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Efficient Palladium Catalysts Containing Original Imidazolium-Tagged Chiral Diamidophosphite Ligands for Asymmetric Allylic Substitutions in Neat Ionic Liquid

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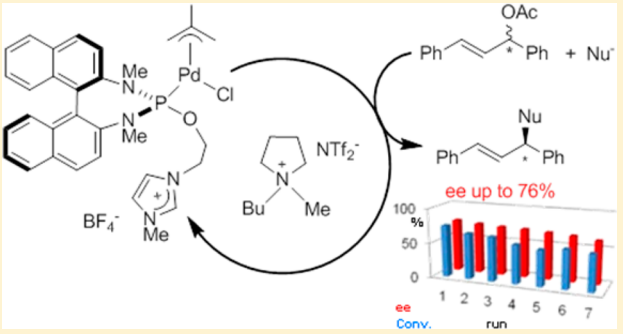
Supporting Information

ABSTRACT: New imidazolium-tagged chiral diamidophosphite ligands, (*S*,*S*)-**a** and (*R*)-**b**, derived from (*S*,*S*)-*N*,*N*′-dibenzyl-1,2-cyclohexanediamine and (*R*)-*N*,*N*′-dimethyl-1,1′-binaphthyl-2,2′-diamine, respectively, and the corresponding palladium allylic complexes of general formula $[PdCl(\eta^3\text{-2-Me-}C_3H_4)(\kappa^1P\text{-L})]BF_4$ (**1a**,**b**) and $[Pd(\eta^3\text{-2-Me-}C_3H_4)(\kappa^1P\text{-L})_2](BF_4)_3$ (**2a**,**b**) were synthesized and fully characterized, including the X-ray crystal structure for **1b**. These original Pd/L catalytic systems were applied in asymmetric allylic alkylation, amination, and sulfonylation using *rac*-3-acetoxy-1,3-diphenyl-1-propene as a substrate in neat ionic liquids, [bmim][PF_6] and [Pyr][NTf_2]. The best results in terms of enantioselectivity were obtained with the catalytic precursor **1b** in [Pyr][NTf_2]. The catalytic phase containing **1b** for the allylic amination could be recycled up to six times without significant loss of asymmetric induction.



INTRODUCTION

Asymmetric allylic substitutions mediated by palladium systems using soft nucleophiles represent one of the most studied enantioselective processes to create carbon−carbon and carbon−heteroatom bonds.[1] Concerning the chiral inductors, phosphorus-based ligands have been largely applied since the first work published by Trost et al.,[2] leading to excellent enantioselectivity.[3] In most cases, homogeneous catalysts in organic solvents are involved, but also palladium colloidal based systems modified by chiral diphosphites have proven to induce a differentiated reactivity due to the surfacelike catalytic behavior.[4] An important remaining challenge in this asymmetric reaction is the use of solvents other than the commonly used volatile organic solvents. For Pd-catalyzed allylic substitutions, ionic liquids (ILs; mainly imidazolium derivatives) have been scarcely used, often applied in nonenantioselective reactions.[5] To the best of our knowledge, previous work reported by some of us constituted by palladium complexes containing chiral diphosphites in imidazolium- and pyrrolidinium-based ionic liquids is the only efficient catalytic system for allylic alkylation and amination, allowing the recycling of the catalytic phase and preserving a high enantioselectivity (more than 95% ee).[6] With the aim to better adapt the catalytic system to an ionic liquid medium, P-donor ligands with ionic moieties seem to stand for an appropriate approach. Actually, chiral P-based ligands containing a phosphate,[7] ammonium,[8] or imidazolium[9] fragment have been conceived, but surprisingly just few of them have been used in asymmetric catalytic processes in IL medium such as in hydrogenation[8a,9a,b] and allylic substitution.[7,8b,9c]

The experience of some of us in the synthesis of original chiral diamidophosphite ligands leads us to the design of imidazolium-tagged derivatives with the aim of their application in asymmetric allylic substitutions in ionic liquids.[10] Diamidophosphite ligands present the advantage of being modular in nature and readily accessible via simple condensation reactions. Moreover, their cyclic structure in which the phosphorus atom is a component of the heterocyclic ring contributes to their stability.

Herein we describe the synthesis of two chiral ionic imidazolium-tagged diamidophosphite ligands, their palladium coordination chemistry, and their application in asymmetric allylic substitutions, such as alkylation, amination, and sulfonylation processes, in neat ionic liquid medium. A comparison with the catalytic behavior of these Pd systems in dichloromethane was also performed.

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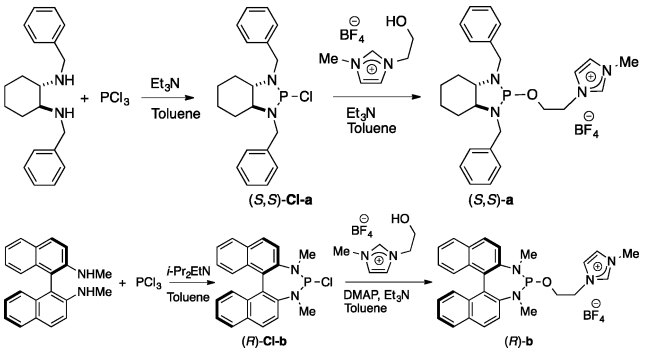
RESULTS AND DISCUSSION

Synthesis and Characterization of Imidazolium-Tagged Chiral Diamidophosphite Ligands, (*S,S*)-a and (*R*)-b. The new homochiral diamidophosphite ligands (*S,S*)-**a** and (*R*)-**b** were prepared through a two-step sequence using enantiomerically pure diamines and the corresponding alcohol hanging from an imidazolium moiety, on the basis of previously reported methodologies (Scheme 1).[9a,10,11] The first step of the synthesis consists of the formation of chlorodiaza derivatives (*S,S*)-**Cl-a** and (*R*)-**Cl-b**, by the reaction of the corresponding diamine with PCl_3 in the presence of an excess of a base (monitoring by ^{31}P NMR). While the intermediate (*S,S*)-**Cl-a** was quantitatively formed after 2 h of stirring at room temperature, (*R*)-**Cl-b** required a longer time (20 h). Both intermediates were not isolated and were used immediately because of their sensitivity to oxygen and moisture.

Scheme 1. Synthesis of Imidazolium-Tagged Chiral Diamidophosphite Ligands (*S,S*)-a and (*R*)-b



The second step of the synthesis corresponds to the condensation of the chlorodiaza derivatives and the alcohol tagged with the imidazolium group in the presence of triethylamine. After 12 h of stirring at room temperature, the diamidophosphite ligands (*S,S*)-**a** and (*R*)-**b** were obtained in global yields of 41% and 87%, respectively. In the case of the synthesis of (*R*)-**b**, the addition of DMAP as a catalyst and excess Et_3N as an HCl scavenger was necessary, reducing the amount of byproducts.[10b,12] Despite the ionic nature of the ligands (*S,S*)-**a** and (*R*)-**b**, they are soluble in commonly used organic solvents, such as CH_2Cl_2, $CHCl_3$, THF, and toluene, and also in ionic liquids (ILs), such as [bmim][PF_6] and [Pyr][NTf_2]. Because of their high tendency to hydrolyze, these new ligands were used without further purification in the formation of the corresponding palladium allylic complexes.

(*S,S*)-**a** and (*R*)-**b** were characterized by mass spectrometry and multinuclear (^{31}P, ^{1}H, and ^{13}C) NMR spectroscopy. Selected NMR data are shown in Table 1. ^{31}P chemical shifts are in the same range as those reported for analogous monodentate diamidophosphites.[10a,13] ^{1}H NMR spectra for both ligands show two signals corresponding to each of the diastereotopic $POCH_2$ methylene protons, coupled to the geminal proton, the phosphorus atom and the vicinal proton. Moreover, two doublets are found for the methyl binaphthylamine substituents of (*R*)-**b**, suggesting that the local C_2 symmetry of the free diamine is lost.

