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New amino-, imino- and oxazolinophosphites based on 1,1′-bi-2-naphtol: coordination and catalytic properties

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Abstract

A series of the new chiral BINOL-based phosphite *P*,*N*-hybrid ligands was prepared. The coordination behavior of all the ligands was studied and the neutral complexes [Rh(CO)Cl(P^N)] were synthesized in order to characterize a degree of the electronic non-symmetry of donating centers. Also the neutral and cationic complexes *cis*-[$PdCl_2(\eta^2$-P^N=)], *cis*-[$PdCl_2(\eta^1$-P^N=)$_2$], *cis*-[$PdCl(\eta^2$-P^N=)(η^1-P^N=)]$^+Cl^-$, [Pd(allyl)(η^2-P^N=)]$^+X^-$ ($X^- = Cl^-$, BF_4^-) were obtained and characterized. The new *P*,*N*-hydrid ligands gave up to 81% ee in the enantioselective Pd-catalyzed alkylation of 3-penten-2-yl carbonate by dimethyl malonate and up to 60% ee in the Rh-catalyzed hydrosilylation of acetophenone and acetylferrocene by diphenylsilane. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *P*,*N*-ligands; Phosphites; Rhodium complexes; Palladium complexes; Pd-catalyzed allylation; Rh-catalyzed hydrosilylation

1. Introduction

In the last 10 years (*R*)- and (*S*)-1,1′-bi-2-naphtol (BINOL) proved to be useful building blocks in the synthesis of chiral phosphite ligands. *P*-mono-, *P*,*P*-bidentate phosphites and *P*,*P*-bidentate phosphinophosphites derived from BINOL were successfully used in the enantioselective catalysis [1–9]. Far less frequently hetero-bifunctional systems, i.e. systems possessing another donor atom (e.g. O, S or N) besides the phosphorus atom have been employed, although the *P*,*O*-ligands were found to give 70–71% ee in the Cu-catalyzed addition of diethylzinc to chalcone [10], and the *P*,*S*-bidentate phosphites gave up to 81% ee in the Pd-, Rh- and Ir-catalysed allylic alkylation reactions [11].

A notable series of the *P*,*N*-bidentate phosphite-oxazolines (**1**) was successfully applied in the Pd-catalyzed allylic alkylation (up to 96% ee) and Cu-catalyzed 1,4-addition of diethylzinc to cyclic enones (up to 96% ee) [9,12,13].

Finally, synthesis and application of the four chiral BINOL based phosphites **2a**–**d** in the Cu-catalyzed conjugate addition of Et_2Zn to 2-cyclohexene-1-one (up to 51% ee) and in the Pd-catalyzed substitution of 1,3-diphenyl-1,2-propenyl acetate by dimethyl malonate (up to 37% ee) were recently reported [14–17].

The present paper aims at obtaining novel *P*,*N*-bidentate phosphite derivatives of BINOL bearing amino, imino and oxazoline functionalities and at studying of their complexation and catalytic properties.

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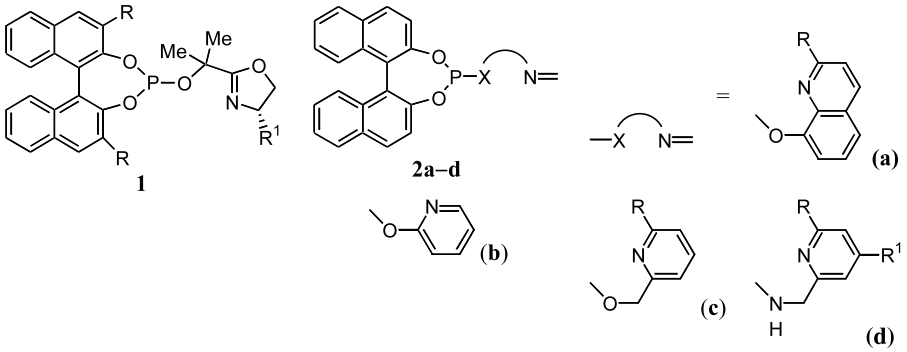


2. Experimental

2.1. General comments

All reactions were performed under Ar in dehydrated solvents.

IR spectra were recorded on a Specord M80 or Nicolet 750 instrument. ^{31}P-, ^{13}C-, ^{1}H-, ^{11}B-, ^{19}F-NMR spectra were recorded on a Bruker AMX-400 instrument (162.0 MHz for ^{31}P; 100.6 MHz for ^{13}C, 400.13 MHz for ^{1}H, 128.34 MHz for ^{11}B, 376.31 MHz for ^{19}F). The complete assignment of all the resonances in ^{13}C-NMR spectra was achieved using DEPT techniques. Chemical shifts (ppm) are given relative to Me_4Si (^{1}H- and ^{13}C-NMR), 85% H_3PO_4 (^{31}P-NMR), $BF_3 \cdot Et_2O$ (^{11}B-NMR), CF_3COOH (^{19}F-NMR). Mass spectra were recorded on a Kratos MS 890 spectrometer (EI), MSVKh TOF spectrometer with ionization by californium-252 fission fragments (plasma desorption technique). Electrospray mass spectra (ES MS) were measured on a Micromass BioQ II-ZS mass spectrometer. Organometallic compound solutions at 5–10 pmol μl^{-1} in THF or MeCN were infused via a Harvard Apparatus Model 11 syringe pump at 5 $\mu l\ min^{-1}$. Spectra were recorded over a mass range of 200–1200 Da and were calibrated relative to a mixed PEG standard. Sedimentation analyses were performed on a MOM-3180 analytical ultracentrifuge according to published techniques [18,19]. Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow).

$[Rh(CO)_2Cl]_2$ [20], $[PdCl_2(COD)]$ [21], $[PdCl(allyl)]_2$ [22], $[PdCl_2(CH_3CN)_2]$ [23], amino- and iminoalcohols **4c** [24], **4d** [25], **4f** [26], **4h** [27], **4k** [28], **4l** [29], **4m** [30] and chlorophosphite **3** [31] were synthesized according to the known procedures. Compounds **4a** (Fluka), **4b** (Aldrich), **4e** (Aldrich), **4n** (Fluka), *rac*-, (*R*)- and (*S*)-BINOL (Fluka) were commercially available. Amino- and iminoalcohols **4g** (quincoridine, Buchler GmbH), **4c**, **4e**–**f**, **4h**–**i**, **4k** were azeotropically dried with C_6H_6 and distilled before use. Compounds **4a**–**b**, **4d**, **4j**, **4l**–**n** and BINOL were dried in vacuum (2 mmHg, 3 h) immediately before use.

Iminoalcohols **4i**, **4j** were synthesized analogously to the known procedures [32].

