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Mixed Phosphite/*N*-Heterocyclic Carbene Complexes: Synthesis, Characterization and Catalytic Studies

Olivier Diebolt,[†,‡] Václav Jurčík,[†] Rosenildo Correa da Costa,[†] Pierre Braunstein,[§] Luigi Cavallo,[∥] Steven P. Nolan,[†,‡] Alexandra M. Z. Slawin,[†] and Catherine S. J. Cazin*[,†,‡,§]

[†]*EaStCHEM School of Chemistry, University of St Andrews, North Haugh, St Andrews KY16 9ST, U.K.,* [‡]*Institute of Chemical Research of Catalonia (ICIQ) Av. Països Catalans 16, 43007 Tarragona, Spain,* [§]*Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université de Strasbourg, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France, and* [∥]*Dipartimento di Chimica, Università di Salerno, Via ponte don Melillo, I-84084 Fisciano (SA), Italy*

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A series of mixed $P(OR)_3$/NHC Pd complexes was synthesized and fully characterized. The steric properties of both types of ligands were computationally determined using X-ray data. These structural studies clearly show that *N*-heterocyclic carbenes modulate their bulkiness with respect to the steric requirements of the coligands. Catalytic studies were performed using this new class of complexes for the Suzuki−Miyaura reaction. It was found that alkoxide or hydroxide bases and/or alcohols were necessary to achieve good catalytic activity. Mechanistic studies were undertaken in order to gain insights into the role of alkoxide groups. These studies suggest that alcohols or alkoxide groups play a major role in the activation of the precatalyst to generate the catalytically active species. Catalytic studies proved these systems to be efficient using 0.1 mol % of Pd loading for the coupling of aryl, benzyl, and heterocyclic chlorides with boronic acids.

Introduction

During the past 30 years, significant efforts have been dedicated to the development of transition metal catalytic systems for cross-coupling reactions.[1] This interest is explained by the fact that these reactions are considered powerful tools for the formation of carbon−carbon and carbon−heteroatom bonds. Among them, the Suzuki−Miyaura reaction[2] is one of the most well-established methods in particular for the synthesis of unsymmetrical biaryls, fragments found in many pharmaceutical compounds and natural products.[3] Systems capable of efficiently promoting such cross-coupling reactions are often based on palladium, and usually in association with strong donor ligands, in particular when the coupling partner is a chloroarene.[4] Hence, efforts have largely focused on the development of systems bearing bulky electron rich phosphines or *N*-heterocyclic carbene ligands.[5] In this respect, it has been shown that while palladacycle **1** does not promote the Suzuki−Miyaura coupling of aryl chlorides, its PR_3-adduct **2** is very efficient, even with deactivated substrates.[6] In this context, the active species was proposed to be a Pd(0) low valent "Pd-PR_3", and it was shown that the orthometalated ligand was released from the metal center during the activation of the Pd(II) precatalyst. Subsequent studies showed that the "reductively eliminated" orthometalated ligand was critical for the lifetime of the active catalyst. Indeed, while the parent chloride-bridged dimers of complexes of type **3** are inactive in the Suzuki−Miyaura coupling of aryl chlorides, their association with electron rich phosphines such as PCy_3 leads to systems (**3** and **4**) of outstanding catalytic performances, with a longevity dependent on the π-acidity of the oxyphosphorus ligand (Figure 1).[7,8]

In contrast, when the phosphite-palladacycles were associated with NHC ligands (complexes of type **5**), the systems were not efficient for the cross-coupling of aryl chlorides with boronic acids.[9] This is rather surprising as *N*-heterocyclic carbenes lead to very efficient systems in Pd-catalyzed cross-coupling chemistry.[10] Furthermore, Jamison showed

*To whom correspondence should be addressed. Phone: +44 1334 463 698. Fax: +44 1334 463 808. E-mail: cc111@st-andrews.ac.uk.

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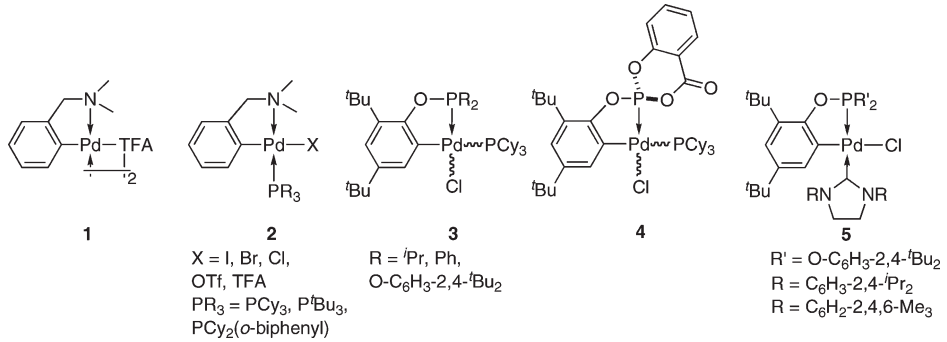

Figure 1. Orthometalated precatalysts.

that synergy between phosphites and NHCs was possible in Ni-catalyzed coupling of alkenes and aldehydes.[11] We reasoned that, in the case of complexes of type **5**, the metalation might render difficult the formation of the active species and therefore be responsible for the lack of reactivity of these complexes in Suzuki−Miyaura reactions involving aryl chorides. We were therefore interested in the development of a versatile synthetic methodology allowing for the generation of palladium complexes bearing a monodendate NHC and a monodendate phosphite ligand.[12] Herein, we report the synthesis and characterization of a range of complexes of the type $[PdCl_2(NHC)\{P(OR)_3\}]$ and their behavior in the Suzuki−Miyaura reaction of aryl chlorides.

Results and Discussion

Synthesis and Characterization of $[PdCl_2(NHC)\{P(OR)_3\}]$. Complexes of the type $[PdCl_2(NHC)\{P(OR)_3\}]$ were obtained by cleavage of the chloride bridges in the parent dimer $[Pd(\mu\text{-}Cl)Cl(NHC)]_2$ with a phosphite ligand. This methodology was applied to a range of phosphites chosen for their diversity in terms of electronic (alkyl, aryl, cyclic) and steric properties (cone angle ranging from 102° to 172°).[13] With respect to the NHC ligand, previous work has clearly shown that, for the Suzuki−Miyaura coupling, *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) leads to high catalytic performances.[14] The present studies on mixed ligands systems was therefore mainly focused on systems bearing the IPr ligand and various phosphites. However, to assess the importance of the NHC ligand, and for comparative purposes, selected complexes bearing the saturated analogue of IPr, *N*,*N*′-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene (SIPr) were studied. In all cases, the synthetic strategy adopted afforded the compounds in high yields and purity (Scheme 1).

