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# Chiral Ionic Phosphites and Diamidophosphites: A Novel Group of Efficient Ligands for Asymmetric Catalysis

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Dedicated to Professor Masakatsu Shibasaki on the occasion of his 60th birthday.

**Abstract:** Seven members of a new class of chiral P-monodentate cationic phosphites and diamidophosphites have been synthesized for the first time and tested as ligands in asymmetric transition metal catalysis. Up to 96% *ee* was achieved in the rhodium-catalyzed asymmetric hydrogenation of functionalized olefins and up to 99% *ee* in the palladium-catalyzed allylic allylation. Applications of the immobilized cationic rhodium complex to asymmetric catalytic synthesis have also been demonstrated.

**Keywords:** allylation; asymmetric catalysis; hydrogenation; P ligands; palladium; rhodium

## Introduction

In 2000 it was reported that monodentate BINOL-derived phosphites,[1] phosphonites,[2] and phosphoramidites[3] are excellent ligands in Rh-catalyzed olefin hydrogenation. Since then this chemistry has been generalized to include other reaction types and other monodentate P ligands,[4] and the first detailed mechanistic study has appeared.[5] None of these chiral ligands has been prepared and used catalytically in ionic form. However, recently a study regarding the use of ionic forms of achiral phosphites in catalysis appeared.[6] Moreover, a chiral ionic phosphoramidite was described, but it was not used directly in catalysis.[7]

Herein we report the synthesis of chiral cationic phosphites and diamidophosphites along with their application in the Rh-catalyzed asymmetric hydrogenation of prochiral olefins and Pd-catalyzed allylation as well as their successful immobilization by ionic interaction on an anionic support.

## Results and Discussion

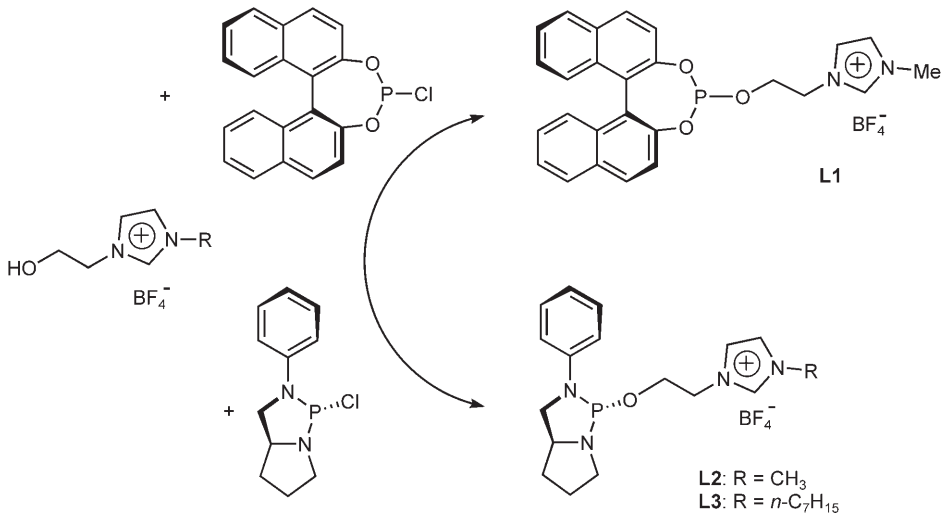
Unlike the traditional synthetic approach to ionic phosphites through quaternization of P,N-bidentate compounds,[6] the novel phosphites and diamidophosphites **L1–L3** were synthesized by a direct phosphorylation of an appropriate ionic liquid in $CH_2Cl_2$ (Scheme 1).

The ligands were isolated in pure form and characterized by NMR spectroscopy and mass spectrometry as well as elemental analysis. Interestingly, despite their ionic nature compounds **L1–L3** are readily soluble in commonly used solvents such as $CH_2Cl_2$, $CHCl_3$ or THF and also ionic liquids. They are stable enough to tolerate washing of their dichloromethane solutions with water.