2.1.1. (2S,3S)-2-[(4-Dimethylamino-benzylidene)-amino]-3-methyl-pentan-1-ol (**4i**)

Yellow viscous oil, 63% yield. $[n]_D^{20} = 1.4411°$. B.p. 165–167 °C (0.8 mmHg, Kugelrohr distillation). ^{13}C-NMR ($CDCl_3$): δ_C CH_3 10.63, 15.15; CH_2 25.10; CH 36.16; $N(CH_3)_2$ 39.51; CH_2O 63.59; CHN 76.59; CH_{Ar} 110.86, 129.33; C_{Ar} 123.58, 151.33; CH= 161.27. ^{1}H-NMR ($CDCl_3$): δ_H (*J*(H,H), Hz) 8.08 (s, 1H, CH=), 7.57 (d, 2H, ^{3}J 8.8, H_{Ar}), 6.67 (d, 2H, ^{3}J 8.8, H_{Ar}), 3.78 (m, 2H, CH_2O), 3.00 (s, 6H, $N(CH_3)_2$), 2.98 (m, 1H, ^{3}J 8.8, NCH), 2.41 (s, br, 1H, OH), 1.69 (m, 1H, CH_2), 1.46 (m, 1H, CH_2), 1.04 (m, 1H, CH), 0.92 (d, 3H, ^{3}J 6.8, CH_3), 0.83 (t, 3H, ^{3}J 7.6, CH_3). Anal. Calc. for $C_{15}H_{24}N_2O$: C, 72.54; H, 9.74; N, 11.28. Found: C, 72.83; H, 10.02; N, 11.00%.

2.1.2. (2S,3S)-2-[(Ferrocenylidene)-amino]-3-methyl-pentan-1-ol (**4j**)

Orange solid, 81% yield. ^{1}H-NMR ($CDCl_3$): δ_H (*J*(H,H), Hz) 8.06 (s, 1H, CH=), 4.72 (m, 1H, Fc), 4.51 (m, 1H, Fc), 4.37 (m, 1H, Fc), 4.34 (m, 1H, Fc), 4.10 (s, 5H, Fc), 3.82 (m, 2H, CH_2O), 2.94 (m, 1H, ^{3}J 8.8, NCH), 1.65 (m, 1H, CH), 1.24 (m, 1H, CH_2), 0.94 (d, 3H, ^{3}J 6.8, CH_3), 0.88 (t, 3H, ^{3}J 7.6, CH_3). ^{13}C-NMR ($CDCl_3$): δ_C (*J*(C,P), Hz) CH_3 10.76, 15.35; CH_2 25.67; CH 30.03; CH_2O 63.79; C_{Fc} 66.97, 68.69, 69.85, 70.17, 70.32; CHN 77.85; C_{Fc} 79.97; CH= 161.91. Anal. Calc. for $C_{17}H_{23}FeNO$: C, 73.66; H, 4.79; N, 4.47. Found: C, 73.75; H, 5.01; P, 4.18%.

2.2. Preparation of ligands

2.2.1. General technique

A solution of the corresponding alcohol (3.5×10^{-3} mol) and Et_3N (0.36 ml, 3.5×10^{-3} mol) in $C_6H_5CH_3$ (20 ml) was added dropwise at 0 °C to a stirred solution

of chlorophosphite (**3**) (1.227 g, 3.5×10^{-3} mol) in $C_6H_5CH_3$ (15 ml). The reaction mixture was warmed to 60 °C, stirred for 1 h and left at 20 °C overnight. Then the solution was filtered and C_6H_{14} (30 ml) was added to precipitate $NEt_3 \cdot HCl$. The mixture was filtered again, the solvent evaporated in vacuum and the residue dried in high vacuum to give the desired product.

*2.2.2. (1′S,2′R)-2-(1′-Benzyl-3′-dimethylamino-2′-methyl-1′-phenyl-propoxy)dinaphtho[2,1-d:1′,2′-f](1,3,2) dioxaphosphepine (**5a**)*

Yellow solid, 89% yield. ^{31}P-NMR ($CDCl_3$): δ_P 152.03, 151.02. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) CH_3 14.47, 14.92; CH 40.53, 43.97 (^3J 9.5); CH_2Ph 44.87 (^3J 8.0), 45.15 (^3J 9.5); $N(CH_3)_2$ 45.53, 45.69; NCH_2 60.63, 60.42; OCPh 88.28, 88.80; C_{Ar} 121.51–147.84. MS (EI, 70 eV): m/z (I, %) 382 (2), 332 (8), 268 (14), 267 (5), 58 (100). Anal. Calc. for $C_{39}H_{36}NO_3P$: C, 78.37; H, 6.07; P, 5.18. Found: C, 78.42; H, 6.10; P, 5.25%.

*2.2.3. (R^{ax})-**5a***

Yellow solid, 87% yield. ^{31}P-NMR ($CDCl_3$): δ_P 152.03.

*2.2.4. (1′R,2′S)-2-(2′-Dimethylamino-1′-phenyl-propoxy)[2,1-d:1′,2′-f](1,3,2) dioxaphosphepine (**5b**)*

White solid, 94% yield. ^{31}P-NMR ($CDCl_3$): δ_P 147.24; 151.44. ^{13}C-NMR ($CDCl_3$): δ_C CH_3 21.20, 22.74; $N(CH_3)_2$ 41.62; NCH 64.68, 65.75; OCH_2 77.83; C_{Ar} 118.79–153.25. MS (EI, 70 eV): m/z (I, %) 448 (1), 422 (97), 268 (100), 252 (7). Anal. Calc. for $C_{31}H_{28}NO_3P$: C, 75.44; H, 5.72; P, 6.28. Found: C, 75.62; H, 5.51; P, 6.11%.

*2.2.5. (R^{ax})-**5b***

White solid, 93% yield. ^{31}P-NMR ($CDCl_3$): δ_P 151.44.

*2.2.6. (2′R)-2-(2′-Dibenzylamino-3′-methyl-butoxy)dinaphtho[2,1-d:1′,2′-f](1,3,2) dioxaphosphepine (**5c**)*

White solid, 92% yield. ^{31}P-NMR ($CDCl_3$): δ_P 142.01, 142.53. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) CH_3 20.10, 20.92; CH 27.40; NCH_2 54.59; NCH 62.90; OCH_2 63.80; C_{Ar} 121.50–148.98. MS (EI, 70 eV): m/z (I, %) 554 (1), 332 (90), 268 (94), 91 (100). Anal. Calc. for $C_{39}H_{36}NO_3P$: C, 78.37; H, 6.07; P, 5.18. Found: C, 78.53; H, 5.84; P, 5.30%.

*2.2.7. (2′R)-2-[2′-(N-pyrrolidine)butoxy]dinaphtho[2,1-d:1′,2′-f](1,3,2) dioxaphosphepine (**5d**)*

White solid, 84% yield. ^{31}P-NMR ($CDCl_3$): δ_P 142.16, 142.78. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) CH_3 10.36; 10.37; CH_2CH_3 20.61; CH_2 (cycl.) 23.21, 23.30; NCH_2 49.84; OCH_2 63.52 (^2J 3.0), 63.60 (^2J 2.5); NCH 64.65; C_{Ar} 121.67–148.80). MS (EI, 70 eV): m/z (I, %) 457 (2, $[M]^+$), 428 (4), 387 (4), 332 (45), 286 (54), 268 (47), 125 (34). Anal. Calc. for $C_{28}H_{28}NO_3P$: C, 73.51; H, 6.17; P, 6.77. Found: C, 73.76; H, 6.00; P, 6.98%.