The corresponding diamidophosphite selenides (*S,S*)-**Se-a** and (*R*)-**Se-b** (Figure 1) were prepared in order to evaluate the electron-donating ability of the ligands toward metal acceptors, on the basis of the magnitude of the coupling contant $^{1}J(^{77}Se-^{31}P)$. These coupling constant values for (*S,S*)-**Se-a** and (*R*)-**Se-b** were found to be 882.9 and 885.3 Hz, respectively, close to those reported for similar diamidophosphite ligands.[10] These data point to the fact that the new ligands (*S,S*)-**a** and (*R*)-**b** exhibit a σ-donor character in the range between that corresponding to phosphines and phosphites (reported values for PPh_3 and $P(OPh)_3$ are $^{1}J_{PSe}$ = 745 and 1039 Hz, respectively[14]).

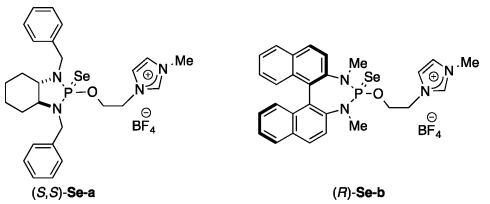


Figure 1. Structures of the diamidophosphite selenides (*S,S*)-**Se-a** and (*R*)-**Se-b**.

Synthesis and Characterization of Palladium Allylic Complexes Containing the Ligands (*S,S*)-a and (*R*)-b: 1a,b and 2a,b. Allyl complexes **1a,b** of general formula [PdCl(η^3-2-Me-C_3H_4)(κ^1*P*-L)]BF_4 (L = (*S,S*)-**a**, (*R*)-**b**) were obtained as a mixture of two diastereomers by reaction of the organometallic precursor [Pd(η^3-2-Me-C_3H_4)(μ-Cl)]$_2$ with the appropriate diamidophosphite ligand (Scheme 2).[10a] The allyl complexes **2a,b** containing 2 equiv of ligand, [Pd(η^3-2-Me-C_3H_4)(κ^1*P*-L)$_2$]$(BF_4)_3$ (L = (*S,S*)-**a**, (*R*)-**b**), were obtained in the same way but in the presence of $AgBF_4$ to remove the chloride ligand (Scheme 2). Complex **2b** was not soluble in nonpolar organic solvents and was scarcely soluble in acetonitrile and acetone but was soluble in the ionic liquids tested ([bmim][PF_6] and [Pyr][NTf_2]).

Table 1. Selected $^{31}P\{^{1}H\}$ and ^{1}H NMR Data for Free and Coordinated Diamidophosphite Ligands[a]

compound	$\delta(^{31}P\{^{1}H\})$	$\delta(^{1}H)$ NC*HN*	$\delta(^{1}H)$ $N_{imi}CH_3$	$\delta(^{1}H)$ $POCH_2$
(*S,S*)-**a**	133.0[b] (s)	8.88 (s)	3.87 (s)	3.90 (m, 1H), 3.48 (m, 1H)
(*R*)-**b**	168.9[b] (s)	8.74 (s)	3.80 (s)	4.32 (dt, $^{2}J_{HH}$ = 16.0, $^{3}J_{HH} \approx {}^{3}J_{HP}$ = 4.0), 4.23 (dt, $^{2}J_{HH}$ = 16.0, $^{3}J_{HH} \approx {}^{3}J_{HP}$ = 4.0)
1a[c]	127.7 (s, maj), 125.9 (s, min)	9.30 (s)	3.85 (s)	4.15 (ov) and 3.40 (m, 1H)
1b[c]	149.9 (s, min), 148.5 (s, maj)	9.35 (br s, maj), 9.31 (br s, min)	3.93 (s, maj), 3.92 (s, min)	4.20 (m, 1H) and 3.98 (m, 1H)
2a[d]	123.0 (d, J_{PP} = 87.4), 121.5 (d, J_{PP} = 87.4)	8.80 (s), 8.75 (s)	3.92 (s)	4.29 and 3.80 (m, ov), 4.48 and 3.93 (m, ov)

[a]Chemical shifts are given in ppm. $^{31}P\{^{1}H\}$ (121.44 MHz, 298 K) and ^{1}H (400 MHz, 298 K) were recorded in $CDCl_3$. Coupling constants are given in Hz. Overlapped signals were assigned from gHSQC spectra. Abbreviations: s, singlet; d, doublet; t, triplet; br, broad; m, multiplet; ov, overlapped. [b]In toluene. [c]Abbreviations: maj, major isomer; min, minor isomer; assigned when isomers are distinguishable. [d]Recorded in acetone-d_6.

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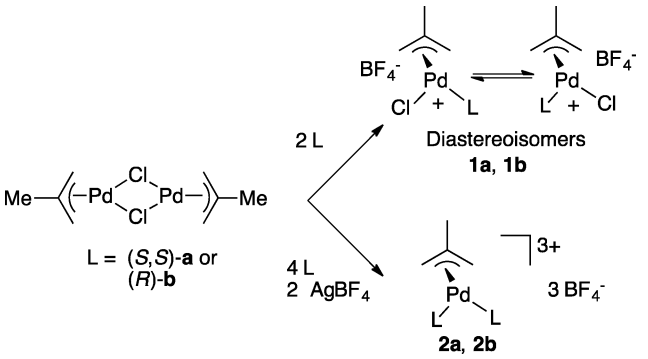
Scheme 2. Synthesis of Allyl Complexes 1a,b and 2a,b (L = (*S*,*S*)-a, (*R*)-b)



These new organometallic compounds, isolated as brown solids, are moderately air stable; they were fully characterized both in the solid state and in solution. A multinuclear (^{31}P, ^{1}H, and ^{13}C) NMR study permitted us to characterize these complexes in solution. Relevant NMR data are summarized in Tables 1 and 2. ^{31}P{^{1}H} NMR spectra showed two sharp signals for **1a,b**, with a 1.2/1 ratio arising from the two disatereoisomers formed, due to the different relative spatial arrangements of the chiral ligand and the allylic group around the metal center.[10a,15]

Table 2. Selected ^{1}H and ^{13}C NMR Data of the Allyl Moiety of Complexes 1a,b and 2a[a]

	1a[b]	1b[b]	2a[c,d]
$H_{syn,trans}$	4.49 (br s)	4.55 (dd, J_{HP} = 9.6, 3.2, min), 4.51 (dd, J_{HP} = 10.0, 3.2, maj)	4.67*, 4.50**
$H_{syn,cis}$	3.44 (ov), 3.42 (ov)	2.88 (br s, min), 2.82 (br s, maj)	
$H_{anti,trans}$	3.43 (ov, maj), 3.26 (s, min)	3.57 (d, J_{HP} = 14.0, maj), 3.54 (d, J_{HP} = 14.0, min)	3.42** (d, J_{HP} = 7), 3.35* (d, J_{HP} = 7)
$H_{anti,cis}$	2.38 (s, min), 2.32 (s, maj)	2.35 (br s, maj), 2.17 (br s, min)	
2-CH_3	1.92 (s)	1.99 (s, min), 1.80 (s, maj)	2.04 (s)
C_{trans}	79.7 (d, J_{CP} = 57.3), 78.6 (d, J_{CP} = 56.3)	81.5 (d, J_{CP} = 44.0), 80.7 (d, J_{CP} = 44.0)	72.6* (d, J_{CP} = 33.0), 71.4** (d, J_{CP} = 42.0)
C_{cis}	55.4 (s), 55.0 (s)	53.3 (br s), 52.1 (br s)	
$C_{central}$	133.8 (s), 133.5 (s)	133.4 (s), 133.3 (s)	137.8 (s)
$C_{2\text{-}CH3}$	23.37 (s)	23.11 (s)	24.3 (s)

[a]Chemical shifts are given in ppm. ^{1}H (400 MHz, $CDCl_3$, 298 K) and ^{13}C (100.6 MHz, 298 K) were recorded in $CDCl_3$. Coupling constants are given in Hz. Trans is with respect to the diamidophosphite ligand. Overlapped signals were assigned from gHSQC spectra. Abbreviations: s, singlet; d, doublet; t, triplet; br, broad; m, multiplet; ov, overlapped. [b]Abbreviations: maj, major isomer; min, minor isomer; assigned when isomers are distinguishable. [c]*/** denotes the two nonequivalent allyl CH_2. [d]Recorded in acetone-d_6.

