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An Atropo-Stereogenic Diphosphane Ligand with a Proximal Cationic Charge: Specific Catalytic Properties of a Palladium Complex Thereof

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A class of cationic diphosphane ligands combining phosphane and amidiniophosphane moieties is illustrated on the *N*-methyl,*N*-naphthylbenzimidazolium framework. The palladium(II) complex thereof is described and compared to the corresponding complex of the analogous neutral diphosphane. Contrary to first-level expectations, the N_2C–P and N_2CP–Pd bonds in the cationic diphosphane complex are not longer than those occurring in its neutral counterpart. In the cationic ligand, the proximal positive charge is indeed conjugated to one phosphanyl group, and the coordination scheme is tentatively interpreted by resonance of the phosphane→metal dative bond (^+N_2C–P:→[Pd]) with a carbene→phosphenium dative bond (N_2C:→[$^+$P:→Pd]). Despite this peculiar structural feature, the electronic σ donation (vs. π acceptation) towards the palladium centre remains lowered in the cationic ligand. This specific property can be a priori valuable in a catalytic process where oxidative addition is not the limiting step. It is indeed shown that although the neutral complex is more active in Suzuki coupling reactions, the cationic complex is more active in Sonogashira-type coupling reactions involving predissociated halide substrates, namely an acyl chloride. These likely atropo-chiral ligands deserve to be resolved for application in asymmetric catalysis.

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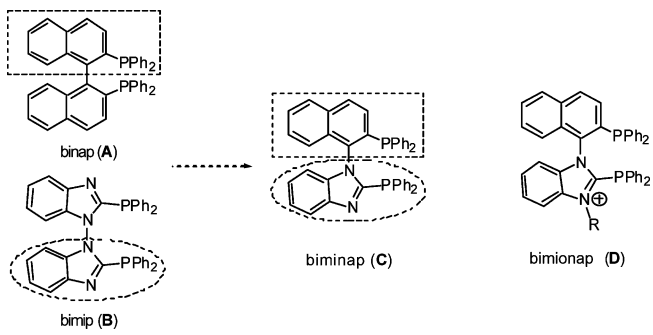
Introduction

Since Noyori's initial report of binap (**A**) based on the chiral 1,1′-binaphthyl scaffold,[1] a wide variety of alternative C_2-symmetric biaryl-bridged diphosphanes have been devised.[2] Among them, the C_2-axially chiral heterobiaryl ligands,[3] first exemplified by Sannicolò on the *N*,*N*′-bisbenzimidazolyl scaffold with bimip (**B**; Scheme 1),[4] provides additional electron-withdrawing properties that may be valuable for specific purposes. Indeed, diphosphane ligands primarily act as Lewis bases, but the exact nature and extent of the electron transfer determine the catalytic properties of the metallic centre. Adjustment of the electronic properties inside the coordination sphere (where catalysis takes place) may be achieved in two ways: (i) by a C_2-symmetric overall electron transfer from equivalent phosphorus atoms or (ii) by a C_1-dissymmetric balance of the transfer between phosphorus atoms of different σ-donating and π-accepting characters. Although many disymmetric (C_1) diphosphanes proved to be efficient in various catalytic applications, a rationale for their design is a priori tricky. However, because sterically optimized ligands for asymmetric catalysis should be C_2 symmetric according to the "quadrant" rule,[5] such ligands must not be far from C_2 symmetry in their optimal form. Given a symmetric diphosphane R_2P–PR_2, a subtle − but sufficient − electronic desymmetrization could be achieved by inserting/substituting a P-bonded moiety on one side of the bridge by a "perturbing linkage" X: pseudosymmetric heterobiaryl scaffolds R_2P–X-PR_2 are thus a priori attractive. With respect to the underlying X–R_2P→M dative bond, electron-withdrawing effects are classically exerted by π retrodonation and σ (–I) induction due to the oxygen linkages of phosph(in)ites (X = O, e.g. the binaphos ligand, which is efficient in asymmetric hydroformylation and hydrogenation catalysis).[6] A shortcoming is, however, the hydrolytic sensitivity of the P–O bonds, and phosphanes may be naturally preferred. In this case, however, the remote desired effects must be amplified



Scheme 1. Hybridization of the C_2-symmetric binap (**A**) and bimip (**B**) ligands into the C_1-symmetric biminap ligand (**C**) and its bimionap iminium salt (**D**).

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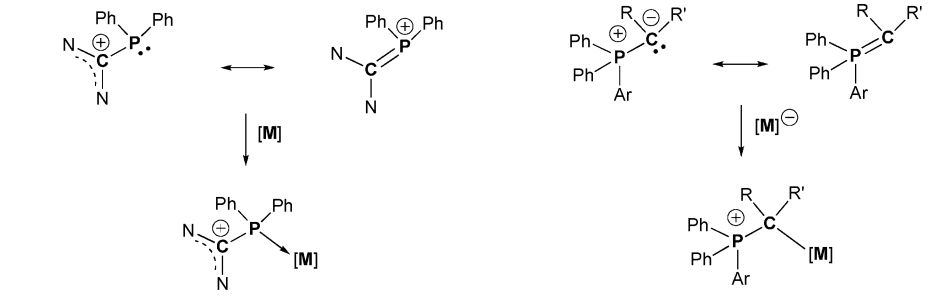

Scheme 2. Analogy between amidiniophosphane ligands (of the C^+P kind) and phosphonium ylide ligands (of the P^+C kind).

by conjugation and/or by doubling the number of electronegative atoms in β positions from the coordinating P^{III} atom, such as the nitrogen atoms in the C_2-symmetric bimip ligand, which was indeed claimed to be a very electron-poor ligand.[4] The pseudo-C_2/C_1-symmetric heterobiaryl version, the naphthylbenzimidazolyl "biminap" ligand (**C**) derived from the hybridization of binap (**A**) and bimip (**B**), is a natural candidate (Scheme 1).

The electron-withdrawing effect of X (an imidazolyl ring in the case of biminap), is of the second order only, but it should culminate in α,β-cationic phosphanes. Cationic phosphanes, the counterparts of the more widely exemplified anionic phosphanes such as tris(3-sulfonatophenyl)-phosphane trisodium salt (tppts),[7] have been used for performing catalysis in aqueous or polar media,[8] or for the design of "true" zwitterionic organometallates.[9] For such purposes, the cationic charge is conjugatively isolated and/or in remote position in order to avoid perturbation of the metal centre. In an opposite purpose, we may wonder about the possible active role of a cationic charge on the catalysis itself. Beyond the through-bond (inductive/mesomeric) effect, the through-space electrostatic (field) effect is also to be considered. In a rigid framework, the resulting steady electrostatic field embedding the metal centre should influence the approach of polar substrates and the selectivity of charge-controlled processes. The biaryl framework of biminap (**C**) could bring the required rigidity and its nitrogen atoms in the ideal sites for cationization: the *N*-methyl-*N*,1′-benzimidazolionaphthyl diphosphane "bimionap" (**D**) is therefore a challenging target (Scheme 1).