The ^{1}H NMR spectra of complexes of type **6** confirm the presence of the CH groups of the NHC by a doublet, a broad doublet, and a broad doublet of doublets integrating for two, four, and two protons, and with chemical shifts in the ranges 7.08−7.21, 7.21−7.36, and 7.48−7.56 ppm, respectively. The *iso*-propyl groups of the NHC appear as two doublets (each integrating for 12 protons) and a pseudoseptuplet integrating for four protons. The chemical shifts of these three signals lie in the ranges 1.01−1.10, 1.13−1.38, and 3.00−3.10 ppm, with coupling constants of 6.9, 6.6−6.7, and 6.8 Hz, respectively. A selective decoupling experiment showed that the two methyl groups of ^{i}Pr are not equivalent, they therefore appear as two doublets because of coupling with the CH proton. The latter is seen as a pseudoseptuplet with an averaged coupling constant, when in theory a quadruplet of quadruplets should be observed. The same observation was made for complexes of type **7** as the ^{i}Pr are seen as two doublets and a pseudoseptuplet. The methylene protons of the NHC backbone give rise to a singlet integrating for four protons (4.12 and 4.17 ppm), characteristic for the saturated carbene SIPr. In all cases (complexes of type **6** and **7**), signals accounting for the presence of the phosphite ligand are observed.

The $^{13}C\{^1H\}$-NMR spectra of complexes of type **6** and **7** contain three singlets associated with the ^{i}Pr groups on the NHC, with chemical shifts in the ranges 22.7−23.6, 26.3−26.7, and 28.7−29.1 ppm. The data obtained for the other characteristic and distinctive C-atoms of the carbene ligands are summarized in Table 1.

For all complexes bearing the IPr ligand, the CH groups of the backbone (C^4 and C^5) are seen as a doublet between 124.8 and 125.3 ppm, with $^4J_{C-P}$ coupling constants between 7.9 and 8.9 Hz. The carbene carbon atoms give rise to a doublet between 167.2 and 171.9 ppm, with $^2J_{CP}$ of ca. 300 Hz. For the complexes bearing a SIPr ligand, C^4 and C^5 are also seen as a doublet, with chemical shifts of 52.5 and 53.6 ppm. The coupling constant $^4J_{CP}$ is comparable to those measured with complexes of type **6**. The carbene carbon atoms are seen as downfield-shifted doublets (194.2 and 198.1 ppm), with coupling constants $^2J_{CP}$ also comparable to those of the unsaturated analogues.

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Scheme 1. Synthesis of the P(OR)$_3$/NHC Mixed Complexes

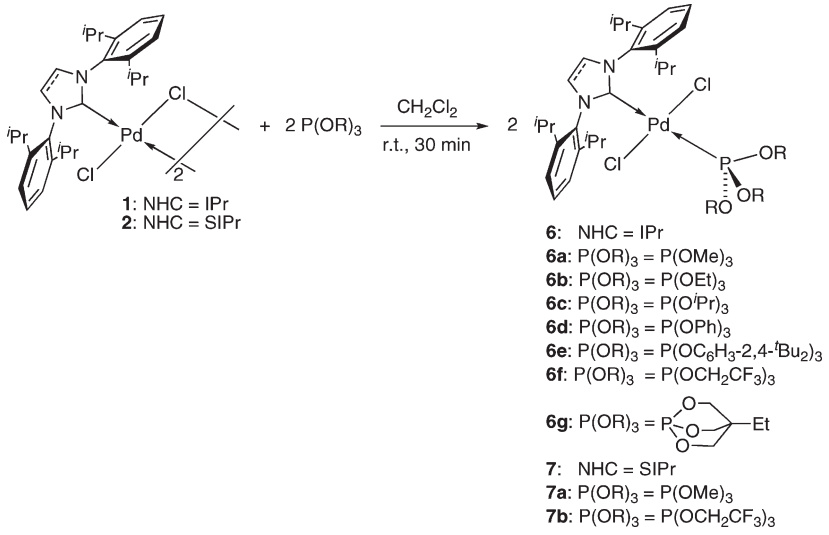

Table 1. Selected ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR Data for Complexes of Types 6 and 7[a]

	C^4C^5		$C_{carbene}$		P
complex	δ_C (ppm)	$^4J_{CP}$ (Hz)	δ_C (ppm)	$^2J_{CP}$ (Hz)	δ_P (ppm)
[PdCl$_2$(IPr){P(OMe)$_3$}] (**6a**)	124.8	8.55	171.1	290.8	107.9
[PdCl$_2$(IPr){P(OEt)$_3$}] (**6b**)	124.8	8.2	171.9	290.9	103.3
[PdCl$_2$(IPr){P(O^{i}Pr)$_3$}] (**6c**)	124.8	7.9	172.6	291.0	97.3
[PdCl$_2$(IPr){P(OPh)$_3$}] (**6d**)	125.3	8.6	167.8	303.7	92.2
[PdCl$_2$(IPr){P(OC$_6$H$_3$-2,4-^{t}Bu$_2$)$_3$}] (**6e**)	125.1	8.9	168.1	306.3	93.1
[PdCl$_2$(IPr){P(OCH$_2$CF$_3$)$_3$}] (**6f**)	125.2	8.65	167.2	302.7	108.8
[PdCl$_2$(IPr)(ETPB)] (**6g**)	125.0	8.6	167.8	300.5	87.7
[PdCl$_2$(SIPr){P(OMe)$_3$}] (**7a**)	52.5	9.2	198.1	272.3	110.0
[PdCl$_2$(SIPr){P(OCH$_2$CF$_3$)$_3$}] (**7b**)	53.6	9.6	194.2	282.6	110.9

[a] Spectra recorded in CD_2Cl_2.

^{31}P-{^{1}H} NMR spectra of all complexes contain one sharp singlet (see Table 1), which is shifted upfield with respect to the shift observed for the corresponding free phosphite.

The structure of complexes **6a**, **6c**, **6d**, **6e**, and **7a** were unambiguously determined by single crystal X-ray diffraction studies (Figure 2).

For complexes of type **3**, the palladium center presents an approximately square planar coordination geometry. These crystal structures invariably show the trans disposition of the phosphite ligand to the *N*-heterocyclic carbene. The angles between adjacent ligands lie in the range 85.837(17)−93.08(5)°, highlighting the distortion of the square planar geometry. The Pd−Cl bond distances of complexes **6a**, **6c**−**e** fall between the values found for the Pd−(μ-Cl) and Pd−Cl distances of the parent dimer [Pd(μ-Cl)Cl(IPr)]$_2$ (Pd-(μ-Cl) 2.4029(9) Å, Pd−Cl 2.2715(9) Å).[15] In terms of electronics, complexes bearing the ligands of better π-acidity have a shorter Pd−P bond length (compare **6c** with **6d**). As expected, due to the trans influence of phosphites, the Pd−C bonds of complexes **6a**, **6c**−**e** are in all cases substantially longer than the Pd−C distance found for the parent dimer [Pd(μ-Cl)Cl(IPr)]$_2$ (1.9553(3) Å).[15] As can be seen from the Pd−C bond lengths found in **6a** and **6c**, compared to **6d** and **6e**, the alkylphosphites have a larger trans influence than the arylphosphites. This influence is mirrored by the ^{13}C-{^{1}H}-NMR shift found for the carbene carbon atom, with the trans influence of the P(OR)$_3$ ligand leading to a downfield shift of the carbene carbon atom (Table 1). The observation that a signal shifts downfield with the increasing trans influence of the ligand trans to it has been previously observed in Pd(II) complexes.[6] As observed with the complexes of type **6**, the trans influence of the phosphite ligand in **7a** leads to a longer Pd−C bond compared to the one found with the parent dimer [Pd(μ-Cl)Cl(SIPr)]$_2$ (1.947(5) Å).[16] As can be seen when comparing the values obtained for complexes **6a** and **7a**, the nature of the *N*-heterocyclic carbene does not have a large influence on the bond lengths and angles around the palladium center. On the other hand, the values obtained with the Samb*V*ca application confirm the slightly larger steric hindrance of SIPr compared to its unsaturated analogue (37.4% V_{Bur} for **7a** vs 36.3% V_{Bur} for **6a**).[17] The calculations performed for the complexes of type **6** (Table 2) show that the % V_{Bur} of the