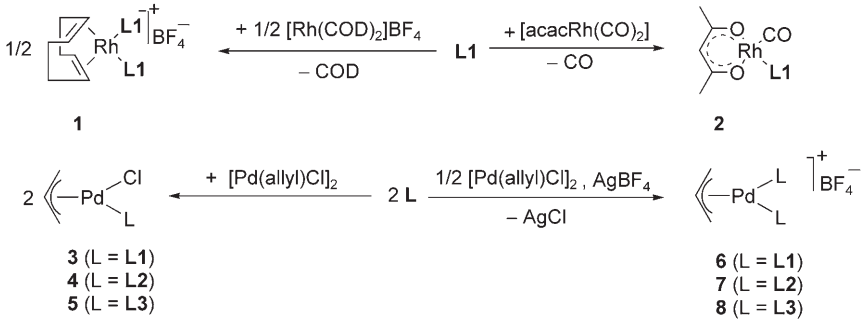
The new compounds act as typical P-monodentate ligands in reactions with $[Rh(COD)_2]BF_4$ and $[Pd(allyl)Cl]_2$ (Scheme 2).[1,8]

The precatalysts **1–8** were characterized by NMR and IR spectroscopy and mass spectrometry. A high $^1J_{P,Rh}$ value for complex **1** (309.6 Hz, in DMSO-$d_6$) indicates pronounced electron-accepting character of cationic phosphite **L1**. The electronic properties of **L1** were also revealed by the $^{31}P$ NMR and IR spectroscopic data of its rhodium(I) carbonyl complex **2**. The $^1J_{P,Rh}$ and ν(CO) data for complex **2** (289.0 Hz; 2012 $cm^{-1}$, in $CHCl_3$) indicate that **L1** is a highly π-accepting aryl phosphite.[9]

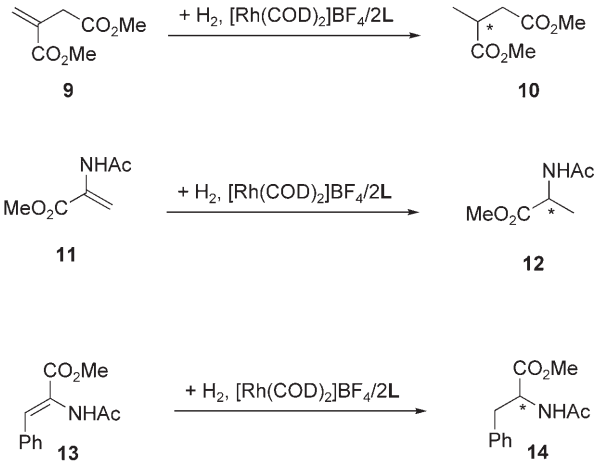
  




**Scheme 1.** Synthesis of cationic ligands **L1–L3**.




**Scheme 2.** Complexation of the ligands **L1–L3** with Rh(I) and Pd(II).




**Scheme 3.** Rh-catalyzed enantioselective olefin-hydrogenation.

The efficacy of the new ionic ligands **L1** and **L3** was evaluated in the Rh-catalyzed asymmetric hydrogenation of olefins **9**, **11** and **13** (Scheme 3).

In these reactions the catalysts formed *in situ* by standard mixing of $[Rh(COD)_2]BF_4$ with two equivalents of an appropriate ionic ligand (Rh/substrate = 1:1000, in $CH_2Cl_2$) led to very different enantioselectivities, depending upon the nature of the chiral auxiliary (Table 1). It is noteworthy that the use of BINOL-based phosphite **L1** provided $\geq$ 93% *ee* and 100% conversion for all substrates (**9**, **11**, **13**). This is in line with the results obtained when using analogous

**Table 1.** Rh-catalyzed hydrogenation of olefins ($CH_2Cl_2$, 1.3 bar $H_2$, 22 °C, 20 h).

| Entry | Substrate | Ligand | Conversion [%] | *ee* [%] |
|---|---|---|---|---|
| 1 | **9** | **L1** | 100[a] | 94 (*S*)[a] |
| 2[b] | **9** | **L1** | 100 | 79 (*S*) |
| 3 | **9** | **L3** | 42 | 58 (*S*) |
| 4 | **11** | **L1** | 100 | 93 (*R*) |
| 5 | **11** | **L3** | 100 | 33 (*R*) |
| 6 | **13** | **L1** | 100 | 96 (*R*) |
| 7 | **13** | **L3** | 59 | 46 (*R*) |

[a] The reaction was also performed for a shorter time (12 h), likewise leading to complete conversion (meaning TOF = 83 $h^{-1}$).

[b] *Reaction conditions:* solvent $[BDMIM]BF_4$; 25 bar $H_2$.

