Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 689 (2004) 2988–2994
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Syntheses of a 2,6-bis-(methylphospholyl)pyridine ligand and its cationic Pd(II) and Ni(II) complexes – application in the palladium-catalyzed synthesis of arylboronic esters

Mohand Melaimi, Claire Thoumazet, Louis Ricard, Pascal Le Floch *

Laboratoire "hétéroéléments et Coordination", UMR CNRS 7653, Ecole Polytechnique, 91128 Palaiseau cedex, France

Received 3 May 2004; accepted 21 June 2004
Available online 31 July 2004

Abstract

2,6-Bis(2,5-diphenylphospholyl-1-methyl)pyridine (**2**) was prepared from the reaction of 2,5-diphenylphospholide anion with 2,6-bis(chloromethyl)pyridine. The X-ray crystal structure of **2** was recorded. Reaction of **2** with $[Pd(COD)Cl_2]$ in the presence of $AgBF_4$ yields the cationic complex $[Pd(2)Cl][BF_4]$ (**3**). The analogous Ni complex $[Ni(2)Br][BF_4]$ (**4**) was prepared in a similar way by reacting ligand **2** with $[NiBr_2(DME)]$ in the presence of $AgBF_4$ and its formulation was confirmed by an X-ray crystal structure study. Complex **3** efficiently catalyzes the coupling between pinacolborane and iodo and bromoarenes with good TON (up to 1×10^5 with iodo derivatives and 8.9×10^3 with bromo derivatives).

Keywords: Arylboronic esters; Catalysis; Complexes; Phosphorus heterocycles; Nickel; Palladium

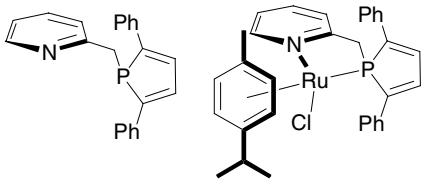
1. Introduction

In recent years, tridentate ligands of the type PXP (X = C, N) have found numerous applications in coordination chemistry and are now increasingly implicated in homogeneous catalysis [1]. It is now well established that the role of ancillary phosphine groups is crucial and a fine tuning of the electronic and stereochemical properties of transition metal complexes can be achieved by adjusting the substitution scheme around phosphorus. However, most systems reported so far incorporate acyclic tertiary phosphine groups and only little attention has been paid to the synthesis and reactivity of mixed PXP ligands featuring phosphorus heterocycles [2]. As part of a large program aimed at exploring the synthesis and potential applications in catalysis of heteroditopic chelates and multidentate ligands incorporating phospholes, we recently reported the synthesis of an easily available bidentate PN ligand featuring a pyridine and the 2,5-diphenylphosphole ring connected by a methylene group. The low sensitivity towards oxidation and the high thermal resistance of this phosphole are two important factors that make it very attractive for the elaboration of robust catalysts. Thus, we recently showed that the chlororuthenium-cymene complex of this 2-(2,5-diphenyl-1-methylphospholy)pyridine ligand exhibited a remarkable activity in the ruthenium-catalyzed transfer hydrogenation of ketones with TON up to 20×10^6 (Scheme 1) [3].

This preliminary result encouraged us in pursuing our investigation on such systems and we logically extended our studies to the synthesis of PNP derivatives featuring a central pyridine unit as ligand. Herein we report the synthesis of the 2,6-bis-(methylphospholyl)pyridine

* Corresponding author. Tel.: +33-1-69334570; fax: +33-1-69333990.
E-mail address: lefloch@poly.polytechnique.fr (P.L. Floch).

0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2004.06.035



Scheme 1.

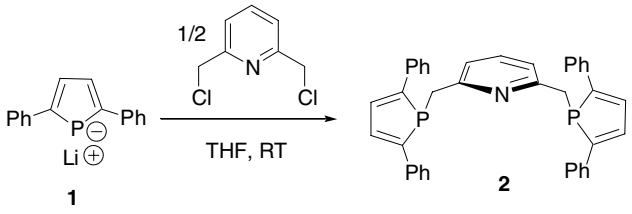
ligand and its PdCl and NiBr complexes as well as their catalytic activity in the Miyaura coupling reaction which allows the synthesis of arylboronic esters.

