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Nickel(II) Complexes of Bidentate N-Heterocyclic Carbene/Phosphine Ligands: Efficient Catalysts for Suzuki Coupling of Aryl Chlorides

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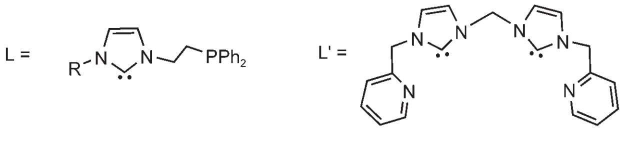
Abstract: Nickel(II) complexes of bidentate N-heterocyclic carbene (NHC)/phosphane ligand L were prepared and structurally characterized. Unlike palladium, which forms $[PdCl_2(L)]$, the stable nickel product isolated is the ionic $[Ni(L)_2]Cl_2$. These Ni^{II} complexes are highly robust in air. Among different N-substituents on the ligand framework, the nickel complex of ligand L bearing *N*-1-naphthylmethyl groups (**2a**) is a highly effective catalyst for Suzuki cross-coupling between phenylboronic acid and a range of aryl halides, including unreactive aryl chlorides. The activities of **2a** are largely superior to those of other reported nickel NHC complexes and their palladium counterparts. Unlike the previously reported $[NiCl_2(dppe)]$ (dppe = 1,2-bis(diphenylphosphino)ethane), **2a** can effectively catalyze the cross-coupling reaction without the need for a catalytic amount of PPh_3, and this suggests that the PPh_2 functionality of hybrid NHC ligand L can partially take on the role of free PPh_3. However, for unreactive aryl chlorides at low catalyst loading, the presence of PPh_3 accelerates the reaction.

Keywords: carbene ligands · cross-coupling · nickel · phosphane ligands · synthetic methods

Introduction

Monoligated palladium complexes containing electron-rich and bulky phosphane or N-heterocyclic carbene (NHC) ligands are widely used in cross-coupling reactions for the formation of C−C, C−N, C−O, and C−S bonds from aryl halides.[1] Some highly effective palladium systems based on electron-rich, bulky ligands of these two classes allowed the use of less expensive, more widely available, but less reactive aryl chlorides as substrates.[1] In particular, NHC ligands are attracting considerable interest because of their easy accessibility, remarkable catalytic activities, and high thermal stability imparted to the palladium catalysts.[2] Recently, research has also been devoted to the synthesis of palladium complexes with polydentate NHC-based ligands. In particular, the combination of nitrogen functionality, such as pyridine, and an NHC moiety has attracted considerable interest.[3–10] The straightforward synthetic procedures involving easily accessible N-substituted imidazoles and pyridine derivatives as starting materials led to diverse polydentate ligands, some of which were applicable in palladium-catalyzed C−C coupling reactions.[4,5,9] For example, the tridentate pincer framework of CNC ligands forms highly robust palladium complexes that show very efficient catalytic activities in the Heck reaction.[9a,f] However, the combination of phosphane and NHC functionalities has received less attention.[11,12] In contrast to monoligated palladium catalysts with electron-rich phosphane or NHC ligands, others and we have shown that bidentate ligand L exhibits only moderate activity in palladium-catalyzed C−C coupling reactions.[11b,12a,c]



On the other hand, the replacement of palladium by nickel catalysts in C−C coupling reactions is being promoted, because nickel is less expensive and can be effectively removed from the final products.[13] Indeed, some of the nickel catalysts have been shown to be more effective than the palladium systems.[13,14] To date, various nickel catalysts

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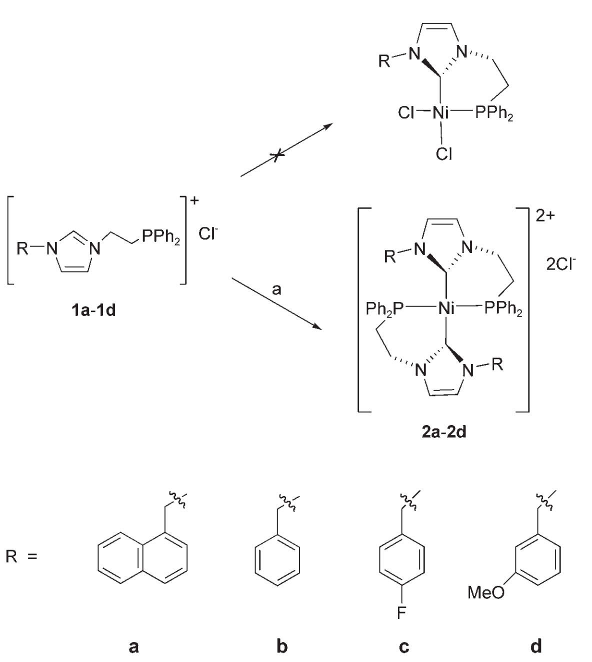
have been shown to catalyze a wide range of Suzuki cross-coupling reactions.[14–19] Among these systems, phosphane ligands are commonly employed.[18,19] For example, Percec et al. have shown that [$NiCl_2$(dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane) in the presence of an excess of PPh_3 is an efficient catalyst for the Suzuki cross-coupling of aryl mesylates and chlorides with both electron-donating (deactivating) and electron-withdrawing (activating) substituents.[19] However, only a very few reports have been made on using nickel NHC complexes as catalysts in Suzuki coupling reactions.[14–16] Notably, MacMillian et al. described a catalytic system, based on [Ni(cod)$_2$]/IMes·HCl (cod = cyclooctadiene, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazole carbene), capable of utilizing aryltrimethylammonium salts for Suzuki coupling reactions. Cavell et al. also reported on the use of nickel(II) NHC complex containing the monodentate tmiy ligand [NiBr(tmiy)$_2$(*o*-tolyl)] (tmiy = 1,3,4,5,-tetramethylimidazol-2-ylidene) in the Suzuki cross-coupling reaction. The activity of this nickel NHC catalyst is, however, limited to reactive aryl bromides.[15]

Recently, we showed that for the nickel(II) complex of the tetradentate NHC/pyridine ligand L′, [Ni(L′)]Br_2, the presence of catalytic amount of PPh_3 significantly enhances its activity in Suzuki coupling of electron-deficient (reactive) and electron-neutral aryl chlorides.[16] The use of a monophosphane (PCy_3; HPR_2, R = alkyl) as a coligand in palladium-catalyzed Suzuki coupling reactions has also been described.[20] The necessity of PPh_3 in our [Ni(L′)]Br_2 system encouraged us to investigate whether nickel(II) complexes of a bidentate ligand with both NHC and phosphane functionalities are more effective catalysts for Suzuki coupling reactions. Therefore, we reinvestigated ligand L and prepared new nickel(II) complexes. Unlike palladium, which forms [$PdCl_2$(L)], the stable nickel complex of L obtained is the ionic [Ni(L)$_2$]Cl_2. Highly robust [Ni(L)$_2$]Cl_2 is indeed much more effective than [$PdCl_2$(L)] in utilizing unreactive, electron-rich aryl chlorides as substrates for Suzuki cross-coupling, even in the absence of PPh_3.