**Table 2.** Rh-catalyzed hydrogenation of dimethyl itaconate **9** using immobilized complex **1**.[a]

| Run | Conversion [%] | *ee* [%] | Rh leaching [ppm][b] |
|---|---|---|---|
| 1 | 100 | 89 (*S*) | 0.83 |
| 2 | 100 | 89 (*S*) | 0.76 |
| 3 | 100 | 88 (*S*) | 0.78 |
| 4 | 87 | 78 (*S*) | 0.67 |
| 5 | 78 | 57 (*S*) | 0.43 |

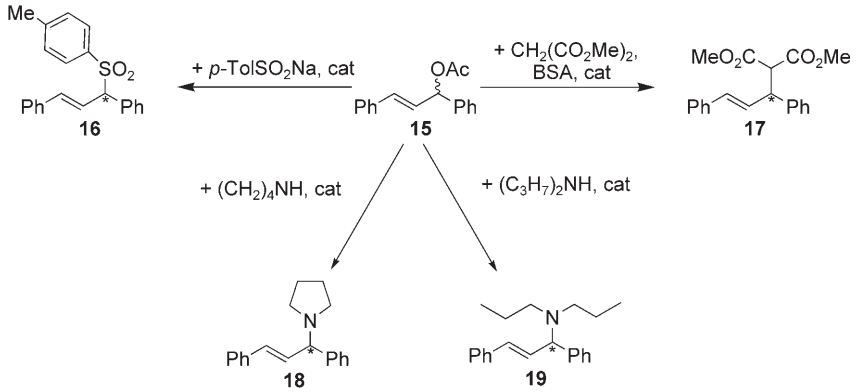
[a] *Reaction conditions:* solvent $CH_2Cl_2$ (5 mL); 22 °C; $H_2$ 1.5 bar; 20 h; substrate/Rh mol ratio 100/1; 0.1 g catalyst.
[b] Percentage of total amount of Rh determinated by ICP of the filtrate.

BINOL-derived monodentate phosphites which are not ionic.[1,4] The experiment described in entry 1 of Table 1 was repeated using the isolated cationic complex **1** as the catalyst, which resulted in the same catalytic profile (100 % conversion; 94 % *ee*). It is interesting to see that considerable reduction in enantioselectivity of the product was observed (Table 1, entry 2) when using the ionic liquid [BDMIM]$BF_4$ as solvent, a phenomenon that was not studied in detail. In this medium the catalyst is completely soluble. It should be noted that the $H_2$ pressure was not varied, although it is known that this parameter in addition to the viscosity of the solvent can effect enantioselectivity.[10] Cationic diamidophosphite **L3** provided only moderate enantioselectivity, up to 58 % *ee*.

We then turned to immobilization by ionic interactions between the doubly cationic Rh-containing precatalysts and an appropriate solid support.[11,12] The goal of immobilization of homogeneous catalysts on supports is to combine the superior activity and selectivity displayed by them with the ease of separation and the possibility of recycling the respective heterogeneous catalysts. We selected phosphotungstic acid ($H_3PW_{12}O_{40}$) on silica as support material, because this is well known for efficient ionic anchoring.[11] The ratio of $H_3PW_{12}O_{40}$ to silica was fixed at 10 wt % heteropoly acid.[11a] Complex **1** was immobilized by direct ion exchange of acidic sites on silica. The rhodium content (1.31 wt %) of the catalyst estimated by energy-dispersive X-ray analysis (EDX) was in good agreement with those obtained from ICP-AES analysis (1.23 wt %). The immobilized catalyst was then tested in the hydrogenation of dimethyl itaconate **9** (Scheme 3) in five consecutive runs. The results are shown in Table 2.

In the first run immobilized catalyst **1** shows good enantioselectivity, although a little lower than that in homogeneous catalysis. Importantly, only 0.83 ppm of Rh was found in the filtrate, demonstrating that very little leaching occurs. This result is also of significance when addressing the question of undesired amounts of transition metals in a reaction product, an issue that is often ignored in academic work. Apart from this positive result, a decrease in activity after run 3 was observed, which defines the limitation of this method. However, we were also interested to use a substrate/Rh mol ratio 1000/1 in order to compare catalytic results which are normally obtained in homogeneous reaction. As before, 0.1 g of catalyst was used, but the concentration of substrate **9** was increased proportionally. Use of immobilized complex **1** and the substrate/Rh mol ratio 1000/1 gave **10** with 90 % *ee* in 77 % conversion. In this case only 0.51 ppm of Rh was detected in the filtrate containing the product, which is a significant observation. Consistently and in accord with a truly asymmetric heterogeneous reaction, no catalytic activity was observed when using solutions recovered after any of the catalytic cycles reported in the present study. Thus, although the solution may contain minute amounts of Rh, in unknown form, it is not enough to catalyze the reaction.

