*C*). Two signals are missing, probably due to signal broading. ^{19}F NMR (282 MHz, $CDCl_3$) δ −153.36, −153.31. Anal. Calcd $C_{39}H_{48}BF_4N_5Pd$ (780.06): C, 60.05; H, 6.20; N, 8.98. Found: C, 59.73; H, 5.98; N, 8.41.

Suzuki−Miyaura Cross-Coupling. A 10 mL crimp vial with a magnetic stir bar was charged with a boronic acid and a base and capped with a PTFE-faced butyl rubber septum. When the reaction was run under argon, the vial was evacuated and filled with argon three times. The aryl chloride, for determination of yields or conversions by GC−MS, dodecane as internal standard, and a stock solution of the precatalyst (10^{-3} M in EtOH) were dissolved in a solvent and added to the vial with a syringe. Subsequently, the reaction mixture was stirred as indicated.

dx.doi.org/10.1021/om5004336 | *Organometallics* 2014, 33, 3966−3976

For the determination of yields or conversions by GC−MS, samplings of 0.1 mL were taken via a syringe and filtered through a silica gel filled pipet with DCM (5 mL). Otherwise, the reaction mixture was filtered through a thin pad of silica gel with DCM (200 mL). After removal of the solvent, the residue was purified by column chromatography on silica gel (isohexane/ethyl acetate). In a few cases where we were not able to separate the product from the aryl chloride, we determined the yield based on the isolated mixture and the ^{1}H NMR spectrum.

Solid-State Structure Determination. Preliminary examination and data collection were carried out on an area detecting system (Kappa-CCD; Nonius, FR590) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) with an Oxford Cryosystems cooling system at the window of a sealed fine-focus X-ray tube. The reflections were integrated. Raw data were corrected for Lorentz, polarization, decay, and absorption effects. The absorption correction was applied using SADABS.[51] After merging, the independent reflections were used for all calculations. The structure was solved by a combination of direct methods[52] and difference Fourier syntheses.[53] All non-hydrogen atom positions were refined with anisotropic displacement parameters. All hydrogen atoms were assigned to calculated positions and then refined using the SHELXL-97 riding-model.[53] Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.[54] All calculations were performed with the programs COLLECT,[55] DIRAX,[56] EVALCCD,[57] SIR97,[52] SHELXS-97,[53] SADABS,[51] and the SHELXL-97 package.[53] For the visualizations, ORTEP-3[58] was employed, and to create the Supporting Information for the publication, ENCIFER[59] was used.

■ ASSOCIATED CONTENT

Supporting Information

CIF files for the crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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