Several cationic binap derivatives bearing ammonium or phosphonium charges at the periphery have been proposed,[10] and in particular, binapium,[11] which is a monophosphane that could not enter the coordination sphere of cationic metals,[12] but which was made P,C-chelating by passing to the corresponding ylide.[13] Phosphonium ylides are actually phosphoniocarbyl ligands that can be regarded as reversed amidiniophosphane ligands. The analogy is not only geometric, but also electronic (Scheme 2): although the σ-donating character is particularly strong for the former "P^+C" ligands (of X-type), it should be particularly weak for the latter "C^+P" ligands (of L-type).

Whereas aryl-bridged phosphane–phosphonium ylide Ph_2P–[Ph_2P^+C] ligands afforded stable and catalytically active complexes,[14] their reverted phosphane–amidiniophosphane Ph_2P–[$N_2C^+PPh_2$] version is hereafter studied with bimionap (**D**) as an example.

The first target is thus biminap (**C**), which will serve to bring out the effect of the cationic charge in a comparative study with its *N*-alkylated product bimionap (**D**). Both ligands are expected to possess an atropo-stereogenic C(aryl)-N(amine) bond. It is worth noting that related non-classical stereogenic elements have been exemplified by C(aryl)–C(amide)[15] and C(aryl)–N(non-amine) bonds in chiral phosphane ligands based on quinazolinone-containing *N*-anilide[16] and *N*-arylimide[17] moieties. Although atropo-stereogenic C(aryl)–N(indoline) bonds were recently described,[18] only few examples of such C(aryl)–N(amine) bonds have been reported.[19]

Results and Discussion

Synthesis of Ligands and Complexes

The synthesis of biminap (**C**) starts from readily available 1-(1-naphthyl)-1*H*-benzimidazole (**1**), which was prepared as reported in the literature by a coupling reaction between benzimidazole and 1-iodonaphthalene in the presence of copper iodide.[20]

Because the most acidic proton of **1** is located at the C-2 position of the benzimidazolyl ring, the addition of one equivalent of BuLi in thf followed by chlorodiphenylphosphane allowed the isolation of monophosphane **2** in 76% yield, which was fully characterized, including by X-ray diffraction analysis.[21] Interestingly, and as described recently,[22] the use of two equivalents of Buli and one equivalent of chlorodiphenylphosphane in Et_2O resulted in the isolation of isomeric monophosphane **3** in 34% yield. In this case, selective monophosphanylation occurs mainly at the most nucleophilic position, namely, the lithiated *ortho* carbon atom of the naphthyl group. Finally, double deprotonation of **1** with two equivalents of BuLi in Et_2O and the addition of the corresponding stoichiometric amount of chorodiphenylphosphane afforded targeted diphosphane **4** in 39% yield.

Despite the presence of different nucleophilic centres (nitrogen and phosphorus atoms), a single equivalent of methyl triflate (MeOTf, a hard methylating reagent) selec-

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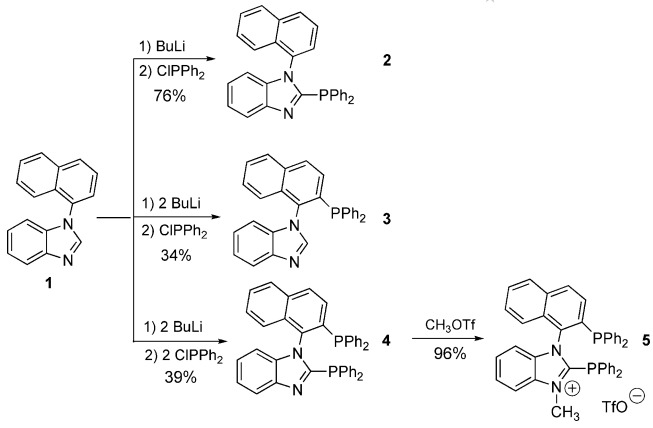
tively reacted with **4** in CH_2Cl_2 to give desired *N*-methylated monocation **5** in 96% yield. The ionic nature of **5** is primarily indicated by its very-low solubility in nonpolar solvents and by the appearance of a ^1H NMR signal at δ = 3.81 ppm corresponding to the *N*-methyl substituent. This

Table 1. Selected bond lengths [Å] from X-ray diffraction studies in the biminap series (**4** and **6**) and bimionap series (**5** and **7**).

	4	6	5	7
C1–P1	1.808(5)	1.824(5)	1.847(3)	1.810(16)
C1–N1	1.333(6)	1.310(8)	1.330(3)	1.353(18)
C1–N2	1.399(6)	1.384(7)	1.349(3)	1.346(18)
P1–Pd	–	2.2467(13)	–	2.249(4)
P2–Pd	–	2.2555(13)	–	2.268(5)
N2–C9	1.434(6)	1.409(9)	1.432(3)	1.450(18)
C10–P2	1.828(5)	1.838(8)	1.833(3)	1.845(15)



Scheme 3. Selective phosphanylation and methylation of the *N*-naphthylbenzimidazole core.

