Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 16 (2005) 1737–1741

Enantioselective Pd-catalyzed *C**–*C*, *C**–*N*, and *C**–*S* bond formation reactions using first *P*,*P*,*N*,*N*-tetradentate chiral phosphites

Vasily N. Tsarev,[a,*] Stanislav I. Konkin,[b] Alexei A. Shyryaev,[b] Vadim A. Davankov[a] and Konstantin N. Gavrilov[b]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilova Str., Moscow 119991, Russian Federation*
[b]*Department of Chemistry, Ryazan State Pedagogic University, 46 Svoboda Str., Ryazan 390000, Russian Federation*

Received 13 October 2004; revised 12 April 2005; accepted 13 April 2005

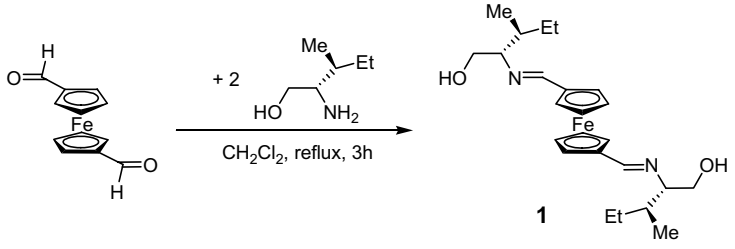
Abstract—Chiral *P*,*P*,*N*,*N*-tetradentate ferrocene-derived iminophosphite and iminodiamidophosphite ligands were synthesized for the first time. The applicability of these ligands in asymmetric *C**–*C*, *C**–*N*, and *C**–*S* bond formation was demonstrated. High enantioselectivity was obtained in the Pd-catalyzed allylic substitution of 1,3-diphenylallyl acetate with dimethyl malonate (up to 90% ee), pyrrolidine (up to 85% ee), and sodium *para*-toluene sulfinate (up to 81%), with the iminodiamidophosphite ligand being the best stereoselector.

1. Introduction

Optically active phosphine- and phosphinite-type ligands are well known in the asymmetric catalysis and synthesis of chiral metal complexes.[1–7] An interesting feature of these compounds is their ability to realize both *P*,*N*- and *P*,*P*-bidentate type of coordination to metal atoms, depending on the ligand/metal molar ratio. In turn, a coordination mode may have a strong impact on catalytic activity and enantioselectivity of the ligands. In recent years, *P*,*N*-bidentate phosphites have been actively used in asymmetric metal complex catalysis,[8,9] but no examples of using chiral *P*,*P*,*N*,*N*-tetradentate phosphite-type ligands are known. Herein, we report the first representatives of *P*,*P*,*N*,*N*-tetradentate chiral phosphites and their successful application in Pd-catalyzed enantioselective allylation.