*2.2.8. (2′S)-2-[(1′-Methyl-pyrrolidinyl-2′)-methoxy]dinaphtho[2,1-d:1′,2′-f](1,3,2) dioxaphosphepine (**5e**)*

White solid, 89% yield. ^{31}P-NMR ($CDCl_3$): δ_P 140.52, 140.62. ^{13}C-NMR ($CDCl_3$): δ_C –$(CH_2)_2$– 22.41, 22.48, 27.70, 27.78; NCH_3 40.91, 40.95; NCH_2 57.12; NCH 64.97; OCH_2 66.23; C_{Ar} 114.76–153.10. MS (EI, 70 eV): m/z (I, %) 429 (2, $[M]^+$), 332 (74), 286 (100), 97 (21). Anal. Calc. for $C_{26}H_{24}NO_3P$: C, 72.72; H, 5.63; P, 7.21. Found: C, 72.49; H, 5.37; P, 6.96%.

*2.2.9. (2′S)-2-[(1′-Benzyl-pyrrolidinyl-2′)-methoxy]dinaphtho[2,1-d:1′,2′-f](1,3,2) dioxaphosphepine (**5f**)*

White solid, 93% yield. ^{31}P-NMR ($CDCl_3$): δ_P 144.06, 144.72. ^{13}C-NMR ($CDCl_3$): δ_C –$(CH_2)_2$– 22.65, 27.60; CH_2Ph 54.02; NCH_2 59.02; NCH 63.16; OCH_2 66.89; C_{Ar} 121–148.35. MS (EI, 70 eV): m/z (I, %) 505 (14, $[M]^+$), 414 (32), 332 (38), 268 (100), 174 (70). Anal. Calc. for $C_{32}H_{28}NO_3P$: C, 76.03; H, 5.58; P, 6.13. Found: C, 75.84; H, 5.29; P, 6.25%.

*2.2.10. (2′R,4′S,5′R)-2-[(5′-Vinylquinuclidyl-2′)methoxy]dinaphtho[2,1-d:1′,2′-f](1,3,2) dioxaphosphepine (**5g**)*

White solid, 85% yield. ^{31}P-NMR ($CDCl_3$): δ_P 142.36, 142.43. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) CHCH$_2$CH 22.91, 23.12; CH_2CH_2CH 26.07, 26.19; CH_2CHCH_2 27.14, 27.25; CHCHCH= 39.13, 39.29; NCH$_2$CH 46.92, 46.98; NCH$_2$CH$_2$ 48.47, 48.57; CHN 55.54, 55.60 (^3J 2.9); OCH_2 64.97 (^2J 3.5), 65.19 (^2J 2.4); CH_2= 114.15, 114.21; CH= 139.67, 139.87; C_{Ar} 121.46–148.40. MS (EI, 70 eV): m/z (I, %) 332 (35), 286 (100), 268 (37), 167 (10). Anal. Calc. for $C_{30}H_{28}NO_3P$: C, 74.83, H, 5.86; P, 6.43. Found: C, 74.56; H, 5.99; P, 6.66%.

*2.2.11. (2′R,S^{ax})-2-{2′-[(4-Dimethylamino-benzylidene)-amino]-3′-methyl-butoxy}dinaphtho[2,1-d:1′,2′-f](1,3,2) dioxaphosphepine ((S^{ax})-**5h**)*

White solid, 94% yield. ^{31}P-NMR ($CDCl_3$): δ_P 145.01. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) CH_3 18.73, 19.69, CH 29.84; $N(CH_3)_2$ 40.06; OCH_2 67.24 (^2J 8.0); NCH 76.73 (^3J 4.1); C_{Ar} 111.42–151.83; CH=N 161.47. MS (EI, 70 eV): m/z (I, %) 748 (100), 415 (3), 332 (89), 315 (7), 286 (57), 268 (97), 252 (7), 216 (7), 203 (33). Anal. Calc. for $C_{34}H_{33}N_2O_3P$: C, 74.44; H, 6.06; P, 5.65. Found: C, 74.22; H, 6.18; P, 5.96%.

*2.2.12. (R^{ax})-**5h***

White solid, 95% yield. ^{31}P-NMR ($CDCl_3$): δ_P 147.85.

*2.2.13. (2′S,3′S)-2-{2′-[(4-Dimethylamino-benzylidene)-amino]-3′-methyl-pentyloxy}-dinaphtho[2,1-d:1′,2′-f](1,3,2) dioxaphosphepine (**5i**)*

White solid, 92% yield. ^{31}P-NMR ($CDCl_3$): δ_P 144.84, 147.42. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) CH_3 10.87, 10.94, 15.53, 15.59; CH_2 25.23, 25.30; CH 36.39, 36.42; $N(CH_3)_2$ 40.06, 40.12; OCH_2 67.07 (^2J 7.8), 67.17 (^2J 10.0); NCH 75.78 (^3J 4.2), 75.92 (^3J 2.2); C_{Ar} 111.43–151.93; CH=N 161.43, 161.86. MS (EI, 70 eV): m/z (I, %) 561 (1, $[M-H]^+$), 748 (100), 332 (92), 315 (10), 286 (9), 268 (92), 252 (12), 231 (7), 217 (22), 161 (19), 147 (71). Anal. Calc. for $C_{35}H_{35}N_2O_3P$: C, 74.72; H, 6.27; P, 5.50. Found: C, 74.86; H, 6.11; P, 5.27%.

*2.2.14. (R^{ax})-**5i***

White solid, 91% yield. ^{31}P-NMR (C_6D_6): δ_P 143.94.

*2.2.15. (S^{ax})-**5i***

White solid, 94% yield. ^{31}P-NMR (C_6D_6): δ_P 144.82.

*2.2.16. (2′S,3′S,R^{ax})-2-{2′-[(Ferrocenylidene)-amino]-3′-methyl-pentyloxy}dinaphtho[2,1-d:1′,2′-f](1,3,2) dioxaphosphepine ((R^{ax})-**5j**)*

Red solid, 88% yield. ^{31}P-NMR (C_6D_6): δ_P 141.36. ^{13}C-NMR (C_6D_6): δ_C (J(C,P), Hz) CH_3 11.40, 15.92; CH_2 25.55; CH 36.71; CH_2O 67.16; C_{Fc} 68.75, 69.16, 69.31, 70.30, 70.40; CHN 76.54 (^3J 3.0); $C_{Fc(ipso)}$ 81.41; C_{Ar} 122.08–149.65, CH= 161.16. MS (EI, 70 eV): m/z (I, %) 627 (4, $[M]^+$), 543 (100), 478 (85), 332 (39), 268 (95). Anal. Calc. for $C_{37}H_{34}FeNO_3P$: C, 70.82; H, 5.46; P, 4.94. Found: C, 71.08; H, 5.64; P, 5.14%.

