Asymmetric Pd-catalyzed allylic amination of 1,3-diphenylallyl acetate with dipropylamine in ionic and molecular solvents

S. E. Lyubimov,[a]★ V. A. Davankov,[a] A. S. Kucherenko,[b] S. G. Zlotin,[b] S. V. Zheglov,[c] K. N. Gavrilov,[c] and P. V. Petrovskii[a]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (495) 135 6471. E-mail: lssp452@mail.ru*

[b] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (495) 135 5328. E-mail: zlotin@ioc.ac.ru*

[c] *S. A. Esenin Ryazan State Pedagogical University, 46 ul. Svobody, 390000 Ryazan, Russian Federation. Fax: +7 (091 2) 77 5498. E-mail: chem@rspu.ryazan.ru*

Asymmetric catalytic allylic amination of 1,3-diphenylallyl acetate with dipropylamine in an ionic liquid, 1-butyl-2,3-dimethylimidazolium tetrafluoroborate, and in THF and CH_2Cl_2 in the presence of palladium complexes of P-monodentate phosphite and phosphoramidite derivatives of *S*-1,1′-bis-2-naphthol was carried out. This gave a product with *ee* of up to 65%. The level of asymmetric induction is retained after three catalyst cycles.

Keywords: chiral phosphites, palladium complexes, asymmetric ammination, ionic liquid, catalyst cycles.

Phosphites and phosphoramidites based on *S*-1,1′-bis-2-naphthol (BINOL) represent a highly efficient group of chiral P-monodentate ligands in asymmetric metal complex catalysis. Using these ligands, excellent results have been achieved in enantioselective Rh-catalyzed hydrogenation,[1,2] Cu-catalyzed conjugated addition,[3,4] Ir-catalyzed allylation, and Pd-catalyzed hydrosilylation—oxidation.[5,6] Recently, we also started the successful use of these ligands in Pd-catalyzed asymmetric allylic substitution.[7,8] As further development of this line of research, this communication describes the use of palladium complexes of P-monodentate phosphite and phosphoramidite BINOL derivatives as catalysts for the allylic amination of 1,3-diphenylallyl acetate with dipropylamine. In addition to common organic solvents, we used an ionic liquid (IL) as the reaction medium. Chiral metal complexes dissolved in the IL combine the advantages of homogeneous and heterogeneous catalysts and, in the last decade, they have attracted increasing attention of researchers (see Ref. 9 and references cited therein). Although the Pd-catalyzed synthesis of racemic 1-((*E*)-1,3-diphenylallyl)pyrrolidine from 1,3-diphenylallyl acetate carried out in the IL was described back in 1999,[10] asymmetric catalytic allyllic amination in the IL has been unknown before our study. In addition, this is the first example of using chiral phosphite-based catalysts in processes with the IL as the solvent.

Results and Discussion

The reaction of P-monodentate phosphites **1a,b** and phosphoramidite **1c** with $[Pd(allyl)Cl]_2$ gave both neutral (**2a—c**) and cationic palladium(II) complexes (**3a—c**) (Scheme 1).

Their composition and structure were established by IR, ^{31}P and ^{13}C NMR spectroscopy, ESI mass spectrometry, and elemental analysis. Note that according to ^{31}P NMR spectroscopy, complexes **2a** and **3b,c** exist as mixtures of *exo*- and *endo*-isomers, whereas for **2b,c** and **3a**, these isomers either undergo fast interconversion or one of them is missing.[7,8] The substantial difference in the chemical shifts of the terminal carbon atoms of the allylic ligand in **2a** ($\Delta\delta_c$ = 24.3), caused by the pronounced *trans*-effect of aryl phosphite **1a**, also deserves attention (*cf.*: the ^{13}C NMR spectrum of the complex [Pd(allyl)(L′)Cl] with a phosphine ligand [(*R*)-1-(2-methoxynaphthalen-1-yl)naphthalen-2-yl]diphenylphosphine (L′) shows $\Delta\delta_c$ = 18.9).[11]

