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A mixed phosphine-iminophosphorane tetradentate ligand: synthesis, coordination to group 10 metal centers and use as catalyst in the Suzuki-Miyaura coupling

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ABSTRACT

A novel tetradentate ligand **1** associating two phosphines and two iminophosphorane moieties was easily synthesized from commercially available bis(diphenylphosphino)methane and ethylenediamine via the preparation of bis(phosphine-aminophosphonium) adduct **1-(HBr)₂**. Deprotonation of this salt afforded the corresponding tetradentate P₂N₂ phosphine-iminophosphorane ligand **1**. Coordination to Ni(II) and Pd(II) metal centers afforded respectively complexes **2** and **3**, characterized by multinuclear NMR and X-Ray analysis. Both cationic complexes adopt a square planar geometry around the metal, all phosphorus and

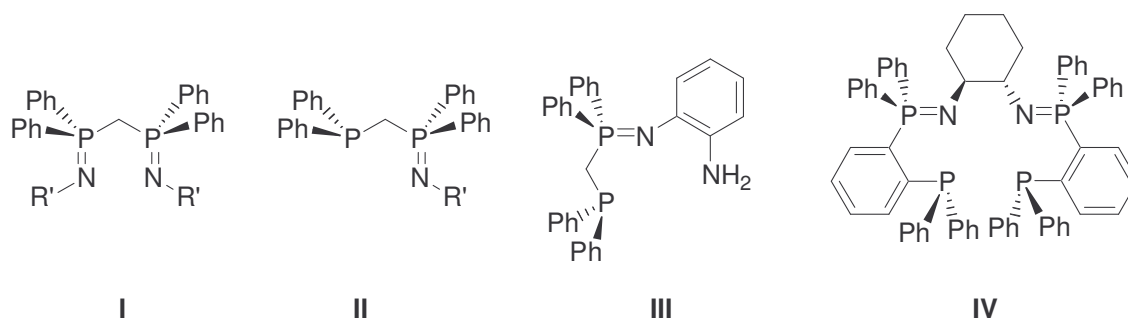
nitrogen atoms being coordinated. Contrary to most iminophosphorane complexes, **2** and **3** could be handled into water without any apparent decomposition. Their catalytic activity was evaluated in the Suzuki-Miyaura coupling. These reactions were conducted either in toluene, in water, or in a biphasic toluene/water medium in presence of a phase-transfer agent. Under these latter conditions, the Pd catalyst **3** (0.1 mol% catalyst loading) could be re-used for 5 cycles without noticeable loss of activity.

INTRODUCTION

Over the past two decades, tetradentate P_2N_2 ligands combining two “soft” phosphines with two “hard” nitrogen atoms, either imine or amide groups, have attracted a considerable attention.¹ In particular, the introduction of chirality within their carbon backbone allowed the elaboration of very efficient enantioselective catalysts. Thus, ruthenium(II) complexes were employed in catalytic cyclopropanation,² epoxydation,³ hydrogenation,⁴ and transfer hydrogenation⁵ reactions, while palladium complexes were nicely exploited by Trost in allylic alkylations⁶ and deracemization reactions.⁷ More recently, Morris and coworkers reported on an efficient iron catalyst featuring a P_2N_2 tetradentate core for the asymmetric hydrogenation of polar bonds.⁸ The efficiency of these tetradentate mixed phosphine-imine ligands prompted us to develop the synthesis of their phosphorus analogs bearing two phosphine and two iminophosphorane (P=N) moieties. We initially postulated that such ligands would exhibit markedly different electronic and steric properties compared to imines derivatives. Indeed, iminophosphoranes do not possess a real π -system and therefore do not exhibit a significant π -accepting capacity. Furthermore, the presence of a remaining lone pair at nitrogen after coordination makes them very good π -donor ligands. The potential of iminophosphoranes in coordination chemistry⁹ is now well established and recent studies have emphasized their utility as ligands in homogeneous catalysis.¹⁰ Nevertheless, in most cases the substitution

pattern at the nitrogen atom is limited to trimethylsilyl, bulky aryl, or phosphonate groups, since the synthesis is achieved through the classical Staudinger reaction,¹¹ which involves the thermal reaction of azides with tertiary phosphines. In order to circumvent this limitation, we recently developed a straightforward route based on the Kirsanov approach which takes place under mild conditions and proceeds through the reaction of phosphine with bromine followed by the subsequent reaction of the bromophosphonium salt formed with primary amines.^{9m,12} We already applied this strategy to a wide range of bidentate N-N **I**,^{12c} bidentate P-N **II**,^{9m,10l} tridentate P-N-N **III** ligands.⁹ⁿ In 2006, we also explored the synthesis of tetradentate phosphine iminophosphorane ligand such as **IV** featuring a P₂N₂ core by combining this synthetic approach with a nitrogen assisted ortho-lithiation process.^{9o} Unfortunately, this potentially interesting tetradentate system proved to be totally reluctant towards coordination of transition metal centres, probably as a result of the rigidity and/or steric bulkiness of the backbone P₂N₂ core. Therefore, we turned our attention to more flexible tetradentate systems.

Chart 1. Iminophosphorane based ligands synthesized by Kirsanov methodology

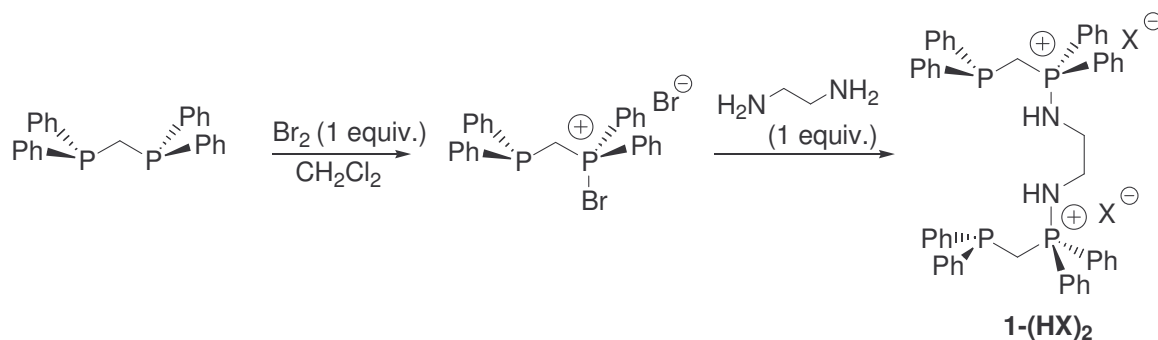


In this paper we report the easy synthesis of a novel mixed tetradentate phosphine-iminophosphorane P₂N₂ ligand which features less rigid ancillary arms. Preliminary studies about the coordinating behavior of this new ligand towards nickel and palladium (II) centers are also reported as well as results concerning the catalytic activity of these complexes in the Suzuki-Miyaura coupling process between boronic acids and aryl halides.

