Tetrahedron 67 (2011) 421–428

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

New bicyclic phosphorous ligands: synthesis, structure and catalytic applications in ionic liquids

Martha V. Escárcega-Bobadilla [a,b], Emmanuelle Teuma [a], Anna M. Masdeu-Bultó [b,*], Montserrat Gómez [a,*]

[a] Laboratoire Hétérochimie Fondamentale et Appliquée, UMR CNRS 5069, Université Paul Sabatier, 118 route de Narbonne, 31120 Toulouse cedex 9, France
[b] Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Marcel.lí Domingo s/n, 43007 Tarragona, Spain

ARTICLE INFO

Article history:
Received 7 September 2010
Received in revised form 2 November 2010
Accepted 4 November 2010
Available online 13 November 2010

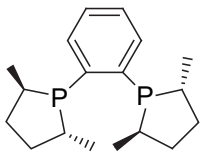
Keywords:
Bicyclophosphanes
Palladium
Ionic liquids
Suzuki C–C cross-coupling
Allylic alkylation

ABSTRACT

New azadioxaphosphabicyclo[3.3.0]octane ligands showing a *trans* arrangement with regard to the two five-membered heterocycles, were obtained as a mixture of three conformers, in agreement with molecular modelling studies. The stability of oxaphosphane ligands was studied under basic catalytic conditions, monitored by NMR spectroscopy. Palladium catalytic systems containing these ligands were active in Suzuki C–C cross-coupling reactions between phenylboronic acid and aryl halides (bromide and chloride derivatives) bearing electron-donor or electron-withdrawing substituents, in both organic and ionic liquid solvents. The catalytic systems showed a high stability even under the most severe reaction conditions used in this work. The ionic liquid catalytic phase could be recycled up to ten times without significant activity loss.

1. Introduction

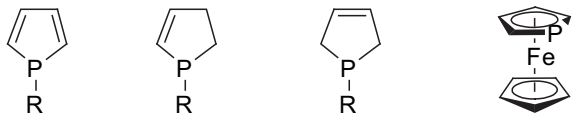
In the field of enantioselective catalysis, a large variety of chiral phosphorous-based ligands has been developed since the pioneering works of Knowles,[1] Horner[2] and Kagan.[3] Looking for high asymmetric inductions, rigid and well-defined coordination environments around the metallic centres besides electronic effects, appeared beneficial to achieve high enantiomeric excesses.[4] Therefore, phosphorous atom placed on a heterocycle can play a crucial role in the asymmetric induction.[5] The noteworthy contribution of Burk and co-workers developing the efficient phospholane DuPhos (Chart 1), which gave excellent enantioselectivities especially in asymmetric hydrogenation,[6] stimulated the catalytic applications of five-membered phosphacycle-based chiral ligands.



DuPhos

Chart 1.

In addition to saturated heterocyclic phospholanes, other five-membered *P*-cyclic ligands, such as phospholes,[7] 2- and 3- phospholenes[8] and phosphaferrocenes[9] (Fig. 1) have been also applied in metal-catalyzed organic processes, including bicyclic backbones, such as phosphanorbornadiene and phosphanorbornene structures described by Mathey and co-workers.[10]



phospholes 2-phospholenes 3-phospholenes phosphaferrocenes

Fig. 1. Skeletons of phosphorous-containing unsaturated five-membered heterocycles.

However, *P*-donor ligands based on fused saturated five-membered bicycle structures have been less commonly applied in catalysis (Fig. 2). The first work was reported by Vedejs and Daugulis preparing P,C-sterogenic phosphabicyclo[3.3.0]octanes used in enantioselective acylations (**A** in Fig. 2).[11] Some years later, Pietrusiewicz and co-workers developed related phospholane and also phospholene (**B** in Fig. 2) ligands to be employed in Pd-catalyzed C–C bond formation reactions.[12] RajanBabu and Yan described the applications in Pd-catalyzed asymmetric allylic alkylations of mono- and bis-phospholanes synthesized from D-mannitol (**C** in Fig. 2).[13] In addition, the work of Buono and co-workers described

* Corresponding authors. Tel.: +34 977558779; fax: +34 977559563 (A.M.M.-B); tel.: +33 561557738; fax: +33 561558204; (M.G); e-mail addresses: annamaria.masdeu@urv.cat (A.M. Masdeu-Bultó), gomez@chimie.ups-tlse.fr (M. Gómez).

0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.11.023

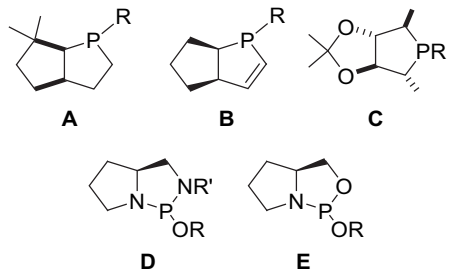
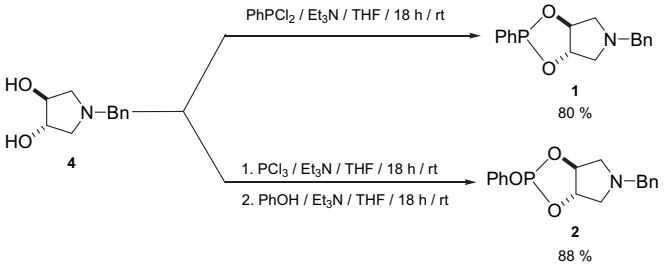


Fig. 2. *P*-heterocyclic ligands placed on fused saturated five-membered bicycle structures.



Scheme 1. Synthesis of oxyphosphanes **1** and **2**.

a diamidophosphite derived from 1,3-diaza-2-phosphabicyclo [3.3.0]octane and its further catalytic uses (Cu-catalyzed enantioselective conjugate addition of diethylzinc to enones and Pd-catalyzed allylic substitutions) (**D** in Fig. 2).[14] Other groups have employed this kind of bicyclic diamidophosphites in asymmetric catalytic processes.[15] Finally, chiral bicyclic phosphoramidites (**E** in Fig. 2) gave high enantiomeric excesses in Rh-catalyzed olefin hydrogenation reactions.[16]

In this context, azadioxaphosphabicyclo[3.3.0]octane compounds (**1** and **2** in Fig. 3) represent a new class of ligands containing two fused five-membered rings derived from tartaric acid. Few reports are described in the literature concerning the synthesis of *trans* fused five-membered heterocycles[17,13] and for the best of our knowledge, only one crystal structure has been described.[18]

Herein, we report the synthesis of phosphonite **1** and phosphite **2** derived from natural tartaric acid and their applications in Pd-catalyzed C–C bond formation processes in organic and ionic liquid solvents. Ionic liquids present different advantages in front of conventional solvents, such as the catalyst recovery for futher recycling, especially interesting in asymmetric catalysis.[19] Bis-(phosphinite) **3**[20] was also studied in order to compare the effect of the rigidity in bicyclic ligands. The robustness of these ligands in [BMI][PF_6] (BMI=1-butyl-3-methyl imidazolium) under catalytic conditions has been proved, in contrast to that observed in toluene. In order to evidence the coordination ability of these ligands, two complexes, **Pd1** and **Pd2**, have been synthesized and fully characterized. A conformational study of the new azadioxaphosphane bicyclo[3.3.0]octane ligands **1** and **2** has been carried out.

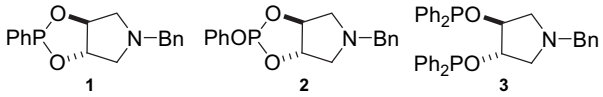


Fig. 3. Azadioxaphosphabicylo[3.3.0]octane compounds **1** and **2**, and the diphosphinite **3**.

2. Results and discussion

2.1. Synthesis and characterization of azadioxaphosphabicyclo[3.3.0]octane compounds

Ligand **1** has been prepared following the methodology reported for related phosphonite compounds,[21] starting from the optically pure (*S*,*S*)-**4** diol[22] by reaction with phenyl dichlorophosphine, giving a white solid in a good yield (80%) after filtration through anhydrous basic alumina to remove the acidic by-products derived from the $PhPCl_2$ (Scheme 1).