2. Results and discussion

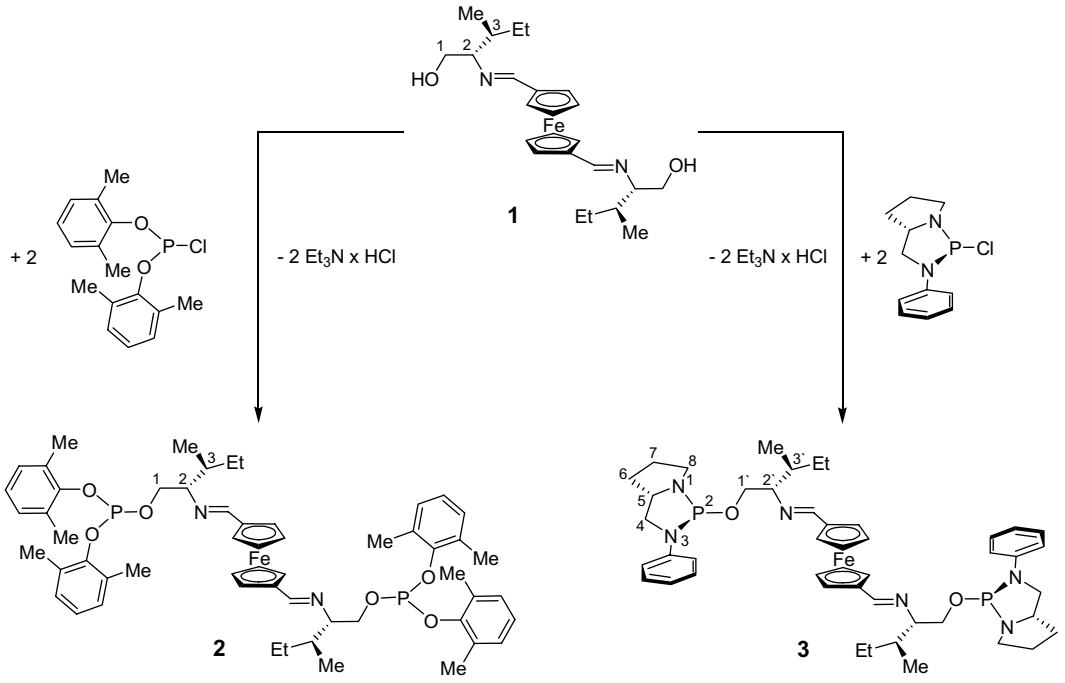
As a starting material for the synthesis of new chiral *P*,*P*,*N*,*N*-tetradentate phosphites, we used imino alcohol **1**, which can be obtained easily and in high yield by the condensation of ferrocene-1,1′-dicarbaldehyde and isoleucinol in CH_2Cl_2 media (Scheme 1).



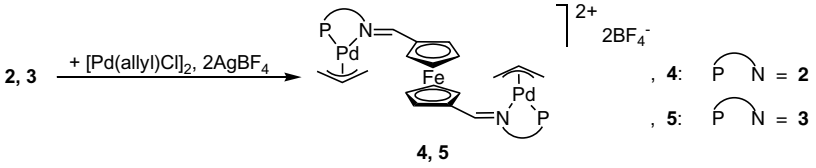
Scheme 1.

* Corresponding author. Tel./fax: +7 095 135 6471; e-mail: tsarev@ineos.ac.ru

0957-4166/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.tetasy.2005.04.010



Scheme 2.



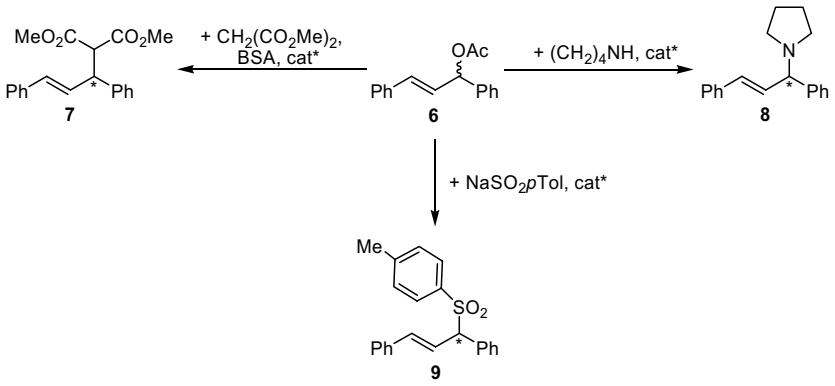
Scheme 3.

It is noteworthy that compound **1** in $CDCl_3$ solution exists exclusively in the imine form, since its ^1H NMR spectrum contains no signals of possible[10] oxazolidine tautomers (see Experimental). *P*,*P*,*N*,*N*-tetradentate iminophosphite **2** and iminodiamidophosphite **3** were synthesized by direct phosphorylation of **1** in benzene (Scheme 2).