Results

Synthesis and spectroscopic characterization of nickel(II) complexes 2a–2d: Ligand precursors [LH]Cl (**1a–1c**), was prepared according to our previous reported procedures.[11b] Initially, complexation of [LH]Cl with nickel was preformed following a procedure analogous to that for their palladium complexes,[11b] that is, one-pot reaction between [LH]Cl and $NiCl_2$ (1:1 molar ratio) with NaOAc as base in DMSO at 75 °C for 3 h. In contrast to palladium, which forms neutral [$PdCl_2$(L)] complexes, subsequent studies showed that the final nickel complex obtained is the ionic [Ni(L)$_2$]Cl_2 (**2a–2d**; Scheme 1). Thus, a 2:1 ratio of [LH]Cl:$NiCl_2$ was required to obtain the optimum yield. However, this original procedure was not suitable for **2b** and **2d**, which were produced with unsatisfactory purity. A more general and cleaner synthetic procedure for **2a–2d** is the metal acetate protocol, which is a common synthetic route for transition-metal NHC complexes from imidazolium salts.[16,21] Hence, direct reaction between [LH]Cl and Ni(OAc)$_2$ (2:1 molar ratio) in DMF at 50 °C for 3 h afforded the same complexes in pure form. Pale yellow compounds **2a–2d** are stable in air and in solution. They have limited solubility in halogenated solvents but dissolve partially in DMF or DMSO. All of them were fully characterized by microanalysis, spectroscopic methods, mass spectrometry, and X-ray crystallography. Even though the silver carbene transfer reaction is a commonly employed method for the preparation of metal NHC complexes,[22] our attempts following this route were unsuccessful.



Scheme 1. Synthesis of [Ni(L)$_2$]Cl_2. Conditions: a) For **2a** and **2c** only $NiCl_2$/NaOAc; for **2a–2d** Ni(OAc)$_2$.

Complexes **2a–2d** exhibit ^{1}H NMR resonances in the diamagnetic range of $\delta = 3.0–9.0$ ppm reflecting the low-spin configuration and hence square-planar coordination environment of the nickel(II) centers. The successful deprotonation of C^2H on the imidazolium moiety was confirmed by the absence of a signal at $\delta \approx 10.5$ ppm. The bidentate coordination of L around the nickel ion can be inferred from the presence of four diastereotopic proton signals for the ethylene linkage in the range of $\delta = 4.0–6.1$ ppm. The singlet $^{31}P\{^1H\}$ NMR resonances for **2a–2d** were observed at $\delta \approx 18–19$ ppm, slightly upfield from those of $\delta = 20–24$ ppm for the palladium complexes. The carbenic carbon atom of **2a** was observed as a triplet at $\delta = 162.8$ ppm, which is in the normal range of other nickel(II) NHC complexes reported in the literature.[7b,23] The carbenic carbon atoms of **2b–2d**, however, were not observed due to insufficient solubility of the compounds. Nevertheless, the NMR data alone were not sufficient to identify whether the nickel(II) complexes are ionic [Ni(L)$_2$]Cl_2 or neutral [$NiCl_2$(L)].

Electrospray ionization mass spectrometry (ESI-MS) studies: Compounds **2a**–**2b** were characterized by mass spectrometry with “soft” electrospray ionization in DMF, which unambiguously confirmed the ionic form $[Ni(L)_2]Cl_2$. The base peak observed in each spectrum corresponds to $[M{-}Cl]^+$, for example, m/z 951.2 for **2a**. Importantly, the doubly charged ion $[M{-}2Cl]^{2+}$ that was also observed in each spectrum confirms the dicationic nature of these complexes in solution. For example, the peak at m/z 449.3 corresponds to dicationic nickel complex **2a** without counterions. Interestingly, in the spectra of **2a**, **2b**, and **2d**, a water molecule, presumably due to the wet DMF solvent used, interacts with the positive ion $[M{-}Cl]^+$ giving rise to the peaks of $[M{-}Cl{+}H_2O]^+$ at m/z 933.1, 850.7, and 911.9, respectively. The association of water with $[M{-}Cl]^+$ is most probably by hydrogen-bonding interaction with the chloride ion. Hydrogen-bonding interactions between water and halide anions are commonly observed.[24] In fact, in the solid-state structure of **2b**, an incorporated water molecule forms a hydrogen bond with a chloride anion (vide infra). All the assignments in the MS spectra show good agreement between the observed and calculated isotopic distributions.

X-ray diffraction studies on 2a–2d: The structures determined at 150 K (Table 1) are shown in Figures 1–4. Each Ni^{II} center in **2a**–**2d** is coordinated by two bidentate L ligands in a distorted square-planar environment with a sum of the four bond angles at Ni1 of 359.3 (**2a**), 360.2 (**2b**), 360.2 (**2c**), and 359.3(**2d**). The two carbene (phosphane) moieties are coordinated *trans* to the two ethylene linkages situated on one side of the coordination plane. Generally, in **2a**–**2d**, the C-Ni-C angle is closer to linearity than the P-Ni-P angle. For example, the C1-Ni1-C29 bond angle in **2a** is 177.3(3)°, whereas the P1-Ni1-P2 angle of 164.57(8)° deviates significantly from the ideal 180°. The Ni−C and Ni−P distances in **2a**–**2d** are within the normal ranges. Although there are numerous nickel NHC complexes reported in the literature,[25] relevant examples containing both phosphane

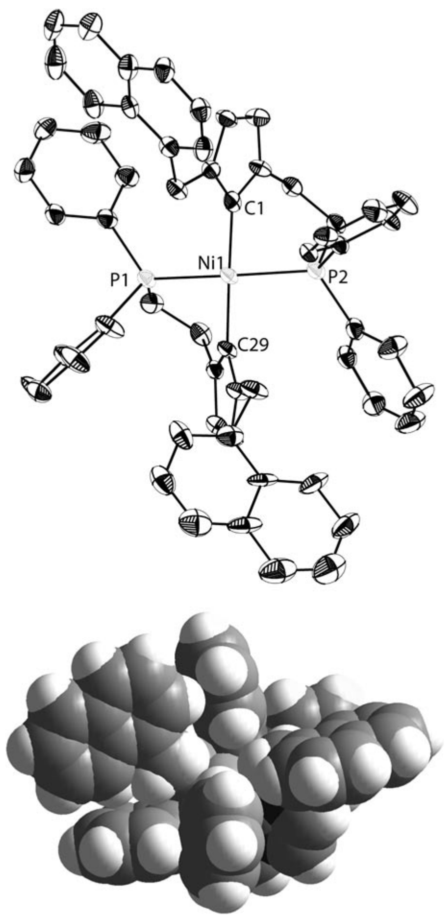


Figure 1. Top: thermal ellipsoid plot of the cationic portion of **2a** at the 35 % probability level (one of the naphthyl groups is disordered and only the major orientation with 0.75 site of occupancy is shown). Selected bond lengths: Ni1−C1 1.914(7), Ni1−C29 1.876(7), Ni1−P1 2.205(2), Ni1−P2 2.185(2) Å. Selected bond angles: C1-Ni1-C29 177.3(3), P1-Ni1-P2 164.57(8), C1-Ni1-P1 96.0(2), C1-Ni1-P2 83.7(2), C29-Ni1-P1 83.4(2), C29-Ni1-P2 96.2(2)°. Bottom: space-filling representation showing the embedment of the nickel ion inside the ligand framework.