$^{31}P\{^1H\}$ NMR spectrum of **1** exhibited two singlets pointing to a mixture of isomers (Fig. 4b). In fact, the ^1H NMR spectrum (Fig. 4a) showed three species with an invariable ratio (1/0.63/0.46) in the

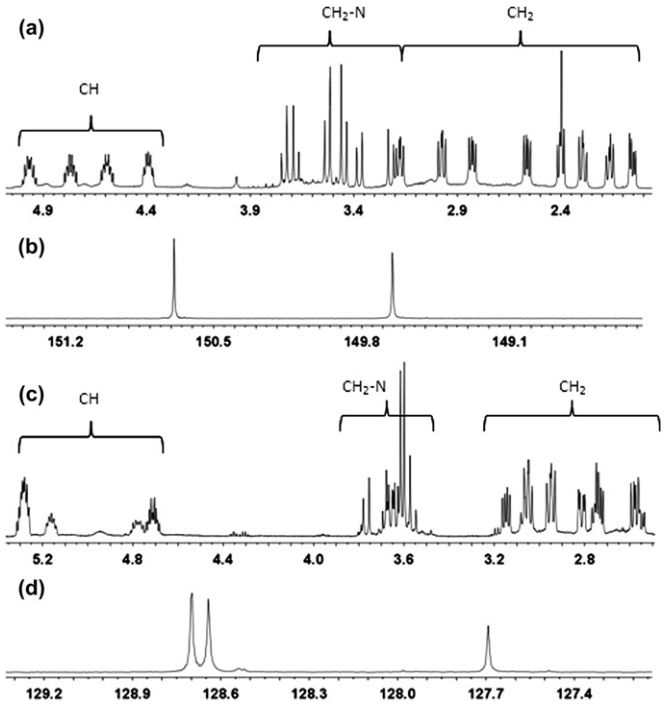


Fig. 4. ^1H (500.13 MHz) and $^{31}P\{^1H\}$ (202.5 MHz) NMR spectra for phosphonite 1 (a, b) and phosphite 2 (c, d) in CD_2Cl_2 and $CDCl_3$, respectively, at 298 K. For ^1H NMR spectra, only the methylene and methinic protons region is exhibited.

studied temperature range (298–193 K). The three isomers could be only distinguished by the signals of the methylene of the benzyl group. The 2D-HSQC experiment confirmed the presence of these three isomers (Fig. S1 in Supplementary data). In order to corroborate this structural behaviour, the new related ligand **2** was prepared following the two-step synthetic methodology for phosphites described elsewhere (Scheme 1).[23] An analogous isomeric behaviour in solution was found by ^1H NMR (isomeric ratio 1/0.9/0.6), but in this case the $^{31}P\{^1H\}$ NMR spectrum showed three singlets (Fig. 4c and d). For both compounds, NOESY experiments at 323 K and 298 K did not reveal exchange signals.

With the aim to understand the nature of these isomers, a modelling study was carried out. Concerning the two five-membered fused rings, a *trans* arrangement is imposed due to the controlled stereochemistry of the two stereogenic carbon atoms. Because of the substituents on P (phenyl or phenoxide for **1** and **2**, respectively) and N (benzyl for both ligands) atoms, two conformations could be possible, *syn* and *anti*, if both groups point to the same or opposite direction, respectively (Fig. 5).

Taking into account that the three isomers are only differentiated by the methylene group of the benzyl substituent on the nitrogen, they might arise from the different relative spatial disposition of this group in the ligand structure (R′ in Fig. 5). This

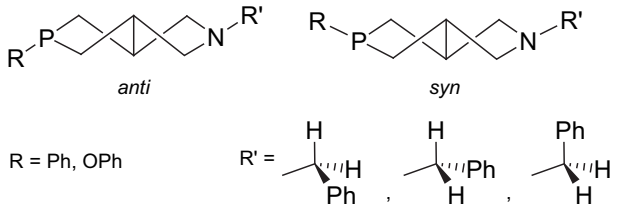


Fig. 5. *Syn* and *anti* conformations for *trans* fused five-membered heterocycles.

fact generates three possible isomers for each *syn* and *anti* conformation. The structures of the six conformations were modelled at semi-empirical PM3 level and their energies calculated by density functional theory (DFT B3LYP) using 6-31G* polarization basis set and pseudopotentials (Figs. S2 and S3 in Supplementary data). For each compound, two conformations exhibited high energy (more than 2.2 kcal/mol in relation to the most stable conformation) and were not considered. The other four conformations of close energy (between 0.01 and 0.36 kcal/mol in relation to the most stable conformation) led to a Boltzmann distribution at 298 K of *ca.* 1/0.75/0.6/0.5 and 1/1/0.9/0.6 for **1** and **2**, respectively (Fig. 6). Conformers *anti*-**1a** and *syn*-**1b** (Fig. 6) cannot probably be discriminated by NMR. In this case, the three conformers (*anti*-**1a** or *syn*-**1b**/*anti*-**1c**/*syn*-**1d**) would be in a relative ratio of 1/0.74/0.53. In the case of **2**, conformers with *anti* arrangement could not be distinguished by NMR, leading to a ratio 1/0.88/0.6 (*anti*-**2**/*syn*-**2c**/*syn*-**2d**). These data are in agreement with the experimental observations (see above). It is important to note that the rotation around the N–Bn bond leads to conformations of different energy, as demonstrated by the corresponding energy calculations (see Figs. S4 and S5 in Supplementary data for ligand **1** and **2**, respectively), in agreement with the interchange lack stated by NMR between the different conformers at rt (see above).

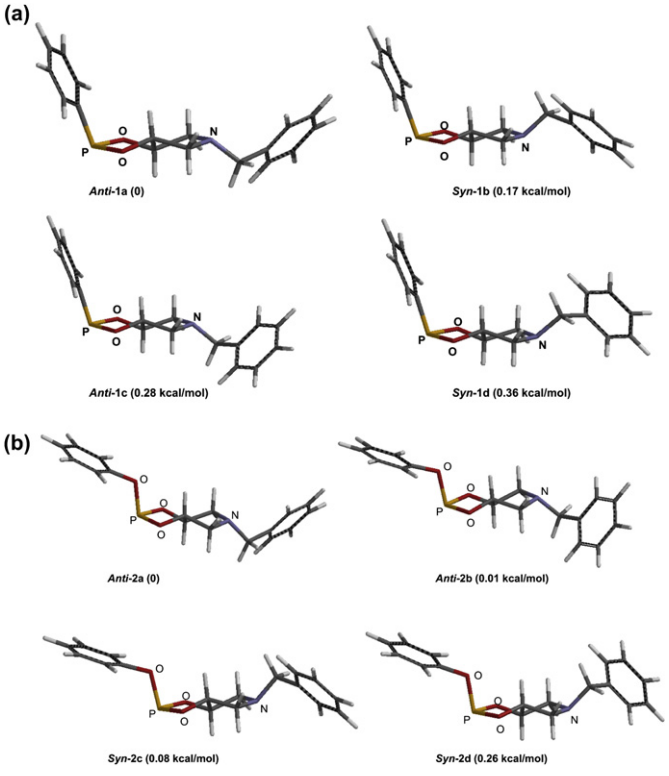


Fig. 6. Modelled structures (PM3(tm)) for the four more stable conformations for: (a) phosphonite 1 and (b) phosphite 2. In brackets, relative energies calculated by DFT.

In order to study the stability of ligands **1**–**3** under catalytic conditions, a $^{31}P\{^{1}H\}$ NMR monitoring study was carried out in toluene and ionic liquids under basic conditions. It is well known that P–O bonds in oxyphosphane ligands can be easily hydrolised to form the corresponding phosphonic acid derivatives.[24] Ligands **1**–**3** dissolved in [BMI][PF_6] in the presence of an aqueous solution of sodium carbonate at 60 °C (conditions used for the catalytic reactions, see below), proved to be stable, without showing any sign of degradation (Fig. 7; for full spectra in the range δ +200 to 0 ppm, see Fig. S6 in Supplementary data). On the contrary, the three ligands quickly decomposed using toluene or [EMI][HPO(O)OMe] (EMI=1-ethyl-3-methyl imidazolium) as solvent (Figs. S7 and S8 in Supplementary data).

