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A Mixed Phosphine−Iminophosphorane Tetradentate Ligand: Synthesis, Coordination to Group 10 Metal Centers, and Use as Catalyst in Suzuki−Miyaura Coupling

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The 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 the bis(phosphine−aminophosphonium) adduct **1-(HBr)$_2$**. Deprotonation of this salt afforded the corresponding tetradentate P_2N_2 phosphine−iminophosphorane ligand **1**. Coordination to Ni(II) and Pd(II) metal centers afforded complexes **2** and **3**, respectively, 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. In contrast to most iminophosphorane complexes, **2** and **3** could be handled in water without any apparent decomposition. Their catalytic activity was evaluated in Suzuki−Miyaura coupling. These reactions were conducted in toluene, water, or a biphasic toluene/water medium in the presence of a phase-transfer agent. Under these last conditions, the Pd catalyst **3** (0.1 mol % catalyst loading) could be reused for five cycles without noticeable loss of activity.

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 considerable attention.[1] In particular, the introduction of chirality within their carbon backbone has allowed the elaboration of very efficient enantioselective catalysts. Thus, ruthenium(II) complexes were employed in catalytic cyclopropanation,[2] epoxidation,[3] hydrogenation,[4] and transfer hydrogenation[5] reactions, while palladium complexes were nicely exploited by Trost in allylic alkylations[6] and deracemization reactions.[7] More recently, Morris and co-workers 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 analogues 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 those of imine 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 chemistry[9] 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

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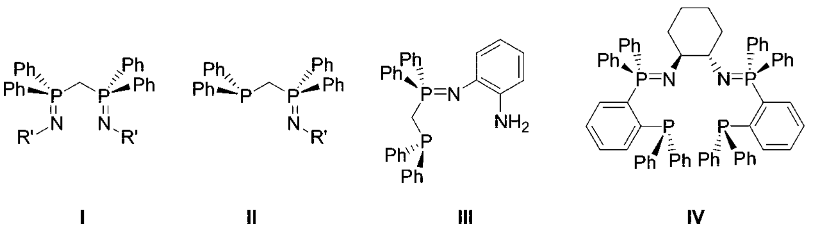
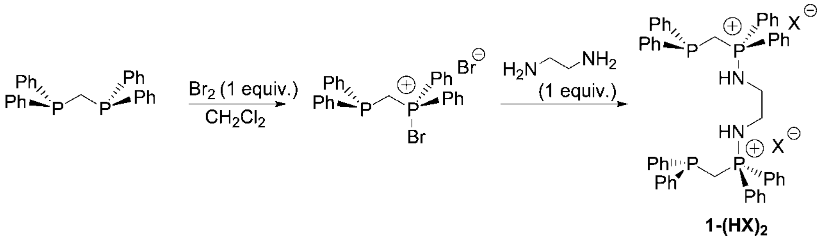
Chart 1. Iminophosphorane-Based Ligands Synthesized by the Kirsanov Method



Scheme 1. Synthesis of the Tetradentate Phosphine−Aminophosphonium Species 1-(HX)$_2$



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] and tridentate P−N−N ligands (**III**) (Chart 1).[9n] In 2006, we also explored the synthesis of tetradentate phosphine−imininophosphorane ligands such as **IV**, featuring a P$_2$N$_2$ core, by combining this synthetic approach with a nitrogen-assisted ortho-lithiation process.[9o] Unfortunately, this potentially interesting tetradentate system proved to be totally resistant toward coordination of transition-metal centers, probably as a result of the rigidity and/or steric bulkiness of the backbone P$_2$N$_2$ core. Therefore, we turned our attention to more flexible tetradentate systems.