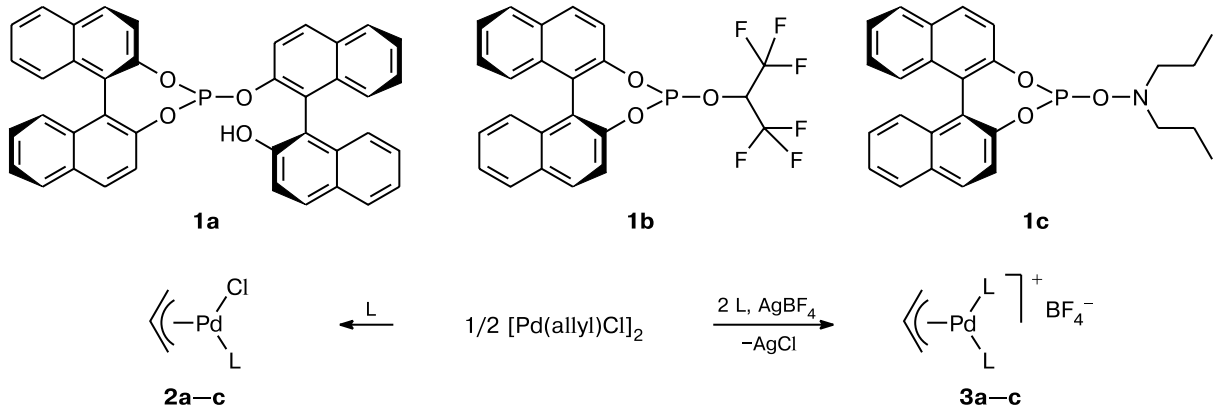
Compounds **2** and **3** were used as catalysts for the asymmetric allylic amination of 1,3-diphenylallyl acetate with dipropylamine (Scheme 2).

The results are summarized in Table 1. When the reaction is carried out in THF or CH_2Cl_2, all metal complexes **2a—c** and **3a—c** demonstrate similar enantioselectivities (50—60% *ee*); in most cases, higher conver-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2478—2481, November, 2005.

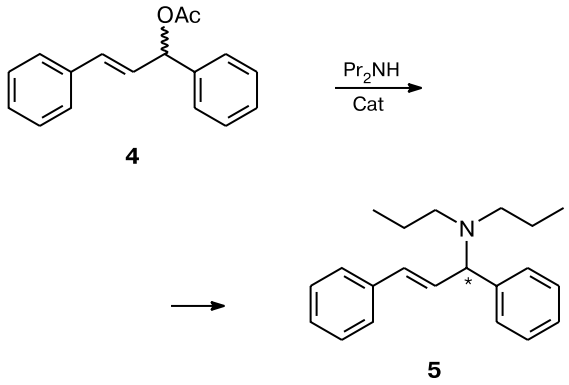
1066-5285/05/5411-2558

Scheme 1



L = **1a**, **1b**, **1c**

Scheme 2



Cat = **2a–c**, **3a–c**.

sion of the starting substrate **4** and higher asymmetric induction are observed in CH_2Cl_2. Generally, the enantioselectivity level attained with compound **2** and **3** (up to 65% *ee*, see Table 1, run 15) is quite comparable with the best result (74% *ee*) obtained when using planar-chiral ruthenium cyclopentadienylphosphine complexes in this reaction.[12] Except for catalysts **2b** and **3b** based on phosphite **1b**, which possess clear-cut electron-withdrawing properties,[8] the other palladium complexes in the IL medium (1-butyl-2,3-dimethylimidazolium tetrafluoroborate, [bdmim]BF_4) provide roughly the same enantioselectivities as in organic solvents, usually with a much higher conversion (in the first cycle). Note that the level of asymmetric induction is retained for the three successive cycles, although the conversion markedly decreases. The loss of the catalyst activity upon recycling is apparently due to the partial washing-out of the complex from the IL during the extraction of the product of catalytic reaction.[10] To prevent this loss, we started investigations into the design and synthesis of chiral phosphite ligands with ionic functional groups.