2.2. Preparation of palladium complexes

With the aim to prove the coordination ability of mono- and bidentated oxaphosphane ligands, palladium complexes [$PdCl_2$(κ^1-*P*-**1**)$_2$] and [$PdCl_2$(κ^2-*P*,*P*-**3**)] were prepared from [$PdCl_2$(COD)] in toluene at 60 °C in the presence of the appropriate ligand **1** and **3**, respectively (Scheme 2).

In the case of **Pd1** containing two monodentate phosphonites **1**, one singlet at δ +130 ppm was observed in the $^{31}P\{^{1}H\}$ NMR spectrum in agreement with Pd related complexes.[25] ^{1}H and ^{13}C NMR spectra showed signals corresponding to only one isomer in the studied temperature range (298–173 K) (Fig. S9 in Supplementary data), pointing to the different ligand conformations are undistinguished upon coordination, in contrast to the free ligand, which exhibits three isomers in solution (see above).

The $^{31}P\{^{1}H\}$ NMR spectrum of **Pd3**, containing a seven-membered metallacycle, showed one singlet at δ +122 ppm, characteristic for Pd complexes coordinated to bidentated phosphinites.[26] The ^{1}H NMR spectrum of **Pd3** was similar to that observed for the free ligand, exhibiting slight changes in the chemical shifts (Fig. S10 in Supplementary data).

2.3. Catalytic results

2.3.1. Suzuki C–C cross-couplings. Reaction between 4-R-bromobenzene derivatives (R=CF_3, OCH_3) and phenylboronic acid under basic biphasic conditions, solvent–H_2O,[27] was carried out using palladium catalysts containing oxyphosphane ligands 1–3. Water was necessary to favour the solubility of sodium carbonate. Catalytic precursors were generated in situ from [$PdCl_2$(COD)] and the appropriate ligand. Toluene and ionic liquids ([BMI][PF_6] and [EMI][HPO(O)OMe]) were used as a reaction medium. The catalytic results are summarized in Table 1.

The three catalytic systems, Pd/**1**, Pd/**2** and Pd/**3**, were active in [BMI][PF_6] and in toluene for both substrates 1-bromo-4-trifluoromethylbenzene and 1-bromo-4-methoxybenzene. Higher conversions were obtained for 1-bromo-4-trifluoromethylbenzene (entries 1, 3, 5, 6 and 8 in Table 1) than for 1-bromo-4-methoxybenzene (entries 2, 4, 7 and 9 in Table 1) as expected by the induced activation when electron-withdrawing substituents are involved.[28] In both catalytic reactions, an excellent chemoselectivity was observed, only giving the expected cross-coupling product. Catalytic system Pd/**3** was more active than Pd/**1** in both toluene and [BMI][PF_6] (entries 1–4 vs 6–9). Catalytic system Pd/**2** gave similar conversion than Pd/**3** in [BMI][PF_6] (entry 5, Table 1).

In order to check the positive influence of the *P*-donor ligands, we evaluated the catalytic behaviour of the Pd system with diol **4**. This compound is one of the plausible by-products formed by hydrolysis of P–O bonds in oxaphosphane ligands. For the most active substrate, 1-bromo-4-trifluoromethylbenzene, in [BMI][PF_6], Pd/**4** system provided *ca.* 80% conversion (entry 10 in Table 1) lower than for Pd/**3** (entry 6 in Table 1) but close to that obtained using Pd/**1**

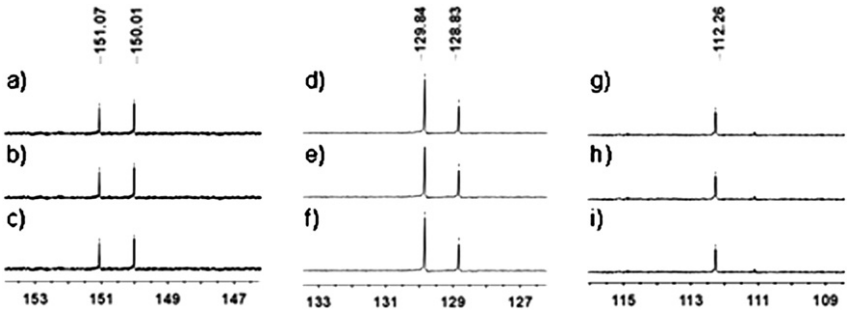
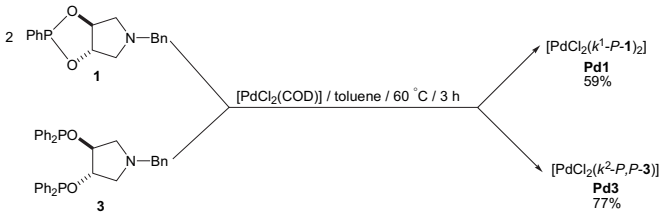
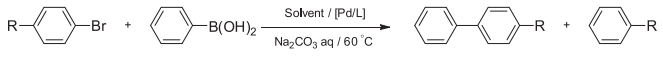


Fig. 7. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, 298 K, $CDCl_3$) spectra of ligands 1 (a, b, c), 2 (d, e, f) and 3 (g, h, i): in [BMI][PF_6] (a, d, g); in [BMI][PF_6] in the presence of Na_2CO_3(aq) at rt (b, e, h) and after heating at 60 °C for 1 h (c, f, i).



Scheme 2. Synthesis of complexes **Pd1** and **Pd3**.

Table 1
Suzuki C–C couplings between 4-R-bromobenzene derivatives (R=CF_3, OCH_3) and phenylboronic acid catalyzed by Pd/**L** systems (*L*=**1**–**3**)[a]



R= CF_3, OMe

Entry	Ligand	Solvent	R	*t* [h]	Conv. (%)
1	**1**	[BMI][PF_6]	CF_3	1	80[b]
2	**1**	[BMI][PF_6]	OMe	15	24[c]
3	**1**	Toluene	CF_3	1	66[b]
4	**1**	Toluene	OMe	15	20[c]
5	**2**	[BMI][PF_6]	CF_3	1	98[b]
6	**3**	[BMI][PF_6]	CF_3	1	91[b]
7	**3**	[BMI][PF_6]	OMe	15	32[c]
8	**3**	Toluene	CF_3	1	94[b]
9	**3**	Toluene	OMe	15	65[c]
10	**4**	[BMI][PF_6]	CF_3	1	79[b,d]
11	—	[BMI][PF_6]	CF_3	1	77[b,e]
12	**3**	[EMI][HPO(O)OMe]	CF_3	1	36[b]
13	**3**	[EMI][HPO(O)OMe]	CF_3	1	5[b,f]
14	**3**	[EMI][HPO(O)OMe]	CF_3	1	0[b,g]

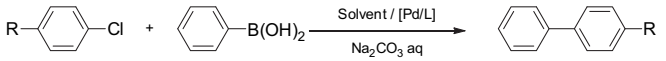
[a] Reaction conditions: Pd:L:arylbromide:phenylboronic acid:sodium carbonate=1:1.2:100:120:250 mmol in 1 cm^3 of [BMI][PF_6] or toluene or [EMI][HPO(O)OMe] and 2 cm^3 of water at 60 °C; all reactions by duplicate.
[b] Determined by ^{19}F NMR and GC–MS.
[c] Determined by ^{1}H NMR and GC–MS.
[d] Cross-coupling product:dehalogenated product=73:26 (in [BMI][PF_6]).
[e] Cross-coupling product:dehalogenated product=85:15.
[f] Without base.
[g] Without base and water.

catalyst (entry 1 in Table 1). However for Pd/**4**, *ca.* 23% of the product corresponded to the dehalogenated substrate, trifluoromethylbenzene. Furthermore, the catalytic mixture became black after time in contrast to yellow solutions obtained using *P*-donor ligands. TEM analysis of the post-catalytic ionic liquid suspension for Pd/**4** system, showed the presence of palladium nanoparticles (PdNP) (Fig. S11 in Supplementary data). Their formation was probably due to the absence of good donor ligands (such as **1**–**3**), which favour the formation of more active and selective catalytic molecular species. The surface reactivity of the PdNP generated in situ could be responsible of the dehalogenation reaction, favoured using heterogeneous catalysts.[29] Similar result was obtained in the absence of any ligand (entry 11 in Table 1). In toluene, only 12% substrate conversion was afforded in the absence of any ligand, mainly giving the corresponding homo-coupling product coming from the substrate (4-4′-CF_3-1,1′-biphenyl).