In this paper we report the easy synthesis of a novel mixed tetradentate phosphine−iminophosphorane P$_2$N$_2$ ligand which features less rigid ancillary arms. Preliminary studies of the coordinating behavior of this new ligand toward nickel(II) 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$_2$N$_2$ ligand (Scheme 1). Reaction of the [Ph$_2$PCH$_2$-PPh$_2$Br]Br salt, obtained by reaction of bromine with dppm (bis(diphenylphosphino)methane) in dichloromethane at low temperature, with 1 equiv of ethylenediamine afforded the **1-(HBr)$_2$** salt. In this reaction $^1/_2$ equiv of ethylenediamine acts as a nucleophile, whereas the second half 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$_2$PCH$_2$PPh$_2$Br]Br salt and all the syntheses 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{^{1}H} NMR spectroscopy at 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.

The corresponding bis(iminophosphorane−phosphine) ligand **1** was then conventionally obtained from **1-(HCl)$_2$** by deprotonation with 2 equiv of MeLi in either THF or toluene (Scheme 2). Complete formation of **1** was first evidenced by ^{31}P{^{1}H} NMR spectroscopy, which shows the appearance of a characteristic AB spin system pattern at δ(THF) −25.4 ppm ($^2J_{PP}$ = 62 Hz) for the PPh$_2$ group and 21.2 ppm ($^2J_{PP}$ = 62 Hz) for the phosphorus atom of the iminophosphorane moiety. After removal of the lithium salts in toluene, ligand **1** was isolated in a satisfactory yield of 83%. The structure of **1** was unambiguously established by NMR spectroscopy, but its high sensitivity toward moisture precluded the obtainment of satisfactory elemental data.

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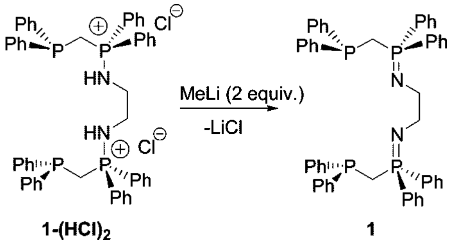
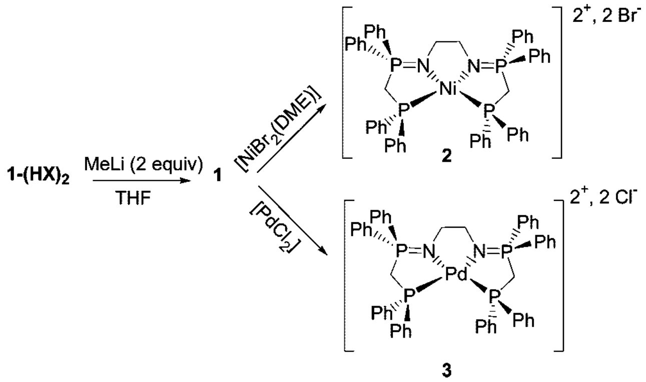
Scheme 2. Preparation of the Tetradentate Phosphine−Aminophosphonium Ligand 1



Scheme 3. Coordination to Ni(II) and Pd(II) Metal Centers



The coordinating ability of **1** toward 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, 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 [NiBr$_2$(DME)] (Scheme 3). Upon addition of the nickel precursor, the color instantly changed from colorless to orange, followed by the precipitation of an orange solid. After removal of the LiBr salts formed in CH$_2$Cl$_2$ and washing with diethyl ether, complex **2** was isolated as a very air- and moisture-stable orange solid in 90% yield. In ^{31}P{^{1}H} 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 PPh$_2$ 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 [PdCl$_2$] 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 toward air and moisture (Scheme 3). As in complex **2**, coordination of phosphorus and nitrogen atoms resulted in a significant downfield shift in ^{31}P{^{1}H} NMR (see the Supporting Information). Several experiments were also carried out using the [Pd(COD)Cl$_2$] complex as starting precursor, but analysis of the crude mixture revealed the presence of different products, among which was complex **3**.

Definitive evidence for the structures 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.