Ligands **2** and **3** are stable under dry conditions and are well soluble in common organic solvents. Their ^{31}P NMR spectra ($CDCl_3$) represent narrow symmetric singlets at δ_p 135.1 and 121.4 ppm correspondingly. The proposed structures of **2** and **3** are also in good agreement with the data of ^{13}C NMR data and MS ESI data for **2** (*m*/*z* ($I_{rel.}$ (%)): 985 $[M]^+$ (100), 880 $[M-2,6\text{-}Me_2\text{–}C_6H_4+H]^+$ (16)). Furthermore the synthesis of **3** is highly stereoselective, since only an epimer with a pseudo-equatorial location of the *exo*-cyclic substituents at the phosphorus atoms was formed. Therefore, both *P**-stereogenic centers have an (*R*) absolute configuration, which is proven by the characteristic $^2J_{C,P}$ coupling (38.7 Hz) for the signal of C(8) atom in the ^{13}C NMR spectrum of **3**. The magnitude of $^2J_{C(8),P}$ seems to be strongly controlled by the dihedral angle associated with the lone-pair orbital of the phosphorus atom and C(8).[11,12]

Cationic palladium bis-chelate complexes were obtained with ligands **2** and **3** (Scheme 3).

Their ^{31}P, ^{13}C NMR, and MS ESI spectral data are in a good agreement with the suggested structures (see Experimental). Several peaks in the ^{31}P NMR spectra of complexes **4** and **5** can be rationalized by the presence of *exo*- and *endo*-isomers for each chelate metalacycle.[11,12] Another notable feature is a significant coordination shift $\Delta\delta_C = \delta_C(\text{complex}) - \delta_C(\text{ligand})$ for the imine carbon atoms in the ^{13}C NMR spectrum of **4** (13.1 and 13.6 ppm). A broad singlet at δ_p 132.7 ppm for the obtained in situ (in $CDCl_3$) complex $[\{Pd(allyl)\}_2(\mathbf{2})]^{2+}2Cl^-$ can be rationalized by fast interconversion of isomers. It is important to note that compounds **2** and **3** do not function as *P*,*P*-bidentate ligands and all attempts to obtain complexes $[Pd(allyl)(L)]^+ X^-$ ($X^- = BF_4^-$, Cl^-) failed. Thus, when the reaction of $[Pd(allyl)Cl]_2$ with 2 equiv of iminophosphite **2** in the presence of 2 equiv of $AgBF_4$ was carried out in $CDCl_3$, only the signals of free ligand **2** and known complex **4** were observed in the ^{31}P NMR spectrum of the reaction mixture. The latter was isolated and found to be identical to the sample of **4** obtained by the alternative method (see above). Similarly, in the ^{31}P NMR spectrum of the reaction mixture $[Pd(allyl)Cl]_2$/2L (L = **2**, in $CDCl_3$)



Scheme 4.

equally intensive singlets of free ligand **2** and complex $[\{Pd(allyl)\}_2(\mathbf{2})]^{2+}2Cl^-$ were found. A long bridge between two phosphorus atoms is likely to be the reason for low *P*,*P*-chelating ability of the ligands.

Ligands **2** and **3** were tested in Pd-catalyzed *C**–*C*, *C**–*N*, and *C**–*S* bond formation reactions (Scheme 4).

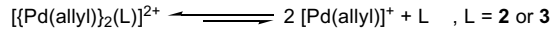
The results achieved in the allylic substitution of **6** by dimethyl malonate are shown in Table 1. Both *P*,*P*,*N*,*N*-tetradentate phosphites **2** and **3** showed high enantioselectivities up to 84% and 90%, respectively. In the case of **2**, CH_2Cl_2 was the solvent of choice, while good asymmetric induction can be reached only with the [Pd(allyl)Cl]$_2$/2L catalytic system (Table 1, entry 4). When P/Pd = 1, enantioselectivity was improved by changing the counterion (Table 1, entries 5 and 6). Conversely, iminodiamidophosphite **3** provided enantiomeric excesses in the range of 71–90%, irrespective of the applied solvent ligand/metal ratio and counterion. Nevertheless, the best result with **3** was also achieved using the [Pd(allyl)Cl]$_2$/2L catalytic system (Table 1, entry 8).