Both complexes with two diamidophosphite ligands, **2a,b**, exhibited nonequivalence of the two phosphorus atoms in the corresponding ^{31}P{^{1}H} NMR spectra. For **2a**, two doublets corresponding to an AA′ spin system at 121.5 and 123.0 ppm appeared with coupling constants ($^{2}J_{PP'}$ = 87.4 Hz) similar to those reported for related *cis*-L,L complexes.[9a] Complex **2b** showed one broad signal at 146.9 ppm when the spectrum was recorded in CD_3COCD_3. However, when the spectrum was recorded in the ionic liquid [Pyr][NTf_2], two broad signals at 153.0 and 147.1 ppm appeared. The phosphorus chemical shifts of these complexes were upfield in comparison to those of the free ligand, as reported for similar compounds.[10a,16]

In relation to ^{1}H NMR spectra, two-dimensional HSQC experiments permitted us to assign unequivocally all the signals. Complexes **1a,b** exhibited two sets of signals for each syn and anti proton of the allyl group, confirming the presence of the two diastereoisomers (Scheme 2), making it possible to correlate the signals for the allylic fragment with the diamidophosphite ligand of each isomer, as shown in Tables 1 and 2. For complex **2a** the presence of only one isomer was confirmed by the existence of one signal for each of the four allylic terminal hydrogen atoms, establishing the nonequivalence of the two coordinated phosphorus atoms. For complex **2b** only broad signals were observed, ruling out a complete attribution.

To elucidate the solution structure and the dynamic behavior of complexes **1a,b**, 2D (NOESY for **1b** and ROESY for **1a**) NMR experiments were carried out. NOE contacts between allylic protons and the diamidophosphite ligand were not observed, but interestingly exchange signals between allylic protons were detected. For both complexes, exchanges between syn/anti allylic protons in positions cis to the phosphorus atom were observed. However, for protons in trans positions only syn/syn and anti/anti proton exchanges were detected, in accordance with a selective opening of the palladium carbon trans to the phosphorus atom. These exchanges point to the well-known $\eta^3-\eta^1-\eta^3$ isomerization process in palladium allylic complexes.[10a,15] Cross peaks assigned to the apparent allyl–palladium rotation were also observed for both complexes.

Crystals of **1b** suitable for an X-ray diffraction study were obtained from a solution of the complex in a mixture of dichloromethane and hexane. Figure 2 shows the molecular view and a selection of bond lengths and angles. The palladium atom exhibits a distorted-square-planar coordination, bonded to one phosphorus, one chlorine, and the allylic carbon atoms. The distances and angles were in the expected range for this

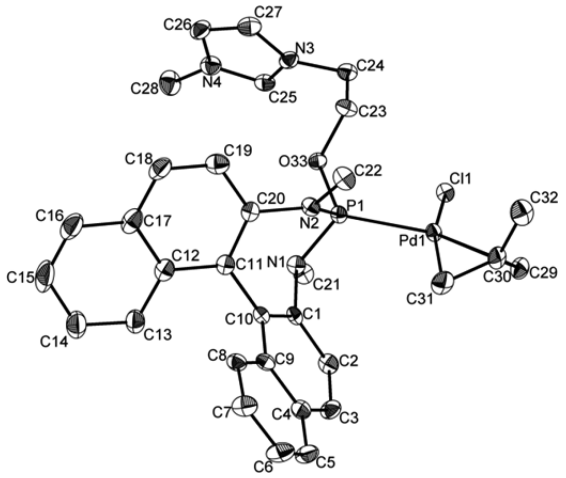


Figure 2. Molecular view of the cation corresponding to complex **1b** (ellipsoids drawn at 50% probability). Hydrogen atoms and the BF_4 anion are omitted for clarity. Selected distances (Å) and angles (deg): Pd(1)–C(31) 2.104(4), Pd(1)–C(29) 2.188(5), Pd(1)–P(1) 2.2626(12), Pd(1)–Cl(1) 2.3784(10), P(1)–O(33) 1.619(3), P(1)–N(2) 1.661(4), P(1)–N(1) 1.687(4), C(29)–C(30) 1.390(6), C(30)–C(31) 1.422(7); P(1)–Pd(1)–Cl(1) 94.79(4), C(29)–C(30)–C(31) 115.4(4).

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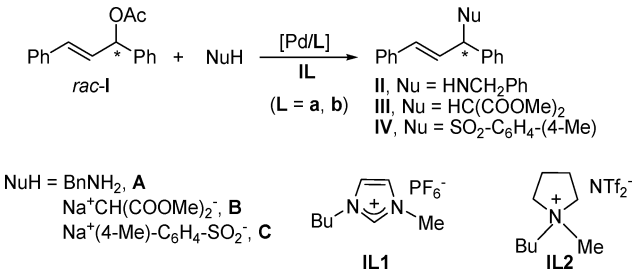
type of complex[10a] and were similar to those of analogous complexes stabilized with phosphoramidites containing a binaphthol moiety.[15,17] The longer Pd−C length placed at a position trans to the phosphorus atom is in agreement with the greater trans influence of the diamidophosphite ligand relative to the chloro ligand. The P−N distances are both shorter than those expected for a single bond, pointing to some extent of a P−N double bond.[18] The values of the angles around the nitrogen atoms are consistent with a significant sp^2 character, in agreement with the partial double-bond character of the P−N bond ($\sum$(N1) = 342.8° and $\sum$(N2) = 357.5°). Bond distance values for the planar imidazolium ring evidence electronic delocalization.

Pd-Catalyzed Asymmetric Allylic Substitutions. The amination (using benzylamine as nucleophile, **A**), alkylation (dimethyl malonate, **B**), and sulfonylation (sodium *p*-toluenesulfinate, **C**) of *rac*-3-acetoxy-1,3-diphenyl-1-propene (*rac*-**I**) were evaluated in neat imidazolium (**IL1**)- and pyrrolidinium-based (**IL2**) ionic liquids using Pd catalytic systems containing the corresponding chiral imidazolium-tagged diamidophosphite ligands (*S*,*S*)-**a** and (*R*)-**b** (Scheme 3).

Scheme 3. Asymmetric Allylic Substitutions in Neat Ionic Liquid Medium Catalyzed by Palladium Systems Containing Imidazolium-Tagged Diamidophosphite Ligands (*S*,*S*)-a and (*R*)-b



We chose the allylic amination as a benchmark reaction in order to study the effect of the solvent in the examined substitutions (Table 3). The named in situ catalytic reactions (generation of the catalytic precursor by mixing $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ and the appropriate ligand in the IL for 30 min at 35 °C) revealed that the nature of the ionic liquid did not trigger important differences in the activity (entries 1 vs 2, 3 vs 4, 5 vs 6, 7 vs 8). Concerning the enantioselectivity, Pd/**b** catalytic systems led to better asymmetric inductions in the pyrrolidium ionic liquid **IL2** than in **IL1** (entries 3 vs 4, 7 vs 8), but no important differences were observed when the corresponding Pd/**a** system was involved (entries 1 and 2). Surprisingly, the catalytic effect of the ligand/metal ratio was dependent on the ligand nature. While the high ligand/Pd ratio (L/Pd = 2.25) triggered a negative effect in the asymmetric induction for the Pd/**a** system in relation to that constituted by L/Pd = 1.25 (entries 1 and 2 vs 5 and 6), for the system Pd/**b**, a significant increase of the enantiomeric excess (up to 73%) was observed using a L/Pd ratio of 2.25, mainly in **IL2** (entries 3 and 4 vs 7 and 8). In any case, the activity increased when an excess of ligand was present (entries 1−4 vs 5−8).