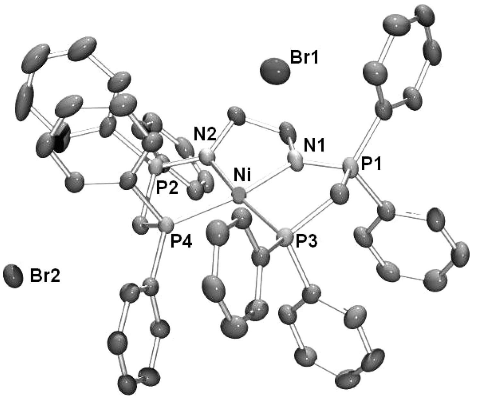


Figure 1. Molecular structure of complex **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected distances (Å) and angles (deg): P3−Ni = 2.155(1), N1−Ni = 1.897(3), N2−Ni = 1.903(3), P4−Ni = 2.154(1), Ni−Br2 = 6.656, 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−P4 = 7.44.

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 are 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 lengths 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). In addition, the two P═N distances at 1.606(3) and 1.608(3) Å are comparable to those recorded for phosphine− iminophosphorane complexes.[9m,13]

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 the ^{31}P NMR spectrum, both nitrogen and phosphorus atoms are coordinated to the metal center; therefore, the chloride atoms remain away from the metal (Pd−Cl > 4.7 Å). Moreover, both the Pd−N and Pd−P bond lengths are in the same range as 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 comment.

The catalytic activity of complexes **2** and **3** in Suzuki−Miyaura cross-coupling reactions was then evaluated.[14] The reaction of phenylboronic acid with bromobenzene was chosen as a model reaction to explore different experimental conditions. Interest-

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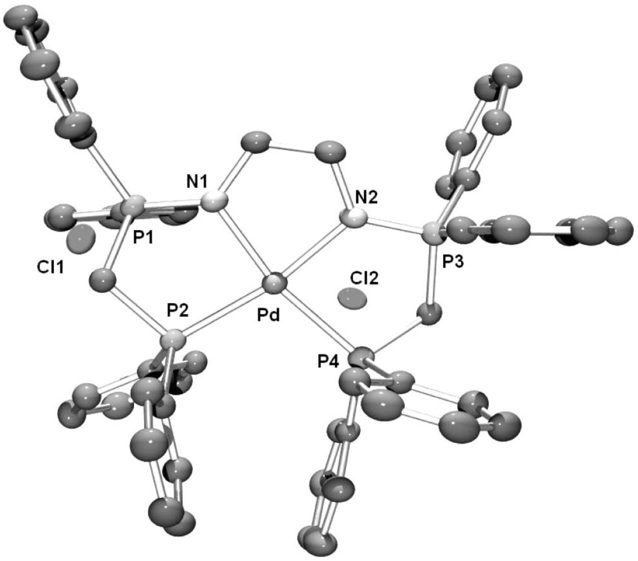
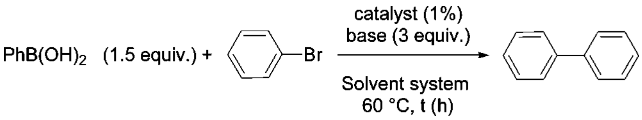


Figure 2. Molecular structure of complex **3**. Thermal ellipsoids are drawn to the 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected distances (Å) and angles (deg): P2−Pd = 2.252(8), N1−Pd = 2.047(2), N2−Pd = 2.023(2), P4−Pd = 2.262(8), Pd−Cl2 = 5.596, 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.