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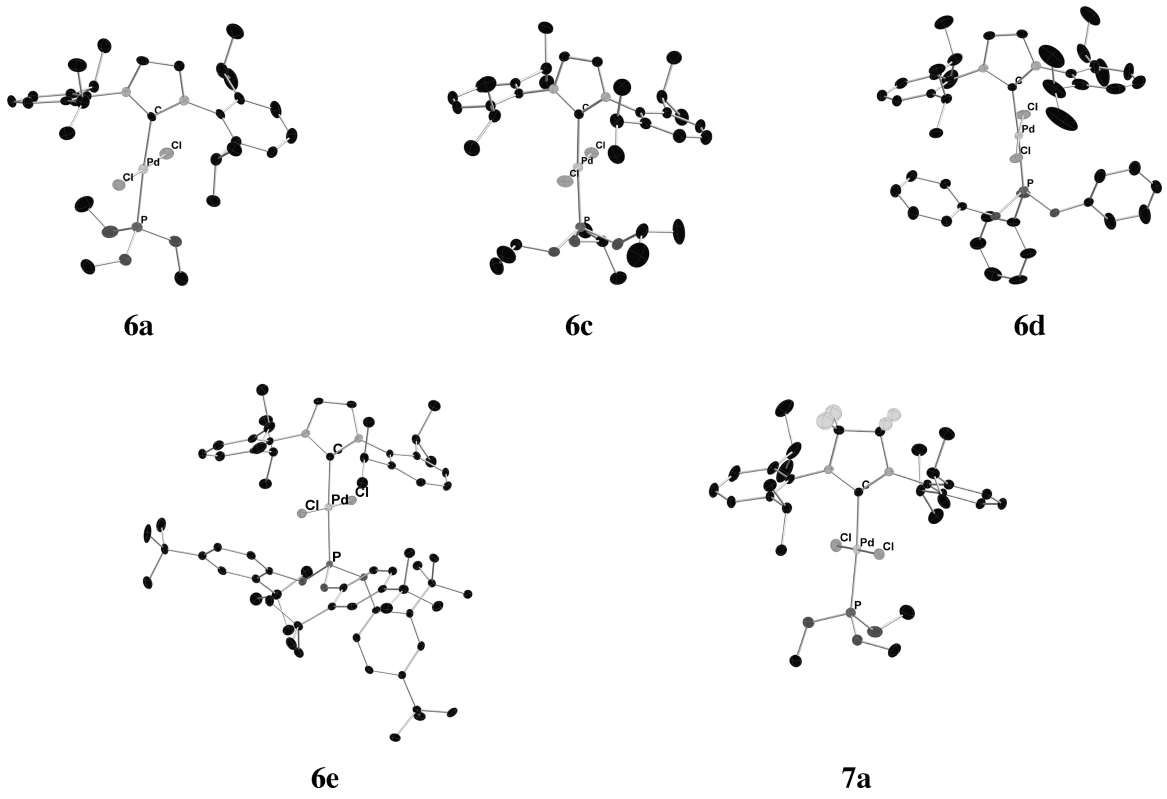
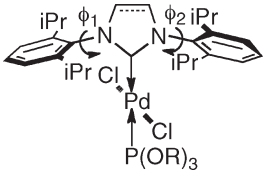


Figure 2. ORTEP plot of the molecular structure of $[PdCl_2(IPr)\{P(OMe)_3\}]$ (**6a**), $[PdCl_2(IPr)\{P(O^iPr)_3\}]$ (**6c**), $[PdCl_2(IPr)\{P(OPh)_3\}]$ (**6d**), $[PdCl_2(IPr)\{P(OC_6H_3\text{-}2,4\text{-}^tBu)_3\}]$ (**6e**), and $[PdCl_2(SIPr)\{P(OMe)_3\}]$ (**7a**). Ellipsoids are represented at 50% probability level, solvent molecule (CH_2Cl_2 for **6e**) and hydrogen atoms are omitted for clarity.

Table 2. $\%V_{Bur}$, Angles ϕ, and Selected Bond Lengths (Å) and Angles (deg) (esd) for 6a, 6c, 6d, 6e, and 7a



complex NHC/P(OR)$_3$	**6a** IPr/P(OMe)$_3$	**6c** IPr/P(O^{i}Pr)$_3$	**6d** IPr/P(OPh)$_3$	**6e** IPr/P(OC$_6$H$_3$-2,4-^{t}Bu)$_3$	**7a** SIPr/P(OMe)$_3$
$\%V_{Bur}$ of NHC	36.3	32.3	32.4	35.1	37.4
$\%V_{Bur}$ of P(OR)$_3$	28.8	30.7	34.3	34.0	29.1
ϕ_1	78.1	86.8	83.3	69.6	66.4
ϕ_2	72.4	83.9	92.2	87.7	72.3
90°-ϕ_{av}[a]	14.8	4.7	2.3	11.3	20.7
Pd−C	2.056(4)	2.0482(11)	2.0357(19)	2.031(2)	2.051(2)
Pd−P	2.2694(12)	2.2845(3)	2.2666(5)	2.2729(7)	2.2710(8)
Pd−Cl1	2.3004(12)	2.2892(3)	2.3006(4)	2.2940(7)	2.2954(7)
Pd−Cl2	2.3113(12)	2.2994(3)	2.2830(4)	2.3063(7)	2.3105(8)
C−Pd−P	177.34(12)	175.04(3)	177.43(5)	176.88(6)	176.10(7)
C−Pd−Cl1	88.88(12)	88.80(3)	93.08(5)	91.15(7)	88.80(7)
C−Pd−Cl2	91.85(12)	90.90(3)	88.81(5)	88.45(7)	91.91(7)
P−Pd−Cl1	92.12(5)	88.500(12)	85.837(17)	90.83(3)	92.75(3)
P−Pd−Cl2	87.20(5)	91.745(12)	92.348(17)	89.74(3)	86.64(3)
Cl1−Pd−Cl2	178.70(5)	179.226(14)	177.38(3)	175.94(2)	178.26(3)

[a] $\phi_{av} = (\phi_1 + \phi_2)/2$.