Table 1. Data of catalytic allylic amination of **4** with dipropylamine using neutral and cationic palladium complexes

Run	Complex	Medium	Cycle	Conversion of **4** (%)	*ee* **5***
1	**2a**	THF		50	3 (+)
2	**2a**	CH_2Cl_2		90	60 (–)
3			1	99	60 (–)
4	**2a**	[bdmim]BF_4	2	92	61 (–)
5			3	59	62 (–)
6	**2b**	THF		12	61 (–)
7	**2b**	CH_2Cl_2		48	60 (–)
8	**2b**	[bdmim]BF_4	1	59	11 (–)
9	**2c**	THF		30	51 (–)
10	**2c**	CH_2Cl_2		87	60 (–)
11			1	96	58 (–)
12	**2c**	[bdmim]BF_4	2	65	58 (–)
13			3	30	58 (–)
14	**3a**	THF		60	51 (–)
15	**3a**	CH_2Cl_2		90	65 (–)
16			1	75	51 (–)
17	**3a**	[bdmim]BF_4	2	45	52 (–)
18			3	15	52 (–)
19	**3b**	THF		28	50 (–)
20	**3b**	CH_2Cl_2		69	53 (–)
21	**3b**	[bdmim]BF_4	1	56	7 (+)
22	**3c**	THF		48	56 (–)
23	**3c**	CH_2Cl_2		38	54 (–)
24			1	97	50 (–)
25	**3c**	[bdmim]BF_4	2	40	51 (–)
26			3	10	51 (–)

* The sign of specific rotation of product **5** is given in parentheses.

Experimental

^{31}P and ^{13}C NMR spectra were recorded on a Bruker AMX-400 (161.98 and 100.61 MHz) instrument relative to 85% H_3PO_4 in D_2O and $CDCl_3$ (δ_C 76.91), respectively. The ^{13}C NMR spectra were assigned using the DEPT procedure. Electrospray mass spectra were measured on a Finnigan LCQ Advantage instrument. IR spectra were measured on a Specord M-80 instrument in $CHCl_3$ in polyethylene cells or in mineral oil between CsI plates. The conversion of substrate **4** and the enantiomeric yield of product **5** were determined by HPLC on a Varian 5000 chromatograph using a Daicel Chiralcel OD-H chiral column (hexane—Pr^iOH—Et_2NH, 1000 : 1 : 1, 0.4 mL min^{-1}, absorption detection at 254 nm, t_1 = 9.5 min, t_2 = 10 min).[12] The optical absorbance was measured on a Perkin—Elmer 341 polarimeter. Elemental analysis was performed at the Laboratory of Organic Microanalysis, A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.

All reactions were carried out under dry argon in anhydrous solvents. Ligands **1a—c** were prepared by procedures we reported previously.[8,13] The synthesis of cationic complexes **3a—c** was described in our previous publications.[8,14] The starting $[Pd(allyl)Cl]_2$ and 1,3-diphenylallyl acetate were prepared by known procedures.[15] Commercial dipropylamine (Acros Organics) was distilled from KOH and then from $LiAlH_4$ immediately prior to use; commercially available $[bdmim]BF_4$ (Fluka) was used.

Preparation of palladium complexes 2a—c (general procedure). A solution of ligands **2a—c** (0.2 mmol) in CH_2Cl_2 was added dropwise to a solution of $[Pd(allyl)Cl]_2$ (0.1 mmol) in the same solvent. The mixture was stirred for 1 h under argon. The product was concentrated and dried *in vacuo*.