*2.2.17. (S^{ax})-**5j***

Red solid, 87% yield. ^{31}P-NMR (C_6D_6): δ_P 135.91.

*2.2.18. (αR)-2-{2′-[Methyl(α-phenylethyl)-imino]phenoxy}dinaphtho[2,1-d:1′,2′-f](1,3,2) dioxaphosphepine (**5k**)*

White solid, 80% yield. ^{31}P-NMR ($CDCl_3$): δ_P 144.94, 145.12. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) CH_3 24.61, 24.92; NCH 69.69, 69.75; C_{Ar} 116.80–151.10; CH=N 154.72, 154.79. MS (EI, 70 eV): m/z (I, %) 438 (18), 332 (22), 268 (28), 252 (5), 105 (100). Anal. Calc. for $C_{35}H_{26}NO_3P$: C, 77.91; H, 4.86; P, 5.74. Found: C, 78.20; H, 4.51; P, 5.99%.

*2.2.19. (S^{ax})-2-{2′-[(Benzylidene)-amino]phenoxy}dinaphtho[2,1-d:1′,2′-f](1,3,2) dioxaphosphepine ((S^{ax})-**5l**)*

Yellow solid, 92% yield. ^{31}P-NMR ($CDCl_3$): δ_P 145.34. ^{13}C-NMR ($CDCl_3$): δ_C C_{Ar} 114.59–147.80, CH= 160.21. MS (EI, 70 eV): m/z (I, %) 511 (81, $[M]^+$), 434 (32), 268 (100), 196 (85). Anal. Calc. for $C_{33}H_{22}NO_3P$: C, 77.49; H, 4.34; P, 6.06. Found: C, 77.27; H, 4.52; P, 6.38%.

*2.2.20. 2-{2′-[(Ferrocenylidene)-amino]-phenoxy}dinaphtho[2,1-d:1′,2′-f](1,3,2) dioxaphosphepine (**5m**)*

Red solid, 90% yield. ^{31}P-NMR (C_6D_6): δ_P 143.72. ^{13}C-NMR ($CDCl_3$): δ_C C_{Fc} 69.12, 69.42, 69.66, 71.36, 71.50; $C_{Fc(ipso)}$ 80.23, C_{Ar} 118.06–148.05; CH= 160.62. MS (EI, 70 eV): m/z (I, %) 619 (41, $[M]^+$), 305 (100), 268 (37), 240 (66). Anal. Calc. for $C_{37}H_{26}FeNO_3P$: C, 71.74; H, 4.23; P, 5.00. Found: C, 71.95; H, 4.53; P, 4.77%.

*2.2.21. (4′S,5′S)-2-[(2′-Methyl-5′-phenyl-2′-oxazolino-4′)methoxy]dinaphtho[2,1-d:1′,2′-f](1,3,2) dioxaphosphepine (**5n**)*

White solid, 90% yield. ^{31}P-NMR ($CDCl_3$): δ_P 139.18, 141.61. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) CH_3 13.95; OCH_2 65.33, 65.92 (^2J 4.5); NCH 74.52 (^3J 2.4), 74.62 (^3J 2.0); OCH_2(Ph) 82.67, 82.86; C_{Ar} 121.24–148.45; C=N 165.89, 166.04. MS (EI, 70 eV): m/z (I, %) 505 (9, $[M]^+$), 332 (45), 315 (6), 286 (4), 268 (98), 252 (5), 174 (2). Anal. Calc. for $C_{31}H_{24}NO_4P$: C, 73.66; H, 4.79; P, 6.13. Found: C, 73.44; H, 4.92; P, 6.07%.

*2.2.22. (R^{ax})-**5n***

White solid, 88% yield. ^{31}P-NMR (C_6D_6): δ_P 142.34.

*2.2.23. (S^{ax})-**5n***

White solid, 90% yield. ^{31}P-NMR (C_6D_6): δ_P 139.49.

2.3. Preparation of Rh complexes

*2.3.1. General technique for complexes **6a–b**, **6d–i**, **6k–l**, **6n***

A solution of the corresponding ligand (3.6×10^{-4} mol) in CH_2Cl_2 (20 ml) was added dropwise to a stirred solution of $[Rh(CO)_2Cl]_2$ (0.070 g, 1.8×10^{-4} mol) in the same solvent (20 ml) at 20 °C. The reaction mixture was stirred at 20 °C for 0.5 h. The excess of the solvent was then removed in vacuum (40 mmHg), and 10 ml of C_6H_{14} was added to the residue. The precipitate obtained was separated by centrifugation, washed up with C_6H_{14} (2 × 10 ml) and dried in vacuum (2 mmHg).

*2.3.2. Complex **6a***

Yellow solid, 82% yield. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) CH_3 19.07, 19.38; CH 43.34 (^3J 10.3), 44.67 (^3J 9.9); CH_2Ph 45.85, 45.98; $N(CH_3)_2$ 47.22, 48.76, 51.16, 51.43; NCH_2 69.15, 69.54; OCPh 91.69 (^2J 8.1), 92.89 (^2J 5.4); C_{Ar} 121.05–148.60. Anal. Calc. for $C_{40}H_{36}ClNO_4PRh$: C, 62.88; H, 4.75; P, 4.05. Found: C, 63.14; H, 4.86; P, 3.81%.

*2.3.3. Complex **6b***

Yellow solid, 90% yield. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) CH_3 13.89, 22.38; $N(CH_3)_2$ 46.46, 48.45, 48.46, 49.29; NCH 71.48, 72.12; OCH_2 76.73 (^2J 4.5),

77.48 (^2J 9.2); C_{Ar} 120.52–147.78. Anal. Calc. for $C_{32}H_{28}ClNO_4PRh$: C, 58.24; H, 4.28; P, 4.69. Found: C, 58.07; H, 4.57; P, 4.79%.

2.3.4. Complex **6d**

Yellow solid, 96% yield. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) CH_3 10.29, 10.64; CH_2CH_3 22.48; CH_2 (cycl.) 23.48, 24.01, 24.99; NCH_2 59.32, 60.28; OCH_2 65.59; NCH 71.88; C_{Ar} 120.98–148.82. Anal. Calc. for $C_{29}H_{28}ClNO_4PRh$: C, 55.83; H, 4.52; P, 4.96. Found: C, 55.67; H, 4.64; P, 4.75%.

2.3.5. Complex **6e**

Yellow solid, 93% yield. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) $-(CH_2)_2-$ 20.30, 21.61, 24.32; NCH_3 45.61, 46.03; NCH_2 59.25, 60.89; NCH 64.00 (^3J 4.9); OCH_2 69.50, 69.63; C_{Ar} 113.92–152.70. Anal. Calc. for $C_{27}H_{24}ClNO_4PRh$: C, 54.43; H, 4.06; P, 5.20. Found: C, 54.71; H, 3.89; P, 5.03%.