It was apparent that the positive effect of ligand excess was due to the suppression of the complex dissociation (Scheme 5).

Even more distinctions were demonstrated by ligands **2** and **3** in Pd-catalyzed *C**–*N*, and *C**–*S* bond formation

Table 1. Enantioselective allylic alkylation of **6** with dimethyl malonate

Entry	Ligand	Catalyst	Solvent	Conversion of **6** (%)	Ee (%)
1	**2**	[Pd(allyl)Cl]$_2$/L	THF	32	17 (*R*)
2	**2**	[Pd(allyl)Cl]$_2$/2L	THF	40	19 (*S*)
3	**2**	[Pd(allyl)Cl]$_2$/L	CH_2Cl_2	76	46 (*R*)
4	**2**	[Pd(allyl)Cl]$_2$/2L	CH_2Cl_2	65	84 (*R*)
5	**2**	**4**	THF	66	86 (*R*)
6	**2**	**4**	CH_2Cl_2	78	81 (*R*)
7	**3**	[Pd(allyl)Cl]$_2$/L	THF	20	71 (*S*)
8	**3**	**[Pd(allyl)Cl]$_2$/2L**	**THF**	**35**	**90 (*S*)**
9	**3**	[Pd(allyl)Cl]$_2$/L	CH_2Cl_2	28	83 (*S*)
10	**3**	[Pd(allyl)Cl]$_2$/2L	CH_2Cl_2	40	78 (*S*)
11	**3**	**5**	THF	80	83 (*S*)
12	**3**	**5**	CH_2Cl_2	99	67 (*S*)



Scheme 5.

Table 2. Enantioselective allylic amination of **6** with pyrrolidine

Entry	Ligand	Catalyst	Solvent	Yield **8** (%)	Ee (%)
1	**2**	[Pd(allyl)Cl]$_2$/L	THF	65	11 (*R*)
2	**2**	[Pd(allyl)Cl]$_2$/2L	THF	57	15 (*R*)
3	**2**	[Pd(allyl)Cl]$_2$/L	CH_2Cl_2	24	1 (*S*)
4	**2**	[Pd(allyl)Cl]$_2$/2L	CH_2Cl_2	46	1 (*R*)
5	**3**	[Pd(allyl)Cl]$_2$/L	THF	73	81 (*R*)
6	**3**	**[Pd(allyl)Cl]$_2$/2L**	**THF**	**75**	**85 (*R*)**
7	**3**	[Pd(allyl)Cl]$_2$/L	CH_2Cl_2	74	66 (*R*)
8	**3**	[Pd(allyl)Cl]$_2$/2L	CH_2Cl_2	71	64 (*R*)
9	**3**	**5**	THF	95	80 (*R*)

reactions. Thus, allylic amination of **6** with pyrrolidine in the presence of iminophosphite **2** proceeded with low enantioselectivity (Table 2, entries 1–4). At the same time, ligand **3** provided good chemical yields and enantiomeric excesses (up to 85% ee).

In the Pd-catalyzed allylic sulfonylation of 1,3-diphenylallyl acetate **6** with sodium *p*-toluene sulfinate in THF, ligand **2** provided no conversion (L/Pd = 1/2 and 1, precatalyst [Pd(allyl)Cl]$_2$). Under the same conditions, iminodiamidophosphite **3** demonstrated rather good results: [Pd(allyl)Cl]$_2$/L {38% yield, 81% ee (*S*)}, [Pd(allyl)Cl]$_2$/2L {35% yield, 75% ee (*S*)} and **5** {79% yield, 66% ee (*S*)}.