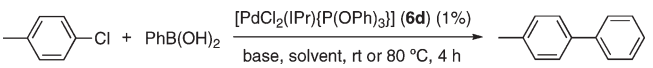
NHC ligand IPr is dependent on the phosphite ligand trans to it. As expected, the $\%V_{Bur}$ of IPr in complexes **6c** and **6d** (32.3 and 32.4) is quite close to that in the DFT optimized geometry of the model complex $[IrCl(IPr)(CO)_2]$,[17a] but it is smaller than the one obtained with **6a**, which is instead surprisingly large (36.3). The anomalous $\%V_{Bur}$ of the IPr ligand in **6a** (and similarly of the SIPr ligand in **7a**) can be associated to the low steric hindrance of the P(OMe)$_3$ phosphite (28.8% V_{Bur}) that allows the NHC *N*-substituents to rotate by ~15° from a nearly orthogonal orientation

relative to the mean NHC plane, see the 90°-ϕ_{av} value in Table 2. This folding of the *N*-substituents results in a higher presence of the NHC ligand in the first coordination sphere around the metal, evidenced by the higher $\%V_{Bur}$. In **6c** and **6d**, instead, the slightly larger steric hindrance of the $P(O^iPr)_3$ and $P(OPh)_3$ phosphites ($\%V_{Bur}$ 30.7 and 34.3, respectively) forces the *N*-substituents of the IPr ligand to be almost orthogonal to the mean NHC ring, see the 90°-ϕ_{av} value quite close to 0° for **6c** and **6d** in Table 2. Finally, a rather large 90°-ϕ_{av} value and, consequently, a rather large $\%V_{Bur}$, is calculated also for the IPr NHC of **6e**, although the $P(OC_6H_3\text{-}2,4\text{-}^tBu_2)_3$ phosphite presents the same $\%V_{Bur}$ as the $P(OPh)_3$ phosphite. This analysis indicates that NHC ligands are rather flexible entities that can modulate their bulkiness in response to the steric requirement of the other ligands, which may be one of the reasons for their effectiveness as ancillary ligands in catalysis.

Catalysis. Optimization of the Reaction Conditions. The reaction conditions for the Suzuki−Miyaura coupling were optimized[18] using as a model reaction the coupling of 4-chlorotoluene with phenyl boronic acid in the presence of 1 mol % of $[PdCl_2(IPr)(P(OPh)_3)]$ (**6d**). To compare the new systems to the orthopalladated complexes of type **5** described by Bedford and co-workers,[9] the reaction was carried out using Cs_2CO_3 as base and 1,4-dioxane as solvent (Table 3, entry 1). While complexes of type **5** performed poorly at 101 °C,[9] complex **6d** led to a good conversion to coupling product (84%) at 80 °C within 4 h. Toluene/K_3PO_4 was also tested as solvent/base mixture because it has been shown to lead to highly active systems in such cross-coupling,[5c] but in the present case, only poor conversion was observed (Table 3, entry 2).

We then investigated the use of alkoxide bases and alcohols. These studies[18] show that the catalytic efficiency of the present system is greatly improved by the use of alcohols and/or hydroxide or alkoxide bases (Table 3, entries 3−6). A concern is that, under such reaction conditions, free phosphites have been shown to undergo transesterification reactions.[19] To ascertain the fact that such reactions would occur on phosphite ligands coordinated to a palladium center, in situ NMR experiments using $[PdCl_2(IPr)\{P(OPh)_3\}]$ (**6d**) were performed.[20] These studies show that several phosphorus-containing species appear when the complex is in the presence of an alcohol and an alkoxide base, together or individually, whereas $[PdCl_2(IPr)\{P(OPh)_3\}]$ (**6d**) is stable in the presence of an nonalcoholic solvent and a nonalkoxide or hydroxide base. Our efforts were therefore focused on the use of 1,4-dioxane with Cs_2CO_3 as it was shown to lead to high conversion to coupling product if heated to 80 °C (Table 3, entry 1). However, when changing the source of 1,4-dioxane, issues of reproducibility arose (fluctuation in conversion to coupling product). Freshly dried and distilled 1,4-dioxane was hence used, and no catalytic activity could be observed. It was found that 2,6-*tert*-butyl-4-methylphenol (BHT), present in 1,4-dioxane as a stabilizer, is likely responsible for the catalytic activity and for the variations in conversion

Table 3. Optimization of Reaction Conditions[a]



entry	solvent	base	temperature (°C)	conv (%)[b]
1	1,4-dioxane	Cs_2CO_3	rt	0
			80	84[c]
2	toluene	K_3PO_4	rt	2
			80	13
3	toluene	KO^tBu	rt	34
			80	81
4	^{i}PrOH	NaOH	rt	62
5	MeOH	K_2CO_3	rt	90
6	**EtOH**	**NaOH**	**rt**	**99**

[a] Reaction conditions: 4-chlorotoluene (0.5 mmol), phenylboronic acid (0.525 mmol), base (0.75 mmol), $[PdCl_2(IPr)\{P(OPh)_3\}]$ **6d** (1 mol % Pd), solvent (1 mL), rt or 80 °C, 4 h. [b] Conversion to coupling product, based on 4-chlorotoluene, determined by GC (average of two runs). [c] Not reproducible.

as the amount of the alcohol could not be controlled.[21] Hence, from the above observations, it appears that the presence of an alcohol is necessary to ensure catalytic activity of complexes of the type $[PdCl_2(NHC)\{P(OR)_3\}]$. This implies that the alcohol plays a role in the activation of the precatalyst, presumably by promoting its reduction from Pd(II) to Pd(0).[22] Mechanistic studies performed by reacting $[PdCl_2(IPr)\{P(OPh)_3\}]$ (**6d**) with ^{i}PrOH in the presence of NaOH showed the formation of acetone. This appears to support a participation of the alcohol in a reduction of the metal center, explaining the need for the presence of an alkoxide group in the catalytic system. Furthermore, mechanistic information gained from in situ NMR studies showed that despite the occurrence of transesterification on the phosphite ligand, the latter might remain coordinated and thus be involved in the catalytic manifold.[20] For these reasons, the catalytic efficiency of complexes of type **6** and **7** was assessed (Table 4) using the optimized reaction conditions found above.

As can be seen in Table 4, most of the studied systems lead to almost complete conversion at room temperature within 4 h, except for the system based on $P(OC_6H_3\text{-}2,4\text{-}^tBu)_3$. The bulkiness of this ancillary ligand might prevent the reduction of the metal center, which is presumed to involve a β-hydride elimination step. Lowering the catalyst loading to 0.1 mol % Pd showed that $[PdCl_2(IPr)\{P(OMe)_3\}]$ (**6a**) and $[PdCl_2(IPr)\{P(O^iPr)_3\}]$ (**6c**) lead to the highest catalytic activity (Table 5, entries 1 and 2) because high conversions were reached after 1.5 h.

A clear trend between the electronic and steric properties of the phosphite ligand and the catalytic performance of the corresponding complex could not be established. The versatility of the catalyst system $[PdCl_2(IPr)\{P(OMe)_3\}]$ (**6a**) at 0.1 mol % loading using EtOH/NaOH was then investigated (Table 6). These results established the broad scope of applications of this precatalyst.