2.3.6. Complex **6f**

Yellow solid, 95% yield. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) $-(CH_2)_2-$ 21.09, 22.54, 23.53, 24.58; CH_2Ph 57.80, 59.72; NCH_2 60.75, 63.17; NCH 63.52 (^3J 3.4), 64.78 (^3J 5.5); OCH_2 65.88 (^2J 8.0), 67.04 (^2J 6.3); C_{Ar} 120.73–147.31. Anal. Calc. for $C_{33}H_{28}ClNO_4PRh$: C, 58.99; H, 4.20; P, 4.61. Found: C, 59.21; H, 4.43; P, 4.34%.

2.3.7. Complex **6g**

Yellow solid, 87% yield. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) $CHCH_2CH$ 22.84; CH_2CH_2CH 25.56, 26.37; CH_2CHCH_2 26.34, 26.37; $CHCHCH=$ 38.57; NCH_2CH 48.49, 48.57; NCH_2CH_2 50.69, 51.23; CHN 60.96 (^3J 5.4), 62.30; OCH_2 66.14 (^2J 3.6), 66.66; $CH_2=$ 115.88, 115.92; $CH=$ 137.29; C_{Ar} 120.89–147.55. Anal. Calc. for $C_{31}H_{28}ClNO_4PRh$: C, 57.47; H, 4.36; P, 4.78. Found: C, 57.81; H, 4.46; P, 4.44%.

2.3.8. Complex (S^{ax})-**6h**

Yellow solid, 92% yield. ^{13}C-NMR ($CDCl_3$): δ_C CH_3 18.13, 19.88; CH 31.34; $N(CH_3)_2$ 39.28; OCH_2 70.24; NCH 78.00; C_{Ar} 110.18–153.17; CH=N 170.41. Anal. Calc. for $C_{35}H_{33}ClN_2O_4PRh$: C, 58.80; H, 4.65; P, 4.33. Found: C, 58.63; H, 4.27; P, 4.63%.

2.3.9. Complex **6i**

Yellow solid, 89% yield. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) CH_3 10.36, 10.51, 14.18, 14.28; CH_2 25.37, 25.50; CH 37.56; $N(CH_3)_2$ 39.71, 40.00; OCH_2 69.41 (^2J 3.1), 70.52; NCH 76.43, 77.24; C_{Ar} 110.63–153.68; CH=N 170.74, 171.10. Anal. Calc. for $C_{36}H_{35}ClN_2O_4PRh$: C, 59.31; H, 4.84; P, 4.25. Found: C, 59.36; H, 4.98; P, 4.02%.

2.3.10. Complex **6k**

Yellow solid, 98% yield. ^{13}C-NMR (Me_2SO-d_6): δ_C (J(C,P), Hz) CH_3 22.25, 22.31; NCH 67.44, 67.77; C_{Ar} 114.83–152.92; CH=N 163.17, 163.77. Anal. Calc. for $C_{36}H_{26}ClNO_4PRh$: C, 61.25; H, 3.71; P, 4.39. Found: C, 61.48; H, 3.93; P, 4.01%.

2.3.11. Complex (S^{ax})-**6l**

Yellow solid, 88% yield. Anal. Calc. for $C_{34}H_{22}ClNO_4PRh$: C, 60.24; H, 3.27; P, 4.57. Found: C, 59.95; H, 3.51; P, 4.73%.

2.3.12. Complex (S^{ax})-**6n**

Yellow solid, 91% yield. Anal. Calc. for $C_{32}H_{24}ClNO_5PRh$: C, 57.20; H, 3.60; P, 4.61. Found: C, 57.47; H, 3.83; P, 4.42%.

2.3.13. Complex (R^{ax})-**6n**

Yellow solid, 90% yield.

2.3.14. Preparation of the complexes **6c**, (R^{ax})-**6j**, **6m**, **6n**

Rh complexes with ligands **5c**, (R^{ax})-**5j**, **5m**, **5n** were synthesized for the NMR experiments as follows: a solution of L* (3.6×10^{-4} mol) in $CDCl_3$ (1.5 ml) was added dropwise to a stirred solution of $[Rh(CO)_2Cl]_2$ (0.070 g, 1.8×10^{-4} mol) in the same solvent (1.5 ml). Then, a 1 ml sample of the reaction solution was transferred to a NMR tube and NMR experiment was carried out.

2.4. Preparation of Pd(II) complexes

2.4.1. General technique for complexes (R^{ax})-**7h** and (S^{ax})-**7i**

A solution of the corresponding ligand (2×10^{-4} mol) in CH_2Cl_2 (15 ml) was added dropwise to a stirred solution of $[PdCl_2(CH_3CN)_2]$ (0.052 g, 2×10^{-4} mol) in the same solvent (15 ml) at 20 °C. The reaction mixture was stirred at 20 °C for 1 h. The excess of the solvent was then removed in vacuum (40 mmHg), and 10 ml of C_6H_{14} was added to the residue. The precipitate obtained was separated by centrifugation, washed with ether (2×10 ml) and dried in vacuum (2 mmHg).

2.4.2. Complex (R^{ax})-**7h**

Yellow solid, 93% yield. IR (CsI, Nujol, cm^{-1}): ν(Pd–Cl) 342, 304. Anal. Calc. for $C_{34}H_{33}Cl_2N_2O_3PPd$: C, 56.25; H, 4.58; P, 4.27. Found: C, 56.58; H, 4.62; P, 4.01%.

2.4.3. Complex (S^{ax})-**7i**

Yellow solid, 95% yield. ^{13}C-NMR ($CDCl_3$): δ_C (J(C,P), Hz) CH_3 9.88, 13.46; CH_2 25.24; CH 37.01; $N(CH_3)_2$ 39.77; OCH_2 69.67 (^2J 4.9); NCH 74.47; C_{Ar} 111.05–155.88; CH=N 171.65. IR (CsI, Nujol, cm^{-1}): ν(Pd–Cl) 338, 300. Anal. Calc. for $C_{35}H_{35}Cl_2N_2O_3PPd$:

C, 56.81; H, 4.77; P, 4.19. Found: C, 56.66; H, 5.00; P, 4.04%.

2.4.4. Complex (R^{ax})-8h

Complex (R^{ax})-**8h** was obtained using the mentioned above for compounds **7h** and **7i** technique from (R^{ax})-**5h** (0.219 g, 4×10^{-4} mol) and [$PdCl_2$(COD)] (0.057 g, 2×10^{-4} mol)

Yellow solid, 90% yield. MS (PD): *m*/*z* (*I*, %) 1238 (7, $[PdClL_2]^+$), 1202 (10), 548 (37), 217 (100). Anal. Calc. for $C_{68}H_{66}Cl_2N_4O_6P_2Pd$: C, 64.08; H, 5.22; P, 4.86. Found: C, 63.94; H, 5.48; P, 4.56%.