In further work the novel ligands **L1–L3** and their neutral and cationic palladium complexes **3–5** and **6–8** were shown to provide excellent enantioselectivities in the asymmetric Pd-catalyzed allylic sulfonylation, amination and alkylation processes (Scheme 4,




**Scheme 4.** Pd-catalyzed enantioselective allylic substitution.

**Table 3.** Pd-catalyzed allylic sulfonylation of **15** with *p*-$TolSO_2Na$ (20 °C, 48 h) and allylic alkylation of **15** with dimethyl malonate (BSA, KOAc, 20 °C, 48 h).

| Entry | Catalyst | L/Pd | Solvent | Conversion [%] | *ee* [%] |
|---|---|---|---|---|---|
| | | *Allylic sulfonylation* | | | |
| 1 | $[Pd(allyl)Cl]_2$/**L1** | 2/1 | THF | 31[a] | 83 (*R*) |
| 2 | **3** | 1/1 | THF | 31[a] | 81 (*R*) |
| 3 | **6** | 2/1 | THF | 73[a] | 99 (*R*) |
| 4 | $[Pd(allyl)Cl]_2$/**L2** | 2/1 | THF | 83[a] | 60 (*S*) |
| 5 | **4** | 1/1 | THF | 43[a] | 44 (*S*) |
| 6 | **7** | 2/1 | THF | 20[a] | 16 (*S*) |
| 7 | $[Pd(allyl)Cl]_2$/**L3** | 2/1 | THF | 18[a] | 55 (*S*) |
| 8 | **5** | 1/1 | THF | 72[a] | 97 (*S*) |
| 9 | **8** | 2/1 | THF | 0[a] | - |
| | | *Allylic alkylation* | | | |
| 10 | $[Pd(allyl)Cl]_2$/**L2** | 2/1 | THF | 68 | 71 (*S*) |
| 11 | $[Pd(allyl)Cl]_2$/**L2** | 2/1 | $CH_2Cl_2$ | 89 | 93 (*S*) |
| 12 | **4** | 1/1 | $CH_2Cl_2$ | 60 | 90 (*S*) |
| 13 | **7** | 2/1 | THF | 66 | 45 (*S*) |
| 14 | **7** | 2/1 | $CH_2Cl_2$ | 70 | 86 (*S*) |
| 15 | $[Pd(allyl)Cl]_2$/**L3** | 2/1 | THF | 46 | 51 (*S*) |
| 16 | $[Pd(allyl)Cl]_2$/**L3** | 2/1 | $CH_2Cl_2$ | 82 | 74 (*S*) |
| 17 | **5** | 1/1 | THF | 20 | 5 (*S*) |
| 18 | **5** | 1/1 | $CH_2Cl_2$ | 0 | - |
| 19 | **8** | 2/1 | THF | 42 | 83 (*S*) |
| 20 | **8** | 2/1 | $CH_2Cl_2$ | 78 | 84 (*S*) |

[a] Isolated yield of product **16**.

**Table 4.** Pd-catalyzed allylic amination of **15** with pyrrolidine and di-*n*-propylamine.[a]

| Entry | Catalyst | L/Pd | Solvent | Conversion [%] | *ee* [%] |
|---|---|---|---|---|---|
| | | *With pyrrolidine* | | | |
| 1 | $[Pd(allyl)Cl]_2$/**L2** | 2/1 | THF | 95 | 90 (*R*) |
| 2 | **4** | 1/1 | THF | 83 | 75 (*R*) |
| 3 | **7** | 2/1 | THF | 90 | 70 (*R*) |
| 4 | $[Pd(allyl)Cl]_2$/**L3** | 2/1 | THF | 62 | 85 (*R*) |
| 5 | **5** | 1/1 | THF | 45 | 93 (*R*) |
| 6 | **8** | 2/1 | THF | 100 | 77 (*R*) |
| | | *With di*-n-*propylamine* | | | |
| 7 | $[Pd(allyl)Cl]_2$/**L2** | 2/1 | THF | 100 | 90 (+) |
| 8 | **4** | 1/1 | THF | 94 | 82 (+) |
| 9 | **7** | 2/1 | THF | 70 | 15 (+) |
| 10 | $[Pd(allyl)Cl]_2$/**L3** | 2/1 | THF | 100 | 97 (+) |
| 11 | **5** | 1/1 | THF | 98 | 94 (+) |
| 12 | **8** | 2/1 | THF | 98 | 61 (+) |

[a] *Reactions conditions:* 20 °C, 48 h.

Table 3 and Table 4). Again, the degree of asymmetric induction was found to depend upon the ligand used.

Using cationic palladium complex **6** with BINOL-based ionic phosphite **L1**, sulfonylated product **16** was obtained in 99 % *ee*, which is the highest enantioselectivity described so far using any ligand.[8a,13] (*S*)-2-Anilinomethylpyrrolidine-derived diamidophosphite **L2** gave moderate to poor enantioselectivity (up to 60 %), while its homologue **L3** possessing an *N*-heptylimidazolium fragment afforded 97 % *ee*. This is a remarkable result which is currently difficult to explain. Interestingly, catalytic systems with a molar ratio of **L3**/Pd = 2 were the least efficient (Table 3, entries 7 and 9).