In conclusion, a synthetic methodology for the synthesis of a range of complexes bearing mixed ligand systems $P(OR)_3$/NHC has been developed. These complexes were fully

(18) For the complete optimization study, see Supporting Information, Table S2.

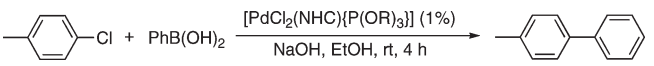
(19) (a) Corbridge, D. E. C. *Phosphorus World. Chemistry, Biochemistry and Technology*; 2005, p 368. (b) Hoffmann, F. W.; Ess, R. J.; Usinger, R. P. *J. Am. Chem. Soc.* **1956**, 5817–5821.

(20) For complete description of the experiments and the corresponding NMR spectra, see Supporting Information.

(21) See Supporting Information, Table S1.

(22) Such a reduction has also been shown to be promoted by water in the case of in situ formed catalytic systems for C−N bond formation: Fors, B. P.; Krattiger, P.; Strieter, E.; Buchwald, S. L. *Org. Lett.* **2008**, *10*, 3505–3508.

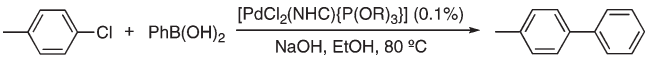
Table 4. Catalysts Screening[a]



entry	catalyst	conv (%)[b]
1	$[PdCl_2(IPr)\{P(OMe)_3\}]$ (**6a**)	> 95
2	$[PdCl_2(IPr)\{P(OEt)_3\}]$ (**6b**)	> 95
3	$[PdCl_2(IPr)\{P(O^iPr)_3\}]$ (**6c**)	82
4	$[PdCl_2(IPr)\{P(OPh)_3\}]$ (**6d**)	> 95
5	$[PdCl_2(IPr)\{P(OC_6H_3\text{-}2,4\text{-}^tBu)_3\}]$ (**6e**)	nr
6	$[PdCl_2(IPr)\{P(OCH_2CF_3)_3\}]$ (**6f**)	> 95
7	$[PdCl_2(IPr)(ETPB)]$[c] (**6g**)	> 95
8	$[PdCl_2(SIPr)\{P(OMe)_3\}]$ (**7a**)	> 95
9	$[PdCl_2(SIPr)\{P(OCH_2CF_3)_3)_3\}]$ (**7b**)	> 95

[a] Reaction conditions: 4-chlorotoluene (0.5 mmol), phenylboronic acid (0.525 mmol), NaOH (0.75 mmol), $[PdCl_2(NHC)\{P(OR)_3\}]$ (1 mol % Pd), EtOH (1 mL), 25 or 80 °C, 4 h. [b] Conversion to coupling product, based on 4-chlorotoluene, determined by GC (average of two runs). [c] ETPB: 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane.

Table 5. Low Catalyst Loading Study[a]



entry	catalyst	time (h)	conv (%)[b]
1	$[PdCl_2(IPr)\{P(OMe)_3\}]$ (**6a**)	1.5	90
2	$[PdCl_2(IPr)\{P(O^iPr)_3\}]$ (**6c**)	1.5	89
3	$[PdCl_2(IPr)\{P(OPh)_3\}]$ (**6d**)	1.5	49
		3	68
4	$[PdCl_2(IPr)\{P(OC_6H_3\text{-}2,4\text{-}^tBu)_3\}]$ (**6e**)	1.5	35
		3	35
5	$[PdCl_2(SIPr)\{P(OMe)_3\}]$ (**7a**)	1.5	58
		3	68

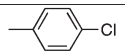
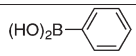
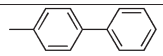
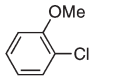
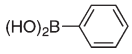
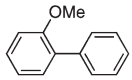
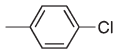
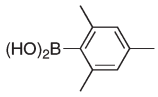
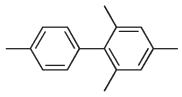
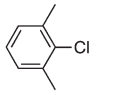
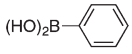
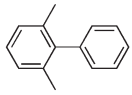
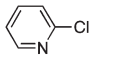
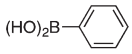
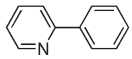
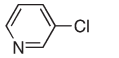
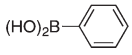
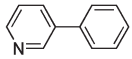
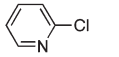
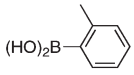
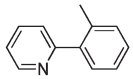
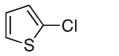
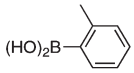
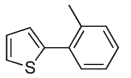
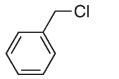
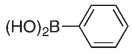
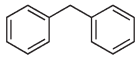
[a] Reaction conditions: 4-chlorotoluene (0.5 mmol), phenylboronic acid (0.525 mmol), NaOH (0.75 mmol), $[PdCl_2(NHC)\{P(OR)_3\}]$ (0.1 mol % Pd), EtOH (1 mL), 80 °C. [b] Conversion to coupling product, based on 4-chlorotoluene, determined by GC (average of two runs).

characterized and X-ray analyses combined with NMR studies showed a correlation of these data with the trans influence of the phosphite ligand. The X-ray data obtained also allowed for a full analysis of the steric properties of the ligands, using the computational tool Samb*V*ca. These investigations emphasize the ability of the *N*-heterocyclic carbene ligands to modulate their bulkiness with respect to the steric requirements of the coligands. Catalytic studies were undertaken in the Suzuki−Miyaura reaction. Mechanistic investigations suggest that the presence of an alkoxide group is necessary to promote the precatalyst activation. Finally, the reported systems proved to be versatile for the efficient cross-coupling of boronic acids with aryl, benzyl and heterocyclic chlorides.

Experimental Section

General Considerations. All reactions were performed under an inert atmosphere of argon or nitrogen using standard Schlenk line and glovebox techniques. Solvents were dispensed from a solvent purification system from Innovative Technology. Flash column chromatography was performed on silica gel 60 (230−400 mesh). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC300 or on a Bruker Avance 400 Ultrashield spectrometer at 298 K unless otherwise stated. Elemental analyses were performed by the Service de Microanalyse, Université de Strasbourg (France), and by the Elemental Analysis Service of the University of St. Andrews.

Table 6. Scope of the Reaction

Entry	ArCl	$ArB(OH)_2$	Product	Yield[b]
1				89
2				98
3				55[c]
4				77[c]
5				99
6				99
7				99
8				88
9				97

[a] Reaction conditions: 4-chlorotoluene (0.5 mmol), boronic acid (0.525 mmol), NaOH (0.75 mmol), $[PdCl_2(IPr)\{P(OMe)_3\}]$ (**6a**) (0.1 mol % Pd), EtOH (1 mL), 80 °C, 24 h (reaction time not optimized). [b] Isolated yield, average of two reactions. [c] 0.5 mol % of catalyst was used.