RESULTS AND DISCUSSION

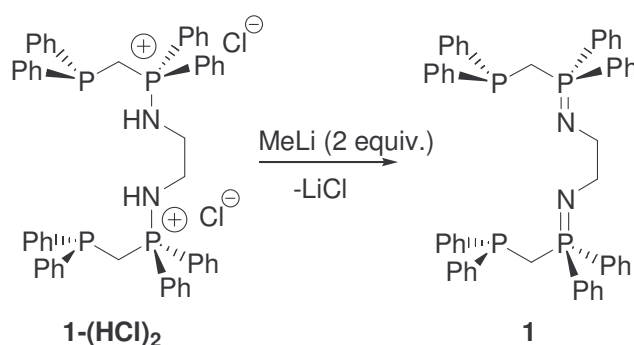
The strategy already employed in our previous studies for the preparation of bidentate phosphine-iminophosphorane ligands was successfully extended to the synthesis of this new tetradentate P_2N_2 ligand (Scheme 1). Reaction of the $[Ph_2PCH_2PPh_2Br]Br$ salt, obtained by reaction of bromine with dppm (bis-diphenylphosphinomethane) in dichloromethane at low temperature, with one equivalent of ethylenediamine afforded salts **1-(HBr)₂**. In this reaction half an equivalent of ethylenediamine acts as a nucleophile whereas the second behaves as a base to trap the hydrogen bromide released. Compound **1-(HBr)₂** which was obtained as a very air and moisture stable powder was characterized by NMR spectroscopy and elemental analysis. Note that, in this reaction sequence, there is no need to isolate the $[Ph_2PCH_2PPh_2Br]Br$ salt and all the synthesis can be carried out in the same flask. In order to avoid any scrambling of the bromide counteranions with chlorides of transition metal precursors, the bis salt **1-(HBr)₂** can be converted to the corresponding chloride derivative by a simple aqueous workup using a saturated NaCl solution. Both salts present similar NMR data and exhibit a characteristic AB spin-system pattern in $^{31}P\{^1H\}$ NMR spectroscopy (δ ($CDCl_3$) = -28.6 ppm ($^2J_{PP} = 70$ Hz) for the phosphine group and 41.2 ppm ($^2J_{PP} = 70$ Hz) for the phosphonium group).

Scheme 1. Synthesis of tetradentate phosphine-aminophosphonium **1-(HX)₂**



The corresponding bis(iminophosphoranephosphine) ligand **1** was then conventionally obtained from **1-(HCl)₂** by deprotonation with two equivalents of MeLi either in THF or toluene (Scheme 2). Complete formation of **1** was first evidenced by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy which shows the appearance of a characteristic AB spin-system pattern at δ (THF) = -25.4 ppm ($^2J_{\text{PP}} = 62$ Hz) for the PPh_2 group and 21.2 ppm ($^2J_{\text{PP}} = 62$ Hz) for the phosphorus atom of the iminophosphorane moiety. After removal of the lithium salts in toluene, ligand **1** was isolated with a satisfactory yield of 83 %. The structure of **1** was unambiguously established by NMR spectroscopy but its high sensitivity towards moisture precluded the obtainment of satisfactory elemental data.

Scheme 2. Preparation of tetradentate phosphine-aminophosphonium **1** ligand

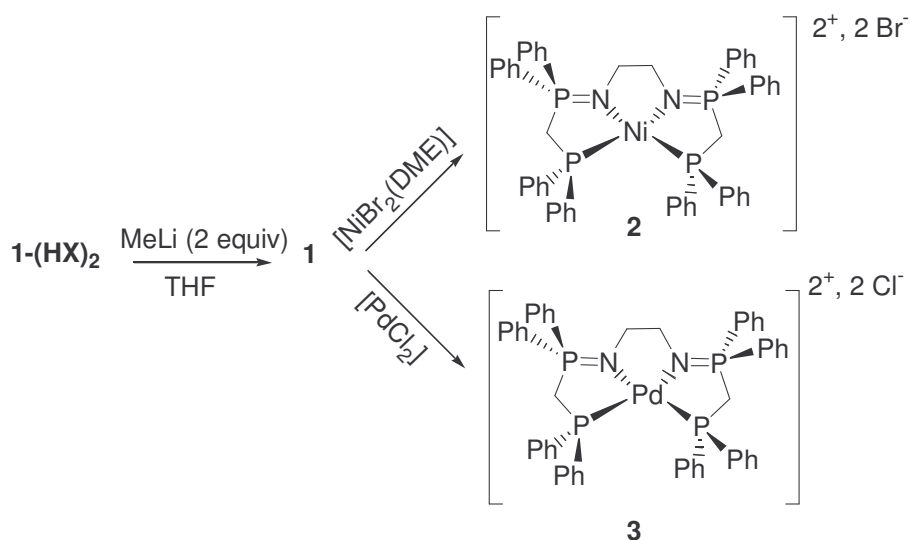


The coordinating ability of **1** towards Ni(II) and Pd(II) metal centers was then evaluated. Interestingly, we noted that there is no need to isolate the free ligand **1** and all experiments were directly conducted from the **1-(HX)₂** salts (X = Cl or Br). Thus, for the

synthesis of the nickel complex **2**, deprotonation of **1-(HBr)₂** was carried *in situ* in THF at low temperature, followed by the subsequent trapping of **1** with [NiBr₂(DME)] (Scheme 3). Upon addition of the nickel precursor, color instantly changed from colorless to orange, followed by the precipitation of an orange solid. After removal of the LiBr salts formed in CH₂Cl₂ and washing with diethyl ether, complex **2** was isolated as a very air and moisture stable orange solid with a 90 % yield. In ³¹P{¹H} NMR, the coordination of both the phosphorus and nitrogen atoms could be ascertained by a significant downfield shift for each phosphorus atoms ($\Delta\delta\sim 55$ ppm for the PPh₂ group and 30 ppm for the phosphorus atom of the iminophosphorane moiety) The fact that complex **2** was not NMR silent suggested that the complex adopts a square planar geometry.

A similar procedure was employed for the synthesis of the palladium complex **3**. In order to avoid any halogen scrambling the **1-(HCl)₂** salt was employed. Whereas the formation of **2** could be achieved *in situ* at room temperature, reaction with the [PdCl₂] complex required heating for 4 h at 60°C. After elimination of LiCl salts, complex **3** was isolated in 85% yield as a yellow solid which was found to be inert towards air and moisture (Scheme 3). Like in complex **2**, coordination of phosphorus and nitrogen atoms resulted in a significant downfield shift in ³¹P{¹H} NMR (see supplementary material available). Several experiments were also carried out using the [Pd(COD)Cl₂] complex as starting precursor but analysis of the crude mixture revealed the presence of different products among which was complex **3**.

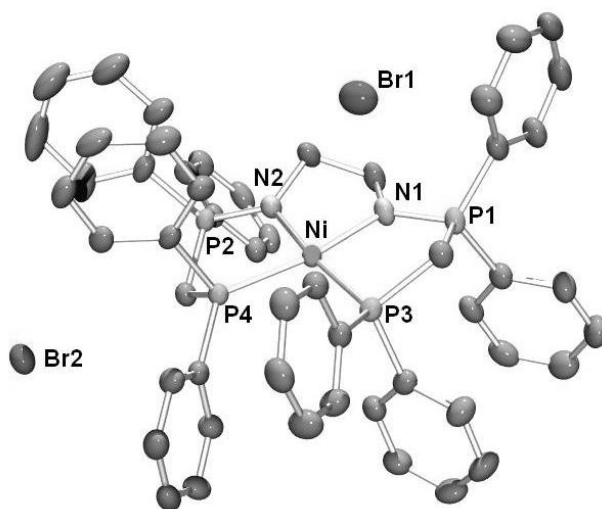
Scheme 3. Coordination to Ni(II) and Pd(II) metal centers



A definitive evidence of the structure of complexes **2** and **3** was given by X-ray crystal structure analyses of both complexes. Suitable crystals of **2** and **3** were conventionally obtained by diffusing hexanes (mixture of isomers) into dichloromethane solutions of the complexes at room temperature.