These results obtained under in situ conditions led us to choose **IL2** for further catalytic study.[19]

With the aim of checking the effect of the catalytic precursor, we also examined the behavior of the preformed complexes

Table 3. Allylic Amination of *rac*-I using Benzylamine as Nucleophile in Neat IL Catalyzed by Pd/L Systems[a]

entry	PdL	L/Pd	IL	conversn (%)[e]	ee of **II** (%)[f]
1	Pd/**a**[b]	1.25	**IL1**	52	33 (*S*)
2	Pd/**a**[b]	1.25	**IL2**	59	30 (*S*)
3	Pd/**b**[b]	1.25	**IL1**	40	43 (*S*)
4	Pd/**b**[b]	1.25	**IL2**	43	57 (*S*)
5	Pd/**a**[b]	2.25	**IL1**	86	<5
6	Pd/**a**[b]	2.25	**IL2**	81	<5
7	Pd/**b**[b]	2.25	**IL1**	93	50 (*S*)
8	Pd/**b**[b]	2.25	**IL2**	96	73 (*S*)
9	**1a**[c]	1	**IL2**	66	46 (*S*)
10	**1b**[c]	1	**IL2**	100	74 (*S*)
11	**1a** + **a**[d]	1.25	**IL2**	66	26 (*S*)
12	**1b** + **b**[d]	1.25	**IL2**	62	76 (*S*)
13[g]	**2a**[c]	2	**IL2**	23	34 (*S*)
14[g]	**2b**[c]	2	**IL2**	0	
15[g]	**2a** + **a**[d]	2.25	**IL2**	50	25 (*S*)
16[g]	**2b** + **b**[d]	2.25	**IL2**	22	50 (*S*)

[a]Reaction conditions: *rac*-**I**/Bn-NH_2/Pd/L = 100/100/1/1.25, 1 mL of IL, 35 °C, 6 h. L = (*S*,*S*)-**a**, (*R*)-**b**. [b]Catalyst generated under in situ conditions by mixing $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ and the appropriate amount of the corresponding ligand. [c]Preformed catalyst used as catalytic precursor. [d]Preformed catalyst in the presence of 0.25% of free ligand used as catalytic precursor. [e]Determined by ^{1}H NMR. [f]Determined by HPLC. [g]Catalytic data for 24 h.

1a,**b**. The activity for both catalysts was better than that observed using the corresponding catalysts generated under in situ conditions (entries 2 and 4 vs 9 and 10); in addition, the asymmetric induction was improved, in particular for **1b**, giving 74% enantiomeric excess (entry 10), analogous to that obtained using a large excess of ligand (entry 8). We added some free ligand in the catalytic mixture (giving a total (*R*)-**b**/Pd ratio of 1.25) with the aim of improving the selectivity. Despite that, only a slight enhancement was observed (76% ee), together with an important decrease in activity (entry 10 vs 12). For **1a** in the presence of added free ligand, the activity was maintained but the selectivity dropped (entry 9 vs 11).

The preformed complexes **2a**,**b** showed low activity (entries 13 and 14). The addition of free ligand improved their activity, leading to low enantiomeric excesses (entries 15 and 16). It is important to note that for **b** the in situ generated catalyst gives a better activity and selectivity than those for the analogous system using the preformed complex **2b** (entry 8 vs 16).

For comparative purposes, we carried out the allylic amination reaction in dichloromethane (Table S1 in the Supporting Information). Using preformed complexes as catalytic precursors, we observed very low activities for **1a**,**b** and **2b** even after 24 h at 40 °C (conversions lower than 12%), except for **2a**, for which high conversion was achieved (up to 72%), but giving the racemic amine **II**.

We also tested the catalytic behavior of the preformed complexes **1a**,**b** in the allylic alkylation of *rac*-**I** using sodium dimethylmalonate as nucleophile (Table 4). Analogously to the allylic amination, complex **1b** induced higher enantioselectiviy than **1a** (entries 1−4), giving up 45% of ee (entry 2). We also observed that the addition of free ligand at the catalytic medium produced a decrease of the asymmetric induction, but in this case the conversion was practically complete after 6h of reaction (entries 3−4). When the nucleophile was generated under the largely employed conditions,[20] it means generating the nucleophile by addition of dimethylmalonate and (*N*,*O*)-

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Table 4. Allylic Alkylation and Sulfonylation of *rac*-I using Sodium Dimethylmalonate (B) and Sodium *p*-Toluenesulfinate (C) as Nucleophiles, Respectively, in Neat IL2 Catalyzed by Pd/L Systems[a]

entry	NuH	PdL	L/Pd	conversn (%)[d]	ee of II (%)[e]
1	B	**1a**[b]	1	11	13 (*R*)
2	B	**1b**[b]	1	64	45 (*R*)
3[f]	B	**1a** + **a**[c]	1.25	87	12 (*R*)
4[f]	B	**1b** + **b**[c]	1.25	100	25 (*R*)
5[g]	B	**1b**[b]	1	81	0
6	B	**2b**[b]	2	38	37 (*R*)
7	B	**2a**[b]	2	23	18 (*R*)
8	C	**1a**[b]	1	85	19 (*S*)
9	C	**1b**[b]	1	70	72 (*S*)

[a]Reaction conditions: *rac*-**I**/NuH/Pd/L = 100/150/1/1.25, 1 mL of **IL2**, 35 °C; 3 h for **B** and 24 h for **C**. L = (*S*,*S*)-**a**, (*R*)-**b**. [b]Preformed catalyst used as catalytic precursor. [c]Preformed catalyst in the presence of 0.25% of free ligand used as catalytic precursor. [d]Determined by ^{1}H NMR. [e]Determined by HPLC for allylic alkylations and by SFC for allylic sulfonylations. [f]Catalytic data for 6 h. [g]Nucleophile generated under in situ conditions by reaction of BSA and dimethyl malonate in the presence of a pinch of potassium acetate.

bis(trimethylsilyl)acetamide (BSA) in the catalytic medium, the racemic alkylated compound **III** was obtained (entry 5), due to the instability of the ligand under these conditions.[21] In contrast to that observed in the allylic amination, complex **2b** was slightly active, but inducing a low asymmetric induction (37% vs 45%, entry 6 vs 2). No significant differences between both processes, amination and alkylation, were observed when **2a** was involved (both low activity and selectivity).

In neat dichloromethane, a similar trend was observed in comparison with that for the allylic amination (Table S2 in the Supporting Information). Conversions were low (up 28% after 24 h) for catalysts **1a**,**b** and **2b**; complex **2a** gave total conversion but induced a moderately high enantioselectivity (65% of ee), in contrast to the lack of asymmetric induction in the case of the allylic amination (Table S1, Supporting Information). This difference could be due to the higher Lewis base behavior of benzylamine in comparison to that of the dimethylmalonate anion, most likely inducing some extent of chiral ligand decoordination. However, in IL, probably due to the ionic interactions between the catalytic species and the solvent, the palladium center is less accessible and consequently the coordination of benzylamine to the metal center is less favored, leading to a significant asymmetric induction (up to 76% ee) in contrast to the racemic mixtures obtained in dichloromethane.

The important differences observed in terms of enantioselectivity could be due to plausible pathways without asymmetric induction, involving palladium nanoparticles, taking into account the trend of ionic liquids to stabilize metallic nanoclusters.[22] For all of the systems studied, the catalytic solutions remained yellow even after 24 h of reaction, without formation of palladium black. The absence of metallic nanoparticles for catalytic solutions, showing asymmetric induction, and also those leading to racemic mixtures was confirmed by transmission electronic microscopy.