$[Pd(\mu\text{-}Cl)Cl(IPr)]_2$ and $[Pd(\mu\text{-}Cl)Cl(SIPr)]_2$ were synthesized according to published procedures.[23,24] All other reagents were purchased and used as received unless otherwise noted.

Synthesis of Complexes. $[PdCl_2(IPr)\{P(OMe)_3\}]$ (6a). A Schlenk tube was charged with $[Pd(\mu\text{-}Cl)Cl(IPr)]_2$ (0.210 g, 0.18 mmol) suspended in dichloromethane (10 mL) and an excess of $P(OMe)_3$ (0.05 mL, 0.42 mmol) was added. The solution was stirred at room temperature for 30 min and then concentrated in vacuo (2 mL). Addition of degassed methanol (5 mL) and concentration to 4 mL led to a precipitate, which was washed with methanol (3 × 5 mL) after removal of the supernatant solution. The complex was obtained as yellow needles (0.164 g, 64%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of methanol in a dichloromethane solution of the complex. ^1H NMR (CD_2Cl_2): δ 1.09 (d, 12H, $^3J_{HH}$ = 6.9 Hz, $CHCH_3$), 1.38 (d, 12H, $^3J_{HH}$ = 6.7 Hz, $CHCH_3$), 3.09 (pseudo sept, 4H, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$), 3.47 (d, 9H, $^3J_{PH}$ = 12.1 Hz, OCH_3), 7.15 (d, 2H, J = 2.3 Hz, CH), 7.33 (br d, 4H, CH), 7.48 (br dd, 2H, CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 23.0 (s, ^{i}Pr), 26.4 (s, ^{i}Pr), 29.0 (s, ^{i}Pr), 53.0 (s, OMe), 124.0 (s, CH aromatic), 124.85 (d, $^4J_{CP}$ = 8.55 Hz, C^4H-C^5H), 130.2 (s, CH aromatic), 135.6 (s, C aromatic), 147.1 (s, C aromatic), 171.1 (d, $^2J_{CP}$ = 290.8 Hz, C carbene). $^{31}P\{^1H\}$ NMR

(23) Viciu, M. S.; Kissling, R. M.; Stevens, E. D.; Nolan, S. P. *Org. Lett.* **2002**, *4*, 2229–2231.
(24) Ma, Y.; Song, C.; Jiang, W.; Xue, G.; Cannon, J. F.; Wang, X.; Andrus, M. B. *Org. Lett.* **2003**, *5*, 4635–4638.

(CD_2Cl_2): δ 107.9 (s). Anal. Calcd for $C_{30}H_{45}Cl_2N_2O_3PPd$: C, 52.22; H, 6.57; N, 4.06. Found: C, 52.11; H, 6.56; N, 3.98.

[$PdCl_2$(IPr){P(OEt)$_3$}] (6b). A Schlenk tube was charged with [Pd(μ-Cl)Cl(IPr)]$_2$ (0.294 g, 0.26 mmol) suspended in dichloromethane (10 mL), and an excess of P(OEt)$_3$ (0.1 mL, 0.58 mmol) was added. The solution was stirred at room temperature for 30 min. Methanol (5 mL) was added, and the reaction mixture was concentrated to 2 mL. The supernatant solution was removed and MeOH (2 mL) was added to the precipitate. The solution was concentrated to 1 mL, the supernatant solution removed with a syringe and the solid was dried in vacuo. The complex was obtained as a yellow solid (0.259 g, 68%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of methanol in a dichloromethane solution of the complex. ^{1}H NMR (CD_2Cl_2): δ 1.08 (t, 9H, $^3J_{HH}$ = 7.0 Hz, OCH_2CH_3), 1.08 (d, 12H, $^3J_{HH}$ = 6.9 Hz, $CHCH_3$), 1.37 (d, 12H, $^3J_{HH}$ = 6.65 Hz, $CHCH_3$), 3.10 (pseudo sept, 4H, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$), 3.85 (m, 6H, OCH_2CH_3), 7.14 (d, 2H, J = 2.2 Hz, CH), 7.33 (br d, 4H, CH), 7.49 (br dd, 2H, CH). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 16.25 (d, $^3J_{CP}$ = 7.0 Hz, O−CH_2-CH_3), 23.0 (s, ^{i}Pr), 26.4 (s, ^{i}Pr), 29.0 (s, ^{i}Pr), 62.3 (s, O-CH_2−CH_3), 124.0 (s, CH aromatic), 124.8 (d, $^4J_{CP}$ = 8.2 Hz, C^4H-C^5H), 130.2 (s, CH aromatic), 135.7 (s, C aromatic), 147.2 (s, C aromatic), 171.9 (d, $^2J_{CP}$ = 290.9 Hz, C carbene). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 103.3 (s). Anal. Calcd for $C_{33}H_{51}Cl_2N_2O_3PPd$: C, 54.14; H, 7.02; N, 3.83. Found: C, 54.02; H, 7.08; N, 3.74.

[$PdCl_2$(IPr){P(O^{i}Pr)$_3$}] (6c). A Schlenk tube was charged with [Pd(μ-Cl)Cl(IPr)]$_2$ (0.221 g, 0.19 mmol) suspended in dichloromethane (10 mL), and P(O^{i}Pr)$_3$ (0.1 mL, 0.40 mmol) was added. The solution was stirred at room temperature for 30 min and concentrated to 5 mL, and cyclohexane (5 mL) was added. The solution was further concentrated to 1 mL, the supernatant solution removed with a syringe, and the precipitate was washed with cyclohexane (2 × 2 mL) and dried in vacuo. The complex was obtained as a shiny yellow solid (0.227 g, 75%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution of the complex. ^{1}H NMR (CD_2Cl_2): δ 1.07 (overlapping d, 30H, $^3J_{HH}$ = 6.2 Hz, $^3J_{HH}$ = 6.9 Hz, $OCHCH_3$ and $CCHCH_3$), 1.37 (d, 12H, $^3J_{HH}$ = 6.7 Hz, $CHCH_3$), 3.11 (pseudo sept, 4H, $^3J_{HH}$ = 6.8 Hz, $CCHCH_3$), 4.62 (m, 3H, $OCHCH_3$), 7.12 (d, 2H, J = 2.2 Hz, CH), 7.33 (br d, 4H, CH), 7.49 (br dd, 2H, CH). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 23.0 (s, ^{i}Pr), 24.05 (d, $^3J_{CP}$ = 4.0 Hz, $OCHCH_3$), 26.5 (s, ^{i}Pr), 29.0 (s, ^{i}Pr), 71.05 (d, $^2J_{CP}$ = 2.0 Hz, $OCHCH_3$), 124.0 (s, CH aromatic), 124.8 (d, $^4J_{CP}$ = 7.9 Hz, C^4H-C^5H), 130.1 (s, CH aromatic), 135.9 (s, C aromatic), 147.3 (s, C aromatic), 172.6 (d, $^2J_{CP}$ = 291.0 Hz, C carbene). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 97.3(s). Anal. Calcd for $C_{36}H_{57}Cl_2N_2O_3PPd$: C, 55.85; H, 7.42; N, 3.62. Found: C, 55.68; H, 7.73; N, 3.41.