A view of one molecule of **2** is presented in figure 1. As expected from NMR data, complex **2** adopts a square planar geometry around the nickel center with a small distortion of 2.23° from planarity (P3-N1-N2-P4 dihedral angle). The four coordination sites are occupied by the two phosphine and the two iminophosphorane ligands, the two bromide counteranions being significantly remote from the metal center (Ni-Br bond distances of 4.9071 and 6.656 Å). The two Ni-P bond lengths are very similar at 2.155(1) and 2.154(1) Å and slightly shorter than those recorded in nickel dibromide complexes of phosphine-iminophosphorane (P, N) complexes (2.303 Å on average).^{9m, 13} Likewise, the Ni-N bond length at 1.897(3) and 1.903(3) Å are shorter than those observed in the previously mentioned (P, N) complexes (2.004 Å on average). Besides, the two P=N distance at 1.606(3) and 1.608(3) Å compare with those recorded for phosphine-iminophosphorane complexes.^{9m, 13}

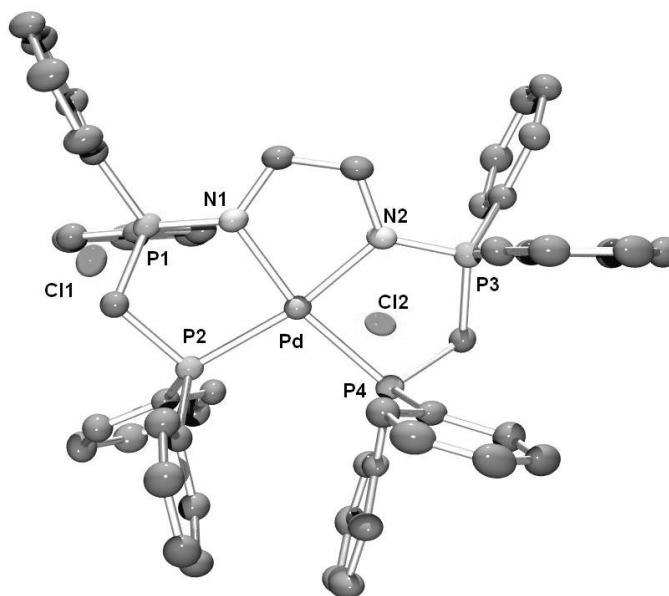
Figure 1. Molecular structure of complex **2**. Thermal ellipsoids are drawn to the 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected distances (Å) and angles (°): P3-Ni = 2.155(1); N1-Ni = 1.897(3); N2-Ni = 1.903(3); P4-Ni = 2.154(1); Ni-Br2 = 6.656; Ni-Br1 = 4.907; P1-N1 = 1.608(3); P2-N2 = 1.606(3); Br1-Ni-Br2 = 118.70; P3-Ni-P4 = 101.51(4); N1-Ni-N2 = 84.50(1); P3-N1-N2-P4 = 2.23; P3-P1-P2-P2 = 7.44.



As can be seen in figure 2, complex **3** also adopts a square planar geometry around the Pd(II) center, with a slight deviation from planarity of 2.46° (P4-N2-N1-P2 dihedral angle). As anticipated from the observed shift in ³¹P NMR spectrum both nitrogen and phosphorus atoms are coordinated to the metal center, so the chloride atoms remained away from the metal (Pd-Cl > 4.7 Å). Moreover, both the Pd-N and Pd-P bond lengths are in the same range of those measured in palladium complexes bearing a phosphine-iminophosphorane bidentate ligand (2.035 and 2.257 Å on average for Pd-N and Pd-P respectively).^{9m} Otherwise, the other metric parameters compare with those of the nickel complex **3** and do not deserve further comments.

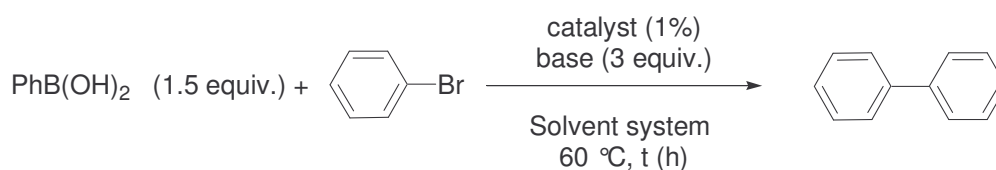
Figure 2. Molecular structure of complex **3**. Thermal ellipsoids are drawn to the 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity.

Selected distances (Å) and angles (°): P2-Pd = 2.252(8); N1-Pd = 2.047(2); N2-Pd = 2.023(2); P4-Pd = 2.262(8); Pd-Cl2 = 5.596; Pd-Cl1 = 4.726; P1-N1 = 1.611(2); P3-N2 = 1.593(2); Cl1-Pd-Cl2 = 163.40; P2-Pd-P4 = 104.57(3); N2-Pd-N1 = 81.1(1); P4-N2-N1-P2 = -2.46; P4-P3-P1-P2 = 2.55.



The catalytic activity of complexes **2** and **3** in the Suzuki-Miyaura cross coupling reactions was then evaluated.¹⁴ Reaction of phenylboronic acid with bromobenzene was chosen as model reaction to explore different experimental conditions. Interestingly, we found that the remarkable stability of **2** and **3** towards moisture allowed the use of water as solvent or co-solvent. It is worth noting that, in the case of bidentate mixed (P, N) ligands, the resulting nickel and palladium complexes are not stable towards moisture. These reactions were thus conducted in different media: either in pure toluene, pure water, or in a biphasic toluene/water mixture in presence of a phase-transfer agent.¹⁵ Results of these preliminary tests are reported in table 1.

Table 1. Suzuki-Miyaura cross-coupling of bromotoluene with phenylboronic acid catalyzed by **2** and **3**^a



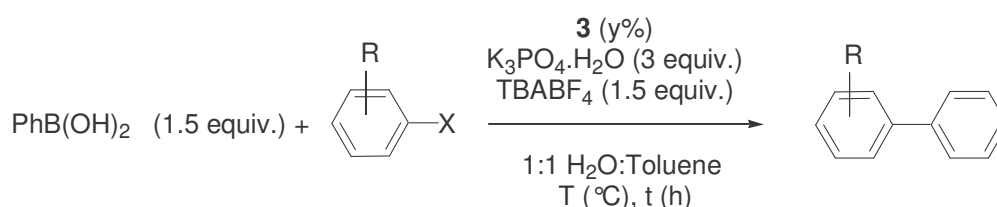
Entry	Catalyst	Base	Solvent System	t (h)	Conversion (%) ^b
1	2	K ₂ CO ₃	H ₂ O	24	47
2	2	K ₂ CO ₃	Toluene	24	66
3	2	K ₃ PO ₄ ·H ₂ O	1:1 H ₂ O:Toluene + TBABF ₄	16	100
4	3	K ₂ CO ₃	Toluene	24	97
5	3	K ₂ CO ₃	1:1 H ₂ O:Toluene + TBABF ₄	8	100
6	3	K ₃ PO ₄ ·H ₂ O	1:1 H ₂ O:Toluene + TBABF ₄	4	100

^a Reactions conditions: 1 mmol of bromobenzene; 1.5 mmol of phenylboronic acid; 4 mL of toluene, H₂O or 1:1 H₂O:toluene + 1.5 mmol of TBABF₄ (TBABF₄ = [N(*n*-C₄H₉)₄]BF₄); 3 mmol of base; 10 μmol of catalyst. ^b Conversions were determined by quantitative GC calibrated with authentic samples.