3. Conclusions

Chiral *P*,*P*,*N*,*N*-tetradentate phosphite-type ligands have shown high efficiency in one of the more widely used asymmetric catalytic processes, namely Pd-catalyzed allylic substitution. Iminodiamidophosphite **3** possessing *P*-stereogenic centers has been found to be a superior stereoselector affording up to 85% ee in the amination of 1,3-diphenylallyl acetate with pyrrolidine. This enantioselectivity is close to the best result (88% ee) achieved in the reaction, to date.[13]

4. Experimental

4.1. General

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a Bruker AMX 400 instrument (400.13 MHz for ^{1}H, 100.6 MHz for ^{13}C and 162.0 MHz for ^{31}P). Complete assignment of all the resonances in ^{1}H and ^{13}C NMR spectra was achieved using literature data,[11,12,14] and in the case of ^{13}C NMR also by the use of DEPT techniques. Chemical shifts are given in ppm relative to Me_4Si (^{1}H), internal $CDCl_3$ (76.91 ppm for ^{13}C NMR), and external 85% aqueous H_3PO_4 solution (0 ppm for ^{31}P NMR). Mass spectra were recorded with a Finnigan LCQ Advantage spectrometer (electrospray ionization technique, ESI). Optical rotations were measured on a Perkin–Elmer 341 polarimeter. Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow). Conversion of substrate **6** and enantiomeric excesses of product **7** were determined using HPLC (Daicel Chiralcel OD-H column) according to the literature.[15] Enantiomeric excesses of compound **8** were determined by HPLC (Daicel Chiralcel OD-H column) as described previously.[16] Enantiomeric excesses of product **9** were determined using HPLC ((*R*,*R*)-WHELK-01 column) according to the literature.[11]

All reactions were carried out under a dry argon atmosphere in freshly dried and distilled solvents; Et_3N and pyrrolidine were twice distilled over KOH and then over a small amount of $LiAlH_4$ before use. Ferrocene-1,1′-dicarbaldehyde was prepared as published.[17] Imino alcohol **1** was synthesized according to the published method.[14] Phosphorylating reagents: bis(2,6-dimethylphenyl) chlorophosphite and (2*R*,5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane were prepared according to previously described methods.[18,12] Starting substrate **6** (1,3-diphenylallyl acetate) and complex [Pd(allyl)Cl]$_2$ for catalysis were synthesized as published.[19] Catalytic experiments: allylic alkylation of substrate **6** with dimethyl malonate (Acros Organics) and allylic sulfonylation with sodium *para*-toluene sulfinate were performed according to appropriate procedures.[12]

4.2. (2*S*,3*S*)-2-(1′,1″-Ferrocenylidenamino)-bis-(3-methylpentanol-1) 1

Deep red solid, 1.42 g (97% yield). $[\alpha]_D^{25} = -86.7$ (*c* 0.06, C_6H_6). ^{1}H NMR ($CDCl_3$): δ 0.80 (t, 6H, $^3J_{H,H}$ = 7.2 Hz, CH_3), 0.89 (t, 6H, $^3J_{H,H}$ = 6.4 Hz, CH_3), 0.97 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 1.57 (m, 2H, CH), 3.0 (m, 2H, CHN), 3.78 (m, 2H, CH_2O), 3.88 (m, 2H, CH_2O), 4.19 (m, 2H, H_{Fc}), 4.39 (m, 2H, H_{Fc}), 4.59 (m, 2H, H_{Fc}), 4.77 (m, 2H, H_{Fc}), 5.62 (br s, 2H, OH), 8.14 (s, 2H, CH=). ^{13}C NMR ($CDCl_3$): δ 10.6 (s, CH_3), 15.0 (s, CH_3), 25.6 (s, CH_2), 36.7 (s, CH), 62.2 (s, CH_2O), 70.1, 71.4, 71.9, 72.2 (all s, C_{Fc}), 78.6 (s, $C_{Fc(ipso)}$), 78.9 (s, CHN), 162.8 (s, CH=). MS (ESI), *m*/*z* (I, %): 441 (100) $[M+H]^+$, 342 (6), 139 (14). Anal. Calcd for $C_{24}H_{36}FeN_2O_2$: C, 65.45; H, 8.24; N, 6.36. Found: C, 65.57; H, 8.31; N, 6.22.