Table 1. Suzuki−Miyaura Cross-Coupling of Bromotoluene with Phenylboronic Acid Catalyzed by 2 and 3[a]



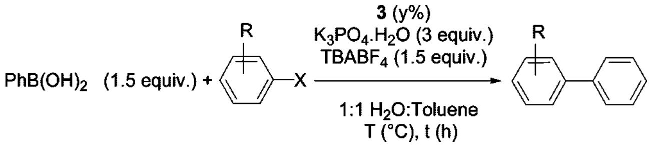
entry	catalyst	base	solvent syst	t (h)	conversion (%)[b]
1	**2**	K_2CO_3	H_2O	24	47
2	**2**	K_2CO_3	toluene	24	66
3	**2**	$K_3PO_4 \cdot H_2O$	1/1 H_2O/toluene + TBABF$_4$	16	100
4	**3**	K_2CO_3	toluene	24	97
5	**3**	K_2CO_3	1/1 H_2O/toluene + TBABF$_4$	8	100
6	**3**	$K_3PO_4 \cdot H_2O$	1/1 H_2O/toluene + TBABF$_4$	4	100

[a] Reaction conditions: 1 mmol of bromobenzene; 1.5 mmol of phenylboronic acid; 4 mL of toluene, H_2O or 1/1 H_2O/toluene + 1.5 mmol of TBABF$_4$ (TBABF$_4$ = [N(n-C_4H_9)$_4$]BF$_4$); 3 mmol of base; 10 μmol of catalyst. [b] Conversions were determined by quantitative GC calibrated with authentic samples.

ingly, we found that the remarkable stability of **2** and **3** toward moisture allowed the use of water as solvent or cosolvent. It is worth noting that, in the case of bidentate mixed P,N ligands, the resulting nickel and palladium complexes are not stable toward moisture. These reactions were thus conducted in different media: in pure toluene, pure water, or a biphasic toluene/water mixture in the presence of a phase-transfer agent.[15] Results of these preliminary tests are reported in Table 1.

As can be seen, whatever the solvent and 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 h). 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 the presence of [N(n-C_4H_9)$_4$]BF$_4$ (TBABF$_4$) as phase-transfer agent. Indeed, complete conversion was observed after 8 h using **3** as catalyst with K_2CO_3 as base. This result must be compared with that obtained in toluene after 1 day (entry 4). Using $K_3PO_4 \cdot H_2O$ as base allowed further improvement, a complete conversion being obtained after 4 h 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	20	0
2	H	Br	0.1	4	60	100
3[c]	H	Br	0.1	12	60	100
4	o-OMe	Br	0.1	16	60	92
5	o,o'-Me	Br	0.1	24	60	51
6	p-CH_3CO	Cl	1	24	60	34
7	o-CN	Cl	1	24	60	44
8	H	Cl	1	24	60	2

[a] Reaction conditions: 1 mmol of bromobenzene; 1.5 mmol of phenylboronic acid; 4 mL of 1/1 H_2O/toluene; 1.5 mmol of TBABF$_4$ (except for entry 3); 3 mmol of base; 1 or 10 μmol 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 TBABF$_4$.

No reaction was observed at room temperature using a 1 mol % loading of catalyst (entry 1). However, at 60 °C, even with 0.1 mol % of catalyst, the coupling was achieved within 4 h (entry 2). Interestingly, we noted that the reaction can be completed in the 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 and 5) and no benzene was produced. Those performances are good for 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 4-chloroacetophenone (entry 6) and 44% for 2-chlorobenzonitrile (entry 7), and no improvement was observed by increasing the 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, ^{31}P NMR spectroscopy allowed us only to observe the signal of the catalyst precursors, and we did not detect any free ligand in the reaction mixture. Therefore, in addition to the fact that the color of the mixture

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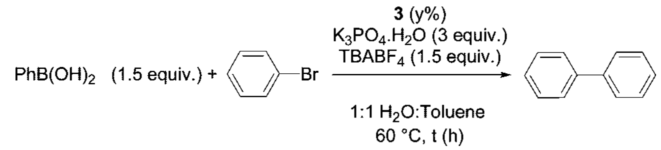
(15) For some examples of Suzuki−Miyaura catalytic reactions in biphasic media see: (a) Bedford, R. B.; Blake, M. E.; Butts, C. P.; Holder, D. *Chem. Commun.* **2003**, 466–467. (b) DeVasher, R. B.; Moore, L. R.; Shaughnessy, K. H. *J. Org. Chem.* **2004**, *69*, 7919–7927. (c) Han, Y.; Huynh, H. V.; 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.