2. Results and discussion

2.1. Synthesis

The synthetic scheme followed for the synthesis of ligand **2** relies on the reactivity of the phospholide anion **1** towards halogenoalkyls. Reaction of two equivalents of phospholide anion **1**, prepared by cleavage of PP bond of the corresponding 1,1′-biphosphole [4], with 2,6-bis-(chloromethyl)pyridine in THF at room temperature cleanly afforded ligand **2** in good yield (86%) (Scheme 2). The formulation of **2** was unambiguously established on the basis of ^{1}H, ^{31}P and ^{13}C NMR data and elemental analyses. Additional evidence was also given by X-ray crystal structure analysis. An ORTEP view of one molecule of **2** is presented in Fig. 1. Selected bond distances and bond angles are listed in Table 1 and crystal data are summarized in Table 2. As can be seen, in the solid state **2** adopts a conformation that minimizes the steric congestion between the two pendant methylenephosphole arms, one phenyl ring of each phosphole subunit partially overlapping with the central pyridine ring (shorter interatomic distance of 3.2 Å). The two phospholyl units are roughly planar, the phosphorus atoms escaping from the plane defined by the four carbon-ring atoms only from 5°. Examination of metric data within the phosphole ring do not deserve further comment and compare with those recorded for the 1,2,5-triphenylphosphole derivative [5].

The synthesis of the cationic palladium complex **3** was achieved by reacting ligand **2** with $[Pd(COD)Cl_2]$ in the presence of $AgBF_4$ as chloride abstractor in dichloromethane at room temperature. Complex **3** was isolated with a very good yield (95%) as an air stable orange solid after purification (Scheme 3). Though the structure of the intermediary complex was not investigated in details, the singlet observed in the ^{31}P NMR spectrum of the crude reaction mixture suggests that a symmetrical complex is formed and that the ancillary phosphole ligands are coordinated ($\delta = 29.5$ ppm). However, on the simple basis of this ^{31}P NMR spectrum, we could not conclude whether this intermediate is a cationic tetracoordinated or a neutral pentacoordinated specie. Indeed, Nelson and Dahlhoff [6] have showed that neutral pentacoordinated complexes can also be formed when 2,6-bis(diphenylphosphinomethyl)-pyridine is used as ligand with Fe, Co and Ni(II) salts. All NMR data and elemental analyzes support the formulation proposed for **3**. Its ^{31}P NMR signal appears as a singlet thus confirming that the two phosphorus atoms are magnetically equivalent and that the structure is symmetric (*trans* arrangement of the phosphole ligands). On the other hand in the ^{1}H NMR spectrum, coordination of the pyridine moiety is evidenced by a significant downfield shift of the H aromatic signals (doublet at 7.68 and triplet at 8.07 ppm with a $^{3}J_{HH} = 7.8$ Hz). In the ^{13}C NMR spectrum, the CH_2 group and Cα and Cβ carbon atoms at phosphorus in the phosphole moieties appear as a AXX′ spin-system pattern, as expected. Unfortunately, despite many



1 2

Scheme 2.

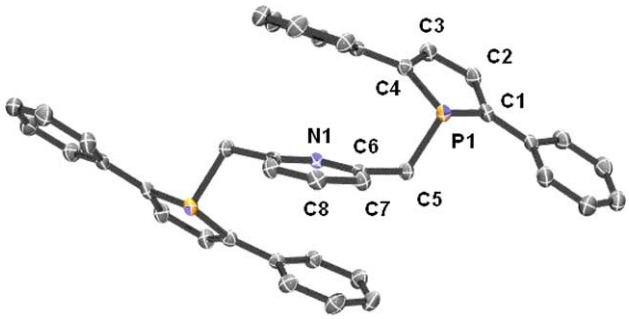


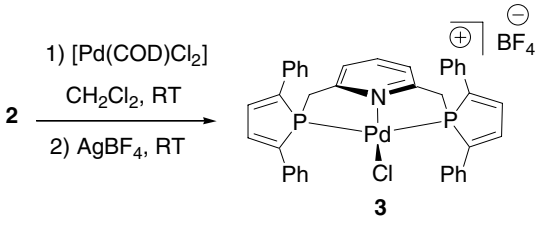
Fig. 1. ORTEP drawing of one molecule of ligand **2**. Ellipsoids are scaled to enclose 50% of the electron density. The numbering is arbitrary and different from that used in the ^{13}C NMR spectrum.

Table 1
Selected interatomic distances (Å) and angles (°) (with e.s.d.s in parentheses) in compound **2**

P1–C1	1.815(2)	P1–C5	1.867(2)
C1–C2	1.358(3)	C5–C6	1.509(2)
C2–C3	1.442(3)	C6–C7	1.392(3)
C3–C4	1.809(2)	C7–C8	1.386(2)
C4–P1	1.809(2)	C6–N1	1.344(2)
C4–P1–C1	91.1(1)	C1–C2–C3	115.2(2)
C4–P1–C5	101.9(1)	C3–C4–P1	109.5(2)
C1–P1–C5	104.0(1)	C6–C5–P1	106.9(1)
C1–C1–P1	108.9(2)	N1–C5–C6	116.2(2)
C4–C3–C2	114.8(2)	C7–C6–C5	121.0(2)