[$PdCl_2$(IPr){P(OPh)$_3$}] (6d). A Schlenk tube was charged with [Pd(μ-Cl)Cl(IPr)]$_2$ (0.302 g, 0.27 mmol) suspended in dichloromethane (10 mL), and an excess of P(OPh)$_3$ (0.15 mL, 0.57 mmol) was added. The solution was stirred at room temperature for 30 min and then concentrated in vacuo (3 mL). Heptane (5 mL) was added and the solution concentrated to 4 mL. The supernatant solution was removed with a syringe, and the precipitate was washed with heptane (3 × 5 mL). The complex was obtained as a yellow powder (0.326 g, 70%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of heptane in a dichloromethane solution of the complex. ^{1}H NMR (CD_2Cl_2): δ 1.04 (d, 12H, $^3J_{HH}$ = 6.9 Hz, $CHCH_3$), 1.21 (d, 12H, $^3J_{HH}$ = 6.6 Hz, $CHCH_3$), 3.00 (pseudo sept, 4H, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$), 6.95−7.17 (m, 17H, CH), 7.32 (br d, 4H, CH), 7.56 (dd, 2H, CH). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 22.9 (s, ^{i}Pr), 26.5 (s, ^{i}Pr), 28.9 (s, ^{i}Pr), 120.6 (d, J_{CP} = 5.5 Hz, CH Ph), 124.3 (s, CH), 124.9 (s, CH), 125.3 (d, $^4J_{CP}$ = 8.6 Hz, C^4H-C^5H), 129.9 (s, CH), 130.5 (s, CH), 135.3 (s, C aromatic), 147.1 (s, C aromatic), 151.0 (d, $^2J_{CP}$ = 6.0 Hz, C−O−P), 167.8 (d, $^2J_{CP}$ = 303.7 Hz, C carbene). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 92.2 (s). Anal. Calcd for $C_{45}H_{51}Cl_2N_2O_3PPd$: C, 61.68; H, 5.87 ; N, 3.20. Found: C, 62.52; H, 6.55; N, 2.69.

[$PdCl_2$(IPr){P(OC$_6$H$_3$-2,4-^{t}Bu$_2$)$_3$}] (6e). A Schlenk tube was charged with tris(2,4-di-*tert*-butylphenyl)phosphite (0.231 g, 0.36 mmol), [Pd(μ-Cl)Cl(IPr)]$_2$ (0.201 g, 0.18 mmol), and dichloromethane (10 mL) was added. The reaction mixture was stirred at room temperature for 30 min, concentrated in vacuo to 5 mL, and methanol (10 mL) was added. The solution was concentrated to 7 mL, the supernatant was removed with a syringe, and the precipitate was washed with methanol (3 × 10 mL). The product was obtained as a pale-yellow powder (0.371 g, 86%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of methanol in a dichloromethane solution of the complex. ^{1}H NMR (CD_2Cl_2): δ 1.01 (d, 12H, $^3J_{HH}$ = 6.9 Hz, $CHCH_3$), 1.13 (d, 12H, $^3J_{HH}$ = 6.6 Hz, $CHCH_3$), 1.29 (br s, 27H, $C(CH_3)_3$), 1.37 (br s, 27H, $C(CH_3)_3$), 3.03 (pseudo sept, 4H, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$), 6.77 (dd, 3H, J = 8.6 Hz, J = 2.6 Hz, CH phosphite), 7.08 (d, 2H, J = 2.3 Hz, CH carbene), 7.21 (br d, 4H, CH carbene), 7.28 (m, 3H, CH phosphite), 7.36−7.48 (m, 5H, CH). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 22.7 (s, ^{i}Pr), 26.4 (s, ^{i}Pr), 28.8 (s, ^{i}Pr), 30.5 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$), 34.6 ($C(CH_3)_3$), 35.3 ($C(CH_3)_3$), 118.8 (d, J_{CP} = 9.8 Hz, CH phosphite), 123.6 (s, CH), 124.0 (s, CH), 125.0 (s, CH), 125.1 (d, $^4J_{CP}$ = 8.9 Hz, C^4H-C^5H), 130.1 (s, CH), 135.4 (s, C NHC), 138.6 (d, J_{CP} = 5.9 Hz, C phosphite), 145.9 (s, C phosphite), 147.0 (s, C NHC), 148.2 (d, J_{CP} = 5.8 Hz, C phosphite), 168.1 (d, $^2J_{CP}$ = 306.3 Hz, C carbene). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 93.1 (s). Anal. Calcd for $C_{70}H_{101}Cl_4N_2O_3PPd$: C, 64.78; H, 7.84; N, 2.16. Found C, 64.77; H, 7.78; N, 2.06.

[$PdCl_2$(IPr){P(OCH$_2$CF$_3$)$_3$}] (6f). A Schlenk tube was charged with [Pd(μ-Cl)Cl(IPr)]$_2$ (0.226 g, 0.20 mmol) suspended in dry THF (2.5 mL), and P(OCH_2CF_3)$_3$ (0.131 g, 88.2 μL, 0.40 mmol) was added. The solution was stirred at room temperature for 30 min. The solvent was then evaporated. The product was obtained analytically pure by recrystallization from THF/pentane. The complex was obtained as a yellow solid (0.260 g, 64%). ^{1}H NMR (CD_2Cl_2): δ 1.10 (d, 12H, $^3J_{HH}$ = 6.9 Hz, $CHCH_3$), 1.38 (d, 12H, $^3J_{HH}$ = 6.7 Hz, $CHCH_3$), 3.01 (pseudo sept, 4H, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$), 4.24 (m, 6H, OCH_2CF_3), 7.21 (d, 2H, J = 2.4 Hz, CH), 7.36 (br d, 4H, CH), 7.52 (br dd, 2H, CH). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 22.9 (s, ^{i}Pr), 26.5 (s, ^{i}Pr), 29.1 (s, ^{i}Pr), 63.6 (q, $^2J_{CF}$ = 37.7 Hz, OCH_2), 122.75 (dq, $^1J_{CF}$ = 278 Hz, $^3J_{CP}$ = 8.7 Hz, CF_3), 124.2 (s, CH aromatic), 125.2 (d, $^4J_{CP}$ = 8.65 Hz, C^4H-C^5H), 130.7 (s, CH aromatic), 135.0 (s, C aromatic), 147.1 (s, C aromatic), 167.2 (d, $^2J_{CP}$ = 302.7 Hz, C carbene). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 108.8 (s). Anal. Calcd for $C_{33}H_{42}Cl_2F_9N_2O_3PPd$: C, 44.34; H, 4.74; N, 3.13. Found: C, 44.19; H, 4.82; N, 3.00.