4.3. Preparation of ligands

4.3.1. General technique. In 25 ml of benzene, the appropriate phosphorylating reagent (3.4×10^{-3} mol) and Et_3N (0.5 ml, 3.4×10^{-3} mol) were dissolved. Then, with vigorous stirring and while being cooled down to 0 °C, imino alcohol **1** (0.75 g, 1.7×10^{-3} mol) was added. The resulting mixture was stirred for 10 min at 0 °C, and then heated to boiling point, then allowed to cool down to 20 °C, after which Et_3N·HCl was filtered off. The solvent was removed in vacuum (40 Torr), and the residue was concentrated and dried in vacuum (1 Torr, 2 h).

4.3.2. (2*S*,3*S*)-2-(1′,1″-Ferrocenylidenamino)-bis-[(3-methylpentyloxy)-bi-(2‴,6‴-dimethylphenyl)phosphite] 2. Deep red oil, 1.54 g (92% yield). $[\alpha]_D^{25} = -73.4$ (*c* 0.06, C_6H_6). ^{13}C NMR ($CDCl_3$): δ 10.9 (s, CH_3), 15.7 (s, CH_3), 17.5, 17.6 (both s, CH_{3Ar}), 25.3 (s, CH_2), 36.3 (s, CH), 63.6 (s, CH_2O), 69.1, 69.5, 71.3, 71.5 (all s, C_{Fc}), 76.4 (s, CHN), 81.3 (s, $C_{Fc(ipso)}$), 123.8–148.9 (C_{Ar}), 160.5 (s, CH=). Anal. Calcd for $C_{56}H_{70}FeN_2O_6P_2$: C, 68.29; H, 7.16; N, 2.84. Found: C, 68.42; H, 7.30; N, 2.76.

4.3.3. (2*R*,5*S*,2′*S*,3′*S*)-2′-(1″,1‴-Ferrocenylidenamino)-bis-{2-(3′-methyl pentyloxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane} 3. Deep red solid, 1.37 g (95% yield). $[\alpha]_D^{25} = -201.9$ (*c* 0.06, C_6H_6). ^{13}C ($CDCl_3$): δ 10.9 (s, CH_3), 15.8 (s, CH_3), 24.9 (s, CH_2), 25.9 (s, C(7)), 31.9 (s, C(6)), 36.1 (s, CH), 48.4 (d, $^2J_{C,P}$ = 38.7 Hz, C(8)), 54.8 (d, $^2J_{C,P}$ = 6.0 Hz, C(4)), 63.0 (d, $^2J_{C,P}$ = 8.8 Hz, C(5)), 63.4 (d, $^2J_{C,P}$ = 5.6 Hz, CH_2O), 69.2, 69.3, 71.2, 71.3 (all s, C_{Fc}), 76.3 (s, CHN), 81.4 (s, $C_{Fc(ipso)}$), 112.8–145.6 (C_{Ar}), 160.1 (s, CH=). Anal. Calcd for $C_{46}H_{62}FeN_6O_2P_2$: C, 65.09; H, 7.36; N, 9.90. Found: C, 65.18; H, 7.39; N, 10.52.

4.4. Preparation of complexes

4.4.1. General technique. A solution of the corresponding ligand (2×10^{-4} mol) in 15 ml of CH_2Cl_2 was added dropwise to a stirred solution of [Pd(allyl)Cl]$_2$ (0.073 g, 2×10^{-4} mol) in 15 ml of the same solvent at 20 °C. The reaction mixture was stirred at 20 °C for 1 h. Then, $AgBF_4$ (0.078 g, 4×10^{-4} mol) in 10 ml of THF was added, the reaction mixture stirred at 20 °C for 0.5 h and filtered. The solvents were then removed in vacuum (40 Torr) and the solid washed up with ether (2×10 ml) and dried in vacuum (1 Torr, 1 h).