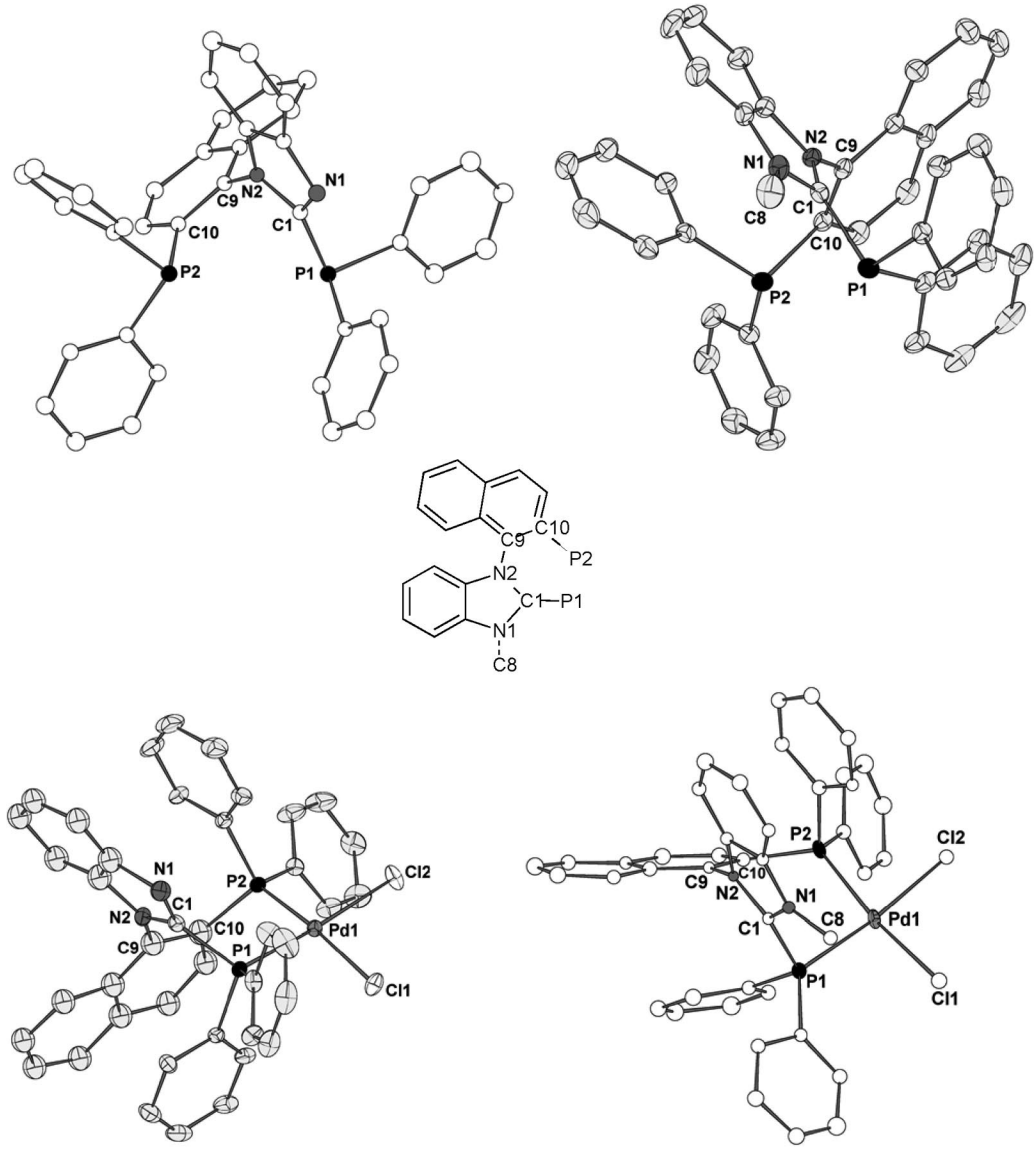


Figure 1. ORTEP views of the X-ray crystal structures of diphosphanes **4** (top left) and **5** (top right) and complexes **6** (bottom left) and **7** (bottom right) [with 30% probability for thermal ellipsoids of all non-hydrogen atoms in **5** and **6**. A common atom numbering scheme (centre) is adopted. All atoms were isotropically refined in **4**, and only Pd and P atoms were anisotropically refined in **7**]. For representative bond lengths, see Table 1.

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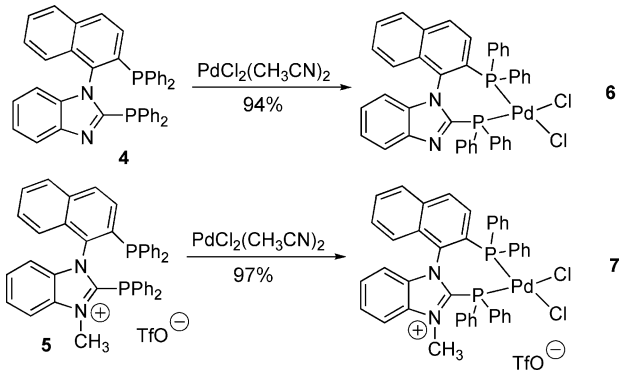
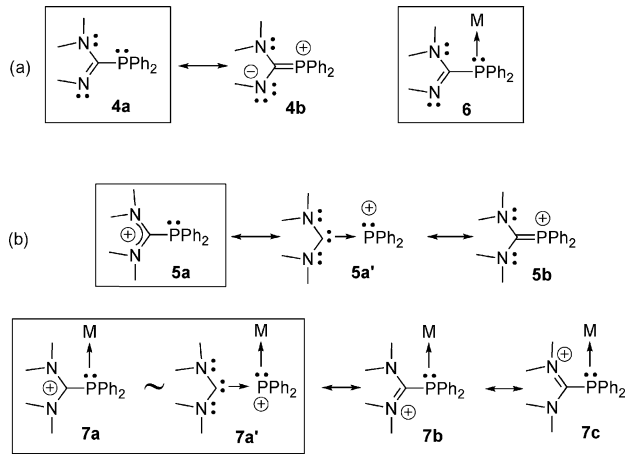
is confirmed in the ^{31}P NMR spectrum by the deshielding of the phosphorus atom connected to the benzimidazolyl from δ = –26.7 ppm in **4** to δ = –18.6 ppm in **5**. In a consistent manner, the second phosphorus atom bonded to the naphthyl moiety is much less but still slightly deshielded (**4**: δ = –18.1 ppm; **5**: δ = –16.3 ppm) (Scheme 3). The structure of diphosphanes **4** and **5** were finally confirmed by X-ray diffraction analysis (Table 1, Figure 1).[21]

Diphosphanes **4** and **5** possessing imidazolyl[23] and imidazolium[24] substituents, respectively, were then envisioned as rigidly chelating ligands. They were thus treated with a stoichiometric amount of $(CH_3CN)_2PdCl_2$ in thf. The corresponding palladium dichloride adducts **6** and **7** were isolated in 94 and 97% yield, respectively (Scheme 4).



Scheme 4. Synthesis of isostructural $PdCl_2$ complexes of biminap **4** and bimionap **5**.

biminap **4** by the $PdCl_2$ unit results in a shortening of the C1–N1 bond from 1.333(6) Å in **4** to 1.310(8) Å in **6** and a lengthening of the C1–P1 bond from 1.808(5) Å in **4** to 1.824(5) Å in **6**. This could be interpreted by some contribution of the zwitterionic imidophosphonium form **4b** in the description of free biminap **4** beside the iminophosphane form **4a** (Scheme 5a): the phosphorus lone pair of electrons is no longer available in complex **6**, and the loss of the possible double bond character of the N_2C–P bond of **4** should indeed result in the observed lengthening upon complexation.



Scheme 5. (a) Resonance description of the imidazolylphosphane end of biminap in the free state (**4**) and the complexed state (**6**); (b) resonance description of the imidazoliophosphane end of bimionap in the free state (**5**) and the complexed state (**7**).

Comparative Analysis of the Structure of Neutral and Cationic Systems

Complexes **6** and **7** were fully characterized by multinuclear NMR spectroscopy and by X-ray diffraction analysis (Table 1, Figure 1).[21] The ^{31}P NMR resonances for **6** and **7** occur at δ = 13.6, 25.4 ppm and δ = 18.8, 24.0 ppm, respectively, which are in the typical range for Pd–diphosphane derivatives. In contrast to **6**, which is air-stable and can be purified by chromatography on silica gel, cationic complex **7** is more sensitive and has to be handled under an inert atmosphere.

In neutral complex **6**, the seven-membered palladacycle is symmetrically twisted (λ/δ configuration with respect to the P1–Pd–P2 unit). This reflects the local C_2 symmetry nearby the two pseudoequivalent phosphorus atoms P1 and P2: as expected, the dissymmetrical backbone exerts a second-order influence. In contrast, in cationic complex **7**, beyond the steric effect of the added *N*-methyl substituent, an internal electronic/electrostatic distortion may help to differentiate the two phosphorus atoms while pushing the whole bridge on the same side of the square planar P_2PdCl_2 moiety (Figure 1).