[$PdCl_2$(IPr)(ETPB)] (6g). A Schlenk tube was charged with 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (ETPB) (0.115 g, 0.71 mmol), [Pd(μ-Cl)Cl(IPr)]$_2$ (0.396 g, 0.35 mmol), and dichloromethane (10 mL) was added. The solution was stirred at room temperature for 30 min, and the solvent was removed in vacuo. The complex was obtained as a yellow powder in a quantitative yield. ^{1}H NMR (CD_2Cl_2): δ 0.73 (t, 3H, $^3J_{HH}$ = 7.7 Hz, CH_2-CH_3), 1.08 (d, 12H, $^3J_{HH}$ = 6.9 Hz, $CHCH_3$), 1.03−1.17 (m, 2H, CH_2-CH_3), 1.37 (d, 12H, $^3J_{HH}$ = 6.65 Hz, $NCHCH_3$), 3.02 (pseudo sept, 4H, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$), 4.11 (d, 6H, $^3J_{HH}$ = 4.5 Hz, OCH_2), 7.11 (d, 2H, J = 2.3 Hz, CH), 7.34 (br d, 4H, CH), 7.51 (br dd, 2H, CH). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 7.1 (s, CH_2-CH_3), 23.3 (s, ^{i}Pr), 23.5 (s, CH_2-CH_3), 26.3 (s, ^{i}Pr), 29.0 (s, ^{i}Pr), 36.1 (d, $^3J_{CP}$ = 31.2 Hz, C ETPB), 74.5 (d, $^2J_{CP}$ = 6.4 Hz, OCH_2), 124.2 (s, CH aromatic), 125.0 (d, $^4J_{CP}$ = 8.6 Hz, C^4H-C^5H), 130.2 (s, CH aromatic), 135.4 (s, C aromatic), 146.9 (s, C aromatic), 167.8 (d, $^2J_{CP}$ = 300.5 Hz, C carbene). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 87.7 (s). Anal. Calcd for $C_{33}H_{47}Cl_2N_2O_3PPd$: C, 54.44; H, 6.51; N, 3.85. Found: C, 54.59; H, 6.63; N, 3.82.

[$PdCl_2$(SIPr){P(OMe)$_3$}] (7a). A Schlenk tube was charged with [Pd(μ-Cl)Cl(SIPr)]$_2$ (1.313 g, 1.16 mmol) dissolved in dichloromethane (25 mL), and an excess of P(OMe)$_3$ (0.3 mL, 2.54 mmol) was added. The solution was stirred at room

temperature for 30 min and then concentrated in vacuo (7 mL). Addition of degassed methanol (10 mL) and concentration to 7 mL led to a precipitate which was washed with methanol (3 × 5 mL) after removal of the supernatant solution. The complex was obtained as a yellow powder (1.305 g, 82%). ^{1}H NMR (CD_2Cl_2): δ 1.29 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CHCH_3), 1.52 (d, 12H, $^3J_{HH}$ = 6.6 Hz, CHCH_3), 3.47 (d, 9H, $^3J_{PH}$ = 12.0 Hz, OCH_3), 3.58 (pseudo sept, 4H, $^3J_{HH}$ = 6.75 Hz, CHCH$_3$), 4.12 (s, 4H, NCH_2), 7.34 (m, 4H, CH), 7.45 (m, 2H, CH). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 23.6 (s, ^{i}Pr), 26.7 (s, ^{i}Pr), 28.7 (s, ^{i}Pr), 52.5 (d, $^4J_{CP}$ = 9.2 Hz, NCH_2), 53.9 (d, $^2J_{CP}$ = 1.5 Hz, OMe), 124.0 (s, CH), 129.0 (s, CH), 135.4 (s, C), 147.9 (s, C), 198.1 (d, $^2J_{CP}$ = 272.3 Hz, C carbene). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 110.0 (s). Anal. Calcd for $C_{30}H_{47}Cl_2N_2O_3PPd$: C, 52.07; H, 6.85; N 4.05. Found: C, 51.37; H, 6.80; N, 3.86.

[PdCl$_2$(SIPr){P(OCH$_2$CF$_3$)$_3$}] (7b). A vial was charged with [Pd(μ-Cl)Cl(SIPr)]$_2$ (0.227 g, 0.20 mmol) suspended in THF (2.5 mL), and P(OCH$_2$CF$_3$)$_3$ (0.088 mL, 0.40 mmol) was added. The solution was stirred at room temperature for 30 min. The solvent was removed in vacuo. Satisfactory elemental analyses on the crude product allowed its use without further purification. The complex was obtained as a yellow powder in a quantitative yield. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of octane in a THF solution of the complex. ^{1}H NMR (CD_2Cl_2): δ 1.29 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CHCH_3), 1.51 (d, 12H, $^3J_{HH}$ = 6.6 Hz, CHCH_3), 3.51 (pseudo sept, 4H, $^3J_{HH}$ = 6.7 Hz, CHCH$_3$), 4.17 (s, 4H, NCH_2), 4.23 (pseudo quint, 6H, J = 8.0 Hz, CH_2CF$_3$), 7.35 (m, 4H, CH), 7.48 (m, 2H, CH). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 23.5 (s, ^{i}Pr), 26,7 (s, ^{i}Pr), 28.8 (s, ^{i}Pr), 53.9 (d, $^4J_{CP}$ = 9.6 Hz, NCH_2), 63.15 (qd, $^2J_{CF}$ = 37.3 Hz, $2J_{CP}$ = 1.0 Hz, O-CH_2), 122.4 (qd, $^1J_{CF}$ = 277.7 Hz, $^3J_{CP}$ = 8.3 Hz, CF_3), 124.2 (s, CH), 129.5 (s, CH), 134.8 (s, C), 147.8 (s, C), 194.2 (d, $^2J_{CP}$ = 282.6 Hz, C carbene). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 110.9 (s). Anal. Calcd for $C_{33}H_{44}Cl_2F_9N_2O_3PPd$: C, 44.24; H, 4.95; N, 3.13. Found: C, 44.98; H, 4.55; N, 3.03.

General Procedure for the Suzuki−Miyaura Reaction. In a glovebox, a 5 mL screwcap-vial fitted with a septum equipped with a magnetic stirring bar was charged with the required amount of base, boronic acid and aryl chloride (if solid). Outside the glovebox, the required amount of aryl chloride (if liquid), catalyst solution and solvent were injected through the septum. The mixture was then stirred at the indicated temperature. The solvent was removed under vacuum and the resulting solid was filtered through a pad of silica (hexanes/dichloromethane). When necessary the product was purified by flash chromatography on silica gel.

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Note Added after ASAP Publication. In the version of this paper that was published on the web on February 19, 2010, the formula preceding ref 12f was incorrect. The formula that appears as of March 15, 2010, is correct.

Supporting Information Available: Calculations of %V_{Bur} for complexes **6a**, **6c**, **6d**, **6e**, and **7a**, crystal data and structure refinement, details of mechanistic investigations including NMR spectra, catalysts optimization, and cross-coupling products details and their ^{1}H and ^{13}C-{^{1}H} NMR spectra. Crystallographic data for complexes **6a**, **6c**, **6d**, CCDC/758461 **6e**, and **7a** in CIF format can also be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CCDC/758458 **6a**, CCDC/758459 **6c**, CCDC/758460 **6d**, CCDC/758461 **6e**, CCDC/758462 **7a**). This material is available free of charge via the Internet at http://pubs.acs.org.