Chloro{(*R*)-2-((*R*)-1,1′-binaphthyl-2′-hydroxy-2-oxy)dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine}(π-allyl)palladium(2+) (2a). Light-yellow powder, m.p. 114—116 °C (with dec.), yield 94%. Found (%): C, 65.99; H, 3.80; P, 4.04. $C_{43}H_{30}ClO_4PPd$. Calculated (%): C, 65.92; H, 3.86; P, 3.95. ^{31}P NMR ($CDCl_3$), δ: 142.8 (71%); 141.9 (29%). ^{13}C NMR ($CDCl_3$) δ for the major isomer: 57.3 (s, CH_2 (allyl, *trans*-Cl)), 81.6 (d, $^2J_{C,P}$ = 47.4 Hz, CH_2 (allyl, *trans*-P)); 112.4, 117.8, 118.0 (br.s, CH (allyl)); 120.2, 121.0, 121.8, 122.9, 123.1, 124.5, 124.9, 125.2, 125.9, 126.7, 126.9, 127.1, 127.3, 127.5, 128.8, 129.1, 129.7, 129.9, 130.1, 130.9, 131.0, 131.4, 131.7, 132.8, 133.6, 133.9, 145.6, 146.7, 146.8, 152.5. IR, ν/cm^{-1}: 3531 (OH, $CHCl_3$); 282 (Pd—Cl, Nujol).

Chloro{(*S*)-2-(hexafluorooisopropyloxy)dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine}(π-allyl)palladium(2+) (2b). White powder, m.p. 120 °C (with dec.), yield 90%. Found (%): C, 47.21; H, 2.85; P, 4.52. $C_{26}H_{18}ClF_6O_3PPd$. Calculated (%): C, 46.94; H, 2.73; P, 4.66. ^{31}P NMR ($CDCl_3$) δ: 149.2. MS, m/z (I_{rel} (%)): 665 $[M]^+$ (100), 614 $[M - CF_3 + H_2O]^+$ (76). IR (Nujol), ν/cm^{-1}: 290 (Pd—Cl).

Chloro{(*S*)-2-(dipropylamino)dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine}(π-allyl)palladium(2+) (2c). White powder, m.p. 104 °C (with dec.), yield 87%. Found (%): C, 58.05; H, 5.35; P, 4.97. $C_{29}H_{31}ClNO_2PPd$. Calculated (%): C, 58.21; H, 5.22; P, 5.18. ^{31}P NMR ($CDCl_3$), δ: 148.3. MS, m/z (I_{rel} (%)): 598 $[M]^+$ (100), 555 $[M - C_3H_7]^+$ (12). IR (Nujol), ν/cm^{-1}: 294 (Pd—Cl).

[Bis{(*R*)-2-((*R*)-1,1′-binaphthyl-2′-hydroxy-2-oxy)-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine)}(π-allyl)palladium(2+) tetrafluoroborate (3a). White powder, m.p. 139—141 °C (with dec.), yield 95%. Found (%): C, 69.67; H, 3.98; P, 4.22. $C_{83}H_{55}BF_4O_8P_2Pd$. Calculated (%): C, 69.45; H, 3.86; P, 4.32. ^{31}P ($CDCl_3$), δ: 142.6. MS, m/z (I_{rel} (%)): 1347 $[M - BF_4]^+$ (8), 1062 $[M - BF_4 - C_{20}H_{13}O_2]^+$ (100). IR, $CHCl_3$), ν/cm^{-1}: 3526 (OH).