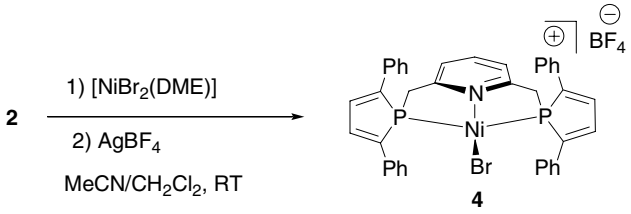
Table 2
Crystallographic data for compound **2**

Molecular formula	$C_{41}H_{33}Cl_6NP_2$
Molecular weight	814.32
Crystal habit	Colorless plate
Crystal dimensions (mm)	$0.20 \times 0.20 \times 0.06$
Crystal system	Monoclinic
Space group	*C*2/*c*
a (Å)	27.206(5)
b (Å)	6.223(5)
c (Å)	22.443(5)
β (°)	94.820(5)
V (Å^3)	3786(3)
Z	4
d (g cm^{-3})	1.429
F(000)	1672
μ (cm^{-1})	0.570
Absorption corrections	Multiple scans; 0.8945 min, 0.9666 max
Diffractometer	KappaCCD
X-ray source	Mo Kα
λ (Å)	0.71069
Monochromator	Graphite
T (K)	150.0(10)
Scan mode	ϕ and ω scans
Maximum θ	27.47
hkl ranges	−35 35; −7 8; −29 29
Reflections measured	7134
Unique data	4314
R_{int}	0.0202
Reflections used	3451
Criterion	>2σ(*I*)
Refinement type	F^2
Hydrogen atoms	Mixed
Parameters refined	231
Reflections/parameter	14
wR_2	0.1201
R_1	0.0436
Weights *a*, *b*	0.0490; 5.9725
Goodness-of-fit	1.045
Difference peak/hole (e Å^{-3})	0.762(0.061)/−0.706(0.061)



Scheme 3.

attempts using different solvents or crystallization techniques, no suitable single crystals of complex **3** could be obtained. The synthesis of the nickel complex **4** was achieved following a similar procedure. Reaction of ligand **2** with [$NiBr_2$(DME)] in a mixture of CH_3CN/dichloromethane (1:1) at room temperature followed by a treatment with $AgBF_4$ furnished **4** in a very good yield (95%) as a brownish solid after purification (Scheme 4). Note that, like in the synthesis of the palladium complex **3**, an intermediate which adopts a symmetrical structure (tetra or pentacoordinated) is transiently formed (broad signal at 30.2 ppm in ^{31}P NMR).



Scheme 4.

All NMR data of complex **4** are very similar to those of the palladium derivative **3** and the magnetic equivalence of the two coordinated pendant methylphosphole ancillary ligands is evidenced in ^{1}H NMR and ^{13}C NMR by the presence of second order spin-system patterns. Fortunately, single crystals of **4** could be grown by slow evaporation of a dichloromethane solution of the complex at room temperature. An ORTEP view of one molecule of **4** is presented in Fig. 2. The most significant bond lengths and bond angles are listed in Table 3 and crystal data are summarized in Table 4. As can be seen, the complex adopts a square planar geometry, the two phosphole ligands lying in a mutually trans configuration. Intramolecular bond distances and bond angles compare with those of dicationic Ni(II) complexes of the (diphenylphosphinomethyl)pyridine ligand [7]. Apart from the spatial arrangement of the four phenyl groups that seem to hinder the access to the metal centre, the structure of **4** deserves no special comments.

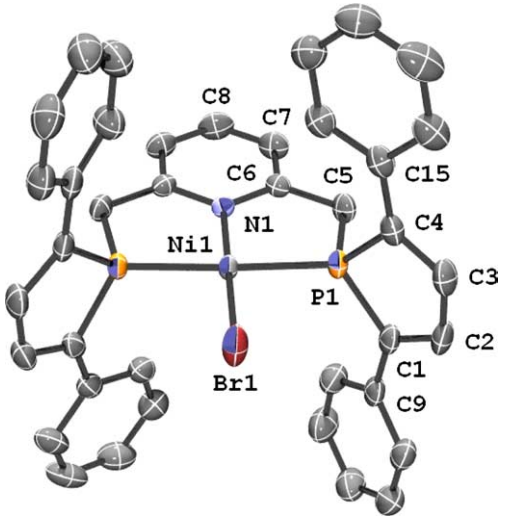


Fig. 2. ORTEP drawing of one molecule of complex **4**. Ellipsoids are scaled to enclose 50% of the electron density. The numbering is arbitrary and different from that used in the ^{13}C NMR spectrum.