2.4.5. General technique for complexes (R^{ax})-9h and (S^{ax})-9l

A solution of the corresponding ligand (4×10^{-4} mol) in CH_2Cl_2 (20 ml) was added dropwise to a stirred solution of [Pd(allyl)Cl]$_2$ (0.073 g, 2×10^{-4} mol) in the same solvent (20 ml) at 20 °C. The reaction mixture was stirred at 20 °C for 1 h. The solvent was then removed in vacuum and the solid was washed up with C_6H_{14} (2×10 ml) and dried in vacuum (2 mmHg).

2.4.6. Complex (R^{ax})-9h

Yellow–orange solid, 92% yield. ^{13}C-NMR ($CDCl_3$): δ_C (*J*(C,P), Hz) CH_3 18.48, 18.97; CH 29.15; $N(CH_3)_2$ 39.63; CH_2 (allyl, *trans*-N) 57.00; OCH_2 64.92 (^2J 14.4); NCH 78.42; CH_2 (allyl, *trans*-P) 80.86 (^2J 42.5); CH (allyl) 121.10; C_{Ar} 111.08–153.96; CH=N 168.04. MS (PD): *m*/*z* (*I*, %) 713 (13, $[Pd(allyl)L(H_2O)]^+$), 695 (7, $[Pd(allyl)L]^+$), 654 (10), 548 (30), 217 (100). Anal. Calc. for $C_{37}H_{38}ClN_2O_3PPd$: C, 60.75; H, 5.24; P, 4.23. Found: C, 61.06; H, 5.53; P, 4.16%.

2.4.7. Complex (S^{ax})-9l

Yellow–orange solid, 95% yield. ^{13}C-NMR ($CDCl_3$): δ_C (*J*(C,P), Hz) CH_2 (allyl, *trans*-N) 57.8, 62.11; CH_2 (allyl, *trans*-P) 81.00 (^2J 22.3), 81.47 (^2J 27.6); CH (allyl) 119.00, 120.31; C_{Ar} 111.16–152.45, CH= 162.27, 162.54. MS (PD): *m*/*z* (*I*, %) 658 (72, $[Pd(allyl)L]^+$), 617 (39), 315 (22), 269 (100). Anal. Calc. for $C_{36}H_{27}ClNO_3PPd$: C, 62.26; H, 3.92; P, 4.46. Found: C, 62.13; H, 4.15; P, 4.22%.

2.4.8. Complex (R^{ax})-10j

Complex (R^{ax})-**10j** was obtained using the mentioned above for compounds **9h** and **9l** technique in THF. But, before the evaporation of the reaction mixture, $AgBF_4$ (0.078 g, 4×10^{-4} mol) was added and the solution was filtered

Red solid, 88% yield. ^{13}C-NMR (C_6D_6): δ_C (*J*(C,P), Hz) CH_3 10.68, 16.00; CH_2 25.63; CH 37.00; CH_2 (allyl, *trans*-N) 54.64; C_{Fc} 61.26, 62.00, 62.34, 62.70, 64.39; CH_2O 66.14 (^2J 11.7); $C_{Fc(ipso)}$ 75.61; CHN 77.10 (^3J 3.4); CH_2 (allyl, *trans*-P) 78.82 (^2J 45.9); CH (allyl) 118.00 (^2J 9.1); C_{Ar} 112.07–147.52; CH= 168.20. ^{19}F-NMR ($CDCl_3$): δ_F −73.87. ^{11}B-NMR ($CDCl_3$): δ_B −1.37. MS (PD): *m*/*z* (*I*, %) 774 (52, $[Pd(allyl)L]^+$), 543 (39), 332 (100). Anal. Calc. for $C_{40}H_{39}BF_4FeNO_3PPd$: C, 55.75; H, 4.56; P, 3.59. Found: C, 55.64; H, 4.28; P, 3.88%.

2.4.9. Pd complexes with ligands 5b, (R^{ax})-5h and 5m

Pd complexes with ligands **5b**, (R^{ax})-**5h** and **5m**, were synthesized for the NMR experiments as follows: a solution of L* (10^{-4} or 2×10^{-4} mol) in $CDCl_3$ (1.5 ml) was added dropwise to a stirred solution of [$PdCl_2$(COD)] (0.0285 g, 10^{-4} mol) in the same solvent (1.5 ml). Then a 1 ml sample of the reaction solution was transferred to a NMR tube and NMR experiment was carried out.

2.5. Catalytic experiments

2.5.1. Pd-catalyzed alkylation of 3-penten-2-yl carbonate with dimethyl malonate

[Pd(π-allyl)Cl]$_2$ (3.6 mg, 1×10^{-5} mol) and the ligand **5** (2.2×10^{-5}–8×10^{-5} mol) were dissolved in the corresponding solvent (4 ml) and the mixture was stirred at room temperature (r.t.) for 20 min. Then, 3-penten-2-yl carbonate (160 mg, 1×10^{-3} mol), dimethyl malonate (132 mg, 1.5×10^{-3} mol), BSA (305 mg, 1.5×10^{-3} mol) and KOAc (2.5 mg) were added to the catalyst and the reaction solution was stirred at r.t. for 24 h. The reaction mixture was then poured into saturated aq. NH_4Cl solution and extracted with ether (2×50 ml). The combined organic extracts were washed with aq. $NaHCO_3$ and water dried (Na_2SO_4), filtered and concentrated in vacuum. Purification by flash chromatography (silica gel, petroleum ether–EtOAc 8:1) gave the allylic alkylation product as a colorless oil. The *S* absolute configuration was ascribed to the product based on the (−) sign of its optical rotation [33]. Enantiomeric excess was determined by chiral GC (fused silica capillary column DP-TFA-γ-CD, 90 °C, He, 1.8 bar).

2.5.2. Rh catalyzed hydrosilylation of ketones 12a,b with diphenylsilane

A mixture of [RhCl(COD)]$_2$ (0.004 g, 8.1×10^{-6} mol) or [IrCl(COD)]$_2$ (0.0054 g, 8.1×10^{-6} mol) and the ligand **5** (16.2–64.8×10^{-6} mol) in $C_6H_5CH_3$ (2 ml) was stirred at r.t. for 45 min. Then acetophenone (**12a**) or acetylferrocene (**12b**) was added, the reaction mixture was stirred for 5 min and cooled down to 0 °C. Cold (0 °C) H_2SiPh_2 (0.2 ml, 10.8×10^{-4} mol) was then added neat and the mixture was stirred at 0 °C for 16 h followed by addition of a solution of *para*-toluenesulfonic acid (1 mg) in MeOH (1 ml) (for **12a**). The solution was stirred over 4 h at r.t. and, in the case of **12a**, excess *p*-$CH_3C_6H_4SO_3H$ was neutralized with $NaHCO_3$. The reaction mixture was evaporated. In the case of 1-

ferrocenylethanol (**13b**), the residue was purified as published [34]; purification of 1-phenylethanol (**13a**) was accomplished by Kugelrohr distillation (1 mmHg, 90–95 °C). The enantiomeric composition of the products was finally determined by chiral GC (Chiraldex B-DM, 30 m × 0.25 mm, He, 120 °C, **13a**) or HPLC ((*R*,*R*)-Whelk-01, 250 × 4 mm^2, C_7H_{16}–Pr^{i}OH = 99:1, 1 ml min^{-1}, 254 nm, **13b**).