With the aim to avoid the addition of a base, we used [EMI][HPO(O)OMe] as solvent, which contains a basic anion, following the encouraging results previously obtained for Heck coupling reactions.[30] In this solvent, Pd/**3** catalytic system using 1-bromo-4-trifluoromethylbenzene as substrate was inactive even in the presence of water (entry 13 in Table 1) and poorly active under aqueous basic conditions (entries 12 and 14 in Table 1).

After these promising results where activation of 1-bromo-4-methoxybenzene was achieved in both toluene and [BMI][PF_6], we evaluated the catalytic behaviour of Pd/**L** systems using less reactive chloroaryl substrates (Table 2).[31]

Table 2
Suzuki C–C couplings between 4-R-chlorobenzene derivatives (R=CF_3, OCH_3, NO_2, NH_2) and phenylboronic acid catalyzed by Pd/**L** systems (*L*=**1**–**3**)[a]



R= CF_3, OMe, NO_2, NH_2

Entry	L	Solvent	R	*t* [h]	Conv. (%)
1	**1**	[BMI][PF_6]	CF_3	15	99[c]
2	**1**	[BMI][PF_6]	OMe	48[b]	91[d]
3	**1**	Toluene	CF_3	15	82[c]
4	**1**	Toluene	OMe	48[b]	85[d]
5	**2**	[BMI][PF_6]	CF_3	15	90[c]
6	**2**	[BMI][PF_6]	OMe	48[b]	26[d]
7	**3**	[BMI][PF_6]	CF_3	15	96[c]
8	**3**	[BMI][PF_6]	OMe	48[b]	31[d]
9	**3**	Toluene	CF_3	15	18[c]
10	**3**	Toluene	OMe	48[b]	55[d]
11	**1**	[BMI][PF_6]	NO_2	15	41[d]
12	**1**	[BMI][PF_6]	NH_2	48[b]	29[d]
13	**3**	[BMI][PF_6]	NO_2	15	35[d]
14	**3**	[BMI][PF_6]	NH_2	48[b]	26[d]

[a] Reaction conditions: Pd:L:arylchloride:phenylboronic acid:sodium carbonate=1: 1.2:100:120: 250 mmol in 1 cm^3 of [BMI][PF_6] or toluene and 2 cm^3 of water at 60 °C; all reactions by duplicate.
[b] *T*=100 °C.
[c] Determined by ^{19}F NMR and GC–MS.
[d] Determined by ^{1}H NMR and GC–MS.

As expected, in relation to the analogous bromo derivatives, the chloroaryl substrates required longer reaction times to achieve high conversions (more than 90% for 1-chloro-4-trifluoromethylbenzene after 15 h of reaction at 60 °C entries 1, 5 and 7 in Table 2). For 1-bromo-4-methoxybenzene, from moderate (31–55% conversion, entries 8 and 10 in Table 2) to excellent conversions (up to 91%, entries 2 and 4 in Table 2) at 100 °C and after

two days of reaction, were obtained. In general for both catalysts, Pd/**1** and Pd/**3**, higher activities were achieved in [BMI][PF_6] than in toluene, in particular for Pd/**1** (for Pd/**1**, see entries 1–2 vs 3–4; for Pd/**3**, see entries 7 vs 9 in Table 2). This behaviour could be due to the ligand degradation in toluene under basic conditions (see above), especially noteworthy at long times and high temperatures. Surprisingly for chloro-substrates, Pd/**1** catalytic system exhibited higher activity than Pd/**3** (entries 1–4 vs 7–10 in Table 2), in contrast to that observed for bromo-substrates (entries 1–8 in Table 1). Pd/**2** gave similar results than Pd/**3** in [BMI][PF_6] (entries 5 and 6, Table 2).

Similar catalytic behaviour was observed using Pd/**1** and Pd/**3** systems in [BMI][PF_6] for activated 1-chloro-4-nitrobenzene (entries 11 and 13, Table 2) and for deactivated 4-chloroaniline (entries 12 and 14, Table 2).

Taking into account the stability of Pd/**3** catalytic system under biphasic [BMI][PF_6]/water conditions, we evaluated the recyclability for the cross-coupling reaction between 1-bromo-4-trifluoromethylbenzene and phenylboronic acid. The ionic liquid catalytic phase could be reused up to ten times without loss of conversion (95–99%), and preserving the chemoselectivity towards the cross-coupling product (Fig. 8).

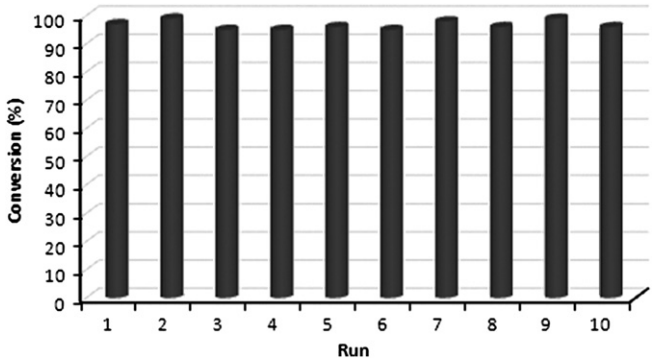
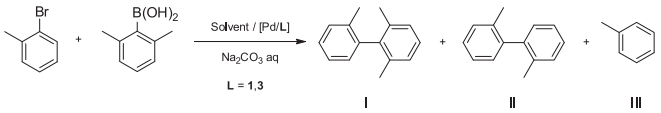


Fig. 8. Histogram representing 1-bromo-4-trifluoromethylbenzene conversion to 4-(trifluoromethyl)-1,1′-biphenyl after each run of recycling using Pd/**3** catalytic system.

2.3.2. Asymmetric Suzuki C–C cross-coupling. In an attempt of performing the asymmetric version of the reaction, several reactants (ortho and diortho substituted iodides and bromides as well as ortho and diortho substituted boronic acids) under different reaction conditions, were tested. Unfortunately, in all cases only the deboronated or dehalogenated products were mainly obtained. The most relevant results are collected in Table 3.

In the case of the catalytic system Pd/**1** in toluene, the desired cross-coupling compound was the main product, although the conversion was low (entry 2 in Table 3). In [BMI][PF_6], only the dehalogenated product was obtained (entry 1, Table 3). Pd/**3** catalytic system mainly gave the dehalogenated and homo-coupling product in [BMI][PF_6] and toluene, respectively (entries 3 and 4, Table 3). At lower temperatures, the catalytic systems were inactive.

Table 3
Asymmetric Suzuki C–C couplings between arylhalide and phenylboronic acid derivatives catalyzed by Pd/**L** systems (*L*=**1**, **3**)[a]

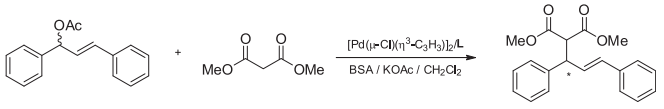


Entry	**L**	Solvent	Conv.[b](%)	Selectivity I:II:III[c](%)
1	**1**	[BMI][PF_6]	100	0:0:100
2	**1**	Toluene	28	82:8:18
3	**3**	[BMI][PF_6]	100	0:0:100
4	**3**	Toluene	100	3:97:0

[a] Reaction conditions: Pd:L:arylhalide:arylboronic acid:sodium carbonate=1:1.2:100:120:250 mmol in 1 cm^3 of [BMI][PF_6] or toluene and 2 cm^3 of water at 100 °C for 24 h; all reactions by duplicate.
[b] Conversion determined by GC–MS.
[c] Determined by GC–MS.