Diamidophosphites **L2** and **L3** were found to be good stereoselectors in the Pd-catalyzed allylic alkylation of **15** (up to 93 and 84 % *ee*, respectively). Both results were obtained in $CH_2Cl_2$ at a molar ratio of L/Pd = 2 (Table 3, entries 11 and 20). It should be noted that under the conditions of catalytic allylic al-

kylation comparable to those described for compounds **L2** and **L3**, NCN-derivatives of (1*R*,2*R*)-*trans*-diaminocyclohexane-based imidazolium-phosphites provided only 42% *ee*.[7] Surprisingly phosphite **L1** and its palladium complexes **3** and **6** showed low asymmetric induction (up to 38% *ee*) in the allylic alkylation of **15** with dimethyl malonate and in the allylic amination of **15** with pyrrolidine and di-*n*-propylamine. These poor results could not be improved despite variation of solvent ($CH_2Cl_2$ and THF), molar ratio **L1**/Pd (1 and 2) and nature of base (BSA and $Cs_2CO_3$).

In the Pd-catalyzed allylic amination of 1,3-diphenylallyl acetate **15** with pyrrolidine (Scheme 4) in THF, both ligands **L2** and **L3** gave **18** with similar enantioselectivity (90 and 93% *ee*, respectively; Table 4, entries 1 and 5).

In allylic amination with di-*n*-propylamine the ligands **L2** and **L3** provided 90 and 97% *ee* and quantitative conversion of **15** (THF, L/Pd = 2, Table 4, entries 7 and 10). The excellent enantioselectivity (97%) achieved in this reaction exceeds the best previously reported result (90% *ee*) shown by the analogues of **L2** and **L3** lacking an ionic liquid fragment.[14] Table 3 and Table 4 show that activity (and enantioselectivity) depend upon the nature of the ligand, a conclusion noted earlier in other systems.[6]

## Conclusions

In summary, we have prepared and characterized the first representatives of a new class of P-monodentate phosphite ligands bearing ionic liquid fragments. In general, they are excellent ligands in Rh-catalyzed olefin hydrogenation (up to 96% *ee*) and in Pd-catalyzed allylic substitution (up to 99% *ee*) in organic solvents. It is noteworthy that in these processes the novel cationic ligands are complementary: BINOL-based phosphite **L1** is an excellent stereoselector for Rh-catalyzed olefin hydrogenation, while (*S*)-2-anilinomethylpyrrolidine-derived diamidophosphites **L2** and **L3** are more efficient in Pd-catalyzed allylation. Our results show that the rhodium complex with the new ligand **L1** can be easily immobilized by ionic interaction with a negatively charged support. On the practical side, this new class of modular P-containing compounds enlarges the structural diversity of chiral phosphites and amidophosphites. This means that they can also be used combinatorially as components in mixtures of monodentate P ligands.[15] The ligands are also attractive candidates for other asymmetric transition metal-catalyzed reactions and for the development of reusable catalytic systems, whereby ionic supports other than the ones used in the present study need to be considered.[12]

## Experimental Section

### General Remarks

IR spectra were recorded on a Specord M80 or Nicolet 750 instruments. $^{31}P$, $^{13}C$ and $^{1}H$ NMR spectra were recorded with a Bruker AMX 400 instrument (162.0 MHz for $^{31}P$, 100.6 MHz for $^{13}C$ and 400.13 MHz for $^{1}H$). Complete assignment of all the resonances in $^{13}C$ NMR spectra was achieved by the use of DEPT techniques. Chemical shifts (ppm) are given relative to $Me_4Si$ ($^{1}H$ and $^{13}C$) and 85% $H_3PO_4$ ($^{31}P$ NMR). Mass spectra were recorded with a Varian MAT 311 spectrometer (EI) and a Finnigan LCQ Advantage spectrometer (electrospray ionization technique, ESI). The rhodium content of the catalyst was determined by energy-dispersive X-ray analysis (EDX) performed on a Hitachi S-3500N scanning electron microscope equipped with an OXFORD EDX system and by inductively coupled plasma atomic emission (ICP-AES, UNICAM PU 700). Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow). The ionic liquid [BDMIM]$BF_4$ was obtained from Fluka; it contains $\leq$0.1% water and $\leq$50 mg halogen as chloride per kg.