Selected geometrical parameters of diphosphanes **4** and **5** and complexes **6** and **7** are listed in Table 1. In the neutral series, coordination induces a decrease in the C10–C9–N2–C1 dihedral angle (**4**: 75.66°; **6**: 64.52°). Complexation of

As in the neutral series, the same trend is observed for the values of the C10–C9–N2–C1 torsion angles in cationic bimionap **5** (73.93°) and its $PdCl_2$ complex **7** (59.76°). In cationic diphosphane **5**, the C1 and N1 atoms exhibit pure sp^2 character (sum of the angles: 359.8 and 360°, respectively), whereas the P1 atom is strongly pyramidalized (sum of the angles: 309.5°). Moreover, the C1–N1 [1.330(3) Å] and C1–P1 [1.847(3) Å] distances correspond to a C=N bond and a C–P bond, respectively. To explain these data, **5** has to be regarded as *C*-phosphanyl-substituted amidinium salt **5a** (or its carbene–phosphenium adduct form **5a′**) rather than as (*C*-diamino)phosphonium salt **5b**. This reveals the superior *p*-donor ability of the nitrogen atoms relative to that of the phosphorus atom. Complexation of cationic diphosphane ligand **5** results in a slight lengthening of the C–N bond length [from 1.330(3) Å in **5** to 1.353(18) Å in **7**], which is thus indicative of a decrease in their double bond character and corresponds to some electron withdrawal from the PPd fragment. The simultaneous important shortening of the C1–P1 bond by ca. Δ = –0.037 Å [from 1.847(3) Å in **5** to 1.810(16) Å in **7**] was however intriguing, because double N_2C=P bond character should involve the P1 lone pair that is simultaneously involved in the P→Pd bond [P1–Pd 2.249(4) Å]. The P1–Pd bond length is in the classical range for similar phosphorus–palladium bonds [e.g., in the (bimip)$PdCl_2$ complex: P–Pd

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≈2.267 Å].[4a] This value is more reliable (esd = 0.004 Å) than the C1–P1 bond length (esd = 0.016 Å), and the relevance of the latter could be questioned with respect to the analytical uncertainty. Another explanation would be that the short $^{+}N_2C$–P bond provided by the X-ray diffraction analysis could reveal the dative nature of the C→P bond, which results in an electron "shift effect". According to a similar effect previously discussed,[25] the distance between the centroids of the electron clouds of C1 and P1 would be shorter than the internuclear distance. The carbene→phosphenium character is indeed expected to be enhanced by complexation of the lone pair of the phosphorus atom of **5** to the palladium atom of **7**.

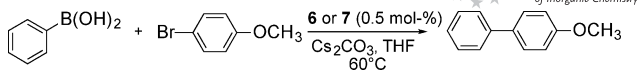
The two-electron interaction between P1 and Pd can thus be summarized by describing complex **7** as the contribution of two kinds of limiting forms: (i) a diaminocarbene–phosphenium form **7a** or **7a′** and (ii) the amidiniophosphane forms **7b** and **7c** (Scheme 5b). The relevance of the "diaminocarbene→phosphenium→metal" coordination scheme is also supported by independent reports. The Lewis amphoteric behaviour of a phosphenium moiety was indeed previously invoked in a dinuclear phosphanylidene complex.[26]

More generally, in the strongly σ-donating N-heterocyclic carbenes (NHCs), the cyclic C–N bonds are slightly longer and the carbenic angle is significantly reduced with respect to the corresponding imidazolium salt.[27] Within the limits of crystallographic errors, the same tendency is observed in the bimionap ligand for the C1–N1 bond (1.330 Å in **5**, 1.353 Å in **7**) and the N1–C1–N2 angle (108.6° in **5**, 107.2° in **7**).

Comparative Analysis of Catalytic Properties of Neutral and Cationic Systems

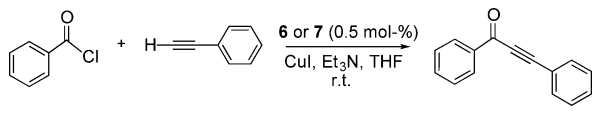
The catalytic properties of biminap and bimionap complexes **6** and **7** were first tested in a classical Suzuki coupling reaction between phenylboronic acid and 4-bromoanisole. In the presence of neutral complex **6** (0.5 mol-%) and in thf as the solvent, the desired biaryl was produced in 73% yield after 12 h at 60 °C. By using cationic catalyst **7** under the same conditions, the coupling product was obtained in 37% yield only. This result is not surprising, because the Suzuki reaction is known to be accelerated by the use of strongly σ-donating diaminocarbene or alkylphosphane ligands facilitating the oxidative addition of the aryl halide, which is the limiting step of the catalytic cycle (Scheme 6).[28] Concerning the challenging aryl chloride substrates, for example, binap was indeed shown to be totally ineffective,[29] and the related and even less-donating biminap (and of course bimionap) ligand was not studied further in this reaction. Moreover, although the biminap ligand could be envisioned for its own, it is here first considered as a neutral reference with respect to bimionap.

A Sonogashira-type coupling reaction was also investigated with the benzoyl chloride and phenylacetylene substrates in a stoichiometric ratio (Scheme 7). Both neutral and cationic catalysts **6** and **7** were found to catalyze the



Scheme 6. A Suzuki–Miyaura coupling reaction catalyzed by biminap (**6**) and cationic bimionap (**7**) complexes.

reaction in the presence of copper iodide (1%) and triethylamine (1.0 equiv.) over a 5-h period to afford diphenylpropynone in 5 and 73% yield, respectively.



Scheme 7. A Sonogashira-type coupling reaction catalyzed by biminap (**6**) and cationic bimionap (**7**) complexes.

This marked difference in catalytic efficiency was studied in more detail by monitoring the yield and conversion by GC analysis (Figure 2). The initial slopes of yield and conversion curves are higher with bimionap complex **7** than those obtained with biminap complex **6**. Although the curves level off after 1 h with biminap complex **6**, the reaction proceeds smoothly over 5 h with bimionap complex **7**. The difference in lifetime of the two catalysts derived from **6** and **7** can be tentatively attributed to some side reaction of the basic/nucleophilic imidazole nitrogen atoms of **6** with the acylium moiety of benzoyl chloride. With either complex, the gap observed between the conversion of phenylacetylene and the yield of diphenylpropynone is due to the formation of unidentified side products.

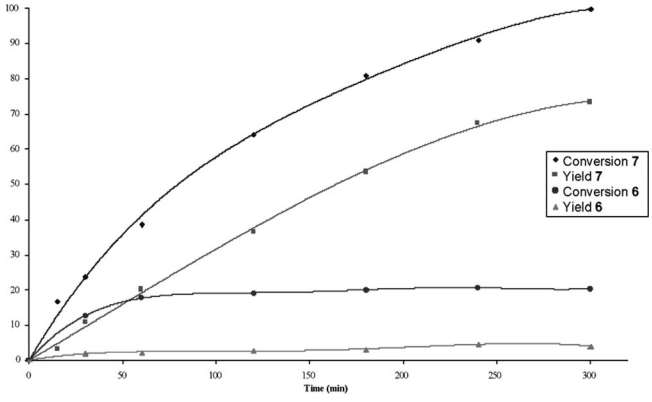


Figure 2. Kinetic curves of the Sonogashira-type coupling reaction depicted in Scheme 7 catalyzed by biminap and cationic bimionap complexes **6** and **7**, respectively; dodecane was used as an internal standard.

It was previously suggested that the mechanism of Sonogashira-type reactions with acyl chlorides obey the same mechanism as the "true" Sonogashira reactions with aryl halides: the acyl chloride oxidatively adds to a Pd^0 species thus to form an acyl Pd^{II} intermediate, which then reacts with the in situ generated copper acetylide.[30] In fact, the dramatic differences displayed in Figure 2, could be simply explained by the difference in electrophilicity of the neutral

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and cationic catalytic intermediates resulting from precursors **6** and **7**, respectively. The scope of this catalytic system with other terminal alkynes is under current investigation.