Table 1. Crystallographic data of **2a**–**2d**.

	2a	**2b**	**2c**	**2d**
formula	$C_{56}H_{50}N_4NiP_2Cl_2{\cdot}3\,CH_3OH$	$C_{48}H_{46}N_4NiP_2Cl_2{\cdot}H_2O$	$C_{48}H_{44}F_2N_4NiPCl_2$	$C_{50}H_{50}N_4NiO_2P_2Cl_2$
M	1066.68	888.45	906.42	930.49
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	Pc	$P2_1/c$	$C2$	$C2/c$
a [Å]	9.7827(4)	11.7417(10)	22.0676(7)	22.1786(11)
b [Å]	11.5029(4)	18.0255(17)	9.0135(3)	9.1773(4)
c [Å]	23.8131(9)	21.264(2)	11.8192(4)	22.9439(9)
β [°]	90.796(2)	103.742(6)	105.591(2)	106.606(2)
V [Å^3]	2679.42(18)	4371.6(7)	2264.41(13)	4475.2(3)
T [K]	150(2)	150(2)	150(2)	150(2)
Z	2	4	2	4
ρ_{calcd} [Mg m^{-3}]	1.322	1.350	1.329	1.381
unique data	6348	9063	2872	5341
parameters	688	523	276	279
R_1[a] [$I > 2\sigma(I)$]	0.0611	0.0600	0.0475	0.0524
wR_2[b] (all data)	0.1720	0.1689	0.1256	0.1606
Flack parameter	0.12(2)	–	0.10(2)	–

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

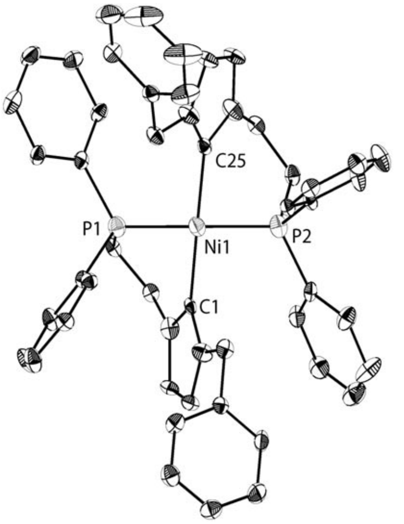


Figure 2. Thermal ellipsoid plot of the cationic portion of **2b** at the 50% probability level. Selected bond lengths: Ni1−C1 1.971(4), Ni1−C25 1.985(4), Ni1−P1 2.1025(13), Ni1−P2 2.1074(13) Å. Selected bond angles: C1-Ni1-C25 179.15(18), P1-Ni1-P2 163.64(5), C1-Ni1-P1 82.82(12), C1-Ni1-P2 94.21(12), C25-Ni1-P1 97.85(13), C25-Ni1-P2 85.29(13)°.

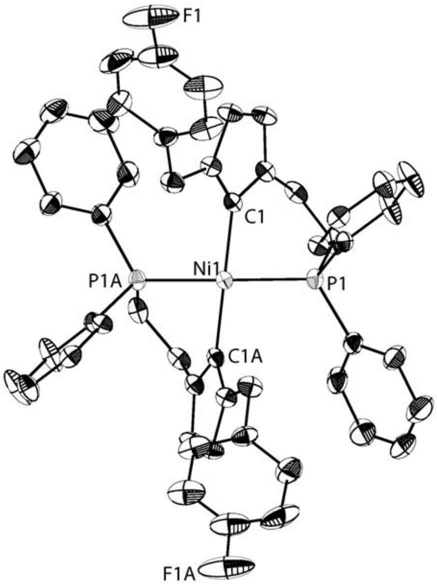


Figure 3. Thermal ellipsoid plot of the cationic portion of **2c** at the 35% probability level. Selected bond lengths: Ni1−C1 1.898(4), Ni1−P1 2.1863(9) Å. Selected bond angles: C1-Ni1-C1A 179.2(3), P1-Ni1-P1A 165.42(7), C1-Ni1-P1 97.23, C1-Ni1-P1A 82.87(11)°.

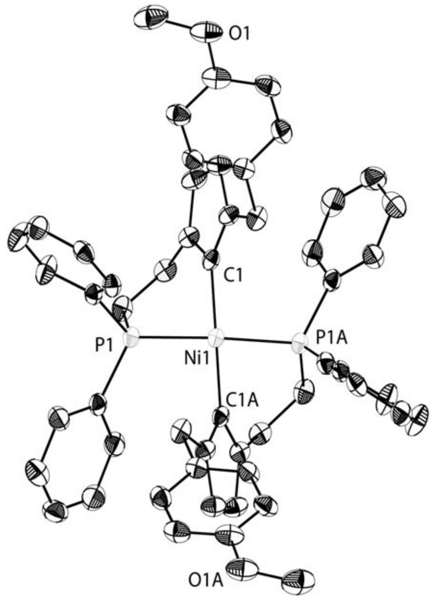


Figure 4. Thermal ellipsoid plot of the cationic portion of **2d** at the 35% probability level. Selected bond lengths: Ni1−C1 1.901(3), Ni1−P1 2.1931(8) Å. Selected bond angles: C1-Ni1-C1A 178.09(19), P1-Ni1-P1A 159.38(5), C1-Ni1-P1 84.44(10), C1-Ni1-P1A 95.22(10)°.

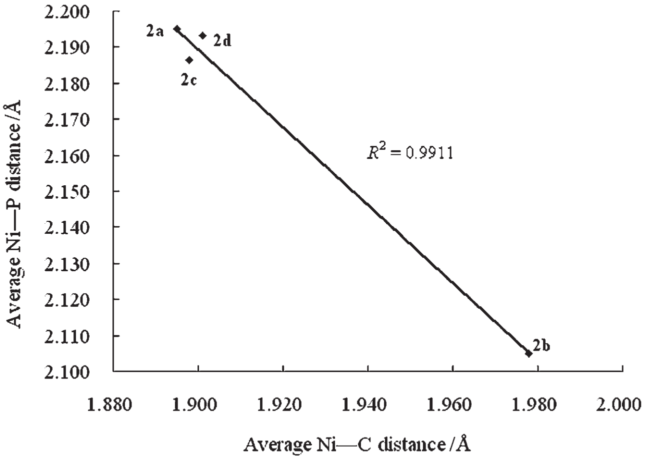


Figure 5. Plot of average Ni−C and Ni−P distances in **2a**–**2d**.

and NHC moieties are rare.[26] Interestingly, even though **2b**–**2d** bear similar N-substituents, a plot of the average Ni−C and Ni−P distances in **2a**–**2d** clearly reveals the significantly longer Ni−C and shorter Ni−P distances in **2b**, which reflect a stronger *trans* influence exerted by the phosphorus atom than by the NHC moiety in **2b** (Figure 5). In fact, the more stable Ni−P bonds in **2b** correlate to its poorer catalytic activity in Suzuki coupling (vide infra). It can be envisaged from the space-filing representation of **2a** that the nickel ion is embedded inside the ligand framework of L, and direct attachment of a bulky group on the nitrogen atom of the imidazole ring will lead to unfavorable overlap with the adjacent phenyl rings; therefore, the methylene spacers appear to be crucial in directing the bulky naphthyl/aryl moieties away from the sterically congested coordination sphere (Figure 1, bottom). In **2a** and **2b**, the chloride ions form Cl···H−O hydrogen-bonding interactions with guest methanol and water molecules, respectively. The geometries of the hydrogen-bonding interactions in **2a** and **2b** are given in the Supporting Information.