These encouraging results prompted us to test a more challenging allylic substitution, such as the sulfonylation reaction (Table 4). The model nucleophile used for this reaction is sodium *p*-toluenesulfinate,[23] exhibiting a very low solubility in the usual organic solvents and consequently rendering this reaction particularly appropriate to be carried out in ionic liquid medium.[24] Actually, complexes **1a**,**b** were both highly active, **1b** being the catalyst inducing a higher asymmetric induction (up to 72% (*S*), entries 8 and 9), analogously to that observed for the alkylation and amination reactions (see above).

An accurate literature search showed us that the attribution of absolute configuration to both enantiomers for the allylic sulfonylation product **IV** was not described.[25] For this reason, we separated the two isomers from a racemic mixture of **IV** by SFC techniques on a semipreparative scale. Both isomers were fully characterized and identified by NMR, polarimetry, and X-ray diffraction on monocrystal (Figure 3), leading us to an unequivocal assignment.

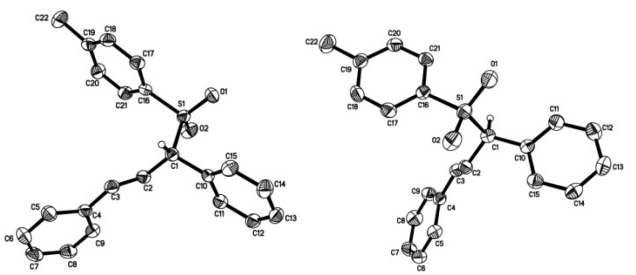

Figure 3. Molecular views of (*S*)-**IV** (left) and (*R*)-**IV** (right) (ellipsoids drawn at shown at 50% probability). For the two compounds, only one of the two independent molecules of the asymmetric unit is shown and H atoms are omitted (except those on the asymmetric carbons).

One of the main interests in using ionic liquids as solvents in catalysis is the feasible immobilization of the metallic catalyst in the IL phase and consequently the catalyst recycling. To the best of our knowledge, only one efficient recyclable system has been reported by some of us, in the case of Pd-catalyzed asymmetric allylic substitutions.[6] We then decided to study the recyclability of the best of our catalytic systems here described, **1b**, applied in the allylic amination for which the highest enantioselectivity was obtained (Table 1). As shown in Figure 4, the activity decreased somewhat after the first run (from 75% to 67%) but was nearly preserved up to the sixth run. The enantioselectivity was almost constant up to the sixth run (for run 1, 88 (*S*)/12 (*R*); for run 6, 83 (*S*)/17 (*R*)). Even when the activity clearly decreased (for run 10, conversion 25%), the selectivity was still quite high (79 (*S*)/21 (*R*)), which points to

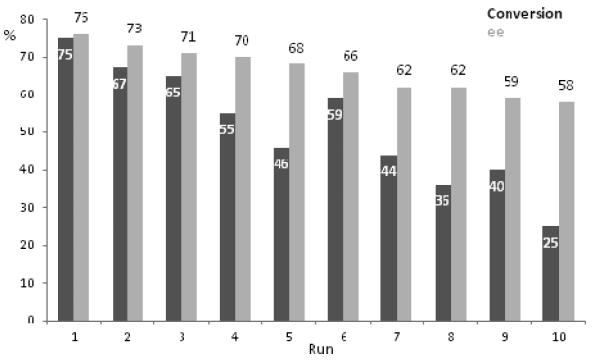

Figure 4. Allylic amination recycling in **IL2** catalyzed by **1b**. Conversion and ee values are represented by black and gray bars, respectively.

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the stability of the ligand under catalytic conditions. The activity clearly decreases after the sixth run due to catalyst deactivation; actually, ICP-MS analyses of the organic products after the first, fifth, and ninth runs showed the absence of palladium, proving that no metal leaching is produced after extraction from the ionic liquid catalytic phase.

CONCLUDING REMARKS

Imidazolium-tagged chiral diamidophosphite ligands L coming from optically pure cyclohexyl and binaphthyl diamines, (*S*,*S*)-**a** and (*R*)-**b**, respectively, have been successfully prepared by a two-step synthetic route. These monodentate phosphanes could stabilize palladium allyl complexes containing one and two ligands per metal, corresponding to complexes of the general formula $[PdCl(\eta^3\text{-2-Me-}C_3H_4)(\kappa^1P\text{-L})]BF_4$ (**1a,b**) and $[Pd(\eta^3\text{-2-Me-}C_3H_4)(\kappa^1P\text{-L})_2](BF_4)_3$ (**2a,b**). Both types of complexes, less sensitive than the related free ligands, were fully characterized in the solid state (including the X-ray crystal structure of **1b**) and in solution by NMR analyses, showing the formation of the expected allylic diastereomers for **1a,b** complexes and also the characteristic palladium allyl dynamic behavior. The ionic character of these palladium systems favors their solubility in ionic liquids, such as those based on imidazolium and pyrrolidinium cations. **1a,b** and **2a,b** complexes have been used as catalytic precursors for asymmetric allylic substitutions of *rac*-3-acetoxy-1,3-diphenyl-1-propene (amination, alkylation, and sulfonylation) in neat ionic liquid, giving better enantioselectivity in $[Pyr][NTf_2]$. The best asymmetric induction was achieved using the preformed complex **1b** as catalyst, leading to 76% ee for the amination and 72% ee for the sulfonylation with conversions higher than 60%, in contrast to the lack of activity observed in dichloromethane. The amination reaction was particularly sensitive to the metal/ligand ratio when ligand (*S*,*S*)-**a** was involved, probably due to the higher lability of (*S*,*S*)-**a** in comparison to (*R*)-**b** in the presence of nucleophile species. The stability of the Pd/**b** catalytic system was proved by its ability to be recycled.

Further studies will seek to exploit the modularity of these ligands to improve their catalytic activity and selectivity.

EXPERIMENTAL SECTION

General Information. All manipulations were performed under a dry nitrogen atmosphere using standard vacuum-line Schlenk techniques. Solvents were purified by standard procedures and distilled under nitrogen; Et_3N and *i*-Pr_2EtN were distilled from CaH_2 and collected over 4 Å molecular sieves before use. 1-(2-Hydroxyethyl)-3-methylimidazolium tetrafluoroborate,[26] (*S*,*S*)-*N*,*N*′-dibenzyl-1,2-cyclohexanediamine,[27] and the dimeric palladium complex $[Pd(\eta^3\text{-2-Me-}C_3H_4)(\mu\text{-Cl})]_2$[28] were prepared as previously described. Ionic liquids **IL1** (1-butyl-3-methylimidazolium hexafluorophosphate) and **IL2** (*N*-butyl-*N*-methylpyrrolidinium bis((trifluoromethyl)sulfonyl)amide) were treated under vacuum at 60 °C overnight prior to use. Other chemicals were used as purchased. ^1H and ^{13}C (standard $SiMe_4$) and ^{31}P (standard H_3PO_4) NMR spectra were recorded on 300 and 400 MHz spectrometers. High-resolution mass spectra were obtained on a time-of-flight instrument using electrospray ionization. Enantiomeric excesses for **II** and **III** were determined by HPLC at 25 °C with a UV PDA detector; enantiomeric excesses for **IV** were determined by SFC with a UV PDA detector at 35 °C.