Table 3. Reuse of the Aqueous Palladium Catalyst Phase for the Suzuki−Miyaura Cross-Coupling of Bromobenzene with Phenylboronic Acid



run	added Pd (mol %)	*t* (h)	conversion (%)[b]	TON[c]
1[a]	0.1	4	100	1000
2[b]	0	4	100	2000
3[d]	0	5	100	3000
4[d]	0	8	100	4000
5[d]	0	12	68	4680

[a] Reaction conditions: 1 mmol of bromobenzene; 1.5 mmol of phenylboronic acid; 4 mL of 1/1 H_2O/toluene; 1.5 mmol of $TBABF_4$; 3 mmol of base; 1 μmol of catalyst. [b] Conversions were determined by quantitative GC calibrated with authentic samples. [c] TON = turnover number, in units of mol of product/mol of catalyst. [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.

did not change 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 an 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 mixture was stirred until completion. Results of these experiments are reported in Table 3. It is worth noting that the extraction of the aqueous phase with dichloromethane allowed us to ascertain by ^{31}P 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 have been 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 byproduct in the aqueous phase. On the basis of this study, we could establish that the TON of our catalyst **3** is approximately 5000 mol of product/mol of catalyst.

Conclusion

We have 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 the 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 the 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, the reusability of the catalyst system was demonstrated; **3** could be re-employed without noticeable loss of activity up to four 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 Considerations. All experiments were performed under an atmosphere of dry nitrogen or argon using standard Schlenk and glovebox techniques. Solvents were freshly distilled under argon from Na/benzophenone (THF, diethyl ether, petroleum ether) or from P_2O_5 (dichloromethane). Bu_4NBF_4[19] and $NiBr_2$(DME)[20] were prepared according to literature procedures. 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 a Bruker Avance 300 spectrometer operating at 300 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si. ^{31}P shifts are relative to an 85% H_3PO_4 external reference. Coupling constants 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'analyze du CNRS", at Gif sur Yvette, France. The GC yields were determined on a PERICHROM 2100 gas chromatograph equipped with a PERICHROM column (SILICONE OV1, CP-SIL 5 CB), 30 m × 0.22 mm.

Synthesis and Characterization of the 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 CH_2Cl_2 (20 mL) at −78 °C. The reaction mixture was stirred for 20 min. $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2): δ −23.2 (d, $J_{PP} = 83$ Hz), 58.6 (d, $J_{PP} = 83$ Hz).

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 1 h at room temperature. The solution was washed twice with brine (20 mL), the organic layer was dried over $MgSO_4$, and the solvent was removed under vacuum to deliver a white solid, which was washed with diethyl ether.

1-(HCl)$_2$: yield 1.513 g (1.68 mmol, 72%). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ −28.6 (d, $^{2}J_{PP} = 70.0$ Hz, P^{III}), 41.2 (d, $^{2}J_{PP} = 70.0$ Hz, P^{V}). ^{1}H ($CDCl_3$) δ 3.22 (4H, bs, N-CH_2), 3.97 (4H, d, $^{2}J_{HP} = 16.0$ Hz, PCH_2P), 7.23 (8H, m, m-H (Ph_2P^{V})), 7.28 (4H, m, p-H (Ph_2P^{V})), 7.33 (8H, m, o-H (Ph_2P^{V})), 7.44 (8H, vtd, $^{3}J_{HH} = 7.5$ Hz, $^{5}J_{PH} = 3.0$ Hz, m-H (Ph_2P^{III})), 7.57 (4H, vt, $^{3}J_{HH} = 7.5$ Hz, $^{3}J_{HP}$ not measurable, p-H (Ph_2P^{III})), 7.77 (8H, dd, $^{3}J_{HH} = 7.5$ Hz,

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(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 the complex $Pd(dba)_2$ under H_2 in THF at room temperature 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 coupling was 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 couplings has not been thoroughly explored, one may propose that a phosphine-substituted 14-VE complex is formed. Preliminary calculations were 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 nonmetallic atoms) and the lanl2dz pseudopotential for palladium. These calculations revealed that a 14-VE palladium(0) complex would only involve coordination of the two phosphine ligands. .