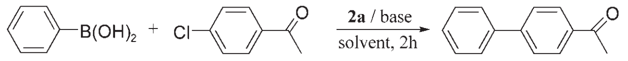
Theoretical studies: Palladium forms neutral 1:1 Pd–L complex [$PdCl_2(L)$], whereas for nickel ionic 1:2 Pd–L complex [$Ni(L)_2$]Cl_2 is the stable product. We believe that the difference has thermodynamic reasons. Therefore, we undertook theoretical investigations on the relative stability of $[Ni(L)_2]Cl_2$ and their palladium counterparts $[PdCl_2(L)]$ on a simplified system and calculated the energy of the reaction shown in Scheme 2 (see Computational Methods). The optimized geometrical parameters of the products **5** (a model for $[PdCl_2(L)]$) and **6** (a model for $[Ni(L)_2]Cl_2$) are in good agreement with the X-ray data. For example, the computed Ni−C and Ni−P distances of **6** are 1.914 and 2.233 Å, respectively, which are comparable to those of the solid-state structures of **2a**, **2c**, and **2d**. The Pd−C and Pd−P distances of **5** (2.014 and 2.274 Å, respectively) are also similar to those obtained for $[PdCl_2(L)]$ from the X-ray structure determinations.[11b] With the CPCM model, the energy of reaction is $-9.8\ \mathrm{kcal\,mol^{-1}}$, and it is $-7.3\ \mathrm{kcal\,mol^{-1}}$ with the 6-311G** basis set. Hence, our computational results indeed show that $[PdCl_2(L)]$ and $[Ni(L)_2]Cl_2$ are energetically more favorable than $[NiCl_2(L)]$ and $[Pd(L)_2]Cl_2$.

Thermogravimetric analysis (TGA): The thermal stability of **2a**–**2d** was studied by TGA on amorphous powders, and the results suggested that the four solids are thermally stable below 200 °C. Their TGA curves are essentially similar, typically with an initial weight loss due to liberation of guest water or solvent molecules and then a gradual weight loss from about 200 to 500 °C. For example, the TGA curve of **2b** shows a weight loss of 3.85 % from 50 to 130 °C, corresponding to the release of two water molecules (calcd 3.98 %), and then decomposition starts to occur at an onset temperature of 237 °C.

Suzuki cross-coupling: We have previously shown that the precatalyst $[Ni(L')]Br_2$ is effective in Suzuki cross-coupling.[16] Undoubtedly, donor-atom dissociations are essential in this bis-chelated Ni^{II} complex to generate vacant sites for the incoming substrates. Also, reduction of Ni^{II} to Ni^0 is required for an initial oxidative addition of an Ar−X bond in the catalytic cycle. Such reduction to Ni^0 can be mediated by bases or reactants (i.e., without the need for an external reducing agent).[18g] The addition of a catalytic amount of reducing PPh_3 should further facilitate this reduction. Since the bidentate ligand L contains the phosphane functionality, we were interested whether $[Ni(L)_2]Cl_2$ represents a simplified catalytic system (without the necessity of PPh_3) for the Suzuki coupling reaction. We tested the catalytic performance of **2a**–**2d** in the cross-coupling between phenylboronic acid and a range of aryl halides with different electronic properties (from reactive, electron-deficient aryl bromides to unreactive, electron-rich aryl chlorides). Initially, we employed similar catalytic conditions as reported for $[NiCl_2(dppe)]$[19] and $[Ni(L')]Br_2$,[16] that is, 1–3 mol % of **2a** as precatalyst in the presence of 2–6 mol % of PPh_3 (1:2 Ni/PPh_3). Further studies indicated that **2a** is still efficient for unreactive, electron-rich aryl chlorides even in the absence of PPh_3.

The different solvent and base combinations for the coupling reaction were studied according to Table 2. The coupling reaction between phenylboronic acid and 4-chloroacetophenone over a period of 2 h was employed as standard reaction for screening purposes. The coupling activity is highly solvent and base dependent. The combination of $K_3PO_4{\cdot}H_2O$/toluene affords quantitative yield (entry 1), whereas no coupling product is obtained when the reaction is conducted in toluene with NaOAc as base (entry 6). The use of Cs_2CO_3 as base in 1,4-dioxane, that is, the conditions used for the $[PdCl_2(L)]$-catalyzed cross-coupling reaction,[11b] was not applicable for the nickel system (entry 9).

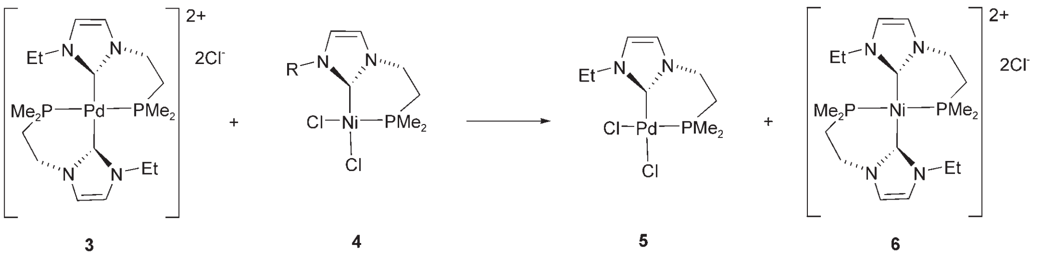
Table 2. Effect of solvents and bases on Suzuki coupling catalyzed by **2a**.[a]



Entry	Base	Solvent	Yield [%]
1	$K_3PO_4{\cdot}H_2O$	toluene	100
2	$K_3PO_4{\cdot}H_2O$	1,4-dioxane	48
3	$K_3PO_4{\cdot}H_2O$	THF	63
4	$K_3PO_4{\cdot}H_2O$	2-propanol	38
5	K_2CO_3	toluene	76
6	NaOAc	toluene	0
7	KOH	toluene	82
8	Cs_2CO_3	toluene	74
9	Cs_2CO_3	1,4-dioxane	11

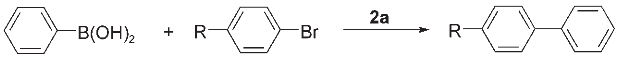
[a] Reaction conditions: 4-chloroacetophenone (1 mmol), phenylboronic acid (1.3 mmol), base (2.6 mmol), Ni catalyst (2 mol %), solvent (3 mL), 2 h, 80 °C, GC yield.

With the optimized solvent/base combination, **2a** can in general catalyze effectively the reaction of de-, un-, and activated aryl bromides with excellent yields; the addition of PPh_3 is not necessary (Table 3). The capability of the catalytic system for the cross-coupling of the less reactive aryl chlorides is summarized in Table 4 (entries 1–7). Quantitative yields of 4-acetylbiphenyl can be obtained from 4-chloroacetophenone over 2 h with or without PPh_3 (entries 1



Scheme 2. Hypothetical reaction between $[Pd(L)_2]Cl_2$ and $[NiCl_2(L)]$.