As can be seen, whatever the solvent and the base used, both complexes **2** and **3** were able to achieve the coupling reaction in moderate to quantitative yield within a reasonable reaction time (from 4 to 24 hours). Though the use of neat water as solvent seems at first very attractive, these conditions were quickly given up because of lower conversion yields compared to experiments carried out in toluene as solvent with the same base (entry 1). This failure may be due to the poor solubility of the substrate in aqueous medium. Nevertheless, we were pleased to see that more satisfactory results could be obtained by using a biphasic water/toluene system in presence of [N(*n*-C₄H₉)₄]BF₄ (TBABF₄) as phase-transfer agent. Indeed, complete conversion was observed after 8h using **3** as catalyst employing K₂CO₃ as

base. This result must be compared with that obtained in toluene after one day (entry 4). Using $K_3PO_4 \cdot H_2O$ as base allowed further improvement, a complete conversion being obtained after 4h using catalyst **3** (entry 6). This first set of results led us to establish that complex **3** is a better catalyst than **2**. Therefore, additional experiments using different functional aryl bromides were exclusively conducted with **3** as catalyst in the water/toluene system, with $K_3PO_4 \cdot H_2O$ as base. These results are summarized in table 2.

Table 2. Suzuki-Miyaura cross-coupling of halogenoarenes with phenylboronic acid catalyzed by **3** in a biphasic H_2O :toluene medium^a



Entry	R	X	y (mol%)	t (h)	T (°C)	Conversion (%) ^b
1	H	Br	1	24	rt	0
2	H	Br	0.1	4	60	100
3 ^c	H	Br	0.1	12	60	100
4	<i>o</i> -OMe	Br	0.1	16	60	92
5	<i>o,o'</i> -Me	Br	0.1	24	60	51
6	<i>p</i> -CH ₃ CO	Cl	1	24	60	34
7	<i>o</i> -CN	Cl	1	24	60	44
8	H	Cl	1	24	60	2

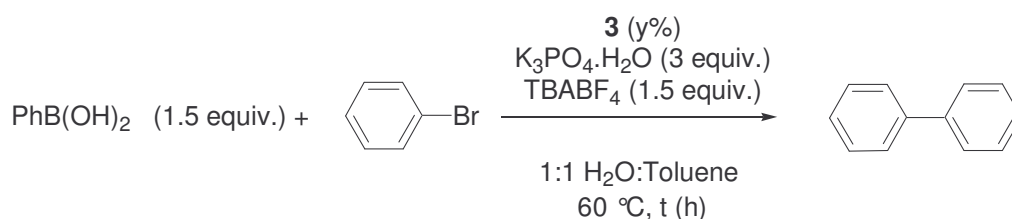
^a Reactions conditions: 1 mmol of bromobenzene; 1.5 mmol of phenylboronic acid; 4 mL of 1:1 H_2O :toluene; 1.5 mmol of TBABF₄ (except for entry 3); 3 mmol of base; 1 or 10 μ mol of complex **3**. ^b Conversions were determined by quantitative GC calibrated with authentic samples. ^c Reaction carried out in a 1:1 H_2O :toluene system without TBABF₄.

No reaction was observed at room temperature using a 1 mol% loading of catalyst (entry 1). However, at 60 °C, even with a 0.1 mol% of catalyst, the coupling was achieved within 4 hours (entry 2). Interestingly, we noted that the reaction can be completed in absence of the phase-transfer agent, but a longer reaction time (compare entries 2 and 3) was needed. The coupling was also carried out with electronically deactivated and hindered bromoarenes (entries 4 and 5). The products were obtained in moderate to excellent yields, and, in every case, conversion to biphenyl never exceeded 2% (entries 4, 5) and no benzene was produced. Those performances are good regarding systems that can achieve this coupling in a biphasic medium.¹⁵ However, even with 1 mol% of catalyst, the coupling of activated chloroarenes only proceeded in low yields: 34% for the 4-chloroacetophenone (entry 6) and 44% for the 2-chlorobenzonitrile (entry 7) and no improvement was observed by increasing temperature. With chlorobenzene, almost no reaction took place (entry 8). It is worth noting that no coupling of aryl chlorides was observed with nickel complex **2** as catalyst. At the end of every catalytic run, ³¹P NMR spectroscopy allowed us not only to observe the signal of the catalyst precursors but we did not detect any free ligand in the reaction mixture. Therefore, in addition to the fact the color of the mixture was not modified during the reaction, the possibility of the formation of nanoparticles which might be the active species was eliminated.^{16, 18}

Having shown that catalyst **3** was efficient under these conditions, we then explored its reusability. Indeed the use of such aqueous/organic system allows an easy separation of the organic products formed from the aqueous catalyst solution. The first run was carried out using 0.1 mol% of catalyst loading and after this initial run, the aqueous layer remaining after toluene extraction was reloaded with base and boronic acid. A solution of bromobenzene in toluene was added and the reaction was allowed to stir until completion. Results of these experiments are reported in table 3. Noteworthy, the extraction of the aqueous phase with dichloromethane allowed us to ascertain by ³¹P NMR spectroscopy that the catalytic precursor

3, was still unchanged after two runs. Though the reaction rate slows down after three runs, no significant loss of activity was noticed until the fifth cycle. No studies aimed at understanding this loss of activity were conducted so far but one may propose that it probably results from the slow decomposition of the catalyst upon long exposure to water and/or mechanical loss during the recycling and the accumulation of salt by-products in the aqueous phase. Based on this study, we could establish that the TON of our catalyst **3** approximate 5000 mol of product per mol of catalyst.

Table 3. Re-use of the aqueous palladium catalyst phase for the Suzuki-Miyaura cross-coupling of bromobezene with phenylboronic acid



Run	Added Pd (mol %)	t (h)	Conversion (%) ^b	TON ^c
1 ^a	0.1	4	100%	1000
2 ^d	0	4	100%	2000
3 ^d	0	5	100%	3000
4 ^d	0	8	100%	4000
5 ^d	0	12	68%	4680

^a Reactions conditions: 1 mmol of bromobenzene; 1.5 mmol of phenylboronic acid; 4 mL of 1:1 H₂O:toluene; 1.5 mmol of TBABF₄; 3 mmol of base; 1 μmol of catalyst. ^b Conversions were determined by quantitative GC calibrated with authentic samples. ^c TON : Turn-Over Number, mol product per mol catalysts. ^d The aqueous catalyst solution from the previous catalyst cycle was used. Only the upper toluene phase was replaced between each cycle, and the reaction mixture was reloaded with phenylboronic acid, bromobenzene, and base.

CONCLUSION

We therefore developed a straightforward synthesis (two steps) of a tetradentate P_2N_2 ligand featuring two phosphine and two iminophosphorane groups. The corresponding Ni(II) and Pd(II) complexes were prepared and fully characterized. Both X-Ray crystal structures evidenced a square planar geometry with the four coordination sites being occupied by the P_2N_2 ligand, while the halide anions remained away from the metal centers. The coordination of iminophosphorane arms proved to be very strong, since both complexes **2** and **3** were found to be stable in water. These complexes were successfully used in Suzuki-Miyaura coupling reactions using a biphasic toluene/water system in presence of a phase transfer agent. For this catalysis, the palladium complex **3** was shown to be more efficient than the nickel complex **2**. Moreover, re-usability of the catalyst system was demonstrated; **3** could be re-employed without noticeable loss of activity up to 5 runs. Further studies aimed at extending the coordination chemistry and applications of ligands such as **1** and their corresponding enantiopure derivatives are currently underway in our laboratories.