Table 3
Selected interatomic distances (Å) and angles (°) (with e.s.d.s in parentheses) in complex 4

P1–C1	1.806(3)	C5–C6	1.487(4)
C1–C2	1.349(5)	C6–N1	1.368(3)
C2–C3	1.447(5)	C6–C7	1.379(4)
C3–C4	1.349(5)	C7–C8	1.369(4)
C4–C15	1.452(5)	P1–Ni1	2.1571(7)
C1–C9	1.466(5)	N1–Ni1	1.911(3)
P1–C5	1.829(3)	Ni1–Br1	2.2709(7)
C4–P1–C1	94.3(2)	P1–C1–C2	106.5(3)
C1–C2–C3	116.4(3)	C2–C3–C4	116.5(3)
C3–C4–P1	106.3(3)	C5–C6–N1	119.1(3)
C6–N1–Ni1	120.9(2)	N1–Ni1-Br1	180.0
P1–Ni1–P1′	176.35(5)	N1–Ni1–P1	88.18(2)

Table 4
Crystallographic data for compound **4**

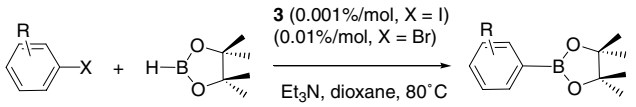
Molecular formula	$C_{39}H_{31}BBrF_4NNiP_2$
Molecular weight	801.02
Crystal habit	Red cube
Crystal dimensions (mm)	$0.20 \times 0.20 \times 0.16$
Crystal system	Rhombohedral
Space group	$R\bar{3}c$
a (Å)	29.2369(4)
c (Å)	21.3678(5)
V (Å^3)	15818.0(5)
Z	18
d (g cm^{-3})	1.514
$F(000)$	7308
μ (cm^{-1})	1.831
Absorption corrections	Multiple scans; 0.7109 min, 0.7583 max
Diffractometer	KappaCCD
X-ray source	Mo Kα
λ (Å)	0.71073
Monochromator	Graphite
T (K)	150.0(10)
Scan mode	ϕ and ω scans
Maximum θ	27.50
hkl ranges	−27 30; −37 26; −18 27
Reflections measured	18844
Unique data	4018
R_{int}	0.0387
Reflections used	3093
Criterion	$>2\sigma(I)$
Refinement type	F^2
Hydrogen atoms	Mixed
Parameters refined	224
Reflections/parameter	13
wR_2	0.1226
R_1	0.0402
Weights a, b	0.0562; 83.345
Goodness-of-fit	1.060
Difference peak/hole (e Å^{-3})	1.960(0.088)/−0.384(0.088)

2.2. Catalysis

The catalytic activities of complexes **3** and **4** were investigated in three cross-coupling processes using low loading of catalyst. In all our experiments, the nickel complex **4** showed no activity. Its palladium analogue **3** yielded better results. Thus, in the reaction of 4-bromoacetophenone with phenylboronic acid to yield biphenyl (Suzuki coupling) [8], no complete conversion was observed (51%) using 0.001% of catalyst after 2 h in toluene under reflux (TON = 51×10^3). A modest conversion yield (42%) was also obtained in the coupling of bromobenzene with styrene (Heck reaction) [9] after 15 h heating in dioxane at 80 °C (TON = 42×10^3) and triethylamine as base. Additional experiments using other solvents such as NMP, MeCN, yielded comparable results. Interestingly, much more significant performances were obtained in the Miyaura cross-coupling process that allows the preparation of arylboronic esters[10] from pinacolborane and halogenoarenes [11]. We found that iodoaromatics are easily converted at 80 °C in dioxanne using 0.001% of catalyst and triethylamine as base (TON about 100×10^3, see Table 5). The conversion of bromoarenes proved to be more difficult to achieve and 0.01% of catalyst was needed to achieve a partial conversion after 40 h of heating (see Scheme 5) (TON between 55 and 89×10^2, see Table 5). However, to the best of our knowledge, the TON obtained with complex **3** as catalyst are the highest reported so far in this Miyaura cross-coupling process.

Table 5
Cross-coupling reaction between iodo and bromoarenes with pinacolborane using complex **3** as catalyst (yields given by GC)

Ar–X (X = I, Br)	T (h)	% cat	Yield (%)	TON (%)
C_6H_5I	48	0.001	100	100×10^3
p-IC_6H_5Ome	48	0.001	100	100×10^3
o-IC_6H_5Ome	48	0.001	93	93×10^3
o-IC_6H_4Me	48	0.001	91	91×10^3
C_6H_5Br	40	0.01	86	86×10^2
p-BrC_6H_4COMe	40	0.01	55	55×10^2
p-BrC_6H_4Ome	40	0.01	89	89×10^2
p-BrC_6H_4Me	40	0.01	81	81×10^2



Scheme 5.