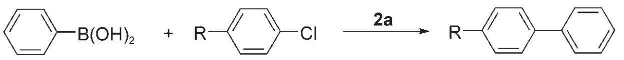
Table 3. Suzuki coupling with aryl bromides catalyzed by **2a**.[a]



Entry	Cat. [%]	PPh_3 [%]	R	*t* [h]	Yield [%]
1	3	6	COMe	3	100[b]
2	3	0	COMe	3	100[b]
3	3	6	H	12	100
4	3	0	H	12	95
5	3	6	OMe	12	100[b]
6	3	0	OMe	12	100[b]

[a] Reaction conditions: aryl bromide (1 mmol), phenylboronic acid (1.3 mmol), $K_3PO_4{\cdot}H_2O$ (2.6 mmol) as base, **2a** (3 mol%), PPh_3 (0–6 mol%), toluene (3 mL), 80 °C, GC yield. [b] NMR yield.

Table 4. Suzuki coupling with aryl chlorides catalyzed by **2a**.[a]



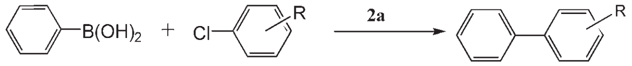
Entry	Cat. [%]	PPh_3(%)	R	*t* [h]	Yield [%]
1	3	6	COMe	2	100[b](95)
2	3	0	COMe	2	100[b](97)
3	3	6	Me	2	100(93)
4	3	0	Me	24	98
5	3	6	OMe	12	91
6	3	6	OMe	24	100[b](99)
7	3	0	OMe	24	96[b](93)
8	2	4	COMe	2	100
9	2	0	COMe	2	100
10	2	4	Me	24	100
11	2	0	Me	24	88
12	2	4	OMe	24	95
13	2	0	OMe	24	91(89)
14	1	2	COMe	2	97
15	1	2	COMe	6	100
16	1	0	COMe	6	90
17	1	2	Me	24	98
18	1	0	Me	24	74
19	1	2	OMe	24	92
20	1	0	OMe	24	77

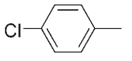
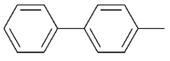
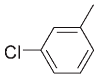
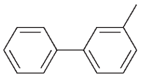
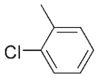
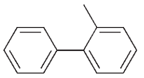
[a] Reaction conditions: aryl chloride (1 mmol), phenylboronic acid (1.3 mmol), $K_3PO_4{\cdot}H_2O$ (2.6 mmol) as base, **2a** (1–3 mol%), PPh_3 (0–6 mol%), toluene (3 mL), 80 °C, GC yield; yields of isolated compounds in parentheses. [b] NMR yield.

and 2). Notably, **2a** can also utilize electron-neutral and electron-rich (unreactive) aryl chlorides as coupling partners for the formation of unsymmetrical biphenyls (Table 4, entries 3–7). For example, even without the addition of 6 mol% PPh_3, 4-methoxybiphenyl can still be obtained in an excellent 93% yield of isolated product from the unreactive 4-chloroanisole within 24 h (Table 4, entries 6 and 7).

In the presence of PPh_3, the catalyst loading can be reduced to 2 or 1 mol% without significant reduction of yield. For example, even with the unreactive 4-chloroanisole, the yields of the products only decreased slightly from 99 to 95 to 92% with catalyst loadings of 3, 2, and 1 mol%, respectively (Table 4, entries 6, 12, and 19). However, in the absence of PPh_3, a low catalyst loading of 1 mol% furnishes only 77% yield of 4-methoxybiphenyl, instead of 96% yield with 3 mol% of the catalyst (Table 4, entries 7 and 20). A good yield of 91% can still be achieved with 2 mol% catalyst loading (Table 4, entry 13). Since $[Ni(L)_2]Cl_2$ contains two bidentate ligands L, one might suspect that **2a** would give poor yields with sterically hindered substrates; however, excellent yields of coupled products can still be obtained over 24 h with 2- and 3-chlorotoluene (Table 5, entries 2 and 3). These activities reflect the fact that the true catalytic species has much less steric bulk than the precatalyst.

Table 5. Suzuki coupling of chlorotoluenes catalyzed by **2a**.[a]



Entry	Substrate	Product	Yield [%]
1			100 (98)
2			100 (67)
3			94 (32)

[a] Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.3 mmol), $K_3PO_4{\cdot}H_2O$ (2.6 mmol), **2a** (3.0 mol%), PPh_3 (6.0 mol%), toluene (3 mL), 80 °C, 24 h, NMR yield; yield without addition of PPh_3 in parentheses.

The difference in catalytic behavior with and without the addition of PPh_3 was subjected to a more detailed kinetic study on the coupling reactions of 4-chloracetophenone and 4-chlorotoluene with 3 mol% of **2a**. For the reactive 4-chloroacetophenone, the addition of PPh_3 is not necessary, because it produces no accelerating effect, as indicated by the superposition of the two curves (Figure 6). However, for less reactive substrates, such as 4-chlorotoluene, the reaction is slightly accelerated in the presence of PPh_3 (Figure 7).

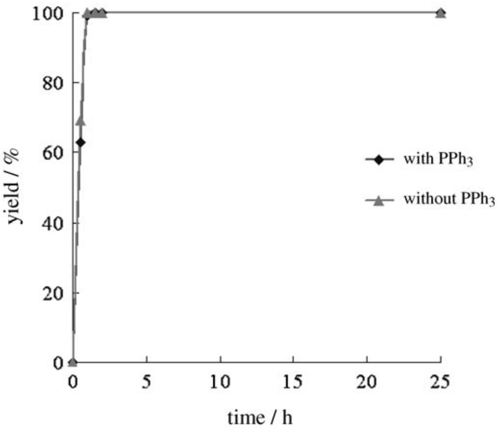


Figure 6. Comparison of the time/yield characteristics of **2a** with and without the addition of PPh_3 in the cross-coupling of phenylboronic acid and 4-chloroacetophenone.

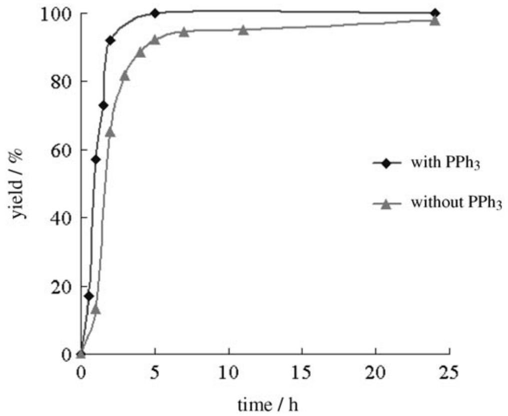
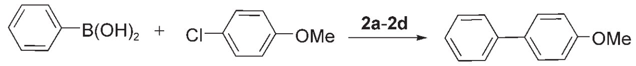


Figure 7. Comparison of the time/yield characteristics of **2a** with and without the addition of PPh_3 in the cross-coupling of phenylboronic acid and 4-chlorotoluene.