2.3.3. Asymmetric allylic alkylation. Palladium/**L** systems were tested in the benchmark allylic alkylation starting from the racemic substrate 3-acetoxy-1,3-diphenyl-1-propene and dimethylmalonate as nucleophile, under basic Trost conditions.[32] The catalytic results are summarized in Table 4. The catalytic precursor was generated in situ form [$PdCl(C_3H_5)]_2$ and the appropriate ligand (**1**–**3**). Pd/**1** was the most active catalytic system in organic solvent, giving full conversion towards the expected product after 1h of reaction (entry 1 vs 2 and 3 in Table 4). This system led to the best asymmetric induction, however only 26% of enantiomeric excess was achieved. Pd/**1** was also used in [BMI][PF_6]. The system was slower than in dichloromethane (entry 4 vs 1 in Table 4), giving also a lower enantioselectivity but towards the opposite enantiomer than that obtained in dichloromethane. The reversal of product configuration depending on the solvent nature (ionic liquid vs dichloromethane) has been also previously reported for copper catalyzed Diels–Alder reactions.[33] This effect can be due to the influence of the anion nature in the catalytic intermediates.

Table 4
Asymmetric allylic alkylation catalyzed by Pd/**L** systems (*L*=**1**–**3**)[a]



Entry	Ligand	Solvent	*t* (h)	Conv.[b](%)	ee[c]%
1	**1**	CH_2Cl_2	1	100	26 (*S*)
2	**2**	CH_2Cl_2	4	100	4 (*R*)
3	**3**	CH_2Cl_2	4	100	10 (*R*)
4	**1**	[BMI][PF_6]	24	74	11 (*R*)

[a] Reaction conditions: Pd:**1**,**2**=2.5, **3**=1.25; Pd:substrate=50 in 4 cm^3 of CH_2Cl_2 or 1 cm^3 [BMI][PF_6] at rt results obtained by duplicate experiments.
[b] Conversion determined by ^1H NMR.
[c] Enantiomeric excess determined by HPLC on a Chiralcel OJ-H column.

3. Conclusions

New azadioxaphosphane bicyclo[3.3.0]octane ligands **1** and **2** derived from natural tartaric acid were prepared and characterized. NMR studies revealed that at least three conformers are present in solution due to the relative spatial disposition of benzyl and phosphorus substituents in both *syn* and *anti* arrangements. Modelling studies are in good agreement with the isomeric ratios observed by NMR spectroscopy. Nevertheless upon palladium coordination to give [$PdCl_2(\kappa^1$-*P*-**1**$)_2$], the conformers are not thus far distinguished.

The catalytic systems Pd/**1**–**3** were highly active and selective in Suzuki C–C cross-couplings with substrates bearing both electron-donor and electron-withdrawing groups for 4-R-bromobenzene and 4-R-chlorobenzene derivatives. Using [BMI][PF_6] as solvent, the systems worked without formation of by-products allowing the activation of C–Cl bonds for substrates containing electron-donor substituents.

It is noteworthy that ligands **1**–**3** showed higher stability under catalytic basic biphasic conditions in [BMI][PF_6] than that observed in toluene and [EMI][HPO(O)OMe]. This behaviour allowed the recycling of the catalytic phase in [BMI][PF_6] up to ten cycles without loss of activity.

Unfortunately, asymmetric Suzuki reactions were not selective towards the desired cross-coupling product, only giving the expected product in a very low yield and selectivity (substrate conversion less than 30% using Pd/**1** catalytic system in toluene). The catalytic evaluation of these chiral ligands for the formation of new stereogenic centre in the Pd-catalyzed asymmetric allylic alkylation model reaction gave low enantioselectivities.

4. Experimental section

4.1. General data

Syntheses were performed using standard Schlenk techniques under nitrogen or argon atmosphere. Organic solvents were dried following the procedures described in literature.[34] *rac*-3-acethoxy-1,3-diphenyl-1-propene was synthesized following the methodology described in the literature.[35] $PhPCl_2$, PCl_3, Ph_2PCl, substrates, boronic acids, dimethylmalonate, potassium acetate, *N*,*O*-bis(trimethylsilyl)acetamide (BSA), $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ and $[PdCl_2(COD)]$ were purchased from Sigma–Aldrich, Acros and Strem chemicals and used without further purification. [BMI][PF_6] and [EMI][HPO(O)OMe] (99.5%) were purchased from Solvionic and treated under reduced pressure at 60 °C for 48 h prior to use. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AV–300 spectrometer (300.13 MHz for ^1H) or a Brucker AV–400 (400.16 MHz for ^1H) or a Brucker AV–500 (500.13 MHz for ^1H). Chemical shifts are expressed in parts per million upfield from $SiMe_4$. NOESY, ^1H and ^{13}C correlation spectra were obtained using standard procedures. TEM experiments were performed at the 'Service Commun de Microscopie Electronique de l'Université Paul Sabatier' on a Philips CM12 electron microscope operating at 120 kV with resolution of 4.5 Å. The images of particles dispersed in [BMI][PF_6] were obtained from a transmission electron microscope running at 120 kV. A drop of solution was deposited on a holey carbon grid and the excess of [BMI][PF_6] was removed in order to obtain a film as thin as possible. Images were recorded on the film of IL lying on the holes of the grid. IR spectra were recorded on an FTIR Nicolet Impact 400 spectrometer. Optical rotations were measured in a Perkin–Elmer 241MC polarimeter.

4.2. (3a*S*,6a*S*)-5-Benzyl-2-phenyltetrahydro-3a*H*-[1,3,2]dioxaphospholo[4,5-*c*]pyrrole, 1

A solution of 100 mg (0.5 mmol) of **4** and 0.72 cm^3 of Et_3N in 6.6 cm^3 of THF were added dropwise to a solution of 0.07 cm^3 of $PhPCl_2$ (0.5 mmol) in 1 cm^3 of toluene at rt. The reaction mixture was stirred overnight affording a white suspension. The suspension was filtered through anhydrous basic alumina under argon atmosphere and solvent was then evaporated, obtaining the monophosphonite as a white powder (120 mg, 80%). $[\alpha]_D^{25}$ +46.7 (*c* 0.97 in CH_2Cl_2) ν_{max} (IR, KBr, pellet)/cm^{-1} 1104 (P–O–C, st, s), 746 (P–O–C, st, w), 828 (P–C, st, w) HRMS (CI–CH_4) found *m*/*z*: 299.1081 $[M]^+$. $C_{17}H_{18}NO_2P$ requires 299.1075.

Isomer 'A' (48%): ^1H NMR (500.13 MHz, CD_2Cl_2, rt): δ=2.30 (m, 1H, CH_2CH), 2.40 (m, 1H, CH_2CH), 2.57 (m, 1H, CH_2CH), 2.98 (m, 1H CH_2CH), 3.53 (d, 1H, CH*H*Bn), 3.45 (d, 1H, C*H*HBn), 4.59 (m, 1H, CH), 4.77 (m, 1H, CH), 7.13–7.65 (m, 10 CHar). ^{13}C NMR (125.5 MHz, CD_2Cl_2, rt): δ=58.5 (*C*H_2CH, J_{CP}=3.8 Hz), 58.9 (*C*H_2CH, J_{CP}=3.8 Hz), 59.8 (CH_2Bn), 79.3 (CH, J_{CP}=11.3 Hz), 84.1 (CH, J_{CP}=8.8 Hz), 127 (CHar), 128.1 (CHar), 128.3 (CHarP, J_{CP}=8.8 Hz), 128.3 (CHar), 128.5 (CHar), 128.6 (CHar), 130 (CHarP, J_{CP}=21.3 Hz), 130.2 (CHar), 138.2 (C*ipso*Bn), 140.1 (C*ipso*P, J_{CP}=23.8 Hz). ^{31}P NMR (121.4 MHz, CD_2Cl_2, rt): δ=149.66.