Conclusions

We developed an efficient short synthesis of a class of atropo-stereogenic neutral monophosphanes **2** and **3** and neutral **4** or cationic **5** diphosphanes. Biminap **4** and bimionap **5** were shown to act as chelating ligands of palladium in neutral and cationic complexes **6** and **7**, respectively. In the cationic ligand, the proximal positive charge is conjugated to one phosphanyl group, and the coordination scheme is tentatively interpreted by resonance of the phosphane→metal dative bond ($^{+}N_2C$–P:→[Pd]) with a carbene→phosphenium dative bond (N_2C:→[$^{+}$P:→Pd]).

Through the study of a Sonogashira-type reaction, we showed that the presence of a proximal cationic charge was able to significantly modify the electronic availability of the neighbouring phosphorus atom, and consequently to tune finely the electronics of the corresponding catalyst. It is important to note that recently, electron-rich ligands have been extensively studied, particularly with the tremendous development of NHCs, but surprisingly, the chemistry of electron-poor ligands remained less explored.

Owing to the known restricted rotation about naphthyl–naphthyl and benzimidazolyl–benzimidazolyl bonds, both the neutral and cationic ligands should be atropo-chiral, and their resolution and applications in asymmetric catalysis can be henceforth envisioned. Efforts in this sense are currently in progress.

Experimental Section

General Remarks: Tetrahydrofuran and diethyl ether were dried and distilled from sodium/benzophenone, and pentane, dichloromethane and acetonitrile were dried and distilled from P_2O_5. All other reagents were used as commercially available. All reactions were carried out under an argon atmosphere by using Schlenk and vacuum-line techniques. Column chromatography was carried out on silica gel (60 Å, C.C 70–200 μm). The following analytical instruments were used. ^{1}H, ^{13}C and ^{31}P NMR: Bruker ARX 250, DPX 300, Avance 400 and 500. Mass spectrometry: Quadrupolar Nermag R10–10H. Elemental analyses: Perkin–Elmer 2400 CHN (flash combustion and detection by catharometry). NMR chemical shifts δ are in ppm, with positive values to high frequency relative to the tetramethylsilane reference; coupling constants J are in Hz. NMR assignment: (b) benzimidazole; (n) naphthalene. Gas chromatographic analyses were performed with a HP-4890 GC. Compound **1** was synthesized according to the reported procedure.[20]

2-(Diphenylphosphanyl)-*N*-(1′-naphthyl)-1*H*-benzimidazole (2): To a solution of **1** (0.42 g, 1.75 mmol) in thf (40 mL) cooled to –78 °C was added tmeda (0.26 mL, 1.75 mmol) and then BuLi (2.5 M in hexane, 0.70 mL, 1.75 mmol). The suspension was slowly warmed to –40 °C and stirred for 1 h. Then, after the addition of chlorodiphenylphosphane (0.32 mL, 1.75 mmol) at –78 °C, the solution was warmed to room temperature and stirred for 2 h. The reaction mixture was washed with a saturated aqueous solution of NH_4Cl (20 mL). After extraction with Et_2O (2 × 20 mL), the organic layer was then dried with $MgSO_4$ and concentrated under vacuum. Purification by chromatography on silica gel (pentane/ethyl acetate, 8:1) gave a solid residue (yield: 0.57 g, 76%). Recrystallization at room temperature from pentane/ethyl acetate afforded white crystals (m.p. 217–220 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.78 (d, $J_{H,H}$ = 6.0 Hz, 1 H, CH), 6.92 (d, $J_{H,H}$ = 9.0 Hz, 1 H, CH), 7.06–7.32 (m, 12 H, CH), 7.36–7.46 (m, 4 H, CH), 7.82–7.91 (m, 3 H, CH) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 110.7 (CH), 120.5 (CH), 122.6 (CH), 122.9 (d, $J_{C,P}$ = 1.0 Hz, CH), 123.7 (CH), 125.2 (CH), 126.8 (CH), 127.2 (CH), 127.3 (CH), 128.3 (CH), 128.3 (d, $J_{C,P}$ = 7.6 Hz, CH) 128.6 (d, $J_{C,P}$ = 7.8 Hz, CH), 129.2 (CH), 129.4 (CH), 130.0 (CH), 130.5 (d, $J_{C,P}$ = 1.0 Hz, 1 C), 132.5 (d, $J_{C,P}$ = 2.0 Hz, 1 C), 133.9 (d, $J_{C,P}$ = 5.5 Hz, 1 C), 134.2 (d, $J_{C,P}$ = 20.8 Hz, CH), 134.3 (C), 134.3 (d, $J_{C,P}$ = 21.1 Hz, CH), 134.6 (d, $J_{C,P}$ = 6.1 Hz, 1 C), 138.4 (d, $J_{C,P}$ = 1.3 Hz, 1 C), 144.2 (d, $J_{C,P}$ = 2.3 Hz, 1 C), 156.1 (d, $J_{C,P}$ = 11.2 Hz, NCN) ppm. ^{31}P NMR (500 MHz, $CDCl_3$): δ = –24.71 ppm. MS (DCI/NH_3): m/z = 429 [M + H]$^+$. $C_{29}H_{21}N_2P$ (428.47): calcd. C 81.29, H 4.94, N 6.54; found C 81.10, H 4.36, N 6.35.

***N*-(2′-Diphenylphosphanyl-1′-naphthyl)-1*H*-benzimidazole (3):** To a solution of **1** (1.0 g, 4.12 mmol) in Et_2O (110 mL) cooled to –78 °C was added tmeda (0.98 g, 8.68 mmol) and then BuLi (1.9 M in hexane, 4.60 mL, 8.68 mmol). The suspension was warmed to room temperature and stirred for 4 h. Then after addition of chlorodiphenylphosphane (0.68 mL, 3.68 mmol) at –78 °C, the solution was slowly warmed to room temperature and stirred for 2 h. After the addition of methanol (0.20 mL, 4.94 mmol), the organic layer was washed with a saturated aqueous solution of NH_4Cl (3 × 20 mL). The organic layer was then extracted with additional Et_2O (60 mL), dried with $MgSO_4$ and concentrated under vacuum. Purification by chromatography on silica gel (pentane/ethyl acetate, 8:1) gave **3** as a white solid (yield: 0.55 g, 34%; m.p. 147–151 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.82 (d, $J_{H,H}$ = 8.1 Hz, 1 H, CH), 7.08 (d, $J_{H,H}$ = 8.5 Hz, 1 H, CH), 7.14 (m, 1 H, CH), 7.20 (m, 2 H, CH), 7.23–7.29 (m, 3 H, CH), 7.30–7.41 (m, 8 H, CH), 7.56 (m, 1 H, CH), 7.76 (d, $J_{P,H}$ = 1.8 Hz, 1 H, NCHN), 7.93–7.98 (m, 3 H, CH) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 111.0 (CH), 120.3 (CH), 122.5 (CH), 122.9 (d, $J_{C,P}$ = 2.5 Hz, CH), 123.5 (CH), 127.7 (CH), 128.0 (CH), 128.2 (CH), 128.5 (d, $J_{C,P}$ = 6.3 Hz, 2 CH), 128.9 (d, $J_{C,P}$ = 7.5 Hz, 2 CH), 129.0 (CH), 129.3 (CH), 129.5 (CH), 129.7 (CH), 131.1 (d, $J_{C,P}$ = 2.5 Hz, 1 C), 133.8 (d, $J_{C,P}$ = 20.1 Hz, 2 CH), 133.9 (d, $J_{C,P}$ = 20.1 Hz, 2 CH), 134.4 (C), 135.6 (C), 135.9 (d, $J_{C,P}$ = 12.6 Hz, 1 C), 136.2 (d, $J_{C,P}$ = 12.6 Hz, 1 C), 136.5 (d, $J_{C,P}$ = 18.9 Hz, 1 C), 136.6 (d, $J_{C,P}$ = 25.2 Hz, 1 C), 143.0 (C), 144.3 (d, $J_{C,P}$ = 2.5 Hz, NCHN) ppm. ^{31}P NMR (500 MHz, $CDCl_3$): δ = –16.56 ppm. MS (DCI/NH_3): m/z = 429 [M + H]$^+$. HRMS (ESI+): calcd. for $C_{29}H_{22}N_2P$ 429.1521; found 429.1516.