We compared the catalytic activities of **2a**–**2d** (Table 6). Entry 1 clearly indicates that **2a** containing the bulkier *N*-1-naphthylmethyl groups is the most active complex. Interestingly, the least reactive compound is **2b**, which contains *N*-phenyl groups and afforded only 37 % yield of 4-methoxybiphenyl. This can be explained by the fact that the stronger Ni–P bonds in **2b**, as shown by the solid-state structure, lead to inefficient phosphane-arm dissociation to generate the coordinatively unsaturated active species and hence poor catalytic activity of the precatalyst. The structure/activity relationship for precatalysts was also explored by Nolan et al. recently.[27] They reported a family of [Pd(allyl)Cl(IPr)] (IPr = *N*,*N'*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) complexes in which the allyl moiety is substituted. As shown by the X-ray structural data, substitution increases the dissymmetry of the allyl ligand around the Pd center, and this allows facile activation of Pd^{II} to Pd^0. The ease of activation translates into a much higher activity of, for example, [Pd(cinnamyl)Cl(IPr)] relative to [Pd(allyl)Cl(IPr)].

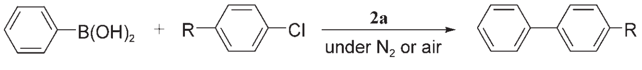
Table 6. Suzuki coupling catalyzed by **2a**–**2d**.[a]



Entry	Catalyst	Yield [%]
1	**2a**	91
2	**2b**	37
3	**2c**	56
4	**2d**	62

[a] Reaction conditions: 4-chloroanisole (1.0 mmol), phenylboronic acid (1.3 mmol), $K_3PO_4{\cdot}H_2O$ (2.6 mmol), nickel catalyst (2.0 mol %), toluene (3 mL), 24 h, 80 °C, GC yield.

Table 7. Effect of conducting Suzuki coupling under N_2 and air.[a]



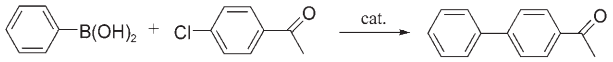
Entry	Atmosphere	R	*t* [h]	Yield [%]
1	N_2	COMe	2	100
2	air	COMe	2	42
3	N_2	Me	24	88
4	air	Me	24	6
5	N_2	OMe	24	91
6	air	OMe	24	41

[a] Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1.3 mmol), $K_3PO_4{\cdot}H_2O$ (2.6 mmol) as base, Ni catalyst (2 mol %), toluene (3 mL), 80 °C, GC yield.

We also briefly investigated the effect of conducting the catalytic reaction in air and compared the results with those performed under nitrogen. Even though **2a**–**2d** are stable in air, Table 7 shows that when the catalytic reactions were conducted in air instead of under nitrogen, drastic reduction of product yields were observed. This can be rationalized by the fact that both the intermediate Ni^0 state and the free phosphane arms are reactive towards oxygen. After irreversible oxidation of phosphane to phosphane oxide by air, the presumed recoordination of the phosphane arm to stabilize the resting states in the catalytic cycle becomes impossible.

The catalytic performance of **2a** was compared with other nickel and palladium catalysts reported in the literature. Nickel complexes of L or dppe are much more effective than $Ni(OAc)_2$ and $NiCl_2$ (Table 8, entries 1–4 and 6, 7).

Table 8. Suzuki coupling catalyzed by different nickel and palladium catalysts.[a]

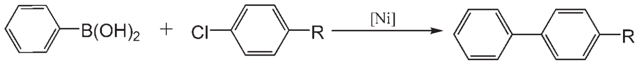


Entry	Catalyst	Cat. [%]	PPh_3 [%]	Yield [%]
1	**2a**	1	2	97
2	**2a**	1	0	88
3	$[NiCl_2(dppe)]$	1	2	90
4	$[NiCl_2(dppe)]$	1	0	55
5	$[NiCl_2(dppe)]$	1	2	26
6	$Ni(OAc)_2{\cdot}4H_2O$	1	2	8
7	$NiCl_2$	1	2	1
8[b]	$[PdCl_2(L)]$ (L = **1a**)	1	0	3
9[b]	$[PdCl_2(L)]$ (L = **1a**)	1	2	22

[a] For entries 1–7: reaction conditions: 4-chloroacetophenone (1 mmol), phenylboronic acid (1.3 mmol), base (2.6 mmol), catalyst (1 mol %), toluene (3 mL), 2 h, 80 °C, GC yield. [b] Cs_2CO_3 (2 mmol) as base, 1,4-dioxane (3 mL) as solvent; other conditions as in entries 1–7.

These complexes are also reactive than $[NiCl_2(PPh_3)_2]$ (Table 8, entry 5). The nickel catalyst with L is much more reactive than its palladium counterpart in catalyzing cross-coupling reaction with the aryl chloride (Table 8, entries 8 and 9). To further differentiate the efficiency between the most reactive **2a** and $[NiCl_2(dppe)]$, their performances in the cross-coupling reactions were compared. For the reactive 4-chloroacetophenone substrate, their activities are comparable when a catalytic amount of PPh_3 is present (Table 9, entries 1 and 2). However, in the absence of PPh_3, **2a** gives a better yield of 88 % instead of 55 % given by $[NiCl_2(dppe)]$ (Table 9, entries 3 and 4). The difference in activities became more evident when the unreactive 4-chloranisole was used as substrate. While **2a** afforded a 92 % yield of 4-methoxybiphenyl, only 48 % yield was recorded

Table 9. Suzuki coupling catalyzed by **2a** and [$NiCl_2$(dppe)].[a]



Entry	Catalyst	PPh_3 [%]	R	*t* [h]	Yield [%]
1	**2a**	2	COMe	2	97
2	[$NiCl_2$(dppe)]	2	COMe	2	90
3	**2a**	0	COMe	2	88
4	[$NiCl_2$(dppe)]	0	COMe	2	55
5	**2a**	2	OMe	24	92
6	[$NiCl_2$(dppe)]	2	OMe	24	48
7	**2a**	0	OMe	24	77
8	[$NiCl_2$(dppe)]	0	OMe	24	28

[a] Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.3 mmol), $K_3PO_4{\cdot}H_2O$ (2.6 mmol), nickel catalyst (1.0 mol%), toluene (3 mL), 80 °C, GC yield.

for [$NiCl_2$(dppe)] with PPh_3 added. In the absence of PPh_3, **2a** still gives a decent yield of 77%, whereas [$NiCl_2$(dppe)] becomes ineffective (Table 9, entries 7 and 8).

Conclusion

We have prepared and characterized Ni^{II} complexes of bidentate phosphane/NHC ligands L. Unlike palladium, which forms [$PdCl_2$(L)], the stable nickel product isolated is the ionic [$Ni(L)_2$]Cl_2, which is consistent with theoretical calculations. These Ni^{II} complexes **2a**–**2d**, in contrast to Ni^0 compounds, have high stability in air, which is a desirable property of a catalyst precursor. Notably, the novel nickel complex **2a** is highly effective in Suzuki cross-coupling of phenylboronic acid with a range of aryl halides, including unreactive aryl chlorides. The activities of [$Ni(L)_2$]Cl_2 are largely superior to those of other reported nickel NHC complexes[15,16] and their palladium counterparts.[11b] Unlike [$NiCl_2$(dppe)][19] **2a** can effectively catalyze cross-coupling without the need for a catalytic amount of PPh_3, and this suggests that the PPh_2 functionality of the hybrid NHC ligand L can partially replace the role of free PPh_3. For unreactive aryl chlorides at low catalyst loading, the presence of PPh_3, however, accelerates the reaction.