Isomer 'B' (30%): ^1H NMR (500.13 MHz, CD_2Cl_2, rt): δ=2.83 (m, 2H, CH_2CH), 3.18 (m, 2H, CH_2CH), 3.74 (d, 1H, CH*H*Bn), 3.68 (d, 1H, C*H*HBn), 4.39 (m, 1H, CH), 4.97 (m, 1H, CH), 7.13–7.65 (m, 10H CHar). ^{13}C NMR (125.5 MHz, CD_2Cl_2, rt): δ=58.0 (*C*H_2CH, J_{CP}=2.5 Hz), 59.8 (*C*H_2CH), 60.3 (CH_2Bn), 78.1 (CH, J_{CP}=11.3 Hz), 84.7 (CH, J_{CP}=16.3 Hz), 127.1 (CHar), 128.2 (CHar), 128.3 (CHarP, J_{CP}=8.8 Hz), 128.6 (CHarP), 128.8 (CHar), 130 (CHarP, J_{CP}=21.3 Hz), 130.3 (CHar), 138.3 (C*ipso*Bn), 140.5 (C*ipso*P, J_{CP}=23.8 Hz). ^{31}P NMR (121.4 MHz, CD_2Cl_2, rt): δ=150.69.

Isomer 'C' (22%): ^1H NMR (500.13 MHz, CD_2Cl_2, rt): δ=2.06 (m, 2H, CH_2CH), 2.17 (m, 2H, CH_2CH), 3.37 (d, 1H, C*H*HBn), 3.22 (d, 1H, CH*H*Bn), 4.39 (m, 1H, CH), 4.97 (m, 1H, CH), 7.13–7.65 (m, 10 CHar). ^{13}C NMR (125.5 MHz, CD_2Cl_2, rt): δ=58.0 (*C*H_2CH, J_{CP}=2.5 Hz), 59.5 (CH_2Bn), 59.8 (*C*H_2CH), 78.1 (CH, J_{CP}=11.3 Hz), 84.7 (CH, J_{CP}=16.3 Hz), 126.9 (CHar), 128.2 (CHar), 128.3 (CHarP, J_{CP}=8.8 Hz), 128.6 (CHar), 128.8 (CHar), 130 (CHarP, J_{CP}=21.3 Hz), 130.3 (CHar), 138.2 (C*ipso*Bn), 140.5 (C*ipso*P, J_{CP}=23.8). ^{31}P NMR (121.4 MHz, CD_2Cl_2, rt): δ=150.69.

4.3. (3a*S*,6a*S*)-5-Benzyl-2-phenoxytetrahydro-3a*H*-[1,3,2]dioxaphospholo[4,5-*c*]pyrrole, 2

PCl_3 0.023 cm^3 (0.26 mmol) was dropwise added to a solution of 50 mg (0.26 mmol) of **4** and 0.072 cm^3 of Et_3N in 20 cm^3 of THF at −110 °C and stirred at 70 °C for 5 h. Then the solvent was removed under reduced pressure and 20 cm^3 of THF were added and mixture cooled at −110 °C, after 24 mg of phenol in 20 cm^3 of THF and 0.036 cm^3 of Et_3N were dropwise added over a period of 15 min. The reaction mixture was stirred 3 h affording a white suspension. The suspension was filtered through anhydrous basic alumina under argon atmosphere and solvent was then evaporated, obtaining the monophosphite as a white powder (73 mg, 88%). $[\alpha]_D^{25}$ +51.5 (*c* 1.1 in CH_2Cl_2) ν_{max} (IR, KBr, pellet)/cm^{-1} 1099 (P–O–Car, st, w), 838 (P–O, st, s), 744 (P–O–C, st, w). HRMS (CI–CH_4) found *m*/*z*: 316.1102 ($[M]^+$H) $C_{17}H_{19}NO_3P$ requires 316.1103.

Isomer 'A' (40%): ^1H NMR (500.13 MHz, $CDCl_3$, rt): δ=2.58 (m, 1H, C*H*HCH), 2.73 (m, 1H, CH*H*CH), 2.95 (m, 1H, CH*H*CH), 3.06 (m, 1H, C*H*HCH), 3.63 (d, 1H, CH*H*Bn), 3.59 (d, 1H, C*H*HBn), 5.28 (m, 1H, CH), 4.71 (m, 1H, CH), 7.01–7.36 (m, 10 CHar). ^{13}C NMR (125.5 MHz, $CDCl_3$): δ=58.3 (*C*H_2CH, J_{CP}=5 Hz), 59.6 (*C*H_2CH), 59.9 (CH_2Bn), 78.4 (CH, J_{CP}=2.5 Hz), 78.6 (CH, J_{CP}=20.1 Hz), 119.6–129.7 (CHar), 133.9 (C*ipso*Bn), 152.4 (C*ipso*P, J_{CP}=8.8 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ=128.7.

Isomer 'B' (36%): ^1H NMR (500.13 MHz, $CDCl_3$, rt): δ=2.55 (m, 1H, C*H*HCH), 2.75 (m, 1H, CH*H*CH), 2.95 (m, 1H, C*H*HCH), 3.058 (m, 1H, CH*H*CH), 3.77 (d, 1H, C*H*HBn), 3.67 (d, 1H, CH*H*Bn), 4.78 (m, 1H, CH), 5.16 (m, 1H, CH), 7.01–7.36 (m, 10 CHar). ^{13}C NMR (125.5 MHz, $CDCl_3$, rt): δ=58.2 (*C*H_2CH, J_{CP}=2.5 Hz), 59.7 (*C*H_2CH), 60.1 (CH_2Bn), 76.5 (CH, J_{CP}=6.3 Hz), 77.4, 119.5–129.7 (CHar), 138.2 (C*ipso*Bn), 152 (C*ipso*P, J_{CP}=6.3 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$, rt): δ=128.64.

Isomer 'C' (24%): ^1H NMR (500 MHz, $CDCl_3$, rt): δ=2.81 (m, 2H, CH_2CH), 3.14 (m, 2H, CH_2CH), 3.60 (d, 1H, C*H*HBn), 3.64 (d, 1H, CH*H*Bn), 5.36 (m, 2H, CH), 7.01–7.36 (m, 10 CHar). ^{13}C NMR (125.5 MHz, $CDCl_3$, rt): δ=59.4 (*C*H_2CH, J_{CP}=2.5 Hz), 60.2 (CH_2Bn), 75.5 (CH, J_{CP}=6.3 Hz), 119.6–129.7 (CHar), 137.7 (C*ipso*Bn), 152 (C*ipso*P, J_{CP}=5). ^{31}P NMR (202.5 MHz, $CDCl_3$, rt): δ=127.69.

4.4. Palladium(II) dichloro-κ^1-P-bis-{(3a*S*,6a*S*)-5-benzyl-2-phenyltetrahydro-3a*H*-[1,3,2]dioxaphospholo[4,5-*c*]pyrrole]}, Pd1

To a solution of 0.046 g (0.154 mmol) of ligand **1** in 20 cm^3 of anhydrous and deoxygenated toluene it was added 0.027 g (0.077 mmol) of the palladium precursor $[PdCl_2(COD)]$. The reaction mixture was then heated at 50 °C and stirred during 2 h. Then the solvent was evaporated under reduced pressure and the precipitate washed with ethyl ether. The complex was obtained as a yellowish powder (0.070 g, 59%). δ_H ^1H NMR (400.16 MHz, CD_2Cl_2, 213 K) δ 3.05 (m, 4H, CH_2CH), 3.16 (m, 4H, CH_2CH), 3.70 (d, 2H,

CH_2Bn), 3.78 (d, 2H, CH_2Bn), 5.04 (br s, 2H, CH), 6.14 (m, 2H, CH), 7.27–7.63 (m, 20H, ar). ^{13}C NMR (125.47 MHz, CD_2Cl_2, rt): δ=57.5 (pt, J_{CP}=5 Hz, *C*H_2CH), 58.3 (pt, J_{CP}=5 Hz, *C*H_2CH), 59.3 *C*H_2Bn, 83 (pt, J_{CP}=2.5 Hz, CH), 83.1 (pt, J_{CP}=2.5 Hz, CH), 127.5 CHar, 127.6 (pt, J_{CP}=7 Hz, CHarP), 128.5 CHar, 128.7 CHar, 130.8 (pt, J_{CP}=5.7 Hz, CHarP), 132.2 CHar, 134.0 (d, J_{CP}=96 Hz, C*ipso*P), 137.5C*ipso*Bn. ^{31}P NMR (121.50 MHz, CD_2Cl_2, rt): δ=130.44. ν_{max} (IR, KBr, pellet)/cm^{-1} 749 (P–C, st, w), 1022 (P–O–Cal, st), 1437 (C–N, st, w), 2961 (C=C, st, w). EA C 52.69, H 4.72, N 3.57. $C_{34}H_{36}Cl_2N_2O_4P_2Pd$ requires C 52.63, H 4.68, N 3.61. HRMS (ESI) found *m*/*z*: 737.0886 $[M]^+$–Cl. $C_{34}H_{36}N_2O_4P_2ClPd$ requires 737.0879.