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

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

$^3J_{HP}$ = 13.0 Hz, o-H (Ph_2P^{III})), 8.16 (2H, bs, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.6 (dd, $^1J_{CP}$ = 34.5 Hz, $^1J_{CP}$ = 66.5 Hz, PCH_2P), 42.55 (d, $^2J_{CP}$ = 9.0 Hz, NCH_2), 120.8 (dd, $^1J_{CP}$ = 98.0 Hz, $^4J_{CP}$ = 1.0 Hz, C^{IV}(Ph_2P^{III})), 128.7 (d, $^3J_{CP}$ = 7.0 Hz, p-CH (Ph_2P^V)), 129.4 (d, $^3J_{CP}$ = 12.5 Hz, m-CH (Ph_2P^V)), 129.4 (s, m-CH (Ph_2P^{III})), 132.9 (d, $^2J_{CP}$ = 21.5 Hz, o-CH (Ph_2P^V)), 133.2 (dd, $^2J_{CP}$ = 11.0 Hz, $^4J_{CP}$ = 2.5 Hz, o-CH (Ph_2P^{III})), 134.3 (d, $^2J_{CP}$ = 2.5 Hz, p-CH (Ph_2P^{III})), 135.3 (dd, $^2J_{CP}$ = 12.5 Hz, $^3J_{CP}$ = 8.5 Hz, C^{IV}(Ph_2P^V)). Anal. Calcd for $C_{52}H_{50}Cl_2N_2P_4$: 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 μL, 0.223 mmol) was added to a suspension of the ligand **1-(HCl)$_2$** (0.111 mmol) in toluene (5 mL) cooled to −78 °C. The cold bath was removed and the solution warmed to room temperature. The insoluble lithium salts were removed by centrifugation. After removal of the solvent under vacuum, the obtained white solid was washed with hexanes (10 mL).

1: yield 76 mg (0.091 mmol, 83%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −27.2 (d, $^2J_{PP}$ = 49.0 Hz, P^{III}), 22.7 (d, $^2J_{PP}$ = 49.0 Hz, P^V). ^1H ($CDCl_3$): δ 3.09 (4H, d, $^2J_{HP}$ = 15.0 Hz, N-CH_2), 4.12 (4H, d, $^2J_{HP}$ = 16.0 Hz, PCH_2P), 7.27 (24H, m, o,m-H (Ph_2P^V) and m-H (Ph_2P^{III})), 7.79 (4H, m, p-H (Ph_2P^V)), 7.81 (8H, m, o-H (Ph_2P^V)), 8.17 (4H, m, p-H (Ph_2P^{III})). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.9 (dd, $^1J_{CP}$ = 29.0 Hz, $^1J_{CP}$ = 81.5 Hz, PCH_2P), 47.7 (d, $^2J_{CP}$ = 22.5 Hz, NCH_2), 127.3 (m, C^{IV}(Ph_2P^{III})), 129.8 (d, $^3J_{CP}$ = 2.0 Hz, m-CH (Ph_2P^V)), 130.1 (d, $^3J_{CP}$ = 2.5 Hz, m-CH (Ph_2P^{III})), 131.8 (d, $^2J_{CP}$ = 9.5 Hz, o-CH (Ph_2P^V)), 132.0 (s, $^2J_{CP}$ = 4.5 Hz, o-CH (Ph_2P^{III})), 132.3 (s, p-CH (Ph_2P^V)), 132.6 (s, p-CH (Ph_2P^{III})), 135.3 (dd, $^2J_{CP}$ = 12.5 Hz, $^3J_{CP}$ = 8.0 Hz, C^{IV}(Ph_2P^V)).