2-(Diphenylphosphanyl)-*N*-(2′-diphenylphosphanyl-1′-naphthyl)-1*H*-benzimidazole (4): To a solution of **1** (1.0 g, 4.11 mmol) in Et_2O (110 mL) cooled to –78 °C was added tmeda (0.98 g, 8.64 mmol) and then BuLi (2.2 M in hexane, 3.95 mL, 8.64 mmol). The suspension was warmed to room temperature and stirred for 4 h. After the addition of chlorodiphenylphosphane (1.6 mL, 8.64 mmol) at –78 °C, the solution was slowly warmed to room temperature and stirred for 2 h. After the addition of MeOH (0.20 mL, 4.94 mmol), the organic layer was washed with a saturated aqueous solution of NH_4Cl (3 × 20 mL). The organic layer was then extracted with additional Et_2O (60 mL), dried with $MgSO_4$ and concentrated under vacuum. Purification by chromatography on silica gel (pentane/ethyl acetate, 8:1) gave **4** as a solid residue (yield: 0.97 g, 39%). Recrystallization at –20 °C from CH_2Cl_2/pentane gave white crystals (m.p. 238–241 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.47 (d, $J_{H,H}$ = 8.1 Hz, 1 H, CH), 6.71 (d, $J_{H,H}$ = 8.4 Hz, 1 H, CH), 6.93

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(td, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 0.9 Hz, 1 H, CH), 7.04 (td, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 1.2 Hz, 1 H, CH), 7.15–7.31 (m, 9 H, CH), 7.33–7.36 (m, 8 H, CH), 7.39–7.48 (m, 3 H, CH), 7.51 (dd, J_{PH} = 2.5 Hz, $J_{H,H}$ = 8.5 Hz, 1 H), 7.59–7.63 (m, 2 H), 7.91 (d, $J_{H,H}$ = 8.0 Hz, 1 H), 8.03 (t, $J_{H,H}$ = 8.0 Hz, 2 H, CH) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 110.9 (CH), 120.4 (CH), 122.3 (CH), 123.3 (d, $J_{C,P}$ = 2.0 Hz, CH), 123.4 (CH), 127.3 (CH), 127.4 (CH), 127.9 (CH), 128.3–128.6 (m, 10 CH), 129.0 (CH), 129.4 (CH), 129.9 (CH), 130.2 (d, $J_{C,P}$ = 2.0 Hz, CH), 131.3 (dd, $J_{C,P}$ = 4.0 Hz, $J_{C,P}$ = 2.0 Hz, 1 C), 133.2 (dd, $J_{C,P}$ = 18.1 Hz, $J_{C,P}$ = 2.0 Hz, 2 CH), 133.3 (dd, $J_{C,P}$ = 19.1 Hz, $J_{C,P}$ = 2.0 Hz, 2 CH), 134.2 (d, $J_{C,P}$ = 1.0 Hz, 1 C), 134.3 (C), 134.3 (d, $J_{C,P}$ = 22.1 Hz, 2 CH), 135.0 (d, $J_{C,P}$ = 22.1 Hz, 2 CH), 135.1 (d, $J_{C,P}$ = 5.0 Hz, 1 C), 136.2 (d, $J_{C,P}$ = 13.1 Hz, 1 C), 136.7 (d, $J_{C,P}$ = 12.1 Hz, 1 C), 137.0 (dd, $J_{C,P}$ = 15.6 Hz, $J_{C,P}$ = 1.5 Hz, 1 C), 137.9 (dd, $J_{C,P}$ = 26.2 Hz, $J_{C,P}$ = 2.0 Hz, 1 C), 138.3 (C), 144.3 (d, $J_{C,P}$ = 1.0 Hz, 1 C), 156.3 (d, $J_{C,P}$ = 9.1 Hz, 1 C) ppm. ^{31}P NMR (500 MHz, $CDCl_3$): δ = –18.10 (d, $^5J_{P,P}$ = 32.8 Hz, P_n), –26.69 (d, $^5J_{P,P}$ = 32.8 Hz, P_b) ppm. MS (DCI/NH_3): *m*/*z* = 613 $[M + H]^+$. $C_{41}H_{30}N_2P_2 \cdot 0.08CH_2Cl_2$ (619.44): calcd. C 79.67, H 4.87, N, 4.53; found C 79.65, H 4.63, N 4.52.