EXPERIMENTAL SECTION

General: All experiments were performed under an atmosphere of dry nitrogen or argon using standard schlenk and glove box techniques. Solvents were freshly distilled under argon from Na/benzophenone (THF, diethylether, petroleum ether), from P_2O_5 (dichloromethane). Bu_4NBF_4 ¹⁹ and $NiBr_2(DME)$ ²⁰ were prepared according to literature procedure. All other reagents and chemicals were obtained commercially and used without further purification, except for ethylenediamine which was distilled under dry nitrogen from calcium hydride. Nuclear magnetic resonance spectra were recorded on Bruker Avance 300 spectrometer operating at 300 MHz for 1H , 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P . 1H and ^{13}C chemical

shifts are reported in ppm relative to Me₄Si. ³¹P are relative to a 85% H₃PO₄ external reference. Coupling constant are expressed in hertz. The following abbreviations are used: b, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; v, virtual. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France. The GC yields were determined on a PERICHRON 2100 gas chromatograph equipped with a PERICHRON column (SILICONE OV1, CP-SIL 5 CB), 30 m x 0.22 mm.

Synthesis and characterization of aminophosphonium salt 1-(HCl)₂: Bromine (120 μL, 2.34 mmol) was added dropwise to a solution of dppm (0.900 g, 2.34 mmol) in CH₂Cl₂ (20 mL) at -78°C. The reaction mixture was stirred for 20 minutes. ³¹P {¹H} (CH₂Cl₂) δ -23.2 (d, *J*_{PP} = 83 Hz), 58.6 (d, *J*_{PP} = 83 Hz).

The ethylenediamine (156 μL, 2.34 mmol) was added to the solution of DPPMBr at -78°C. The cold bath was removed and the reaction mixture was stirred for 1h at room temperature. The solution was washed twice with brine (20 mL), the organic layer was dried over MgSO₄ and the solvent was removed under vacuum to deliver a white solid, which was washed with diethyl ether.

1-(HCl)₂ (1.513 g, 1.68 mmol, 72%). ³¹P {¹H} (CDCl₃) δ -28.6 (d, ²*J*_{PP} = 70,0 Hz, P^(III)), 41.2 (d, ²*J*_{PP} = 70,0 Hz, P^(V)). ¹H (CDCl₃) δ 3.22 (4H, bs, N-CH₂), 3.97 (4H, d, ²*J*_{HP} = 16.0 Hz, PCH₂P), 7.23 (8H, m, m-H (Ph₂ P^(V))), 7.28 (4H, m, p-H (Ph₂ P^(V))), 7.33 (8H, m, o-H (Ph₂ P^(V))), 7.44 (8H, vtd, ³*J*_{HH} = 7.5 Hz, ⁵*J*_{PH} = 3.0 Hz, m-H (Ph₂ P^(III))), 7.57 (4H, vt, ³*J*_{HH} = 7.5 Hz, ³*J*_{HP} non measurable, p-H (Ph₂ P^(III))), 7.77 (8H, dd, ³*J*_{HH} = 7.5 Hz, ³*J*_{HP} = 13.0 Hz, o-H (Ph₂ P^(III))), 8.16 (2H, bs, NH). ¹³C {¹H} (CDCl₃) δ 23.6 (dd, ¹*J*_{CP} = 34.5 Hz, ¹*J*_{CP} = 66.5 Hz, PCH₂P), 42.55 (d, ²*J*_{CP} = 9.0 Hz, NCH₂), 120.8 (dd, ¹*J*_{CP} = 98.0 Hz, ⁴*J*_{CP} = 1.0 Hz, C^{IV}(Ph₂ P^(III))), 128.7 (d, ³*J*_{CP} = 7.0 Hz, p-CH-(Ph₂ P^(V))), 129.4 (d, ³*J*_{CP} = 12.5 Hz, m-CH-(Ph₂ P^(V))), 129.4 (s, m-CH-(Ph₂ P^(III))), 132.9 (d, ²*J*_{CP} = 21.5 Hz, o-CH-(Ph₂ P^(V))), 133.2 (dd, ²*J*_{CP} = 11.0

Hz, $^4J_{CP} = 2.5$ Hz, o-CH-(Ph₂P^(III))), 134.3 (d, $^2J_{CP} = 2.5$ Hz, p-CH-(Ph₂P^(III))), 135.3 (dd, $^2J_{CP} = 12.5$ Hz, $^3J_{CP} = 8.5$ Hz, C^{IV}(Ph₂P^(V))). Anal. Calc. for C₅₂H₅₀Cl₂N₂P₄: C, 69.87; H, 5.61; N, 3.12. Found: C, 69.79; H, 5.64; N, 3.13.

Synthesis and characterization of iminophosphorane 1: MeLi (140 μ L, 0.223 mmol) was added to a suspension of ligand **1-(HCl)₂** (0.111 mmol) in toluene (5 mL) cooled at -78°C. The cold bath was removed and the solution allowed to warm to room temperature. The insoluble lithium salts were removed by centrifugation. After removal of solvent under vacuum, the obtained white solid was washed with hexanes (10 mL).

1 (76 mg, 0.091 mmol, 83%). ³¹P {¹H} (C₆D₆) δ -27.2 (d, $^2J_{PP} = 49.0$ Hz, P^(III)), 22.7 (d, $^2J_{PP} = 49.0$ Hz, P^(V)). ¹H (CDCl₃) δ 3.09 (4H, d, $^2J_{HP} = 15.0$ Hz, N-CH₂), 4.12 (4H, d, $^2J_{HP} = 16.0$ Hz, PCH₂P), 7.27 (24H, m, o,m-H (Ph₂P^(V)) and m-H (Ph₂P^(III))), 7.79 (4H, m, p-H (Ph₂P^(V))), 7.81 (8H, m, o-H (Ph₂P^(V))), 8.17 (4H, m, p-H (Ph₂P^(III))). ¹³C {¹H} (CDCl₃) δ 26.9 (dd, $^1J_{CP} = 29.0$ Hz, $^1J_{CP} = 81.5$ Hz, PCH₂P), 47.7 (d, $^2J_{CP} = 22.5$ Hz, NCH₂), 127.3 (m, C^{IV}(Ph₂P^(III))), 129.8 (d, $^3J_{CP} = 2.0$ Hz, m-CH-(Ph₂P^(V))), 130.1 (d, $^3J_{CP} = 2.5$ Hz, m-CH-(Ph₂P^(III))), 131.8 (d, $^2J_{CP} = 9.5$ Hz, o-CH-(Ph₂P^(V))), 132.0 (s, $^2J_{CP} = 4.5$ Hz, o-CH-(Ph₂P^(III))), 132.3 (s, p-CH-(Ph₂P^(V))), 132.6 (s, p-CH-(Ph₂P^(III))), 135.3 (dd, $^2J_{CP} = 12.5$ Hz, $^3J_{CP} = 8.0$ Hz, C^{IV}(Ph₂P^(V))).

Synthesis and characterization of nickel complex 2: MeLi (140 μ L, 0.223 mmol) was added to a suspension of ligand **1-(HCl)₂** (0.111 mmol) in THF (5 mL) cooled at -78°C. The cold bath was removed and the solution allowed to warm to room temperature. Then, [NiBr₂(DME)] (35 mg, 0.111 mmol) was added and the solution turned immediately from colorless to red. After stirring 30' at room temperature, an orange solid precipitated, which was isolated by filtration. This solid was dissolved in CH₂Cl₂ (5 mL) to remove the insoluble lithium salts. After removal of solvent under vacuum, the obtained orange solid was washed with Et₂O (10 mL).