Synthesis and Characterization of Nickel Complex 2. MeLi (140 μL, 0.223 mmol) was added to a suspension of the ligand **1-(HCl)$_2$** (0.111 mmol) in THF (5 mL) cooled to −78 °C. The cold bath was removed and the solution warmed to room temperature. Then, [$NiBr_2$(DME)] (35 mg, 0.111 mmol) was added, and the solution turned immediately from colorless to red. After stirring for 30 min at room temperature, an orange 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 orange solid was washed with Et_2O (10 mL).

2: yield 104 mg (0.10 mmol, 90%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.9 (vt, $^2J_{PP}$ = 17.0 Hz, $^3J_{PP}$ = 17 Hz, P^{III}), 49.2 (vt, $^2J_{PP}$ = 17.0 Hz, $^3J_{PP}$ = 17 Hz, P^V). ^1H NMR ($CDCl_3$): δ 2.91 (4H, bs, N-CH_2), 4.36 (4H, bs, PCH_2P), 7.13 (12H, m, p,m-H (Ph_2P^{III})), 7.40 (12H, m, p,m-H (Ph_2P^V)), 7.81 (16H, m, o-H (Ph_2P^V and Ph_2P^{III})). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.43 (d, $^1J_{CP^V}$ = 77.5 Hz, PCH_2P), 66.45 (d, $^2J_{CP}$ = 13.0 Hz, NCH_2), 123.3 (s, C^{IV}(Ph_2P^{III})), 124.0 (s, C^{IV}(Ph_2P^V)), 127.95 (vt, $^3J_{CP}$ = 6.5 Hz, $^5J_{CP}$ = 6.3 Hz, m-CH (Ph_2P^{III})), 128.3 (d, $^3J_{CP}$ = 14.0 Hz, m-CH (Ph_2P^V)), 131.0 (s, p-CH (Ph_2P^{III})), 132.4 (s, p-CH (Ph_2P^V)), 132.5 (d, $^2J_{CP}$ = 11.0 Hz, o-CH (Ph_2P^V)), 134.0 (vt, $^2J_{CP}$ = 5.5 Hz, $^4J_{CP}$ = 5.5 Hz, o-CH (Ph_2P^{III})). Anal. Calcd for $C_{52}H_{48}N_2P_4NiBr_2$: 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 the ligand **1-(HCl)$_2$** (0.111 mmol) in THF (5 mL) cooled to −78 °C. The cold bath was removed and the solution warmed to room temperature. Then, [$PdCl_2$] (20 mg, 0.111 mmol) was added and the solution was heated to 60 °C using an oil bath. After the mixture was stirred for 4 h 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: yield 95 mg (0.095 mmol, 85%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.9 (dd, $^2J_{PP}$ = 14.0 Hz, $^3J_{PP}$ = 10.0 Hz, P^{III}), 46.9 (dd, $^2J_{PP}$ = 14.0 Hz, $^3J_{PP}$ = 10.0 Hz, P^V). ^1H NMR ($CDCl_3$): δ 3.24 (4H, bs, N-CH_2), 4.61 (4H, vt, $^2J_{HP}$ = 9.5 Hz, PCH_2P), 7.09 (12H, m, p,m-H (Ph_2P^{III})), 7.40 (12H, m, p,m-H (Ph_2P^V)), 7.57 (8H, m, o-H (Ph_2P^{III})), 7.90 (8H, m, o-H (Ph_2P^V)). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 38.2 (dd, $^1J_{CP^{III}}$ = 85.0 Hz, $^1J_{CP^V}$ = 15.5 Hz, PCH_2P), 54.2 (d, $^2J_{CP^V}$ = 13.0 Hz, N-CH_2), 122.5 (d, $^1J_{CP^V}$ = 88.5 Hz, C^{IV}(Ph_2P^{III})), 124.5 (dd, $^1J_{CP^{III}}$ = 55.0 Hz, $^3J_{CP^{III}}$ = 4.1 Hz, C^{IV}(Ph_2P^{III})), 129.1 (vt, $^3J_{CP}$ = 5.5 Hz, $^5J_{CP}$ = 5.7 Hz, m-CH (Ph_2P^{III})), 129.7 (d, $^2J_{CP}$ = 12.5 Hz, m-CH (Ph_2P^V)), 132.3 (s, p-CH (Ph_2P^{III})), 133.7 (d, $^4J_{CP}$ = 3.0 Hz, p-CH (Ph_2P^V)), 133.9 (d, $^2J_{CP}$ = 11.0 Hz, o-CH (Ph_2P^V)), 134.9 (vt, $^2J_{CP}$ = 6.5 Hz, $^4J_{CP}$ = 6.5 Hz, o-CH (Ph_2P^{III})). Anal. Calcd for $C_{52}H_{48}N_2P_4PdCl_2$: 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 mol % of catalyst, a Schlenk was charged with a mixture of aryl halide (1.0 mmol; 105 μL for bromobenzene, 102 μL for chlorobenzene, 128 μL for 4-chloroacetophenone, 137.5 mg for 2-chlorobenzonitrile), phenylboronic acid (1.5 mmol, 183 mg), base (3.0 mmol; 691 mg for $K_3PO_4 \cdot H_2O$, 414 mg for K_2CO_3), precatalyst (0.01 mmol; 10.4 mg for nickel complex **2**, 10.0 mg for palladium complex **3**), and [N(n-C_4H_9)$_4$]BF_4 (1.5 mmol, 493 mg). To the mixture was added degassed water (2.0 mL) and toluene (2.0 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 cooled and an exact amount of *n*-heptane (100 μL) was introduced (as internal standard). The organic layer was dried and filtered on a short $MgSO_4$ column and analyzed by quantitative GC, first calibrated with authentic samples.