2-(Diphenylphosphanyl)-*N*-(2′-diphenylphosphanyl-1′-naphthyl)-*N*′-methyl-1*H*-benzimidazolium Trifluoromethanesulfonate (5): To a solution of **4** (0.49 g, 0.80 mmol) in CH_2Cl_2 (20 mL) cooled to –78 °C was added methyl trifluoromethanesulfonate (0.09 mL, 0.80 mmol). The solution was then warmed to room temperature and stirred for 12 h. After concentration under vacuum, the residue was washed with Et_2O (40 mL) to afford a white solid (yield: 0.59 g, 96%). Recrystallization at –20 °C from CH_3CN/Et_2O gave white crystals (m.p. 217–220 °C). ^{1}H NMR (500 MHz, CD_3CN): δ = 3.81 (s, 3 H, CH_3), 6.55 (d, $J_{H,H}$ = 8.5 Hz, 1 H, CH), 6.97 (dd, $J_{H,H}$ = 8.5 Hz, $J_{H,H}$ = 0.7 Hz, 1 H, CH), 7.09 (td, $J_{H,H}$ = $J_{H,P}$ = 8.4 Hz, $J_{H,H}$ = 1.3 Hz, 1 H, CH), 7.15–7.33 (m, 11 H, CH), 7.36–7.47 (m, 7 H, CH), 7.49–7.56 (m, 3 H, CH), 7.58–7.66 (m, 2 H, CH), 7.95 (d, $J_{H,H}$ = 8.6 Hz, 1 H, CH), 8.04 (d, $J_{H,H}$ = 8.3 Hz, 1 H, CH), 8.16 (d, $J_{H,H}$ = 8.5 Hz, 1 H, CH) ppm. ^{13}C NMR (500 MHz, CD_3CN): δ = 34.7 (CH_3), 113.3 (CH), 113.6 (CH), 121.2 (q, $J_{C,F}$ = 320.8 Hz, $CF_3SO_3^-$), 121.6 (d, $J_{C,P}$ = 2.1 Hz, CH), 126.6 (dd, $J_{C,P}$ = 1.7, $J_{C,P}$ = 7.5 Hz, 1 C), 127.6 (CH), 127.8 (CH), 128.0 (d, $J_{C,P}$ = 7.8 Hz, 1 C), 128.4 (CH), 128.6 (CH), 128.8 (CH), 128.9 (d, $J_{C,P}$ = 8.5 Hz, CH), 129.0 (d, $J_{C,P}$ = 6.5 Hz, CH), 129.4 (d, $J_{C,P}$ = 7.8 Hz, CH), 129.5 (CH), 129.6 (CH), 129.8 (d, $J_{C,P}$ = 7.2 Hz, CH), 129.9 (CH), 131.0 (CH), 131.3 (CH), 132.0 (CH), 133.0 (d, $J_{C,P}$ = 20.0 Hz, CH), 133.1 (d, $J_{C,P}$ = 20.0 Hz, CH), 133.8 (C), 133.9 (C), 134.2 (d, $J_{C,P}$ = 22.1 Hz, CH), 134.3 (d, $J_{C,P}$ = 2.4 Hz, 1 C), 134.3 (d, $J_{C,P}$ = 8.4 Hz, 1 C), 134.4 (C), 134.5 (C), 134.6 (d, $J_{C,P}$ = 23.1 Hz, CH), 136.3 (dd, $J_{C,P}$ = 17.1 Hz, $J_{C,P}$ = 1.8 Hz, 1 C), 153.6 (d, $J_{C,P}$ = 57.6 Hz, 1 C) ppm. ^{31}P NMR (500 MHz, CD_3CN): δ = –16.32 (d, $^5J_{P,P}$ = 35.5 Hz, P_n), –18.63 (d, $^5J_{P,P}$ = 35.5 Hz, P_b) ppm. MS (DCI/NH_3): *m*/*z*: 627 $[M]^+$. HRMS (ESI+): calcd. for $C_{42}H_{33}N_2P_2$ 627.2119; found 627.2128.

Palladium Complex 6: A mixture of complex $PdCl_2(CH_3CN)_2$ (0.15 g, 0.57 mmol) and **4** (0.35 g, 0.57 mmol) was dissolved in thf (20 mL) at –20 °C and stirred for 2 h. After concentration under vacuum, purification by chromatography on silica gel (acetone/CH_2Cl_2) gave a yellow solid (yield: 0.42 g, 94%). Recrystallization at –20 °C from CH_3CN afforded yellow crystals (m.p. 260–265 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.46 (d, $J_{H,H}$ = 8.2 Hz, 1 H, CH), 6.75–6.79 (m, 3 H, CH), 6.90–6.94 (m, 1 H, CH), 6.95–7.06 (m, 4 H, CH), 7.17 (ddd, $J_{H,H}$ = 1.1 Hz, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 8.3 Hz, 1 H, CH), 7.21 (dd, $J_{H,H}$ = 8.9 Hz, $J_{H,P(n)}$ = 9.8 Hz, 1 H, CH), 7.28 (ddd, $J_{H,H}$ = 1.4 Hz, $J_{H,H}$ = 7.0, $J_{H,H}$ = 8.4 Hz, 1 H, CH), 7.43–7.55 (m, 7 H, CH), 7.59 (br. d, $J_{H,H}$ = 8.3 Hz, 1 H, CH), 7.63 (br. d, $J_{H,H}$ = 8.5 Hz, 1 H, CH), 7.66–7.71 (m, 2 H, CH), 7.72 (d, $J_{H,H}$ = 8.3 Hz, 1 H, CH), 7.78–7.86 (m, 6 H, CH) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 121.0 (CH) 121.2 (d, $J_{C,P(b)}$ = 56.4 Hz, 1 C), 123.2 (d, $J_{C,P(n)}$ = 54.8 Hz, 1 C), 123.7 (CH), 124.2 (CH), 124.8 (CH), 126.8 (d, $J_{C,P(b)}$ = 69.9 Hz, 1 C), 127.5 (d, $J_{C,P(b)}$ = 12.9 Hz, 2 CH), 128.0 (CH), 128.1 (d, $J_{C,P(n)}$ = 11.7 Hz, 2CH), 128.2 (CH), 128.3 (d, $J_{C,P(b)}$ = 11.7 Hz, 2 CH), 128.4 (CH), 128.4 (d, $J_{C,P(n)}$ = 5.6 Hz, CH), 128.5 (d, $J_{C,P(n)}$ = 11.9 Hz, 2 CH), 128.7 (CH), 129.3 (d, $J_{C,P(n)}$ = 6.0 Hz, 1 C), 129.5 (dd, $J_{C,P(b)}$ = 4.6 Hz, $J_{C,P(n)}$ = 46.2 Hz, 1 C), 129.9 (d, $J_{C,P(n)}$ = 9.1 Hz, CH), 131.3 (d, $J_{C,P(b)}$ = 3.1 Hz, CH), 131.4 (d, $J_{C,P(n)}$ = 2.8 Hz, CH), 131.5 (d, $J_{C,P(b)}$ = 2.5 Hz, CH), 131.6 (d, $J_{C,P(n)}$ = 2.6 Hz, CH), 134.1 (d, $J_{C,P(n)}$ = 4.2 Hz, 1 C), 134.7 (CH), 134.8 (d, $J_{C,P(n)}$ = 10.6 Hz, 2 CH), 134.9 (d, $J_{C,P(b)}$ = 10.4 Hz, 2 CH), 135.2 (d, $J_{C,P(n)}$ = 1.8 Hz, 1 C), 135.5 (d, $J_{C,P(b)}$ = 13.1 Hz, 2 CH), 135.8 (C), 143.1 (d, $J_{C,P(b)}$ = 13.6 Hz, 1 C), 144.8 (dd, $J_{C,P(b)}$ = 78.8 Hz, $J_{C,P(n)}$ = 6.3 Hz, 1 C) ppm. ^{31}P NMR (500 MHz, $CDCl_3$): δ = +13.60 (P_b), +25.40 (P_n) ppm. MS (ESI+): *m*/*z* = 753 $[M – Cl]^+$. HRMS (ESI+): calcd. for $C_{41}H_{30}N_2P_2ClPd$ 753.0608; found 753.0610.