Synthesis of Diamidophosphites (*S*,*S*)-a and (*R*)-b. The diamidophosphites (*S*,*S*)-**a** and (*R*)-**b** were prepared by following the method described in the literature for similar ligands with some modifications.[10]

(S,S)-a. (*S*,*S*)-*N*,*N*′-Dibenzyl-1,2-diaminecyclohexane (0.41 g, 1.40 mmol) and NEt_3 (0.60 mL, 4.30 mmol) were dissolved in 10 mL of toluene. PCl_3 (0.16 mL, 1.80 mmol) dissolved in 5 mL of toluene was added dropwise at 0 °C, and the mixture was stirred for 2 h at room temperature. After evaporation to dryness the oil was dissolved in 10 mL of toluene and NEt_3 (0,6 mL, 4.3 mmol) and a solution of 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate (0.30 g, 1.4 mmol) in acetonitrile (2 mL) and THF (4 mL) was added dropwise. After it was stirred overnight at room temperature 1 mL of hexane was added. The mixture was cooled to 4 °C and the white precipitate of amine hydrochloride was filtered off. The solvent was removed under vacuum, and a waxy brown oil was obtained and used without further purification. Yield: 0.37 g (41%). HRMS (ESI; *m*/*z*): $C_{26}H_{34}BF_4N_4OP$ 449.2445 $[M - BF_4]^+$. $[\alpha]_D^{25}$ = +98.4° (*c* 1.0, CH_2Cl_2). ^{31}P NMR (toluene, 121.44 MHz; δ (ppm)): 133.0 (s). ^1H NMR ($CDCl_3$, 300 MHz; δ (ppm), *J* (Hz)): 8.88 (s, 1H, NC*H*N), 7.46−7.10 (12H, 10C*H*(Ar) + 2NC*H*), 4.37−3.88 (7H, 4CH_2(Bn) + 1OCH_2 + 2NCH_2), 3.87 (s, 3H, CHNCH_3), 3.48 (m, 1H, 1OCH_2), 2.95 (m, 1H, C*H*(Cy)), 2.52 (m, 1H, C*H*(Cy)), 1.97−0.95 (8H, CH_2(Cy)). ^{13}C NMR ($CDCl_3$, 100 MHz; δ (ppm), *J* (Hz)): 140.2 (d, $^2J_{CP}$ = 7.0, 1C, *C*(Ar)), 139.9 (d, $^2J_{CP}$ = 3.0, 1C, *C*(Ar)), 136.7 (s, 1C, NCHN), 129.0−126.9 (10C, *C*H(Ar)), 123.0 (s, 2C, NCH), 67.9 (d, $^2J_{CP}$ = 7.0, 1C, *C*H(Cy)), 66.1 (d, $^2J_{CP}$ = 9.0, 1C, *C*H(Cy)), 61.3 (d, $^2J_{CP}$ = 5.0, 1C, OCH_2), 51.0 (d, $^3J_{CP}$ = 3.0, 1C, NCH_2), 50.2 (d, $^2J_{CP}$ = 32.0, 1C, CH_2(Bn)), 47.7 (d, $^2J_{CP}$ = 15.0, 1C, CH_2(Bn)), 36.2 (s, 1C, NCH_3), 30.0 (d, $^3J_{CP}$ = 2.0, 1C, CH_2(Cy)), 29.6 (d, $^3J_{CP}$ = 3.0, 1C, CH_2(Cy)), 24.1 (s, 1C, CH_2(Cy)), 24.0 (s, 1C, CH_2(Cy)).

(R)-b. (*R*)-*N*,*N*′-Dimethyl-1,1′-binaphthyl-2,2′-diamine (0.5 g, 1.6 mmol) and freshly dried and distilled *i*-Pr_2EtN were dissolved in 10 mL of toluene. PCl_3 (0.30 mL, 3.50 mmol) dissolved in 5 mL of toluene was added dropwise at 0 °C. After it was stirred for 20 h at room temperature, the mixture was evaporated to dryness. To the solid obtained dissolved in toluene (10 mL) and NEt_3 (0.60 mL, 4.3 mmol) was added a catalytic amount of DMAP (2.6 mg, 0.021 mmol). Then a solution of 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate (0.30 g, 1.4 mmol) in acetonitrile (2 mL) and THF (4 mL) was added dropwise over 6 h. After the mixture was stirred overnight at room temperature, 1 mL of hexane was added. The mixture was cooled to 4 °C, and the amine hydrochloride was filtered off. The solvent was removed under vacuum, and a yellow solid was obtained and used without further purification. Yield: 0.77 g (87%). HR-MS (ESI; *m*/*z*): $C_{28}H_{28}BF_4N_4OP$ 485.2111 $[M - BF_4 + H_2O]^+$. $[\alpha]_D^{25}$ = −394.96° (*c* 1.0, CH_2Cl_2). ^{31}P NMR (toluene, 121.44 MHz; δ (ppm)): 168.9 (s). ^1H NMR ($CDCl_3$, 400 MHz; δ (ppm), *J* (Hz)): 8.74 (s, 1H, NC*H*N), 7.92−6.95 (14H, 12C*H*(Ar) + 2NC*H*), 4.32 (dt, $^2J_{HH}$ = 16.0, $^3J_{HH}$ = $^3J_{HP}$ = 4.0, 1H, OCH_2), 4.23 (dt, $^2J_{HH}$ = 16.0, $^3J_{HH}$ = $^3J_{HP}$ = 4.0, 1H, OCH_2), 3.95 (m, 2H, NCH_2), 3.80 (s, 3H, CHNCH_3), 3.01 (d, $^3J_{HP}$ = 12.0, 3H, CH_3(NMe)), 2.83 (d, $^3J_{HP}$ = 8.0, 3H, CH_3(NMe)). ^{13}C NMR ($CDCl_3$, 100 MHz; δ (ppm), *J* (Hz)): 144.3 (d, $^2J_{CP}$ = 8.0, 1C, *C*(Ar)), 142.1 (d, $^2J_{CP}$ = 7.0, 1C, *C*(Ar)), 136.9 (s, 1C, NCHN), 132.9−121.0 (20C, 6C(Ar) + 12CH(Ar) + 2NCH), 61.1 (d, $^2J_{CP}$ = 9.0, 1C, OCH_2), 51.0 (d, $^3J_{CP}$ = 6.0, 1C, NCH_2), 37.9 (d, $^2J_{CP}$ = 44.0, 1C, CH_3(NMe)), 36.2 (s, 1C, NCHCH_3), 35.1 (d, $^2J_{CP}$ = 26.0, 1C, CH_3NMe).

General Procedure for the Synthesis of Selenide Derivatives (*S*,*S*)-Se-a and (*R*)-Se-b. The selenide derivatives were prepared following the method described in the literature.[10b] A 0.15 mmol amount of the corresponding diamidophosphite dissolved in 2 mL of toluene in the presence of 2.4 mmol of selenium powder was stirred under N_2 for 24 h at room temperature. The reaction mixture was filtered through Celite. The compounds were characterized by ^{31}P NMR (101 MHz) in toluene.

(S,S)-Se-a. ^{31}P NMR ($CDCl_3$, 121.44 MHz; δ (ppm), *J* (Hz)): 87.6 (d, J_{PSe} = 882.9).

(R)-Se-b. ^{31}P NMR (toluene, 121.44 MHz; δ (ppm), *J* (Hz)): 90.3 (d, J_{PSe} = 885.3).

General Procedure for the Synthesis of $[PdCl(\eta^3\text{-2-Me-}C_3H_4)(\kappa^1P\text{-L})]BF_4$ (1a,b). For **1a,b**, 0.17 g (0.44 mmol) of $[Pd(\eta^3\text{-2-Me-}C_3H_4)(\mu\text{-Cl})]_2$ was dissolved in 5 mL of CH_2Cl_2 and 0.88 mmol of the corresponding diamidophosphite in toluene (10 mL) was added

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at 0 °C. The mixture was stirred at room temperature overnight and the solvent removed under reduced pressure. After washing with ether a brownish solid was obtained in both cases.