X-ray Crystallographic Data for 2 and 3. Orange needles of **2** and yellow blocks of **3** crystallized by slow diffusion of hexanes into saturated solutions of **2** and **3**, respectively. Data were collected on a Nonius Kappa CCD diffractometer using a Mo Kα (λ = 0.710 73 Å) X-ray source and a graphite monochromator. CCDC 681401 and 681402 contain the supplementary crystallographic data for this paper (for complexes **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, U.K.; 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 created using ORTEP III for Windows.

Crystal data for **2**: triclinic, $P\bar{1}$, a = 12.498(1) Å, b = 13.157(1) Å, c = 16.541(1) Å, α = 86.688(1)°, β = 86.511(1)°, γ = 78.482(1)°, V = 2657.3(3) Å^3, Z = 2, ρ_{calcd} = 1.516 g cm^{-3}, 11 661 unique reflections (θ < 27.1°), 604 parameters, R1 = 0.0546 ($I > 2\sigma(I)$), wR2 = 0.1604 (all data), GOF = 1.055. Crystal data for **3**: triclinic, $P\bar{1}$, a = 12.819(1) Å, b = 13.213(1) Å, c = 14.508(1) Å, α = 89.216(1)°, β = 76.579(1)°, γ = 81.103(1)°, V = 2365.9(3) Å^3, Z = 2, ρ_{calcd} = 1.457 g cm^{-3}, 12 204 unique reflections (θ < 28.7°), 580 parameters, R1 = 0.0429 ($I > 2\sigma(I)$), wR2 = 0.1239 (all data), GOF = 1.014.

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Supporting Information Available: Crystallographic data for **2** and **3** as CIF files and tables and figures 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.

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