2 (104 mg, 0.10 mmol, 90%). ^{31}P { ^1H } (CDCl_3) δ 31.9 (vt, $^2J_{\text{PP}} = 17.0$ Hz, $^3J_{\text{PP}} = 17$ Hz, $\text{P}^{(\text{III})}$), 49.2 (vt, $^2J_{\text{PP}} = 17.0$ Hz, $^3J_{\text{PP}} = 17$ Hz, $\text{P}^{(\text{V})}$). ^1H (CDCl_3) δ 2.91 (4H, bs, N-C H_2), 4.36 (4H, bs, PCH_2P), 7.13 (12H, m, p,m-H ($\text{Ph}_2 \text{P}^{(\text{III})}$)), 7.40 (12H, m, p,m-H ($\text{Ph}_2 \text{P}^{(\text{V})}$)), 7.81 (16H, m, o-H ($\text{Ph}_2 \text{P}^{(\text{V})}$ and $\text{Ph}_2 \text{P}^{(\text{III})}$)). ^{13}C { ^1H } (CDCl_3) δ 24.43 (d, $^1J_{\text{CP(V)}} = 77.5$ Hz, PCH_2P), 66.45 (d, $^2J_{\text{CP}} = 13.0$ Hz, NCH_2), 123.3 (s, $\text{C}^{\text{IV}}(\text{Ph}_2 \text{P}^{(\text{III})})$), 124.0 (s, $\text{C}^{\text{IV}}(\text{Ph}_2 \text{P}^{(\text{V})})$), 127.95 (vt, $^3J_{\text{CP}} = 6.5$ Hz, $^5J_{\text{CP}} = 6.3$ Hz, m-CH-($\text{Ph}_2 \text{P}^{(\text{III})}$)), 128.3 (d, $^3J_{\text{CP}} = 14.0$ Hz, m-CH-($\text{Ph}_2 \text{P}^{(\text{V})}$)), 131.0 (s, p-CH-($\text{Ph}_2 \text{P}^{(\text{III})}$)), 132.4 (s, p-CH-($\text{Ph}_2 \text{P}^{(\text{V})}$)), 132.5 (d, $^2J_{\text{CP}} = 11.0$ Hz, o-CH-($\text{Ph}_2 \text{P}^{(\text{V})}$)), 134.0 (vt, $^2J_{\text{CP}} = 5.5$ Hz, $^4J_{\text{CP}} = 5.5$ Hz, o-CH-($\text{Ph}_2 \text{P}^{(\text{III})}$)). Anal. Calc. for $\text{C}_{52}\text{H}_{48}\text{N}_2\text{P}_4\text{NiBr}_2$: C, 59.86; H, 4.64 ; N , 2.68. Found: C, 59.80; H, 4.51 ; N , 2.71.

Synthesis and characterization of palladium complex 3: MeLi (140 μL , 0.223 mmol) was added to a solution of ligand **1-(HCl) $_2$** (0.111 mmol) in THF (5 mL) cooled at -78°C . The cold bath was removed and the solution allowed to warm to room temperature. Then, $[\text{PdCl}_2]$ (20 mg, 0.111 mmol) was added and the solution was heated to 60°C using an oil bath. After stirring 4 hours at 60°C , a yellow solid precipitated, which was isolated by filtration. This solid was dissolved in CH_2Cl_2 (5 mL) to remove the insoluble lithium salts. After removal of solvent under vacuum, the obtained yellow solid was washed with Et_2O (10 mL).

Crystals suitable for X-ray diffraction were obtained by slow diffusion of petroleum ether into a solution of **3** in dichloromethane at room temperature.

3 (95 mg, 0.095 mmol, 85%). ^{31}P { ^1H } (CDCl_3) δ 28.9 (dd, $^2J_{\text{PP}} = 14.0$ Hz, $^3J_{\text{PP}} = 10.0$ Hz, $\text{P}^{(\text{III})}$), 46.9 (dd, $^2J_{\text{PP}} = 14.0$ Hz, $^3J_{\text{PP}} = 10.0$ Hz, $\text{P}^{(\text{V})}$). ^1H (CDCl_3) δ 3.24 (4H, bs, N- CH_2), 4.61 (4H, vt, $^2J_{\text{HP}} = 9.5$ Hz PCH_2P), 7.09 (12H, m, p,m-H ($\text{Ph}_2 \text{P}^{(\text{III})}$)), 7.40 (12H, m, p,m-H ($\text{Ph}_2 \text{P}^{(\text{V})}$)), 7.57 (8H, m, o-H ($\text{Ph}_2 \text{P}^{(\text{III})}$)), 7.90 (8H, m, o-H ($\text{Ph}_2 \text{P}^{(\text{V})}$)). ^{13}C { ^1H } (CDCl_3) δ 38.2 (dd, $^1J_{\text{CP(III)}} = 85.0$ Hz, $^1J_{\text{CP(V)}} = 15.5$ Hz, PCH_2P), 54.2 (d, $^2J_{\text{CP(V)}} = 13.0$ Hz, N- CH_2), 122.5 (d, $^1J_{\text{CP(V)}} = 88.5$ Hz, $\text{C}^{\text{IV}}(\text{Ph}_2 \text{P}^{(\text{III})})$), 124.5 (dd, $^1J_{\text{CP(III)}} = 55.0$ Hz, $^3J_{\text{CP(III)}} = 4.1$ Hz, $\text{C}^{\text{IV}}(\text{Ph}_2 \text{P}^{(\text{III})})$),

129.1 (vt, $^3J_{CP}= 5.5$ Hz, $^5J_{CP}= 5.7$ Hz, m-CH-(Ph₂ P^(III))), 129.7 (d, $^2J_{CP}= 12.5$ Hz, m-CH-(Ph₂ P^(V))), 132.3 (s, p-CH-(Ph₂ P^(III))), 133.7 (d, $^4J_{CP}= 3.0$ Hz, p-CH-(Ph₂ P^(V))), 133.9 (d, $^2J_{CP}= 11.0$ Hz, o-CH-(Ph₂ P^(V))), 134.9 (vt, $^2J_{CP}= 6.5$ Hz, $^4J_{CP}= 6.5$ Hz, o-CH-(Ph₂ P^(III))). Anal. Calc. for C₅₂H₄₈N₂P₄PdCl₂: C, 62.32; H, 4.83 ; N, 2.80. Found: C, 62.40; H, 4.92 ; N, 2.75.

General procedure for Suzuki-Miyaura catalytic cross-coupling: In a typical run at 1% molar of catalyst, a schlenk was charged with a mixture of aryl halide (1.0 mmol, 105 μ L for bromobenzene, 102 μ L for chlorobenzene, 128 μ L for 4-chloroacetophenone, 137.5 mg for 2-chlorobenzonitrile), phenylboronic acid (1.5 mmol, 183 mg), base (3.0 mmol, 691 mg for K₃PO₄.H₂O, 414 mg for K₂CO₃), precatalyst (0.01 mmol, 10.4 mg for nickel complex **2**, 10.0 mg for palladium complex **3**), and [N(*n*-C₄H₉)₄]BF₄ (1.5 mmol, 493 mg). To the mixture was added degassed water (2.5 mL) and toluene (2.5 mL). The reaction mixture was then vigorously stirred at the appropriate temperature and the progress of the reaction was monitored by GC. After the desired reaction time, the solution was allowed to cool and an exact amount of *n*-heptane (100 μ L) was introduced (as internal standard). The organic layer was dried and filtered on a short MgSO₄ column and analyzed by quantitative GC, first calibrated with authentic samples.