4.4.2. [{Pd(allyl)}$_2$(2)]$^{2+}$2BF$_4^-$ 4. Red solid, 0.26 g (91% yield). Mp 162–164 °C (dec). ^{31}P ($CDCl_3$): δ 120.9 (s, 20%), 121.1 (s, 17%), 121.8 (s, 42%), 121.7 (s, 21%). ^{13}C NMR ($CDCl_3$): δ 10.5, 10.6 (both s, CH_3), 13.3, 13.6 (both s, CH_3), 17.4, 17.5, 18.0, 18.1 (all s, CH_{3Ar}), 25.1, 25.4 (both s, CH_2), 37.2, 37.6 (both s, CH), 53.4, 55.8 (both s, $CH_{2(allyl)}$, *trans*-N), 70.9, 71.3 (both s, CH_2O), 68.2–74.2 (all s, C_{Fc}), 75.4, 75.5 (both s, CHN), 79.0, 79.7 (both s, $C_{Fc(ipso)}$), 81.5 (br d, $^2J_{C,P}$ 41.7 Hz, $CH_{2(allyl)}$, *trans*-P), 125.8, 126.1 (both d, $^2J_{C,P}$ = 5.3 and 4.9 Hz, $CH_{(allyl)}$), 122.3–148.7 (C_{Ar}), 173.6, 174.1 (both s, CH=). MS (ESI), *m*/*z* (I, %): 640

(22) $[M-2BF_4]^{2+}$, 1132 (19) $[M-2BF_4-Pd(allyl)]^+$, 612 (100). Anal. Calcd for $C_{62}H_{80}B_2F_8FeN_2O_6P_2Pd_2$: C, 51.23; H, 5.55; N, 1.93. Found: C, 51.45; H, 5.71; N, 2.09.

4.4.3. $[\{Pd(allyl)\}_2(3)]^{2+}$ $2BF_4^-$ 5. Brick-red solid, 0.25 g (94% yield). Mp 149–151 °C (dec). ^{31}P ($CDCl_3$): δ 121.6 (s, 24%), 121.7 (br s, 50%), 121.8 (s, 26%). MS (ESI), *m/z* (I, %): 572 (100) $[M-2BF_4]^{2+}$, 1231 (7) $[M-BF_4]^+$. Anal. Calcd for $C_{52}H_{72}B_2F_8FeN_6O_2P_2Pd_2$: C, 47.41; H, 5.51; N, 6.38. Found: C, 47.64; H, 5.76; N, 6.61.

4.5. Pd-catalyzed allylic amination of 1,3-diphenyl acetate with pyrrolidine

4.5.1. General procedure. A solution of $[Pd(allyl)Cl]_2$, (3.7×10^{-3} g, 1×10^{-5} mol) and the appropriate ligand (1×10^{-5} mol -2×10^{-5} mol) in 5 ml of the appropriate solvent was stirred for 40 min. Then 1,3-diphenylallyl acetate (0.1 ml, 5×10^{-4} mol) was added and the solution stirred for 15 min, then freshly distilled pyrrolidine (0.12 ml, 1.5 mol) was added and the reaction mixture stirred for 48 h. After that, a resulting solution was filtered through Celite. The solvent was removed in vacuum (40 Torr), and the residue concentrated and dried in vacuum (10 Torr, 12 h) to obtain ((*E*)-1,3-diphenylallyl)pyrrolidine **8** as a cream crystalline solid. All spectroscopic data of compound **8** are in good agreement with the published data.[16]

Acknowledgements

The authors thank Dr. A. V. Korostylev (Leibniz-Institut für Organische Katalyse an der Universitat Rostock, Germany) for his assistance in the preparation of the manuscript. The authors gratefully acknowledge receiving the chiral HPLC columns (*R*,*R*) WHELK-01 from Regis Technologies (U.S.A.) and Chiralcel OD-H from Daicel Chemical Industries, Ltd. (Japan). This work was partially supported by the Russian Foundation for Basic Research (Grant No. 03-03-32181) and Grant of the President of RF for young scientists—doctors of sciences (No. MD—21.2003.03).