Optical yields of product **16** were determined using HPLC [(*R*,*R*)-WHELK-01 column) according to the literature.[16] Conversion of substrate **15**[17] and optical purity of products **17**[17] and **18**[18] were determined using HPLC (Daicel Chiralcel OD-H column) as described previously. Optical yields of product **19** were determined using HPLC (Chiralcel OD-H column) according to the literature.[19] All reactions were carried out under a dry argon atmosphere in freshly dried and distilled solvents.

***Phosphorylating reagents:*** ($S_{ax}$)-2-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2] dioxaphosphepine and (2*R*,5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane were prepared as published.[8a,20] The 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate and starting substrate **15** were synthesized as published.[21,22] Dimethyl malonate, BSA [*N*,*O*-bis(trimethylsilyl)acetamide] and sodium *p*-toluenesulfinate were commercially available. $[Pd(allyl)Cl]_2$,[22] $[acacRh(CO)_2]$[23] and $[Rh(COD)_2]BF_4$[24] on the $H_3PW_{12}O_{40}/SiO_2$ support[11a,f] were synthesized using literature procedures. Rhodium(I) complex **2** was synthesized for the $^{31}P$ NMR and IR experiments in chloroform, analogously to the known procedures.[9] The syntheses of palladium(II) complexes followed techniques similar to that reported.[8a]

***Catalytic experiments:*** allylic sulfonylation of substrate **15** with sodium *p*-toluenesulfinate, allylic alkylation with dimethyl malonate, allylic amination with pyrrolidine, and allylic amination with dipropylamine were performed according to the appropriate procedures.[8,14]

### Preparation of 1-(2-Hydroxyethyl)-3-heptylimidazolium Tetrafluoroborate

A mixture of 1-(2-hydroxyethyl)-3-hepthylimidazolium chloride (obtained similar to the literature[6] without characterization) (8.0 g, 0.032 mol), $KBF_4$ (12.6 g, 0.1 mol) and dry acetonitrile (50 mL) was heated to reflux with stirring for 48 h. Upon cooling, the white precipitate was filtered off and washed with acetonitrile (3×20 mL). The organic fil-

trate was concentrated in vacuum to give a liquid product; yield: 8.0 g (84%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 8.71$ (s, 1H), 7.44 (s, 1H), 7.26 (s, 1H), 5.28 (s, 1H), 4.28 (t, $J =$ 4.6 Hz, 2H), 4.13 (m, 2H), 3.87 (t, 2H), 1.84 (m, 2H), 1.29 (m, 4H), 1.24 (m, 4H), 0.84 (t, 6.8 Hz, 3H); MS (ESI): *m/z* (I,%) = 211 (100, $[M-BF_4]^+$); elemental analysis (%) calcd. for $C_{12}H_{23}N_2OBF_4$: C 48.34, H 7.78, N 9.4; found: C 48.41, H 7.81, N 9.37.

## General Procedure for Preparation of Ligands

A solution of the appropriate phosphorylating reagent (2.8 mmol) in $CH_2Cl_2$ (15 mL) was added dropwise to a vigorously stirred solution of an ionic liquid (2.8 mmol) and $NEt_3$ (3 mmol) in $CH_2Cl_2$ (15 mL). The mixture was stirred for additional 3 h. The obtained solution was washed with water (200 mL), dried over $Na_2SO_4$, filtered, and concentrated. The residue was purified by flash chromatography (silica gel, $CH_2Cl_2$) to give the desired product; yields: 40–67%.

**($S_{ax}$)-1-{2-(Dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine)oxyethyl}-3-methylimidazolium tetrafluoroborate (L1):** White solid; yield: 0.66 g (40%; mp 60 °C. $^{31}$P NMR ($CDCl_3$): $\delta = 140.9$; $^{13}$C NMR ($CDCl_3$): $\delta = 147.7$ (d, $^2J_{C,P} =$ 6.6 Hz), 146.6 (d, $^2J_{C,P} = 3.3$ Hz), 133.5, 133.0, 132.4, 132.1, 131.3, 130.8, 130.5, 130.4, 128.8, 128.3, 128.0, 126.9, 126.7, 126.5, 125.2, 124.3, 123.5, 122.8, 121.3, 121.0, 117.8, 62.1 (d, $^2J_{C,P} = 8.4$ Hz, $OCH_2$), 49.9 (d, $^3J_{C,P} = 5.8$ Hz, $NCH_2$), 35.7 (s, $NCH_3$); MS (ESI): *m/z* (I,%) = 441 (100, $[M-BF_4]^+$), 426 (7, $[M-BF_4-CH_3]^+$); elemental analysis: calcd. (%) for $C_{26}H_{22}BF_4N_2O_3P$: C 59.12, H 4.20, N 5.30; found: C 59.18, H 4.24, N 5.24.