Palladium-catalyzed allylic amination of 1,3-diphenylallyl acetate with dipropylamine. *Method A.* The specified palladium complex (0.02 mol) was dissolved in THF or CH_2Cl_2 (5 mL). Then 1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol) was added, the mixture was stirred for 15 min, and freshly distilled dipropylamine (0.2 mL, (1.5 mmol) was added. The reaction mixture was stirred for 48 h and filtered through celite. The solvent was evaporated *in vacuo* (40 Torr) and the residue was dried for 12 h *in vacuo* (10 Torr) to give 1,3-diphenyl-2-propenyl-di-*n*-propylamine (**5**) as a colorless crystalline compound. The ^1H NMR and mass spectra of compound **5** fully correspond to published data.[12]

Method B. The specified palladium complex (0.02 mol) was dissolved in $[bdmim]BF_4$ (1 mL). Then 1,3-diphenylallyl acetate (0.1 mL, 0.5 mmol) was added, the mixture was stirred for 15 min, and freshly distilled dipropylamine (0.2 mL, 1.5 mmol) was added. The reaction mixture was stirred for 48 h and extracted with diethyl ether (7×4 mL), and the ether layer was filtered through silica gel and concentrated *in vacuo*. Recycling was attained by repeated addition of the starting components to the solution of the complex in the ionic liquid under the same conditions.

The authors are grateful to the Daicel Chemical Industries Ltd. company (Japan) for the provided chiral column Daicel Chiralcel OD-H.

This work was supported by the Foundation for the Support of Russian Science.

References

1. A. Alexakis and C. Benhaim, *Eur. J. Org. Chem.*, 2002, 3221.
2. K. N. Gavrilov, O. G. Bondarev, A. I. Polosukhin, *Usp. Khim.*, 2004, **73**, 726 [*Russ. Chem. Rev.*, 2004, **73**, 671 (Engl. Transl.)].
3. M. T. Reetz and G. Mehler, *Tetrahedron Lett.*, 2003, **44**, 4593.
4. M. van den Berg, R. M. Haak, A. J. Minnaard, A. H. M. de Vries, J. G. de Vries, and B. L. Feringa, *Adv. Synth. Catal.*, 2002, **344**, 1003.
5. X. Jia, R. Guo, X. Li, X. Yao, and A. S. C. Chan, *Tetrahedron Lett.*, 2002, **43**, 5541.
6. G. Lipowsky and G. Helmchen, *Chem.Commun.*, 2004, 116.
7. V. N. Tsarev, S. E. Lyubimov, A. A. Shiryaev, S. V. Zheglov, O. G. Bondarev, V. A. Davankov, A. A. Kabro, S. K. Moiseev, V. N. Kalinin, and K. N. Gavrilov, *Eur. J. Org. Chem.*, 2004, 2214.
8. K. N. Gavrilov, S. E. Lyubimov, S. V. Zheglov, E. B. Benetsky, and V. A. Davankov, *J. Mol. Catal. A: Chemical*, 2005, **231**, 255.

9. E. V. Starodubtseva, M. G. Vinogradov, V. A. Pavlov, L. S. Gorshkova, V. A. Ferapontov, *Izv. Akad. Nauk. Ser. Khim.*, 2004, 2079 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2172].
10. W. Chen, L. Xu, C. Chatterton, and J. Xiao, *Chem. Commun.*, 1999, 1247.
11. P. G. A. Kumar, P. Dotta, R. Hermatschweiler, and P. S. Pregosin, *Organometallics*, 2005, **24**, 1306.
12. Y. Matsushima, K. Onitsuka, T. Kondo, T.-aki Mitsudo, and S. Takahashi, *J. Am. Chem. Soc.*, 2001, **123**, 10405.
13. K. N. Gavrilov, I. S. Mikhel´, *Zh. Neorgan. Khim.*, 1994, **39**, 439 [*Russ. J. Inorg. Chem.*, 1994, **39**, 439 (Engl. Transl.)].
14. K. N. Gavrilov, S. E. Lyubimov, P. V. Petrovskii, S. V. Zheglov, A. S. Safronov, R. S. Skazov, and V. A. Davankov, *Tetrahedron*, 2005, **61**, 10514.
15. P. R. Auburn, P. B. McKenzie, and B. Bosnich, *J. Am. Chem. Soc.*, 1985, **107**, 2033.

Received September 7, 2005;
in revised form October 21, 2005