References

1. *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley: New York, 2000, p 864.
2. *Comprehensive Asymmetric Catalysis: Supplement 2*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 2004, p 136.
3. Zhang, W.; Hirao, T.; Ikeda, I. *Tetrahedron Lett.* **1996**, *37*, 4545–4548.
4. Gomez, M.; Jansat, S.; Muller, G.; Panyella, D.; van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Goubitz, K.; Fraanjie, J. *Organometallics* **1999**, *18*, 4970–4981.
5. Zhang, A.; Feng, Y.; Jiang, B. *Tetrahedron: Asymmetry* **2000**, *11*, 3123–3130.
6. Zhang, A.; Jiang, B. *Tetrahedron Lett.* **2001**, *42*, 1761–1763.
7. Karshtedt, D.; Bell, A. T.; Tilley, T. D. *Organometallics* **2003**, *22*, 2855–2861.
8. Guiry, P. J.; Saunders, C. P. *Adv. Synth. Catal.* **2004**, *346*, 497–537, and references therein.
9. Gavrilov, K. N.; Bondarev, O. G.; Polosukhin, A. I. *Russ. Chem. Rev.* **2004**, *73*, 671–699, and references therein.
10. Miao, C. K.; Sorcek, R.; Jones, P.-J. *Tetrahedron Lett.* **1993**, *34*, 2259–2262.
11. Gavrilov, K. N.; Bondarev, O. G.; Tsarev, V. N.; Shyriaev, A. A.; Lyubimov, S. E.; Kucherenko, A. S.; Davankov, V. A. *Russ. Chem. Bull.* **2003**, *52*, 122–125.
12. Tsarev, V. N.; Lyubimov, S. E.; Shiryaev, A. A.; Zheglov, S. V.; Bondarev, O. G.; Davankov, V. A.; Kabro, A. A.; Moiseev, S. K.; Kalinin, V. N.; Gavrilov, K. N. *Eur. J. Org. Chem.* **2004**, *10*, 2214–2222.
13. Breeden, S.; Wills, M. *J. Org. Chem.* **1999**, *64*, 9735–9738.
14. Gavrilov, K. N.; Bondarev, O. G.; Lebedev, R. V.; Shiryaev, A. A.; Lyubimov, S. E.; Polosukhin, A. I.; Grintselev-Knyazev, G. V.; Lyssenko, K. A.; Moiseev, S. K.; Ikonnikov, N. S.; Kalinin, V. N.; Davankov, V. A.; Korostylev, A. V.; Gais, H.-J. *Eur. J. Inorg. Chem.* **2002**, *6*, 1367–1376.
15. Kodama, H.; Taiji, T.; Ohta, T.; Furukawa, I. *Tetrahedron: Asymmetry* **2000**, *11*, 4009–4015.
16. Smyth, D.; Tye, H.; Eldred, C.; Alcock, N. W.; Wills, M. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2840–2849.
17. Balavoine, G. G. A.; Doisneau, G.; Fillebeen-Khan, T. *J. Organomet. Chem.* **1991**, *412*, 381–382.
18. Polosukhin, A. I.; Bondarev, O. G.; Lyubimov, S. E.; Korostylev, A. V.; Lyssenko, K. A.; Davankov, V. A.; Gavrilov, K. N. *Tetrahedron: Asymmetry* **2001**, *12*, 2197–2204.
19. Auburn, P. R.; McKenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033–2046.