**(2*R*,5*S*)-1-{2-(3-Phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane)oxyethyl}-3-methylimidazolium tetrafluoroborate (L2):** White solid; yield: 0.52 g (54%); mp 65 °C. $^{31}$P NMR ($CDCl_3$): $\delta = 122.4$; $^{13}$C NMR ($CDCl_3$): $\delta = 145.2$ (d, $^2J_{C,P} =$ 16.0 Hz, $C_{Ph}$), 129.3 (s, $CH_{im}$), 129.1 (s, $CH_{Ph}$), 123.2 (s, $CH_{im}$), 122.8 (s, $CH_{im}$), 119.1 (s, $CH_{Ph}$), 114.6 (d, $^3J_{C,P} =$ 12.4 Hz, $CH_{Ph}$), 63.3 (d, $^2J_{C,P} = 8.8$ Hz, C-5), 59.9 (d, $^2J_{C,P} =$ 5.1 Hz, $OCH_2$), 54.8 (d, $^2J_{C,P} = 6.6$ Hz, C-4), 50.6 (s, $NCH_2$), 48.6 (d, $^2J_{C,P} = 37.9$ Hz, C-8), 36.0 (s, $NCH_3$), 32.3 (s, C-6), 26.2 (d, $^3J_{C,P} = 3.6$ Hz, C-7); MS (ESI): *m/z* (I,%) = 331 (100, $[M-BF_4]^+$), 266 (8, $[M-BF_4-C_4H_3N]^+$); elemental analysis: calcd. (%) for $C_{17}H_{24}BF_4N_4OP$: C 48.83, H 5.78, N 13.40; found: C 48.89, H 5.83, N 13.37.

**(2*R*,5*S*)-1-{2-(3-Phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane)oxyethyl}-3-heptylimidazolium Tetrafluoroborate (L3):** White solid; yield: 0.8 g (67%); mp 58 °C. $^{31}$P NMR ($CDCl_3$): $\delta = 122.1$; $^{13}$C NMR ($CDCl_3$): $\delta = 144.8$ (d, $^2J_{C,P} =$ 15.3 Hz, $C_{Ph}$), 129.8 (s, $CH_{im}$), 128.8 (s, $CH_{Ph}$), 122.7 (s, $CH_{im}$), 121.5 (s, $CH_{im}$),118.7 (s, $CH_{Ph}$), 114.3 (d, $^3J_{C,P} =$ 11.7 Hz, $CH_{Ph}$), 62.9 (d, $^2J_{C,P} = 8.8$ Hz, C-5), 59.5 (s, $OCH_2$), 54.4 (d, $^2J_{C,P} = 7.3$ Hz, C-4), 50.3 (s, $NCH_2$), 49.5 (s, $NCH_{2\ heptyl}$), 48.0 (d, $^2J_{C,P} = 37.9$ Hz, C-8), 31.7 (s, C-6), 26.0 (s, C-7); 31.1, 29.5, 28.1, 25.6 and 22.1 (s, $CH_{2\ heptyl}$), 13.6 (s, $CH_3$); MS (ESI): *m/z* (I,%) = 415 (100, $[M-BF_4]^+$), 330 (7, $[M-BF_4-C_6H_{13}]^+$); elemental analysis: calcd. (%) for $C_{23}H_{36}BF_4N_4OP$: C 54.99, H 7.22, N, 11.15; found: C 55.04, H 7.27, N 11.12.

## Cationic Rhodium Complex

**$[Rh(COD)(L1)_2]^+$ $[BF_4]^-$ (1):** Yellow solid; yield: 95%; mp 104 °C. MS (ESI): *m/z* (I,%) = 364 (100, $[M-3\ BF_4]^{3+}$); elemental analysis: calcd. (%) for $C_{60}H_{56}B_3F_{12}N_4O_6P_2Rh$: C 53.21, H 4.17, N 4.14; found: C 53.27, H 4.20, N 4.11.

## Neutral Palladium Complexes

**[Pd(allyl)(L1)Cl] (3):** White solid; yield: 97%; mp 120 °C. $^{31}$P NMR ($CDCl_3$): $\delta = 141.4$: MS (ESI): *m/z* (I,%) = 624 (100, $[M-BF_4]^+$), 441 (18, $[L-BF_4]^+$); IR (nujol): ν(Pd–Cl) = 274 $cm^{-1}$; elemental analysis: calcd. (%) for $C_{29}H_{27}BClF_4N_2O_3PPd$: C 48.98, H 3.83, N 3.94; found: C 49.02, H 3.87, N 3.90.