To summarize, we reported here the first example of a PNP pincer ligand featuring ancillary phosphole as ligands. Further studies aimed at exploring the catalytic activity of this new type of ligands and their functional derivatives are under progress in our laboratories and will be reported in due course.

3. Experimental

3.1. General procedure

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and

glove-box techniques and dry deoxygenated solvents. Dry THF, ether, dioxane and hexanes were obtained by distillation from Na/benzophenone and dry CH_2Cl_2 and $CDCl_3$ from P_2O_5. Dry CD_2Cl_2 was distilled and stored, like $CDCl_3$, on 4 Å Linde molecular sieves. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz for ^1H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P. Solvent peaks are used as internal reference relative to Me_4Si for ^1H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference and coupling constants are expressed in Hertz. The following abbreviations are used: b, broad; s, singlet; d, doublet; t, triplet; m, multiplet; p, pentuplet; sext, sextuplet; sept, septuplet; v, virtual. Mass spectra were obtained at 70 eV with a HP 5989B spectrometer coupled to a HP 5980 chromatograph by the direct inlet method. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France. [$NiBr_2$(DME)] [12], [Pd(COD)Cl_2] [13], 2,6-bis-(chloromethyl)pyridine [14] and triphenylphosphole[15] were prepared according to literature procedures. All other reagents and chemicals were obtained commercially and used as received.

3.2. Synthesis of ligand (2)

To a freshly prepared solution of phospholide anion **1** (6 mmol) in THF (50 mL) at room temperature was added 2,6-bis(chloromethyl)pyridine (528 mg, 3 mmol). After stirring for 20 min at this temperature, the complete formation of **2** was attested by ^{31}P NMR spectroscopy. After evaporation of the solvent, hexanes (100 mL) was added and the resulting mixture was filtered. After evaporation of hexanes, compound **2** was obtained as a yellow powder which was re-crystallized in MeOH. Yield: 1.482 g (86%). ^{31}P NMR ($CDCl_3$, 25 °C): δ −1.9; ^1H NMR ($CDCl_3$, 25 °C): δ 3.02 (s, 4 H, PCH_2), 5.93 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H *meta* of pyridine), 6.67 (t, $^3J_{HH}$ = 7.7 Hz, 1H, H *para* of pyridine), 6.98 (d, $^3J_{PH}$ = 9.5 Hz, 4H, Hβ of phosphole), 7.18–7.51 (m, 20H, CH of phenyl groups); ^{13}C NMR ($CDCl_3$, 25 °C): δ 33.4 (d, $^3J_{PC}$ = 20.3 Hz, CH_2), 118.7, (s, C *meta* of pyridine); 125.1–133.4 (phenyl groups and C *para* of pyridine), 137.7 (d, $^3J_{PC}$ = 13.6 Hz, Cα of phosphole), 152.4 (d, $^2J_{PC}$ = 4.5 Hz, Cβ of phosphole); 153.7 (s, C *ortho* of pyridine); MS, *m/z* (relative intensity): 575 (M^+, 90%). Anal. Calc. for $C_{39}H_{31}NP_2$: C, 81.38; H, 5.43. Found: C, 81.31; H, 5.37%.

3.3. Synthesis of complex (3)

Ligand **2** (161 mg, 0.2 mmol) was added to a solution of [Pd(COD)Cl_2] (57 mg, 0.2 mmol) in dichloromethane (3 mL) at room temperature. After 10 min of stirring at this temperature, $AgBF_4$ (39 mg, 0.2 mmol) was added and the reaction mixture was stirred at room temperature for one hour. Then, filtration on celite allowed the elimination of AgCl salt and the solvent was evaporated yielding a viscous orange oil which was washed with hexanes (3 × 20 mL) to remove 1,5-cyclooctadiene. Complex **3** was obtained as an orange solid. Yield: 152 mg (95%). ^{31}P NMR (CD_2Cl_2, 25 °C): δ = 33.2; ^1H NMR (CD_2Cl_2, 25 °C): δ 4.34 (vt, $A_2A'_2XX'$, $\sum J_{PH}$ = 10.8 Hz, 4 H, CH_2), 7.32–7.40 (m, 12 H, H *meta* and H *para* of phenyls), 7.47 (vt, $A_2A'_2XX'$, $\sum J_{PH}$ = 30.9 Hz, 4H, Hβ of phosphole), 7.68 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, H *meta* of pyridine), 7.77 (m, 8 H, H *ortho* of phenyl groups), 8.07 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, H *para* of pyridine); ^{13}C NMR (CD_2Cl_2, 25 °C): δ 39.1 (vt, AXX′, $\sum J_{PC}$ = 21.6 Hz, PCH_2), 125.4 (vt, AXX′, $\sum J_{PC}$ = 13.8 Hz, C *meta* pyridine), 127.4 (vt, AXX′, $\sum J_{PC}$ = 7.6 Hz, C *ortho* phenyl), 130.0 (s, C *meta* or *para* of phenyl), 130.1 (s, C *meta* or *para* of phenyl), 132.1 (vt, AXX′, $\sum J_{PC}$ = 14.8 Hz, C*ipso* of phenyl), 138.2 (vt, AXX′, $\sum J_{PC}$ = 20.53 Hz, Cβ of phosphole), 138.8 (vt, AXX′, $\sum J_{PC}$ = 50.3 Hz, Cα of phosphole), 142.6 (s, C *para* of pyridine), 162.8 (vt, AXX′, $\sum J_{PC}$ = 9.1 Hz, C *ortho* pyridine); Anal. Calc. for $C_{39}H_{31}BClF_4NP_2Pd$: C, 58.24; H, 3.88. Found: C, 58.11; H, 3.76%.