For nickel and palladium complexes containing monodentate ligand L″ (L″ = bulky phosphane and NHC), the monoligated species [M^0(L″)] is the generally accepted active species for initial oxidative addition of a C–X bond.[1] For the formation of an active species from the coordinatively saturated tetraligated Ni^{II} complexes **2a**–**2d**, reduction to Ni^0 and ligand dissociation can be assumed. Since NHC ligands are stronger σ donors than a PPh_2 moiety, dissociation of the phosphane arm is more likely to occur. In fact, the poor activities of **2b** among [$Ni(L)_2$]Cl_2 can be correlated with its stronger Ni–P bond compared to the other complexes, as evidenced from their solid-state structures. Even though the catalyst precursors are highly stable in air, the sensitivity of the catalytic systems towards air is also in line with the involvement of air-sensitive intermediates (Ni^0 state, free phosphane arm). The scope of the nickel complexes in other C–C coupling reactions is being investigated.

Experimental Section

General procedure: All reactions were performed under a dry nitrogen atmosphere by standard Schlenk techniques. All solvents used were purified according to standard procedures.[28] Commercially available chemicals were purchased from Aldrich or Acros. The ligand precursors **1a**–**1d** were synthesized according to the literature procedure. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded at 300.13, 75.48, and 121.49 Hz, respectively, on a Bruker AV-300 spectrometer. Chemical shifts for ^{1}H and ^{13}C spectra are reported in parts per million relative to residual signal of $CDCl_3$ (^{1}H: $\delta = 7.24$ ppm; ^{13}C: $\delta = 77.0$ ppm) or [D_6]DMSO (^{1}H: $\delta = 2.50$ ppm; ^{13}C: $\delta = 39.5$ ppm). ^{31}P NMR chemical shifts are reported relative to 85% H_3PO_4 external standard (^{31}P: $\delta = 0.0$ ppm). Elemental analyses and ESI mass spectrometry were performed on a Heraeus CHN-OS Rapid Elemental Analyzer and a Finnigan/Thermo Quest MAT 95XL, respectively, at the Instruments Center of National Chung Hsing University, Taiwan. GC analyses were performed on a Varian CP-3800 GC-FID system equipped with a CP-Sil 5 CB capillary column (length: 30 mm, ID: 0.33 mm, film thickness: 1.0 μm). Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer Pyris 6 TGA Thermogravimetric Analyzer under flowing N_2 gas (40 mL min^{-1}), and the heating rate was 20 °C min^{-1}.

Preparation of 2a

Method A: A mixture of **1a** (0.270 g, 0.591 mmol), $NiCl_2$ (0.038 g, 0.295 mmol), and NaOAc (0.0484 g, 0.591 mmol) in dried DMSO (5 mL) was stirred at 75 °C for 3 h. After cooling, the solvent was completely removed under vacuum. The residue was washed twice with water (25 mL) and THF (25 mL). Subsequently, the yellow solid was collected on a frit and dried under vacuum overnight. Yield: 0.19 g, 67%.

Method B: A mixture of **1a** (0.900 g, 1.97 mmol) and $Ni(OAc)_2{\cdot}4H_2O$ (0.245 g, 0.985 mmol) in dried DMF (5 mL) was stirred at 50 °C for 3 h. The subsequent workup procedure was same as that of method A. Yield: 0.65 g, 68%; m.p. 196–198 °C; elemental analysis calcd (%) for $C_{56}H_{50}Cl_2N_4P_2Ni$: C 69.41, H 5.20, N 5.79; found: C 69.42, H 5.21, N 5.75; ^{1}H NMR ([D_6]DMSO): $\delta = 4.64$ (d, ^2J(H,H) = 13.9 Hz, 2H; NC$H_A$$H_B$), 4.98 (br s, 2H; PC$H_2CH_2$), 5.31 (br s, 2H; PC$H_2CH_2$), 6.01 (s, 2H; imi-H), 6.23 (d, ^2J(H,H) = 13.9 Hz, 2H; NC$H_A$$H_B$), 6.46 (d, ^3J(H,H) = 7.5 Hz, 2H; Ar-H), 6.86 (d, ^3J(H,H) = 7.5 Hz, 2H; Ar-H), 7.08 (m, 4H; CH_2-Ar), 7.27–8.19 ppm (m, 32H; Ar-H, imi-H, Ph-H); ^{13}C{^{1}H} NMR ([D_6]DMSO): $\delta = 25.8$, 47.6, 51.1, 122.9, 123.6, 125.3, 125.9, 126.7, 127.3, 128.0, 129.2 (d, J(C,P) = 13.0 Hz, CH), 129.8, 130.2, 130.8, 131.1, 131.5, 132.9, 133.6, 134.4, 162.8 ppm (t, ^2J(C,P) = 35.5 Hz, Ni–C); ^{31}P{^{1}H} NMR ([D_6]DMSO): $\delta = 19.4$ ppm (s); ESI-MS (DMF): *m/z* (%): 951.2 (6) $[M-Cl+H_2O]^+$, 933.1 (100) $[M-Cl]^+$, 449.3 (60) $[M-2Cl]^{2+}$.

Preparation of 2b: The compound was prepared by a similar procedure to method B for **2a**. Compound **1b** (0.120 g, 0.295 mmol) and $Ni(OAc)_2{\cdot}4H_2O$ (0.367 g, 0.147 mmol) were used. A pale yellow powder was obtained. Yield: 0.090 g, 70%; m.p. 195–200 °C; elemental analysis calcd (%) for $C_{48}H_{46}N_4P_2Cl_2Ni$: C 66.34, H 5.34, N 6.45; found: C 66.33, H 5.31, N 6.46; ^{1}H NMR ([D_6]DMSO): $\delta = 4.18$ (d, ^2J(H,H) = 15.4 Hz, 2H; NC$H_A$$H_B$), 4.87 (br s, 2H; PC$H_2CH_2$), 5.17 (br s, 2H; PC$H_2CH_2$), 5.78 (d, ^2J(H,H) = 15.4 Hz, 2H; PC$H_A$$H_B$), 6.29 (s, 2H; imi-H), 6.67 (m, 4H; CH_2-Ar), 7.06–7.99 ppm (m, 32H; Ar-H, imi-H, Ph-H); ^{13}C{^{1}H} NMR ([D_6]DMSO): $\delta = 26.0$, 47.5, 53.6, 123.4, 125.5, 129.0, 129.2, 130.0, 131.1, 132.8, 134.2 ppm; the carbenic carbon was not observed due to insufficient solubility of the compound; ^{31}P{^{1}H} NMR ([D_6]DMSO): $\delta = 18.8$ ppm (s); ESI-MS (DMF): *m/z* (%): 850.7 (15) $[M-Cl+H_2O]^+$, 832.1 (100) $[M-Cl]^+$, 399.3 (80) $[M-2Cl]^{2+}$.