1a. Yield: 0.11 g (22%). Mp: 154−158 °C dec. ^{31}P NMR ($CDCl_3$, 121.44 MHz; δ (ppm)): 127.7 (s, major isomer); 125.9 (s, minor isomer). ^{1}H NMR ($CDCl_3$, 400 MHz; δ (ppm), J (Hz), mixture of two isomers): 9.30 (s, 1H, NC*H*N), 7.65 (s, 1H, NC*H*), 7.50−7.00 (11H, 10C*H*(Ar) + 1NC*H*), 4.70−3.70 (10H, 3CH_2(Bn) + 3CHNCH_3 + 1OCH_2 + 2NCH_2 + 1$H_{syn,trans}$), 3.68−3.20 (3H, 1OCH_2 + 1$H_{anti,trans}$ + 1$H_{syn,cis}$), 3.11 (m, 2H, 1CH_2(Bn) + 1C*H*(Cy)), 2.80 (m, 1H, C*H*(Cy)), 2.40−2.30 (1H, $H_{anti,cis}$), 2.13−1.47 (7H, 4CH_2(Cy) + 3CH_3(allyl)), 1.47−0.96 (4H, CH_2 (Cy)). ^{13}C NMR ($CDCl_3$, 100 MHz; δ (ppm), J (Hz), mixture of two isomers): 138.8 (s, 1C, *C*(Ar)), 137.6 (s, 1C, *C*(Ar)), 133.8; 133.5 (1C, *C*(allyl)), 129.5−126.5 (11C, 10*C*H(Ar) + 1NC*H*N), 124.1 (s, 1C, NCH), 122.5 (s, 1C, NCH), 79.7; 78,6 (d, $^{2}J_{CP,trans}$= 57.3; $^{2}J_{CP,trans}$= 56.3, 1C, *C*H_2(allyl)), 68.0; 67.7 (s, 1C, *C*H(Cy)), 65.6 (s, 1C, *C*H(Cy)), 63.1; 63.0 (d, $^{2}J_{CP}$ = 13.0, $^{2}J_{CP}$ = 12.0, 1C, O*C*H_2), 55.4; 55.0 (s, 1C, *C*H_2(allyl)), 50.0−46.4 (3C, 2CH_2(Bn) + 1N*C*H_2), 36.2 (s, 1C, CHN*C*H_3), 30.0−23.5 (4C, *C*H_2(Cy)), 23.4 (s, 1C, *C*H_3(allyl)). Anal. Calcd for $C_{30}H_{41}BClF_4N_4OPPd$: C, 49.14; H, 5.64; N, 7.64. Found: C, 49.83; H, 5.99; N, 7.98.

1b. Yield: 0.29 g (43%). Mp: 180−184 °C dec. ^{31}P NMR ($CDCl_3$, 121.44 MHz; δ (ppm)): 149.9 (s, minor isomer); 148.5 (s, major isomer). ^{1}H NMR ($CDCl_3$, 400 MHz; δ (ppm), J (Hz), mixture of two isomers): 9.35; 9.31 (bs, 1H, NC*H*N), 8.07−7.04 (14H, 12C*H*(Ar) + 2NC*H*), 4.60−4.40 (2H, 1$H_{syn,trans}$ + 1NCH_2), 4.35−4.15 (2H, 1NCH_2 + 1CH_2O), 4.05−3.85 (4H, 1CH_2O + 3CHNCH_3), 3.57; 3.54 (d, $^{2}J_{HP}$ = 14.0, 1H, $H_{anti,trans}$), 3.28; 3.19 (d, $^{3}J_{HP}$ = 12.0, 3H, CH_3(NMe)), 3.07; 2.95 (d, $^{3}J_{HP}$ = 12.0, $^{3}J_{HP}$ = 8.0, 3H, CH_3(NMe)), 2.88; 2.82 (bs, 1H, $H_{syn,cis}$), 2.35; 2.17 (bs, 1H, $H_{anti,cis}$), 1.99; 1.80 (s, 3H, CH_3(allyl)). ^{13}C NMR ($CDCl_3$, 100 MHz; δ (ppm), J (Hz), mixture of two isomers): 141.5−121.2 (24C, 8*C*(Ar) + 1*C*(allyl) + 12C*H*(Ar) + 1NC*H*N + 2NCH), 81.5; 80.7 (d, $^{2}J_{CP,trans}$= 44.0, 1C, *C*H_2(allyl)), 62.9 (d, $^{2}J_{CP}$ = 8.0 1C, O*C*H_2), 53.3; 52.1 (bs, 1C, *C*H_2(allyl)), 50.3; 50.2 (s, 1C, NCH_2), 39.3; 39.0 (d, $^{2}J_{CP}$ = 19.0, $^{2}J_{CP}$ = 18.0 1C, CH_3(NMe)), 36.3 (s, 1C, CHNCH_3), 35.7; 35.5 (d, $^{2}J_{CP}$ = 4.0, $^{2}J_{CP}$ = 3.0, 1C, NCH_3), 23.2 (s, 1C, *C*H_3 (allyl)). Anal. Calcd for $C_{32}H_{35}BClF_4N_4OPPd$: C, 51.16; H, 4.70; N, 7.46. Found: C, 49.81; H, 4.83; N, 7.20.

General Procedure for the Synthesis of [Pd(η^3-2-Me-C_3H_4)-(κ^1*P*-L)$_2$](BF$_4$)$_3$ (2a,b). To a solution of the appropiate ligand (1.6 mmol) in toluene (7 mL) was added a solution of [Pd(η^3-2-Me-C_3H_4)(μ-Cl)]$_2$ (0.16 g, 0.41 mmol) in CH_2Cl_2 (10 mL) dropwise. The mixture was cooled to 0 °C, and a solution of $AgBF_4$ (0.16 g, 0.82 mmol) in THF (10 mL) was added. The mixture was stirred for 1 h at room temperature (protected from the light). The AgCl that formed was filtered and the solvent was removed. The pasty solid that was obtained was washed and stirred several times with ether until a brownish solid was obtained.

2a. Yield: 0.24 g (22%). Mp: 99−108 °C dec. HR-MS (ESI; m/z): 353.1512 $[M]^{3+}$. ^{31}P NMR (CH_2Cl_2/toluene, 121.44 MHz; δ (ppm), J (Hz)): 123.0 (d, $^{2}J_{PP}$= 87.4), 121.5 (d, $^{2}J_{PP}$= 87.4). ^{1}H NMR (acetone-d_6, 400 MHz; δ (ppm), J (Hz)): 8.80 (s, 1H, NC*H*N), 8.75 (s, 1H, NC*H*N), 7.73−7.15 (24H, 20C*H*(Ar) + 4NC*H*), 4.68−3.75 (24H, 8CH_2(Bn) + 6CHNCH_3 + 4OCH_2 + 2H_{syn} + 4NCH_2)), 3.45−2.94 (6H, 4C*H*(Cy) + 2H_{anti}), 2.10−1.09 (19H, 16CH_2(Cy) + 3CH_3 (allyl)). ^{13}C NMR (acetone-d_6, 100 MHz; δ (ppm), J (Hz)): 140.1−139.6 (2C, *C*(Ar)), 138.0−137.5 (3C, 2*C*(Ar) + 1*C*(allyl)), 130.0−128.1 (22C, 20CH(Ar) + 2NCHN)), 124.7 (s, 2C, NCH), 123.5 (s, 2C, NCH), 72.6 (d, $^{2}J_{CP,trans}$ = 33.0, 1C, CH_2(allyl)), 71.4 (d, $^{2}J_{CP,trans}$ = 42.0, 1C, CH_2(allyl)), 68.1 (d, $^{2}J_{CP}$ = 29.0, 2C, *C*H(Cy)), 67.3 (d, $^{2}J_{CP}$ = 24.0, 2C, CH(Cy)), 63.5 (pt, $^{2}J_{CP}$ = 17.0 2C, OCH_2), 50.5−49.6 (2C, CH_2(Bn)), 49.0 (s, 2C, NCH_2), 47.6−47.0 (2C, *C*H_2(Bn)), 36.6 (s, 2C, NCH_3), 29.9−28.8 (4C, CH_2(Cy)), 25.0−24.0 (5C, 4CH_2(Cy)) + 1CH_3 (allyl)). Anal. Calcd for $C_{56}H_{75}B_3F_{12}N_8O_2P_2Pd$: C, 50.91; H, 5.72; N, 8.48. Found: C, 48.85; H, 5.89; N, 7.85.