4.5. Palladium(II) dichloro-κ^2-P,P-(3*S*,4*S*)-1-benzyl-3,4-bis (diphenylphosphinooxy)pyrrolidine], Pd3

To a solution of 0.043 g (0.077 mmol) of ligand **3** in 20 cm^3 of anhydrous and deoxygenated toluene it was added 0.027 g (0.077 mmol) of the palladium precursor [$PdCl_2$(COD)]. The reaction mixture was then heated at 50 °C and stirred during 2 h. Then the solvent was evaporated under reduced pressure and the precipitate washed with ethyl ether. The complex was obtained as a yellowish powder. (44 mg, 77%). ^1H NMR (300.13 MHz, CD_2Cl_2, rt): δ=2.59 (m, 2H, CH_2CH), 2.85 (m, 2H, CH_2CH), 3.40 (d, 1H, CH_2Bn), 3.64 (d, 1H, CH_2Bn), 4.81 (2H, m, 2CH), 7.055–8.1 (25H, m, ar). ^{13}C NMR (75.47 MHz, CD_2Cl_2, rt): δ=57.3 (pt, J_{CP}=3.5, 3.5 Hz, CH_2), 59.8 (CH_2), 77.2 (CH_2Bn), 80.6 (2CH), 127.5 (CHar), 127.9 (pt, J_{CP}=6 Hz, CHarP), 128.4 (CHar), 128.7 (CHar), 128.8 (pt, J_{CP}=6 Hz, CHarP), 130.8 (dd, J_{CP}=27.8, 27 Hz, C*ipso*P), 131.2 (CHar), 132.1 (pt, J_{CP}=6 Hz, CHarP), 133.1 (CHar), 134.9 (pt, J_{CP}=6.8 Hz, CHarP), 135.1 (dd, J_{CP}=135.1, 93.8 Hz, C*ipso*P), 136.8C*ipso*Bn. ^{31}P NMR (121.4 MHz, CD_2Cl_2, rt): δ=121.79; ν_{max} (IR, KBr, pellet)/cm^{-1} 1047 (P–O–C, st, s), 745 (P–O–C, st, w), 717 (O–C, st, w), HRMS (CI–CH_4) found *m*/*z*: 702.0712 $[M]^+$–Cl. $C_{35}H_{33}NO_2P_2ClPd$ requires 702.0710.

4.6. General procedure for catalytic Suzuki C–C coupling in ionic liquids

Dichloro(cycloocta-1,5-diene)-palladium(II) (2.8 mg, 0.01 mmol) and the corresponding ligand (0.012 or 0.024 mmol) were dissolved in 1 cm^3 of the corresponding ionic liquid and stirred for 30 min under vacuum at rt, giving a colourless or yellowish solution. After this time, the substrate (1 mmol), the boronic acid (1.5 mmol) and Na_2CO_3 (265.0 mg, 2.5 mmol) dissolved in 2 cm^3 of deoxygenated water were consecutively added, forming a biphasic system. The mixture was then heated at 60 or 100 °C during 1, 24 or 48 h and then cooled at rt. The catalytic mixture was extracted with ethyl ether (5×2 cm^3) then the organic phase washed with 1 cm^3 of NaOH 1 M, 1 cm^3 of water and dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, yielding the product either as a solid or as yellow oil.

4.7. General procedure for catalytic Suzuki C–C coupling in organic solvent

Dichloro(cycloocta-1,5-diene)-palladium(II) (2.8 mg, 0.01 mmol) and the corresponding ligand (0.012 or 0.024 mmol) were dissolved in 1 cm^3 of freshly distilled toluene and allowed to stir for 30 min, forming a colourless or yellowish solution. After this time, the substrate (1 mmol), the boronic acid (1.5 mmol) and Na_2CO_3 (265.0 mg, 2.5 mmol) dissolved in 2 cm^3 of deoxygenated water were consecutively added, forming a biphasic system. The mixture was then heated at 60 or 100 °C during 1, 24 or 48 h and then cooled at rt. The catalytic mixture was extracted with ethyl ether (5×2 cm^3) then the organic phase washed with 1 cm^3 of NaOH 1 M, 1 cm^3 of water and dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, yielding the product either as a solid or as a yellow oil.

4.8. General procedure for catalytic asymmetric allylic alkylation in ionic liquid

[Pd(μ-Cl)(η^3-C_3H_3)]$_2$ 3.7 mg (0.02 mmol) and 0.1 mmol of ligand were disolved in 1 cm^3 of [BMI][PF_6] and stirred under vacuum for 30 min then 252 mg (1 mmol) of substrate (*rac*-3-acethoxy-1,3-diphenyl-1-propene), 396 mg (1 mmol) of dimethylmalonate, 610 mg and 3 mg of potassium acetate were added at rt.

After the reaction, the products were extracted with diethyl ether and then extracted with NH_4Cl 10% and water. The organic phase was dried over $MgSO_4$, filtered and solvent was removed under vacuum.

4.9. General procedure for catalytic asymmetric allylic alkylation in organic solvent

[Pd(μ-Cl)(η^3-C_3H_3)]$_2$ 3.7 mg (0.02 mmol) and 0.05 or 0.1 mmol of the corresponding ligand were dissolved in 1 cm^3 of CH_2Cl_2 and stirred for 30 min then 252 mg (1 mmol) of substrate (*rac*-3-acethoxy-1,3-diphenyl-1-propene) dissolved in 1 cm^3 of CH_2Cl_2, 396 mg (1 mmol) of dimethylmalonate in 1 cm^3 of CH_2Cl_2, 610 mg of BSA dissolved in 1 cm^3 of CH_2Cl_2 and 3 mg of potassium acetate were added. After the reaction, 10 cm^3 of diethyl ether were added and then extracted with NH_4Cl 10% and water. The organic phase was dried over $MgSO_4$, filtered and solvent was removed under vacuum.

Acknowledgements

We gratefully acknowledge the financial support of the Centre National de la Recherche Scientifique, the UniversitéPaul Sabatier, the Ministerio de Ciencia e Innovaciónn (CTQ2007-63510PPQ and CSD2006-0003) and Generalitat de Catalunya (CTP 2007ITT-00007). M.V. Escárcega-Bobadilla thanks Generalitat de Catalunya and European Social Fund for a pre-doctoral fellowship (FI and BE2008).

Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2010.11.023.