X-ray Crystallography data for **2 and **3**:** Orange needles of **2** and yellow blocks of **3** crystallized by slow diffusion of hexanes into a saturated solution of respectively **2** and **3**. Data were collected on a Nonius Kappa CCD diffractometer using a Mo K α ($\lambda= 0.71073$ Å) X-ray source and a graphite monochromator. CCDC 681401 and 681402 contain the supplementary crystallographic data for this paper (for complex **2** and **3** respectively). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. The crystal structure was solved using SIR 97 and Shelxl-97. ORTEP drawings were made using ORTEP III for Windows.

Crystal data for **2**: triclinic, P-1, $a = 12.498(1) \text{ \AA}$, $b = 13.157(1) \text{ \AA}$, $c = 16.541(1) \text{ \AA}$, $\alpha = 86.688(1)^\circ$, $\beta = 86.511(1)^\circ$, $\gamma = 78.482(1)^\circ$, $V = 2657.3(3) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc}} = 1.516 \text{ g cm}^{-3}$, 11661 unique reflections ($\theta < 27.1^\circ$), 604 parameters, $R1 = 0.0546 [I > 2\sigma(I)]$, $wR2 = 0.1604$ (all data), GOF = 1.055; Crystal data for **3**: triclinic, P-1, $a = 12.819(1) \text{ \AA}$, $b = 13.213(1) \text{ \AA}$, $c = 14.508(1) \text{ \AA}$, $\alpha = 89.216(1)^\circ$, $\beta = 76.579(1)^\circ$, $\gamma = 81.103(1)^\circ$, $V = 2365.9(3) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc}} = 1.457 \text{ g cm}^{-3}$, 12204 unique reflections ($\theta < 28.7^\circ$), 580 parameters, $R1 = 0.0429 [I > 2\sigma(I)]$, $wR2 = 0.1239$ (all data), GOF = 1.014.

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SUPPORTING INFORMATION

Crystallographic data for **2** and **3** as CIF files and tables giving crystallographic data for **2** and **3** (including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters). This material is available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES

(1) (a) Jeffery, J. C.; Rauchfuss, T. B.; Tucker, P. A. *Inorg. Chem.* **1980**, 19, 3306-3316; (b) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, 30, 97-102; (c) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, 103, 2921-2943.

(2) (a) Bachmann, S.; Furler, M.; Mezzetti, A. *Organometallics* **2001**, 20, 2102-2108; (b) Bonaccorsi, C.; Bachmann, S.; Mezzetti, A. *Tetrahedron: Asymmetry* **2003**, 14, 845-854.

(3) (a) Stoop, R. M.; Bachmann, S.; Valentini, M.; Mezzetti, A. *Organometallics* **2000**, 19, 4117-4126; (b) Wong, W. K.; Chen, X. P.; Chik, T. W.; Wong, W. Y.; Guo, J. P.; Lee, F. W. *Eur. J. Inorg. Chem.* **2003**, 3539-3546.

(4) (a) Gao, J. X.; Wan, H. L.; Wong, W. K.; Tse, M. C.; Wong, W. T. *Polyhedron* **1996**, 15, 1241-1251; (b) Li, T. S.; Churlaud, R.; Lough, A. J.; Abdur-Rashid, K.; Morris, R. H. *Organometallics* **2004**, 23, 6239-6247; (c) Li, T.; Bergner, I.; Haque, F. N.; Iuliis, M. Z. D.; Song, D.; Morris, R. H. *Organometallics* **2007**, 26, 5940-5949.

(5) (a) Gao, J. X.; Ikariya, T.; Noyori, R. *Organometallics* **1996**, 15, 1087-1089; (b) Gao, J. X.; Xu, P. P.; Yi, X. D.; Yang, C. B.; Zhang, H.; Cheng, S. H.; Wan, H. L.; Tsai, K. R.; Ikariya, T. *J. Mol. Catal. A-Chem.* **1999**, 147, 105-111; (c) Gao, J. X.; Zhang, H.; Yi, X. D.; Xu, P. P.; Tang, C. L.; Wan, H. L.; Tsai, K. R.; Ikariya, T. *Chirality* **2000**, 12, 383-388.

(6) (a) Trost, B. M.; van Vranken, D. L. *Angew. Chem.-Int. Edit. Engl.* **1992**, 31, 228-230; (b) Trost, B. M.; Organ, M. G.; Odoherly, G. A. *J. Am. Chem. Soc.* **1995**, 117, 9662-9670; (c) Trost, B. M.; Breit, B.; Peukert, S.; Zambrano, J.; Ziller, J. W. *Angew. Chem.-Int. Edit. Engl.* **1995**, 34, 2386-2388; (d) Trost, B. M.; Lee, C. B.; Weiss, J. M. *J. Am. Chem. Soc.* **1995**, 117, 7247-7248; (e) Trost, B. M.; Bunt, R. C. *Angew. Chem.-Int. Edit. Engl.* **1996**, 35, 99-102; (f) Trost, B. M.; van Vranken, D. L. *Chem. Rev.* **1996**, 96, 395-422; (g) Trost, B. M.; Radinov, R.; Grenzer, E. M. *J. Am. Chem. Soc.* **1997**, 119, 7879-7880; (h) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1998**, 120, 815-816.

(7) (a) Trost, B. M.; Organ, M. G. *J. Am. Chem. Soc.* **1994**, *116*, 10320-10321; (b) Trost, B. M.; Krische, M. J.; Radinov, R.; Zanoni, G. *J. Am. Chem. Soc.* **1996**, *118*, 6297-6298; (c) Trost, B. M.; Patterson, D. E. *J. Org. Chem.* **1998**, *63*, 1339-1341.

(8) Sui-Seng, C.; Freutel, F.; Lough, A. J.; Morris, R. H. *Angew. Chem. Int. Edit.* **2008**, *47*, 940-943.

(9) (a) Aparna, K.; Babu, R. P. K.; McDonald, R.; Cavell, R. G. *Angew. Chem. Int. Edit.* **1999**, *38*, 1483-1484; (b) Babu, R. P. K.; McDonald, R.; Decker, S. A.; Klobukowski, M.; Cavell, R. G. *Organometallics* **1999**, *18*, 4226-4229; (c) Cavell, R. G.; Babu, R. P. K.; Kasani, A.; McDonald, R. *J. Am. Chem. Soc.* **1999**, *121*, 5805-5806; (d) Aparna, K.; Cavell, R. G.; Ferguson, M. *J. Am. Chem. Soc.* **2000**, *122*, 726-727; (e) Babu, R. P. K.; McDonald, R.; Cavell, R. G. *Organometallics* **2000**, *19*, 3462-3465; (f) Babu, R. P. K.; Aparna, K.; McDonald, R.; Cavell, R. G. *Inorg. Chem.* **2000**, *39*, 4981-4984; (g) Al-Benna, S.; Sarsfield, M. J.; Thornton-Pett, M.; Ormsby, D. L.; Maddox, P. J.; Brès, P.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **2000**, 4247-4257; (h) Aparna, K.; McDonald, R.; Babu, R. P. K.; Cavell, R. G. *Angew. Chem. Int. Edit.* **2001**, *40*, 4400-4401; (i) Cavell, R. G.; Babu, R. P. K.; Aparna, K. *J. Organomet. Chem.* **2001**, *617-618*, 158-169; (j) Ruther, T.; Cavell, K. J.; Braussaud, N. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2002**, 4684-4693; (k) Jones, N. D.; Lin, G.; Gossage, R. A.; MacDonald, R.; Cavell, R. G. *Organometallics* **2003**, *22*, 2832-2841; (l) Lin, G.; Jones, N. D.; McDonald, R.; Cavell, R. G. *Angew. Chem. Int. Edit.* **2003**, *42*, 4054-4057; (m) Boubekour, L.; Ricard, L.; Mézailles, N.; Le Floch, P. *Organometallics* **2005**, *24*, 1065-1074; (n) Boubekour, L.; Ulmer, S.; Ricard, L.; Mézailles, N.; Le Floch, P. *Organometallics* **2006**, *25*, 315-317; (o) Boubekour, L.; Ricard, L.; Mézailles, N.; Demange, M.; Auffrant, A.; Le Floch, P. *Organometallics* **2006**, *25*, 3091-3094.