**[Pd(allyl)(L2)Cl] (4):** White solid; yield: 93%; mp 112 °C. $^{31}$P NMR ($CDCl_3$): $\delta = 122.2$; MS (ESI): *m/z* (I,%) = 514 (24, $[M-BF_4]^+$), 331 (100, $[L-BF_4]^+$); IR (nujol): ν(Pd–Cl) = 268 $cm^{-1}$; elemental. analysis: calcd. (%) for $C_{20}H_{29}BClF_4N_4OPPd$: C 39.96, H 4.86, N 9.32; found: C 40.01, H 4.89, N 9.30.

**[Pd(allyl)(L3)Cl] (5):** White solid; yield: 96%; mp 98 °C. $^{31}$P NMR ($CDCl_3$): $\delta = 122.6$ (53%), 122.4 (47%); MS (ESI): *m/z* (I,%) = 598 (100, $[M-BF_4]^+$), 415 (39, $[L-BF_4]^+$); IR (nujol): ν(Pd–Cl) = 270 $cm^{-1}$; elemental analysis: calcd. (%) for $C_{26}H_{41}BClF_4N_4OPPd$: C 45.57, H 6.03, N 8.18; found: C 45.60, H 6.07, N 8.13.

## Cationic Palladium Complexes

**$[Pd(allyl)(L1)_2]^+$ $[BF_4]^-$ (6):** White solid; yield: 94%; mp 89 °C. $^{31}$P NMR ($CDCl_3$): $\delta = 139.9$ and 138.2 (2d, $^2J_{P,P} =$ 120.2 Hz, AB system); MS (ESI): *m/z* (I,%) = 1203 (6, $[M-BF_4]^+$), 441 (100, $[L-BF_4]^+$); elemental analysis: calcd. (%) for $C_{55}H_{49}B_3F_{12}N_4O_6P_2Pd$: C 51.18, H 3.83, N 4.34; found: C 51.23, H 3.87, N 4.31.

**$[Pd(allyl)(L2)_2]^+$ $[BF_4]^-$ (7):** White solid; yield: 97%; mp 81 °C. $^{31}$P NMR ($[D_6]$DMSO): $\delta = 124.1$ (broad s); elemental analysis: calcd. (%) for $C_{37}H_{53}B_3F_{12}N_8O_2P_2Pd$: C 41.51, H 4.99, N 10.47; found: C 41.57, H 5.04, N 10.44.

**$[Pd(allyl)(L3)_2]^+$ $[BF_4]^-$ (8):** White solid; yield: 93%; mp 84 °C. $^{31}$P NMR ($CDCl_3$): $\delta = 115.9$ (broad s); elemental analysis: calcd. (%) for $C_{49}H_{77}B_3F_{12}N_8O_2P_2Pd$: C 47.50, H 6.26, N 9.04; found: C 47.56, H 6.29, N 9.01.

## Immobilization of Complex 1

$H_3PW_{12}O_{40}/SiO_2$ support (400 mg) was suspended in 5 mL of $CH_2Cl_2$ and stirred at room temperature for 15 min. The complex **1** (30 mg) was dissolved in 3 mL of $CH_2Cl_2$ and added to the support suspension. After 3 h of stirring, the solid was collected by filtration and washed thoroughly with 30 mL portions of $CH_2Cl_2$ until the washings were colorless (approximately 5 times). Finally, the catalyst was dried under vacuum for 3 h. The resulting catalyst loading was 13.1 mgRh/g.

## Procedure for Hydrogenation in $[BDMIM]BF_4$

A dry autoclave under argon atmosphere was charged with a mixture of the rhodium complex **1** (1.25 mg; $2 \times 10^{-3}$ mmol) and 316 mg (2 mmol) of substrate **9** in 2 mL of $[BDMIM]BF_4$. Hydrogen was blown through, and hydrogen at 25 bar was introduced. Hydrogenation was subsequently carried out for 20 h. Following extraction with hexane ($3 \times$ 5 mL), conversion was determined by gas chromatography (GC). To determine the *ee* value, about 1.5 mL of the reac-

tion solution were passed through a small amount of silica gel prior to the GC analysis. The hydrogenation experiments were carried out in a parallel manner using 8 flasks.

### Typical Hydrogenation Reaction using Immobilized Complex 1

Hydrogenation of dimethyl itaconate with **1** was carried out in at room temperature and 1.5 bar of hydrogen for 20 h. The immobilized catalyst 100 mg was added to a solution of 1.26 mmol of dimethyl itaconate in 5 mL of $CH_2Cl_2$. The heterogeneous catalyst was recycled with standard methods (the catalyst was filtered off, washed with 3 mL of $CH_2Cl_2$ and reused in the next cycle at the same substrate/catalyst ratio).

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