References and notes

1. Knowles, W. S.; Sabacky, M. J. *Chem. Commun.* **1968**, 1445–1446.
2. Horner, L.; Siegel, H.; Büthe, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 942–948.
3. (a) Kagan, H. B.; Dang, T. P. *Chem. Commun.* **1971**, 481–482; (b) Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc.* **1972**, *94*, 64298–64301.
4. For recent selected reviews, see: (a) Marinetti, A.; Carmichael, D. *Chem. Rev.* **2002**, *102*, 201–230; (b) Thang, W.; Zhang, X. *Chem. Rev.* **2003**, *103*, 3029–3070.
5. *Phosphorus Ligands in Asymmetric Catalysis*; Börner, A., Ed.; Wiley-VCH: Weinheim, 2008, Chapter 2.
6. Burk, M. J.; Feaster, J. E.; Harlow, R. L. *Organometallics* **1990**, *9*, 2653–2655.
7. For selected reviews, see: (a) Lescop, C.; Hissler, M. In *Tomorrow's Chemistry Today*; Pignataro, B., Ed.; Wiley-VCH: New York, NY, 2008, pp 295–319; (b) Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, *94*, 1375–1411.
8. (a) *Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Mathey, F., Ed.; Pergamon: Oxford, 2001; (b) Leca, F.; Sauthier, M.; le Guennic, B.; Lescop, C.; Toupet, L.; Halet, J.-F.; Réau, R. *Chem. Commun.* **2003**, 1774–1775; (c) Leca, F.; Lescop, C.; Toupet, L.; Réau, R. *Organometallics* **2004**, *23*, 6191–6201; (d) Pakulski, Z.; Kwiatosz, R.; Pietrusiewicz, K. M. *Tetrahedron* **2005**, *61*, 1481–1492; (e) Leca, F.; Fernández, F.; Muller, G.; Lescop, C.; Réau, R.; Gómez, M. *Eur. J. Inorg. Chem.* **2009**, 5583–5591.
9. (a) Fu, G. C. *Acc. Chem. Res.* **2006**, *39*, 853–860; (b) Ganter, C. In *Phosphorus Ligands in Asymmetric Catalysis*; Börner, A., Ed.; Wiley-VCH: Weinheim, 2008, Chapter 4.3.
10. Selected papers: (a) Mathey, F.; Mercier, F.; Charrier, C. *J. Am. Chem. Soc.* **1981**, *103*, 4595–4597; (b) Siutkowski, M.; Mercier, F.; Ricard, L.; Mathey, F. *Organometallics* **2006**, *25*, 2585–2589; (c) Clochard, M.; Mattmann, E.; Mercier, F.; Ricard, L.; Mathey, F. *Org. Lett.* **2003**, *5*, 3093–3094.
11. Vedejs, E.; Daugulis, O. *J. Am. Chem. Soc.* **1999**, *121*, 5813–5814.
12. Pakulski, Z.; Demchuk, O. M.; Frelek, J.; Luboradzki, R.; Pietrusiewicz, K. M. *Eur. J. Org. Chem.* **2004**, 3913–3918.
13. Yan, Y.-Y.; RajanBabu, T. V. *Org. Lett.* **2000**, *2*, 199–202.

14. (a) Brunel, J. M.; Constantieux, T.; Buono, G. *J. Org. Chem.* **1999**, *64*, 8940–8942; (b) Delapierre, G.; Constantieux, T.; Brunel, J. M.; Buono, G. *Eur. J. Org. Chem.* **2000**, 2507–2511; (c) Delapierre, G.; Brunel, J. M.; Constantieux, T.; Buono, G. *Tetrahedron: Asymmetry* **2001**, *12*, 1345–1352.
15. (a) Breeden, S.; Wills, M. *J. Org. Chem.* **1999**, *64*, 9735–9738; (b) Lyubimov, S. E.; Davankov, V. A.; Petrovskii, P. V.; Loim, N. M. *Russ. Chem. Bull.* **2004**, *56*, 2094–2096; (c) Gavrilov, K. N.; Lyubimov, S. E.; Bondarev, O. G.; Maksimova, M. G.; Zheglov, S. V.; Petrovskii, P. V.; Davankov, V. A.; Reetz, M. T. *Adv. Synth. Catal.* **2007**, *349*, 609–616; (d) Gavrilov, K. N.; Lyubimov, S. E.; Zheglov, S. V.; Benetsky, E. B.; Petrovskii, P. V.; Rastorguev, E. A.; Grishina, T. B.; Davankov, V. A. *Adv. Synth. Catal.* **2007**, *349*, 1085–1094; (e) Gavrilov, K. N.; Benetsky, E. B.; Grishina, T. B.; Rastorguev, E. A.; Maksimova, M. G.; Zheglov, S. V.; Davankov, V. A.; Schäffner, B.; Börner, A.; Rosset, S.; Bailat; Alexakis, G. A. *Eur. J. Org. Chem.* **2009**, 3923–3929.
16. Bondarev, O. G.; Goddard, R. *Tetrahedron Lett.* **2006**, *47*, 9013–9015.
17. (a) Köck, M.; Grube, A.; Seiple, I. B.; Baran, P. S. *Angew. Chem., Int. Ed.* **2007**, *46*, 6586–6594; (b) Paquette, L. A.; Morwick, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 1230–1241; (c) Paquette, L. A.; Hamme, A. T., II; Kuo, L. H.; Doyon, J.; Kreuzholz, R. *J. Am. Chem. Soc.* **1997**, *119*, 1242–1253; (d) Paquette, L. A.; Kuo, L. H.; Tae, J. *J. Org. Chem.* **1998**, *63*, 2010–2021.
18. Mori, M.; Saitoh, F.; Uesaka, N.; Okamura, K.; Date, T. *J. Org. Chem.* **1994**, *59*, 4993–4998.
19. Trindade, A. F.; Gois, P. M. P.; Afonso, C. A. M. *Chem. Rev.* **2009**, *109*, 418–514.
20. Yatagai, M.; Yamagishi, T.; Hida, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 823–826.
21. (a) Nagel, U.; Kinzel, E.; Andrade, J.; Prescher, G. *Chem. Ber.* **1986**, *119*, 3326–3343; (b) Zhao, B.; Peng, X.; Wang, Z.; Xia, C.; Ding, K. *Chem.—Eur. J.* **2008**, *14*, 7847–7857.
22. Hui, A.; Zhang, J.; Wang, Z. *Synth. Commun.* **2008**, *38*, 2374–2384.
23. Reetz, M. T.; Mehler, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 3889–3890.
24. Quin, L. D. *A Guide to Organophosphorus Chemistry*; Wiley Interscience: New York, NY, 2000.
25. (a) Couch, D. A.; Robinson, S. D.; Wingfield, J. N. *J. Chem. Soc., Dalton Trans.* **1974**, *12*, 1309–1313; (b) Giménez-Pedrós, M.; Aghmiz, A.; Ruiz, N.; Masdeu-Bultó, A. M. *Eur. J. Inorg. Chem.* **2006**, 1067–1075.
26. Sharma, R. K.; Nethaj, M.; Samuelson, A. G. *Tetrahedron: Asymmetry* **2008**, *19*, 655–663.
27. Xin, B.; Zhang, Y.; Liu, L.; Wang, Y. *Synlett* **2005**, 3083–3086.
28. (a) Lai, Y. C.; Chen, H. Y.; Hung, W. C.; Lin, C. C.; Hong, F. E. *Tetrahedron* **2005**, *61*, 9484–9489; (b) Jutand, A.; Mosleh, A. *Organometallics* **1995**, *14*, 1810–1817.
29. Fernández, F.; Cordero, B.; Durand, J.; Muller, G.; Malbosc, F.; Kihn, Y.; Teuma, E.; Gómez, M. *Dalton Trans.* **2007**, *47*, 5572–5581 and references there cited.
30. Jansat, S.; Durand, J.; Favier, I.; Malbosc, F.; Pradel, C.; Teuma, E.; Gómez, M. *ChemCatChem* **2009**, *1*, 244–246.
31. (a) Zaft, A.; Beller, M. *Chem.—Eur.J.* **2000**, *6*, 1830–1833; (b) Beller, M.; Zapf, A. *Synlett* **1998**, 792–793.
32. Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143–1145.
33. Goodrich, P.; Hardacre, C.; Paun, C.; Pârvulescu, V. I.; Podolean, I. *Adv. Synth. Catal.* **2008**, *350*, 2473–2476.
34. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, 1988.
35. von Matt, P.; Lloyd Jones, G. C.; Minidis, A. B. E.; Pfaltz, A.; Macko, L.; Neuberger, M.; Zehnder, M.; Rüegger, H.; Pregosin, P. S. *Helv. Chim. Acta* **1995**, *78*, 265–284.