2b. Yield: 0.53 g (49%). Mp: 177−180 °C dec. HR-MS (ESI; m/z): 365.1189 $[M]^{3+}$. ^{31}P NMR ([Pyr][NTf$_2$], 121.44 MHz; δ (ppm)): 153.0 (bs), 147.1 (bs). ^{31}P NMR (acetone-d_6, 121.44 MHz; δ (ppm)): 146.9 (bs). ^{1}H NMR (acetone-d_6, 300 MHz; δ (ppm), J (Hz)): 8.89 (bs, 2H, NC*H*N), 8.43−6.94 (28H, 24C*H*(Ar) + 4NC*H*N), 4.78−2.70 (30H, 6CHNCH_3 + 4OCH_2 + 4NCH_2 + 2H_{syn} + 2H_{anti} + 12CH_3(NMe)), 2.88 (bs, 3H, 3CH_3 (allyl)). Anal. Calcd for $C_{60}H_{63}B_3F_{12}N_8O_2P_2Pd$: C, 53.11; H, 4.68; N, 8.26. Found: C, 47.77; H, 4.68; N, 7.59.

Although elemental analysis results for **2a**,**b** complexes are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.

General Procedure for Pd-Catalyzed Allylic Substitutions of *rac*-I in IL. *Allylic Amination.* Reactions were carried out into an Schlenk tube under Ar at 35 °C. A 0.01 mmol amount of the palladium catalytic precursor (preformed complex—**1a**, **1b**, **2a**, or **2b**—or generated under in situ conditions by stirring [PdCl(η^3-C_3H_5)]$_2$ and the appropriate amount of the corresponding ligand for 30 min) was dissolved in 1 mL of IL. Then, 1 mmol of *rac*-3-acetoxy-1,3-diphenyl-1-propene and 1 mmol of benzylamine were added to the solution. The mixture was stirred at room temperature for the desired time. At the end of the reaction, the products were extracted with cyclohexane and filtered over Celite. The solvent was then removed under reduced pressure. Conversions were determined by ^{1}H NMR. Enantiomeric excesses were determined by HPLC on a Chiralcel-OJ-H chiral column, using heptane/isopropyl alcohol 90/10 as eluent and a flow of 1 mL/min.

Allylic Alkylation. The procedure was analogous to that described for allylic amination, using 1.5 mmol of Na(CH(COOMe)$_2$). Conversions were determined by ^{1}H NMR. Enantiomeric excesses were determined by HPLC on a Chiralcel-OJ-H chiral column, using heptane/isopropanol 80/20 as eluent and on a Chiralcel-OD chiral column using heptane/isopropyl alcohol 98/2 as eluent and a flow of 1 mL/min for both columns.

Allylic Sulfonylation. The procedure was analogous to that described for allylic amination, using 1.5 mmol of Na(*p*-Me$C_6H_4SO_2$). Conversions were determined by ^{1}H NMR. Enantiomeric excesses were determined by SFC on a Chiralpak OJ-H column, with CH_3CN 20% as eluent and a flow of 4 mL/min under 100 bar of CO_2.

Preparation of *rac*-IV: Separation of Both Enantiomers. [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ (0.01 mmol, 2 mg) and triphenylphosphine (0.05 mmol, 13.12 mg) were dissolved in 4 mL of dichloromethane and stirred for 30 min. *rac*-3-Acetoxy-1,3-diphenyl-1-propene (0.5 mmol, 126 mg) dissolved in 0.2 mL of CH_2Cl_2 was added, followed by *p*-toluenesulfonic acid sodium salt (0.7 mmol, 136 mg), and the mixture was stirred at 100 °C for 24 h. The reaction mixture was extracted with pentane (10 × 1 mL), the sample was filtered through SiO_2, and the solvent was evaporated under reduced pressure. Yield: 113 mg (65%). ^{1}H NMR ($CDCl_3$, 300 MHz; δ (ppm), J (Hz)): 2.44 (s, 3H), 4.85 (dd, J = 0.6, J = 7.5, 1H), 6.60 (d, J = 7.5, 1H), 6.64 (dd, J = 15.6, J = 7.5, 1H) 7.25 (d, J = 8.3, 2H), 7.3−7.5 (m, 10H), 7.57 (d, J = 8.3, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz; δ (ppm)): 21.6 (CH_3), 75.4 (CH), 120.3 (CH), 126.8 (2 CH), 128.6 (2 CH), 128.7 (2 CH), 129.3 (2 CH), 129.4 (2 CH), 129.7 (CH), 132.5 (C), 134.5 (C), 136.0(C), 138.0 (CH), 144.6 (C).

Both enantiomers were separated by semipreparative SFC analysis and crystallized from diethyl ether/pentane solution. For (*S*)-**IV**, $[\alpha]_D^{25}$ = +22.4° (*c* 0.33 g/100 mL, CH_3CN); for (*R*)-**IV**, $[\alpha]_D^{25}$ = −22.4° (*c* 0.33 g/100 mL, CH_3CN).

General Procedure for the Recycling of the Pd-Catalyzed Allylic Amination. After each run, the reaction mixture was cooled to room temperature and extractions were carried out using cyclohexane (3 × 5 mL) from the ionic liquid phase. Under these conditions, neither the ionic liquid nor catalyst (palladium species and ligand) was extracted (checked by NMR and ICP-MS analyses). Upon extractions, the catalytic ionic liquid phase was then treated under vacuum in order to remove the volatiles. The corresponding amounts of substrate (*rac*-**I**) and nucleophile ($BnNH_2$) were then added for starting a new run.

Crystallographic Data. *Data for **1b**.* A prismlike specimen of $C_{33}H_{38}BCl_3F_4N_4OPPd$, approximate dimensions 0.190 × 0.210 × 0.340 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped with a

dx.doi.org/10.1021/om4011577 | *Organometallics* XXXX, XXX, XXX−XXX

multilayer monochromator and a Mo high brilliance Incoatec Microfocus source (λ = 0.71073 Å) at a temperature of 100(2) K.

The frames were integrated with the Bruker SAINT software package using a Bruker SAINT algorithm.[29] Data were corrected for absorption effects using the multiscan method SADABS.[30] The structure was solved and refined using the Bruker SHELXTL software package.[31]

Data for (R)-IV and (S)-IV. Intensity data were collected at a temperature of 193(2) K on a Bruker-AXS APEX II Quazar diffractometer ((*R*)-**IV**) using a 30 W air-cooled microfocus source (ImS) with focusing multilayer optics and on a Bruker-AXS SMART APEX II diffractometer ((*S*)-**IV**) with graphite-monochromated Mo Kα radiation (wavelength 0.71073 Å) by using ϕ and ω scans. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied.[29,30] The structures were solved by direct methods, using SHELXS-97[31] and refined using the least-squares method on F^2. All non-H atoms were treated anisotropically. The hydrogen atoms were fixed geometrically and treated as a riding model. H atoms on the asymmetric carbons were located in difference Fourier maps and included in the subsequent refinement without using restraints.

For crystallographic data, see Table S3 in the Supporting Information.

CCDC-969637 (**1b**), CCDC-969512 ((*R*)-**IV**), and CCDC-969513 ((*S*)-**IV**) contain supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF files giving NMR spectra for ligands (*S*,*S*)-**a** and (*R*)-**b** and complexes **1a**,**b** and **2a**,**b**, catalytic procedures and data for the allylic substitutions in CH_2Cl_2, and crystallographic data for **1b**, (*R*)-**IV**, and (*S*)-**IV**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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