Preparation of 2c: The compound was prepared by following similar procedures to methods A and B for **2a**. Method A: Compound **1c** (0.310 g, 0.729 mmol), $NiCl_2$ (0.473 g, 0.364 mmol), and NaOAc (0.598 g, 0.729 mmol) were used. A pale yellow solid was obtained. Yield: 0.178 g, 54%. Method B: Compound **1c** (0.200 g, 0.470 mmol) and Ni-

$(OAc)_2\cdot 4H_2O$ (0.585 g, 0.235 mmol) were used. A pale yellow solid was obtained. Yield: 0.12 g, 57 %; m.p. 197–200 °C; elemental analysis calcd (%) for $C_{48}H_{44}F_2N_4P_2Cl_2Ni$: C 63.70, H 4.90, N 6.19; found: C 63.67, H 4.93, N 6.18; ^{1}H NMR ([D$_6$]DMSO): $\delta=4.02$ (d, ^2J(H,H) = 13.5 Hz, 2H; NCH_AH$_B$), 4.90 (br s, 2H; PCH_2CH$_2$), 5.18 (br s, 2H; PCH_2CH$_2$), 5.92 (d, ^2J(H,H) = 13.5 Hz, 2H; NCH$_A$$H_B$), 6.28 (s, 2H; imi-H), 6.67 (m, 4H; CH_2-Ar), 7.01 (m, 4H; Ar-H), 7.09 (t, $^3J_{HF}=9.0$ Hz, 4H; *m*-Ar-H), 7.31–8.04 ppm (m, 22H; Ar-H, imi-H, Ph-H); ^{13}C{^{1}H} NMR ([D$_6$]DMSO): $\delta=$ 25.8, 47.6, 52.7, 116.0 (J(C,F) = 21.5 Hz), 116.2, 123.4, 125.6, 129.5 (J-(C,F) = 25.1 Hz), 130.5, 131.2, 131.3, 132.7, 134.3, 162.4 ppm (J(C,F) = 245.3 Hz); the carbenic carbon atom was not observed due to insufficient solubility of the compound. ^{31}P{^{1}H} NMR ([D$_6$]DMSO): $\delta=17.8$ ppm (s); ESI-MS (DMF): *m/z* (%): 869.2 (100) $[M-Cl]^+$, 417.3 (55) $[M-2Cl]^{2+}$.

Preparation of 2d: The compound was prepared by following a similar procedure to method B for **2a**. Compound **1d** (0.240 g, 0.549 mmol) and $Ni(OAc)_2\cdot 4H_2O$ (0.683 g, 0.274 mmol) were used. A pale yellow solid was obtained. Yield: 0.12 g, 47 %; m.p. 194–196 °C; elemental analysis calcd (%) for $C_{50}H_{50}N_4O_2P_2Cl_2Ni$: C 64.64, H 5.43, N 6.03; found: C 64.60, H 5.41, N 6.00; ^{1}H NMR ([D$_6$]DMSO): $\delta=3.72$ (s, 6H; OCH$_3$), 4.09 (d, ^2J(H,H) = 13.9 Hz, 2H; NCH_AH$_B$), 4.86 (br s, 2H; PCH_2CH$_2$), 5.23 (br s, 2H; PCH_2CH$_2$), 5.68 (d, ^2J(H,H) = 13.9 Hz, 2H; NCH$_A$$H_B$), 6.17 (s, 2H; imi-H), 6.58 (m, 4H; CH_2-Ar), 6.83–8.02 ppm (m, 30H; Ar-H, imi-H, Ph-H); ^{13}C{^{1}H} NMR ([D$_6$]DMSO): $\delta=25.8$ (^1J(C,P) = 17.8 Hz), 47.5, 53.2, 55.6, 114.6, 123.0, 125.3, 125.5, 129.5, 130.0, 130.7, 131.1, 132.5, 132.9, 134.3, 159.8 ppm; the carbenic carbon atom was not observed due to insufficient solubility of the compound; ^{31}P{^{1}H} NMR ([D$_6$]DMSO): $\delta=19.4$ ppm (s); ESI-MS (DMF): *m/z* (%): 911.9 $[M-Cl+H_2O]^+$, 895.1 $[M-Cl]^+$, 429.6 (10) $[M-2Cl]^{2+}$.

Suzuki coupling reactions: In a typical reaction, a mixture of aryl halide (1.0 mmol), phenyboronic acid (1.3 mmol), base (2.6 mmol), catalyst (1–3 mol %), and triphenylphosphane (0–6 mol %) in toluene (3 mL) was stirred at 80 °C for an appropriate period of time (0.5–24 h) under nitrogen or in air. The solution was allowed to cool to ambient temperature for GC analysis or standard workup. GC yields were calculated by using benzophenone (with 4-acetylbiphenyl and 4-phenyltoluene as products) or biphenyl (with 4-phenylanisole as product) as internal standards. In the standard workup, the solvent was removed completely under vacuum. A 1:1 mixture of diethyl ether/water (20 mL) was added. The organic layer was washed, separated, further washed with another 10 mL of diethyl ether, and dried with anhydrous $MgSO_4$. The solution was then filtered. The solvent and any volatile substances were removed completely under high vacuum to give a crude product which was either subjected to flash chromatography or analyzed by ^{1}H NMR spectroscopy.

X-ray data collection: Crystals of **2a** were obtained by vapor diffusion of diethyl ether into a methanol solution. Those of **2b**–**2d** were similarly obtained with the solvent combination of DMF/diethyl ether. Typically, the crystals were removed from the vial with a small amount of mother liquor and immediately coated with silicon grease on a glass slide. A suitable crystal was mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker APEX II with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å) at 150(2) K. Crystallographic data for **2a**–**2d** are listed in Table 1 and selected bond lengths and angles are given in the captions of Figures 1–4, respectively.

Solution and structure refinements. All structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares methods against F^2 with SHELXL-97.[29] Tables of neutral atom scattering factors, f' and f'', and absorption coefficients came from a standard source.[30] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model, except H1A of methanol in **2a**, which was located from the difference Fourier map and refined isotropically, and those of water in **2b**, which were located but not refined. CCDC 299434–299437 (**2a**–**2d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. A more detailed description of the structures is provided in the Supporting Information.

Computational methods: Gradient-corrected density functional theory (DFT) was used with the hybrid B3LYP functional, which consists of three-parameter mixing of the nonlocal exchange functional of Becke[31] and correlation functional of Lee, Yang, and Parr.[32] The quality of basis functions is essential, especially for the metals, in the computations. For Ni and nonmetal atoms, 6-31G* basis sets were used in geometry optimizations, and subsequent single-point calculations used the 6-311G** basis set. For Pd, we used the basis set of Hay and Wadt[33] (including effective core potential) LAN(L)$_2$DZ, augmented with a set of functions (3s3p2d3f) suggested by Langhoff et al.[34] Solvation effects of DMSO (dielectric constant $\varepsilon=46.7$) were evaluated using the conductor polarizable continuum model (CPCM) of Barone and Cossi[35] In this model, the solvation free energy is accounted for. The molecular free energy of the solute embedded in a continuum medium is computed with this method, in which the solute is polarized by the solvent, and the solute–solvent dispersion–repulsion energy is evaluated. It has been shown that the CPCM model provides predictions for the free energy of hydration that are comparable with experimental results. All calculations were carried out by using the Gaussian 03 program suite, Revision C.02.[36]

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