3.4. Synthesis of complex (4)

Ligand 2 (161 mg, 0.2 mmol) was added to a mixture of [$NiBr_2$(DME)] (61 mg, 0.2 mmol) in dichloromethane/acetonitrile (2 mL/2 mL) at room temperature. After stirring for 10 min, $AgBF_4$ (39 mg, 0.2 mmol) was added and the reaction mixture was stirred at room temperature for one hour. After filtration on celite, the solvents were evaporated yielding complex **4** as a brown powder. Crystallization of **4** was achieved in dichloromethane at room temperature. Yield: 152 mg (95%). ^{31}P NMR (CD_3CN, 25 °C): δ = 32.3. ^1H NMR (CD_3CN, 25 °C): δ 4.35 (vt, $A_2A'_2XX'$, $\sum J_{PH}$ = 8.4 Hz, 4 H, CH_2), 7.40–7.46 (m, 12 H, H *meta* and H *para* of phenyls), 7.59 (vt, $A_2A'_2XX'$, $\sum J_{PH}$ = 30.6 Hz, 4H, Hβ of phosphole), 7.62 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, H *meta* of pyridine), 7.96 (m, $^3J_{HH}$ = 7.5 Hz; 8 H, H *ortho* of phenyl groups), 8.10 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, H *para* of pyridine); ^{13}C NMR (CD_3CN, 25 °C): δ 35.2 (vt, AXX′, $\sum J_{PC}$ = 20.4 Hz, PCH_2), 122.7 (vt, AXX′, $\sum J_{PC}$ = 11.5 Hz, C *meta* pyridine), 124.62 (s, C *ortho* phenyl), 127.25 (s, C *meta* or *para* of phenyl), 127.47 (s, C *meta* or *para* of phenyl), 129.8 (vt, AXX′, $\sum J_{PC}$ = 13.5 Hz, C*ipso* of phenyl), 135.97 (vt, AXX′, $\sum J_{PC}$ = 16.6 Hz, Cβ of phosphole), 137.4 (vt, AXX′, $\sum J_{PC}$ = 50.7 Hz, Cα of phosphole), 139.7 (s, C *para* of pyridine), 161.8 (vt, AXX′, $\sum J_{PC}$ = 23.6 Hz, C *ortho* pyridine). Anal. Calc. for $C_{39}H_{31}BBrF_4NP_2Ni$: C, 58.48; H, 3.90. Found: C, 58.51; H, 3.81%.

3.5. General procedure for the coupling of bromoacetophenone with phenylboronic acid and bromobenzene with styrene

4-bromoacetophenone (10 mmol) and phenylboronic acid (15 mmol) were added to a solution of catalyst **3** (0.001%) with potassium carbonate (20 mmol) in toluene (20 mL). Then the mixture was heated at 110 °C for 2 h and the progress of the reaction was monitored by GC.

Styrene (2.4 mmol) and bromobenzene (1.6 mmol) were added to a solution of catalyst **3** (0.001%) in dioxane (4 mL). Triethylamine (3.2 mmol) was then added and the mixture was allowed to heat at 110 °C for 15 h. The progress of the reaction was monitored by GC.