Palladium Complex 7: A mixture of complex $PdCl_2(CH_3CN)_2$ (0.31 g, 1.18 mmol) and **5** (0.92 g, 1.18 mmol) was dissolved in thf (50 mL) at –20 °C and stirred for 2 h. After concentration under vacuum, the residue was washed with Et_2O (50 mL) to afford an orange solid (yield: 1.1 g, 97%). Recrystallization at –20 °C from CH_2Cl_2/pentane gave yellow crystals (m.p. 206–210 °C). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 3.98 (s, 3 H, CH_3), 6.56 (d, $J_{H,H}$ = 8.5 Hz, 1 H, CH), 6.91 (m, 1 H, CH), 7.03 (*pseudo*-td, $J_{H,P(n)}$ = 2.9 Hz, $J_{H,H}$ = 7.8 Hz, 2 H, CH), 7.14 (m, 1 H, CH), 7.19 (dd, $J_{H,P(n)}$ = 9.9 Hz, $J_{H,H}$ = 8.9 Hz, 1 H, CH), 7.38 (ddd, $J_{H,H}$ = 8.3 Hz, $J_{H,H}$ = 7.0 Hz, $J_{H,H}$ = 1.3 Hz, 1 H, CH), 7.61–7.76 (m, 16 H, CH), 7.78–7.84 (m, 5 H, CH), 8.43 (ddd, $J_{H,P(b)}$ = 13.4 Hz, $J_{H,H}$ = 7.9 Hz, $J_{H,H}$ = 1.7 Hz, 2 H, CH) ppm. ^{13}C NMR (500 MHz, CD_2Cl_2): δ = 36.8 (CH_3), 113.7 (CH), 114.3 (CH), 120.7 (q, $J_{C,F}$ = 323.3 Hz, $CF_3SO_3^-$), 122.0 (d, $J_{C,P(b)}$ = 22.0 Hz, 1 C), 123.3 (d, $J_{C,P(n)}$ = 56.6 Hz, 1 C), 123.4 (d, $J_{C,P(b)}$ = 61.5 Hz, 1 C), 124.9 (CH), 126.3 (d, $J_{C,P(n)}$ = 64.1 Hz, 1 C), 128.0 (CH), 128.3 (d, $J_{C,P(n)}$ = 6.7 Hz, CH), 128.6 (CH), 128.7 (CH), 128.8 (d, $J_{C,P(b)}$ = 17.8 Hz, CH), 128.8 (d, $J_{C,P(b)}$ = 12.1 Hz, 1 C), 128.9 (d, $J_{C,P(n)}$ = 15.5 Hz, 2 CH), 129.4 (CH), 129.5 (d, $J_{C,P(b)}$ = 12.9 Hz, 2 CH), 130.3 (CH), 130.4 (CH), 131.9 (d, $J_{C,P(n)}$ = 3.8 Hz, 1 C), 132.1 (CH), 132.2 (CH), 132.3 (CH), 132.9 (C), 133.1 (d, $J_{C,P}$ = 2.6 Hz, CH), 133.5 (d, $J_{C,P}$ = 2.7 Hz, CH), 134.3 (d, $J_{C,P(n)}$ = 10.8 Hz, 2 CH), 134.5 (d, $J_{C,P(b)}$ = 14.6 Hz, 1 C), 135.1 (C), 135.2 (2 CH), 135.3 (C), 135.4 (CH), 146.1 (d, $J_{C,P(b)}$ = 29.4 Hz, 1 C) ppm. ^{31}P NMR (500 MHz, CD_2Cl_2): δ = +18.80 (P_b), +24.05 (P_n) ppm. HRMS (ESI+): calcd. for $C_{42}H_{33}N_2P_2Cl_2Pd$ 803.0531; found 803.0424.

General Procedure for Suzuki–Miyaura C–C Coupling: A mixture of boronic acid (0.18 g, 1.5 mmol), *p*-bromoanisole (0.12 mL, 1.0 mmol), Cs_2CO_3 (0.66 g, 2.0 mmol) and **6** or **7** (0.5 mol-%) in dry thf (3 mL) was stirred at 60 °C for 12 h. The reaction mixture was quenched with H_2O (3 mL) and extracted with Et_2O (3 × 5 mL). The organic layer was then dried with $MgSO_4$ and concentrated in vacuo. Purification by chromatography on silica gel (pentane/CH_2Cl_2, 5:1), gave a white solid (for **6**: 0.34 g, 73%; for **7**: 0.07 g, 37%).

General Procedure for Sonogashira Coupling: A mixture of **6** or **7** (0.5 mol-%) and CuI (7 mg, 0.036 mmol, 1 mol-%) were dissolved in dry thf (15 mL). Then, benzoyl chloride (0.42 mL, 3.64 mmol), phenylacetylene (0.24 mL, 3.64 mmol), dodecane (0.82 mL, 3.64 mmol) and Et_3N (0.51 mL, 3.64 mmol) were successively added. The catalysis was performed at room temperature for the desired time. Timing was immediately commenced when Et_3N was added. Reaction samples (0.5 mL), obtained at specified time inter-

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Table 2. Crystal structure determination of compounds **2**, **4**, **5**, **6** and **7**.

	2	**4**	**5**	**6**	**7**
Empirical formula	$C_{29}H_{21}N_2P$	$C_{41}H_{30}N_2P_2$	$C_{43}H_{33}F_3N_2O_3P_2S$	$C_{47}H_{39}Cl_2N_5P_2Pd$	$C_{46}H_{39}Cl_8F_3N_2O_3P_2PdS$
Formula mass	428.47	612.65	776.75	913.11	1208.86
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$
T [K]	180	150	180	180	160
a [Å]	8.9789(10)	10.2697(9)	13.0218(4)	11.0920(3)	14.3280(10)
b [Å]	14.7578(17)	16.9795(11)	14.5941(5)	12.6067(3)	21.585(2)
c [Å]	17.1572(18)	18.6210(19)	19.5513(6)	30.3522(8)	16.0520(10)
α [°]	90	90	90	90	90
β [°]	98.101(13)	104.535(11)	97.463(3)	96.552(2)	94.928(6)
γ [°]	90	90	90	90	90
V [Å^3]	2250.8(4)	3143.1(5)	3684.1(2)	4216.53(19)	4946.0(7)
$D_{calcd.}$ [g cm^{-3}]	1.26	1.30	1.40	1.44	1.62
Z	4	4	4	4	4
μ [mm^{-1}]	0.141	0.172	0.234	0.683	0.969
Refl. measured	22314	31507	34589	39285	46650
Refl. unique/R_{int}	4326	6184	9861	11201	11116
Refl. with $I > n\sigma(I)$	1413 (n = 2.1)	1848 (n = 2)	4877 (n = 1.2)	5732 (n = 3)	2313 (n = 2)
Nv	134	181	487	375	280
R	0.0515	0.0471	0.0454	0.0546	0.0601
R_w	0.0587	0.0552	0.0459	0.0614	0.0695
GooF	1.14	1.15	1.13	1.10	1.15
$\Delta\rho_{max}/\Delta\rho_{min}$ [e Å^{-3}]	0.40/0.27	0.39/0.25	0.42/0.48	1.81/1.06	1.44/0.78

vals, were purified after washing with a saturated aqueous solution of NH_4Cl (0.5 mL) and then filtered through silica gel. Conversion and yield were only determined by GC. It was checked that the presence of the internal standard does not affect the results (the same kinetic curves are obtained in the absence of dodecane).

Crystal Structure Determination of Compounds 2, 4, 5, 6 and 7: Intensity data were collected with an Xcalibur Oxford Diffraction diffractometer or with an IPDS Stoe diffractometer by using a graphite-monochromated Mo-K_α radiation source and equipped with an Oxford Cryosystems Cryostream Cooler Device. Structures were solved by direct methods by using SIR92 and refined by full-matrix least-squares procedures on F by using the PC version of the CRYSTALS program. Atomic scattering factors were taken from the International Tables for X-ray Crystallography. In case of weak diffracting crystals (**2**, **4** and **7**), we were not able to refine all atoms anisotropically (Table 2). Hydrogen atoms were refined by using a riding model. Absorption corrections were introduced by using the MULTISCAN program.

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