(10) (a) Cadierno, V.; Crochet, P.; Garcia-Alvarez, J.; Garcia-Garrido, S. E.; Gimeno, J. *J. Organomet. Chem.* **2002**, *663*, 32-39; (b) Cadierno, V.; Diez, J.; Crochet, P.; Garcia-Garrido, S. E.; Garcia-Granda, S.; Gimeno, J. *Dalton Trans.* **2002**, 1465-1472; (c) Cadierno, V.; Crochet, P.; Diez, J.; Garcia-Alvarez, J.; Garcia-Garrido, S. E.; Garcia-Granda, S.; Gimeno, J.; Rodriguez, M. A. *Dalton Trans.* **2003**, 3240-3249; (d) Cadierno, V.; Diez, J.; Gimeno, J. *Chem. Commun.* **2004**, 2716-2717; (e) Cadierno, V.; Diez, J.; Garcia-Alvarez, J.; Gimeno, J. *Organometallics* **2005**, *24*, 2801-2810; (f) Gamer, M. T.; Rastätter, M.; Roesky, P. W.; Steffens, A.; Glanz, M. *Chem. Eur. J.* **2005**, *11*, 3165-3172; (g) Panda, T. K.; Zulys, A.; Gamer, M. T.; Roesky, P. W. *Organometallics* **2005**, *24*, 2197-2202; (h) Panda, T. K.; Zulys, A.; Gamer, M. T.; Roesky, P. W. *J. Organomet. Chem.* **2005**, *690*, 5078-5089 (i) Rastätter, M.; Zulys, A.; Roesky, P. W. *Chem. Commun.* **2006**, 874-876; (j) Rastätter, M.; Zulys, A.; Roesky, P. W. *Chem. Eur. J.* **2007**, *13*, 3606-3616; (k) Wiecko, M.; Roesky, P. W.; Burlakov, V. V.; Spannen, A. *Eur. J. Inorg. Chem.* **2007**, 876-881; (l) Buchard, A.; Auffrant, A.; Klemp, C.; Vu-Do, L.; Boubekeur, L.; Le Goff, X. F.; Le Floch, P. *Chem. Commun.* **2007**, 1502-1504.

(11) (a) Gololobov, Y. G.; Kasukhin, L. F. *Tetrahedron* **1992**, *48*, 1353. (b) Johnson, A. W. In *Ylides and Imines of Phosphorus*; Wiley: New York, 1999; p 403.

(12) (a) Kirsanov, A. V. *Izv. Akad. Nauk. SSSR* **1950**, 426. (b) Sauthier, M.; Forniés-Camer, J.; Toupet, L.; Réau, R. *Organometallics* **2000**, *19*, 553-562. (c) Demange, M.; Boubekeur, L.; Auffrant, A.; Mezailles, N.; Ricard, L.; Le Goff, X.; Le Floch, P. *New. J. Chem.* **2006**, *30*, 1745-1754; (d) Cantat, T.; Mézailles, N.; Auffrant, A.; Le Floch, P. *Dalton Trans.* **2008**, DOI: 10.1039/b717600g.

(13) Buchard, A.; Auffrant, A.; Le Goff, X.-F.; Le Floch, P. unpublished results

(14) (a) Miyaura, N., In *Metal-Catalyzed Cross-Coupling Reactions*, ed.; Diederich, F.; de Meijere, A., Wiley-VCH: Weinheim, 2004. For some examples of palladium systems bearing tetradentate ligands used in Suzuki-Miyaura coupling, see (b) Phan, T. S. N.; Khan, J.; Styring, P. *Tetrahedron* **2005**, *61*, 12065; (c) Phan, T. S. N.; Brown, D. H.; Styring, P. *Tetrahedron Letters* 2004, *45*, 7915.

(15) For some examples of Suzuki-Miyaura catalytic reactions in biphasic media see: (a) Bedford, R. B.; Blake, M. E.; Butts, C. P.; Holder, D. *Chem. Commun.* **2003**, 466-467; (b) DeVasher, R. B.; Moore, L. R.; Shaughnessy, K. H. *J. Org. Chem.* **2004**, *69*, 7919-7927; (c) Han, Y.; Huynh, H. V.; Tan, G. K. *Organometallics* **2007**, *26*, 6581-6585; (d) Moore, L. R.; Western, E. C.; Craciun, R.; Spruell, J. M.; Dixon, D. A.; O'Halloran, K. P.; Shaughnessy, K. H. *Organometallics* **2008**, *27*, 576-593.

(16) As suggested by reviewers additional experiments aimed at ruling out the formation of colloids or nanoparticles were carried out. Palladium colloids were generated by the reduction of Pd(dba)₂ complex under H₂ in THF at RT in the presence of the free ligand (0.2 equiv.) (Chaudret's method).¹⁷ After purification the insoluble black powder obtained was tested as catalyst (1 mol %) in the coupling processes (with toluene as solvent and in biphasic medium) but no couplings were observed under these conditions.

(17) Jansat, S.; Gomez, M.; Philippot, K.; Muller, G.; Guiu, E.; Claver, C.; Castillon, S.; Chaudret, B. *J. Am. Chem. Soc.* **2004**, *126*, 1592-1593.

(18) Though the mechanism of these coupling has not been thoroughly explored one may propose that a phosphine substituted 14 VE complex is formed. Preliminary calculations carried out within the framework of DFT on a model ligand (in which phenyl groups were replaced by H atoms) using the B3PW91 functional and a combination of the 6-31G* basis set

(for all non-metallic atoms) and the lanl2dz pseudo potential for palladium. These calculations revealed a 14 VE palladium(0) complex would only involve coordination of the two phosphine ligands.

(19) Kryshnal, G. V.; Zhdankina, G. M.; Zlotin, S. G. *Eur. J. Org. Chem.*, **2005**, *13*, 2822-2827.

(20) R. B. King, *Organometallic Syntheses*, Academic Press, New York, 1965, Vol. 1, pp. 170.

A mixed phosphine-iminophosphorane tetradentate ligand: synthesis, coordination to group 10 metal centers and use as catalyst in the Suzuki-Miyaura coupling

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A novel tetradentate phosphine-iminophosphorane ligand was easily synthesized, and the corresponding Ni(II) and Pd(II) complexes were isolated and characterized. They demonstrated an amazing stability in water which allows their use in catalytic Suzuki-Miyaura reactions performed in a biphasic toluene/water medium.