3.6. General procedure for the coupling of pinacolborane with iodo and bromoaromatics and characterizations of arylboronic esters

Pinacolborane (2.4 mmol), the halogenoaromatic (iodo or bromo derivative) (1.6 mmol) and triethylamine (4.8 mmol) were successively added to a solution of catalyst **3** (0.001% for iodo- and 0.01% for bromo derivatives) in distilled dioxane (10 mL). The reaction mixture was heated at 80 °C and the progress of the reaction was monitored by GC. At the end of the reaction, the solvent was evaporated and diethylether (10 mL) was added. After filtration and washing of the ammonium salts with ether (2×10 mL), the solvent was evaporated. Then, the oily residue obtained was purified by column chromatography using silicagel (important: the silicagel must be previously treated with a mixture of hexanes Et_3N (95/5) to avoid any acidic promoted decomposition of the boronic esters). The boronic ester was eluted with hexanes as solvent. Formulations of boronic esters were confirmed by comparison of ^1H and ^{13}C NMR data with literature values.

4,4,5,5-Tetramethyl-2-phenyl-[1,3,2]dioxaborolane (from iodobenzene): Yield (after chromatography): 313 mg (96%). For characterizations, see T. Ishiyama, M. Murata, N. Miyaura, J. Org. Chem. 60 (1995) 7508.

2-(4-Methoxy-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (from p-methoxy-iodobenzene): Yield (after chromatography): 359 mg (96%). For characterizations, see [11j].

2-(2-Methoxy-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (from o-methoxy-iodobenzene): Yield (after chromatography): 318 mg (85%). For characterizations, see [11d].

4,4,5,5-Tetramethyl-2-p-tolyl-[1,3,2]dioxaborolane (from p-tolyl-iodobenzene): Yield (after chromatography): 315 mg (90%). For characterizations, see [11d].

1-[4-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolane-2-yl)-phenyl]-ethanone (from p-bromo-acetophenone): Yield (after chromatography): 335 mg (85%). For characterizations, see [11k].

4,4,5,5-Tetramethyl-2-o-tolyl-[1,3,2]dioxaborolane (from o-bromotoluene): Yield (after chromatography): 273 mg (78%). For characterizations, see [11k].

3.7. X-ray crystal structures of compounds 2 and 4

Single crystals of compound **2** were obtained by slow evaporation of a chloroform solution of the compound at room temperature. Single crystals of **4** were grown by slow evaporation of a dichloromethane solution of the complex at room temperature. Data were collected on a Nonius Kappa CCD diffractometer using a Mo Kα ($\lambda = 0.71073$ Å) X-ray source and a graphite monochromator. Experimental details are described in Tables 1 and 3. The crystal structure was solved using SIR97 [16] and SHELXL-97 [17]. ORTEP drawings were made using ORTEP III for Windows [18].

4. Supplementary material

Crystallographic (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications Nos. CCDC 235565 for compound **2** and CCDC 235565 for compound **4**. Copies of the data can be obtained free of charge, on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

The authors thank the CNRS (Centre National de la Recherche Scientifique) and the Ecole Polytechnique for the financial support of this work.

References

[1] (a) See, for example: M.H.P. Rietveld, D.M. Grove, G. van Koten, New J. Chem. 21 (1997) 751;
(b) C.M. Jensen, Chem. Commun. (1999) 2443;
(c) B. Rybtchinski, D. Milstein, Angew. Chem. Int. Ed. Engl. 38 (1999) 871;
(d) A. Vigalok, D. Milstein, Acc. Chem. Res. 34 (2001) 798;
(e) M. Albrecht, G. Van Koten, Angew. Chem. Int. Ed. Engl. 40 (2001) 3750;
(f) M.E. Van der Boom, D. Milstein, Chem. Rev. 103 (2003) 1759;
(g) J.T. Singleton, Tetrahedron 59 (2003) 1837;
(h) E. Drent, P.H.M. Budzelaar, Chem. Rev. 96 (1996) 663;
(i) Q. Jiang, D. Van Plew, S. Murtuza, X. Zhang, Tetrahedron Lett. 37 (1996) 797;
(j) D. Hermann, M. Gandelman, H. Rozenberg, L.J.W. Shimon, D. Milstein, Organometallics 21 (2002) 812;
(k) K.K. Hii, M. Thornton-Pett, A. Jutand, R.P. Tooze, Organometallics 18 (1999) 1887;