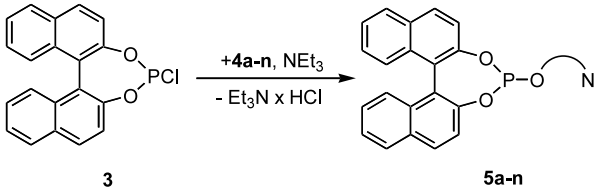
2.6. Calculation of the cone angles θ_R

Cone angles θ_R of the substituents for compounds **5i** and **5j** were determined using published approach [35]. Configurations were taken from the structures obtained by computer calculations using MM2 method.

3. Results and discussion

3.1. Synthesis of the new *P*,*N*-ligands

The new *P*,*N*-hybrid ligands **5a**–**n** were synthesized in 80–95% yields by the one-step phosphorylation of corresponding amino- and imino alcohols:



All the ligands **5a**–**n** are stable in dry conditions for several months and, except **5l** and **5m**, contain C*-stereocenters. The new ligands divide into two groups: possessing sp^3- (**5a**–**g**) or sp^2-nitrogen atoms (**5h**–**n**). The former can bear both acyclic (**5a**–**c**) and cyclic (**5d**–**g**) amino group. The imino groups in the latter ligands are all of acyclic nature (except **5n**, which is a special case), but the structure of the *N*-containing part varies widely. Notably, ligands **5b**–**j** and **5l**–**n** lead to six-membered chelate rings, while **5a** and **5k** can form seven-membered chelates. Therefore, the discussed *P*,*N*-ligands possess the identical phosphorus-containing fragment, but the amino alcohol part varies in the amino group structure, length of the carbon bridge and

Table 1
IR data for compounds **6a**–**n**

Compound	ν(CO) (cm^{-1})		ν(Rh–Cl) (cm^{-1}) (Nujol)
	($CHCl_3$)	(KBr)	
6a	2036	2024	295
6b	2038	2024	302
6c	2025	–	–
6d	2035	2018	300
6e	2038	2017	297
6f	2035	2023	295
6g	2036	2024	294
(S^{ax})-**6h**	2022	2012	298
6i	2026	2011	291
(R^{ax})-**6j**	2030	–	–
6k	2036	2024	292
(S^{ax})-**6l**	2042	2024	298
6m	2038	–	–
(S^{ax})-**6n**	2036	2024	304
(R^{ax})-**6n**	2035, 2020	2024, 2012	306 (br)

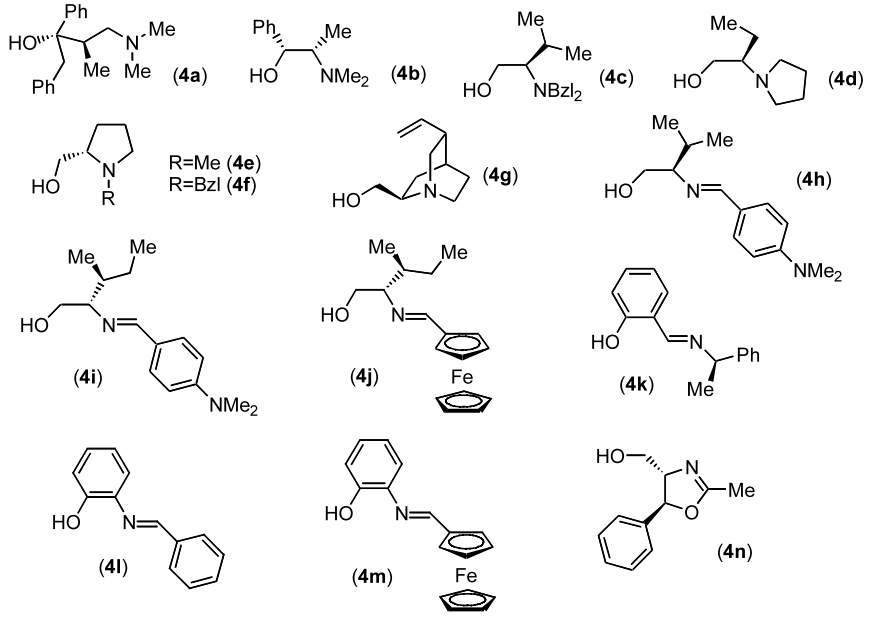


Table 2
^{31}P-NMR data for complexes **6a**–**n** (in $CDCl_3$)

Complex	δ_P (^1J(P,Rh), Hz)
6a	139.42 (310.7), 134.10 (303.0)
6b	146.41 (285.4), 144.22 (285.2)
6c	141.24 (283.8), 141.28 (284.6), 140.35 (286.7), 140.31 (286.2), 140.04 (283.9), 139.99 (285.0)
6d	143.60 (288.5), 140.97 (286.4)
6e	145.41 (286.7), 145.00 (286.1)
6f	146.72 (287.0), 144.83 (287.4)
6g	146.81 (289.2), 145.37 (289.2)
(S^{ax})-**6h**	147.59 (274.7)
6i	147.17 (276.8), 147.05 (276.2)
(R^{ax})-**6j**	145.53 (281.0)
6k [a]	147.80 (287.2), 146.41 (289.9)
(S^{ax})-**6l**	155.33 (283.6), 148.0 (284.6)
6m	153.94 (297.9), 150.30 (290.7), 149.82 (292.1)
(S^{ax})-**6n**	144.67 (275.7)
(R^{ax})-**6n**	150.26 (262.0), 143.00 (276.7)

[a] The data were obtained in DMSO-d_6.

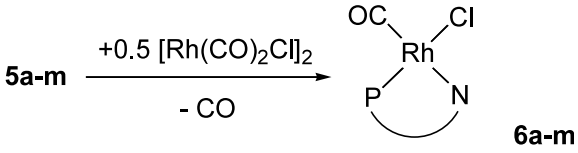
Table 3
^{13}C-NMR data for complexes **6a**–**b**,**d**–**i** (in $CDCl_3$)

Complex	δ_C (^1J(C,Rh) ^2J(C,P), Hz)
6a	184.10 (68.9, 19.1), 183.55 (67.5, 19.5)
6b	184.32 (67.9, 18.3), 183.45 (67.8, 18.5)
6d	183.57 (70.2, 15.1), 182.71 (70.2, 16.4)
6e	184.10 (69.5, 19.7), 183.50 (69.4, 19.5)
6f	184.11 (69.7, 18.9), 183.39 (69.9, 18.8)
6g	184.11 (69.5, 19.3), 183.41 (69.2, 19.5)
(S^{ax})-**6h**	187.91 (70.6, 17.2)
6i	187.79 (69.7, 18.7), 186.10 (71.4, 17.0)

in number and position of C*-chiral centers. Such a variability allows to investigate the influence of the mentioned factors upon complexation and catalytic properties of the novel *P*,*N*-hybride ligands. Most of the discussed compounds were synthesized from the cheap racemic BINOL. That allowed us to develop the methods of synthesis of the ligands and to study their complexation without using expensive chiral BINOL. But for catalytic tests a few ligands were obtained from optically active BINOL. For these compounds an absolute configuration of the BINOL frame (S^{ax} or R^{ax}) is shown (see Section 2).