(l) R.A. Gossage, L.A. Van de Kuil, G. Van Koten, Acc. Chem. Res. 31 (1998) 423.
[2] R. Sablong, C. Newton, P. Dierkes, J.A. Osborn, Tetrahedron Lett. 37 (1996) 4933.
[3] C. Thoumazet, M. Melaimi, L. Ricard, F. Mathey, P. Le Floch, Organometallics 22 (2003) 1580.
[4] (a) C. Charrier, H. Bonnard, F. Mathey, J. Org. Chem. 47 (1982) 2376;
(b) F. Mathey, F. Mercier, F. Nief, J. Fischer, A. Mitschler, J. Am. Chem. Soc. 104 (1982) 2077.
[5] (a) P. Coggon, J.F. Engel, A.T. McPhail, L.D. Quin, J. Am. Chem. Soc. 92 (1970) 5779;
(b) L.D. Quin, in: F. Mathey (Ed.), Phosphorus–carbon Heterocyclic Chemistry: The Rise of a New Domain, Pergamon, Amsterdam, 2001, p. 219.
[6] W.V. Dahlhoff, S.M. Nelson, J. Chem. Soc. A (1971) 2184.
[7] (a) J.T. Mague, S.W. Hawbaker, J. Chem. Cryst. 27 (1997) 603;
(b) W. Haase, Z. Anorg. Allg. Chem. 404 (1974) 273.
[8] (a) See, for example: A. Suzuki, in: F. Diedrich, P.J. Stang (Eds.), Metal-catalyzed Cross-coupling Reactions, Wiley-VCH, Weinheim, Germany, 1998 (Chapter 2);
(b) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457;
(c) J.P. Wolfe, S.L. Buchwald, Angew. Chem. Int. Ed. Engl. 38 (1999) 2413;
(d) A. Zapf, M. Beller, Chem. Eur. J. 6 (2000) 1830;
(e) A.F. Littke, C. Dai, G.C. Fu, J. Am. Chem. Soc. 122 (2000) 4020;
(f) X. Sava, L. Ricard, F. Mathey, P. Le Floch, Organometallics 19 (2000) 4899.
[9] (a) See, for example: I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009;
(b) N.J. Whitcombe, K.K. Hii, S.E. Gibson, Tetrahedron 57 (2001) 7449;
(c) A.F. Littke, G.C. Fu, J. Am. Chem. Soc. 123 (2001) 6989;
(d) A.F. Littke, G.C. Fu, Angew. Chem. Int. Ed. Engl. 41 (2002) 4176;
(e) A. De Meijere, F.E. Meyer, Angew. Chem. Int. Ed. Engl. 33 (1994) 2379;
(f) D. Morales-Morales, R. Redon, C. Yung, C.M. Jensen, Chem. Commun. (2000) 1619.
[10] (a) For the use of arylboronic esters in biology and applications in electron transfer sensors, see respectively: A.H. Solowy, W.J. Tjarks, B.A. Barnum, F.-G. Rong, R.F. Barth, I.M. Wyzlic, J.G. Wilson, Chem. Rev. 98 (1998) 1515;
(b) T.D. James, P. Linnane, S. Shinkai, J. Chem. Soc. Chem. Commun. (1996) 281.
[11] (a) See, for example: M. Doux, N. Mezailles, M. Melaimi, L. Ricard, P. Le Floch, Chem. Commun. (2002) 1566;
(b) M. Melaimi, F. Mathey, P. Le Floch, J. Organomet. Chem. 640 (2001) 197;
(c) T.A. Ahiko, T. Ishiyama, N. Miyaura, Chem. Lett. (1997) 811;
(d) M. Murata, T. Oyama, S. Watanabe, Y. Masuda, J. Org. Chem. 65 (2000) 164;
(e) T. Ishiyama, K. Ishida, N. Miyaura, Tetrahedron 57 (2001) 9813;
(f) O. Baudoin, D. Guénard, F. Guéritte, J. Org. Chem. 65 (2000) 9268;
(g) A. Fürstner, G. Seidel, Org. Lett. 4 (2002) 541;
(h) T. Ishiyama, J. Takagi, A. Kamon, N. Miyaura, J. Organomet. Chem. 687 (2003) 284;
(i) A.S. Abreu, N.O. Silva, P.M.T. Ferreira, M. Queiroz, Tetrahedron Lett. 44 (2003) 6007;
(j) T. Ishiyama, Y. Itoh, T. Kitano, N. Miyaura, Tetrahedron Lett. 38 (1997) 3447;
(k) M. Murata, S. Watanabe, Y. Masuda, J. Org. Chem. 62 (1997) 6458.
[12] R.B. King, Organometallic Syntheses, Academic, New York, 1965 p. 71.
[13] D. Drew, J.R. Doyle, in: R.J. Angelici (Ed.), Inorganic Syntheses, 1990, p. 348.
[14] W.B. Austin, N. Billow, W.J. Kellegan, K.S.Y. Lan, J. Chem. Soc. Chem. Commun. (1958) 3594.
[15] B. Lukas, R.M.G. Roberts, J. Silver, A.S. Wells, J. Organomet. Chem. 256 (1983) 103.
[16] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, SIR97, an integrated package of computer programs for the solution and refinement of crystal structures using single crystal data.
[17] G.M. Sheldrick, SHELXL-97, Universität Göttingen, Göttingen, Germany, 1997.
[18] L.J. Farrugia: ORTEP-3, Department of Chemistry, University of Glasgow.