3.2. Complexation of the new *P*,*N*-hybride ligands with $[Rh(CO)_2Cl]_2$

On the base of **5a**–**m** chelate chlorocarbonyl Rh(I) complexes **6a**–**m** were obtained. ν(CO) frequency in the IR spectra and spin-coupling ^1J(P,Rh) parameters in the ^{31}P-NMR spectra of such Rh(I) complexes are the sensitive indicators, which allow to make a conclusion about electronic properties of the coordinated *P*,*N*-ligands (in particular, about π-acidity of the phosphorus atom and about the degree of electronic non-symmetry of the ligand on the whole [36–38]).



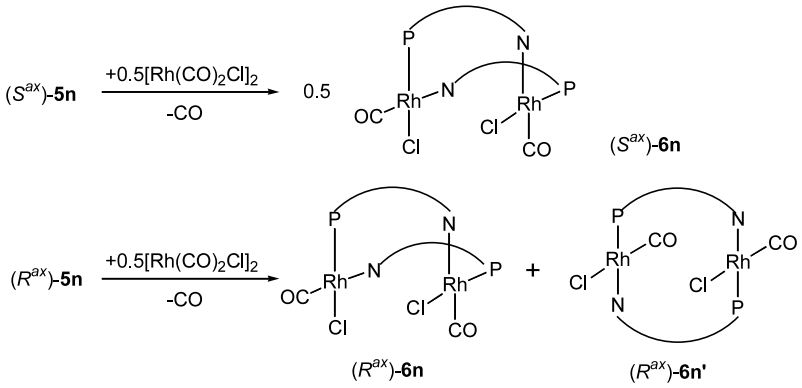
The chelate structure of the products is supported by ES MS data, for in the ES mass spectrum of complex **6i** the peak of $[M-Cl]^+$ cation ($m/z = 693$) has 100% intensity. The selected spectral data for complexes **6a**–**m** are summed up in Tables 1–3. It should be noted that the values ν(CO) and ^1J(P,Rh) for compounds **6a**–**m** (Tables 1 and 2) exceed the analogous values not only for the complexes with aminophosphines (by 30–35 cm^{-1} and 80–100 Hz, respectively) but even for the complexes with most aminophosphites (by 7–10 cm^{-1} and 10–15 Hz, respectively [37,38]). This clearly indicates the strong π-acceptor ability of phosphorus centers in ligands **5a**–**m**. So, the BINOL block can make two sufficient contributions into the structure of *P*,*N*-hybrid phosphite ligands, namely, to provide axial chirality and greatly increase π-acidity of phosphorus atoms. Increasing of the *P*-center π-acidity in *P*,*N*-bidentate ligands is well known to favour high chemical and optical yields in the allylation, hydroboration–oxidation and hydrosilylation–oxidation of alkenes, hydrosilylation of ketones processes [39,40].

When designing chiral *P*,*N*-bidentate ligands, one should keep in mind not only the π-acceptor ability of the phosphorus center but the δ-donor ability of the nitrogen one, as well. Thus, for a series of ferrocene-based phosphinopyrazoles the optical yields in the Rh-catalyzed hydroboration–oxidation of alkenes [36,41] and in the Pd-catalyzed hydrosilylation–oxidation of alkenes [42] were shown to grow with the increasing of the electron-donor ability of the pyrazole fragment. In connection with the fact, a concept of electronically non-symmetric ligands was suggested by Togni and coworkers [36] (the stronger π-acceptor the *P*-center and δ-donating the *N*-center are, the more electronically non-symmetric the compound is). A quantitative estimation of the parameter is possible by means of ν(CO) value in IR spectrum of the corresponding chlorocarbonyl complex [Rh(CO)Cl(PN)] [36,38]. In particular, for structurally analogous complexes bearing the same phosphorus and different nitrogen centers, a compound with a smaller ν(CO) value possesses a stronger δ-donating nitrogen-containing center, and, therefore, is more electronically non-symmetric. From this point of view, the most electronically non-symmetric ligands among **5a**–**n** are iminophosphites **5i**,**h** and aminophosphite **5c** bearing a distant *N*-dibenzyl amino group (see Table 1). The growth of the electron-donating ability of the

nitrogen-containing moiety leads to a decrease in ^1J(P,Rh) for **6i**,**h** against **6a**,**d**,**g** (Table 2).

Other spectral data for **6a**–**m** are also in good agreement with their suggested structure. ν(Rh–Cl) frequencies (Table 1) are typical for terminal chlorine ligands [37]. ^1J(C,Rh) values are in the 68–75 Hz range (Table 3), which is characteristic for *cis*-[Rh(CO)Cl(P^N)] chelate complexes [37,38]. ^2J(C,P) values (Table 3) prove the *cis*-position of the carbonyl and the phosphorus atom [37]. A comparison of ^{13}C-NMR spectral data for free and coordinated ligands (see Section 2) reveals marked downfield coordination shifts of peaks of the carbon atoms neighbor to donor atoms. For example, coordination shifts $\Delta\delta_C = \delta_C$(complex) − δ_C(ligand) for the azomethine carbon atoms of imino-phosphites **5i**,**h** reach a value of 9 ppm.

Notably, complexation of compound **5n** proceeds in a different way. Two optically pure diastereomers ((S^{ax})-**5n** and (R^{ax})-**5n**) were specially synthesized from (*S*)- and (*R*)-BINOL and their coordination behavior investigated. The ES mass spectra of both obtained Rh complexes showed intensive easily recognizable peaks $[2M-Cl]^+$ ($m/z = 1307$), which clearly indicate the formation of dimer products. Recently, we showed that insertion of the phosphorus or nitrogen atoms of *P*,*N*-bidentate ligands into cycles can prevent the ligands from chelation [46]. Most probably, in the case of complexation of ligands **5n**, the dimers are formed because of similar reasons. Interestingly, ligand (S^{ax})-**5n** gives selectively the product with *cis*-location of the nitrogen and phosphorus atoms at Rh, but (R^{ax})-**5n** leads to the mixture of *cis*- and *trans*-products:



The mononuclear structure of metal-complexes **6a**–**m** was additionally proved (in the case of **6d** and **6e**) by sedimentation analysis using ultracentrifuge. Measuring of the diffusion coefficient in DMF gave the diameter of the sphere (14.0 Å for **6d** and 12.4 Å for **6e**), in which a molecule of the complex can be inscribed. This estimation agrees well with the results of a computer calculation of the molecule structure using MM2 method [43] (13.9 Å for **6d** and 13.8 Å for **6e**). In addition, the molecular weight of complex **6e** has been determined by the same method equal to 632 ± 6% (calculated M_r = 596).

Compounds **6c**,**m**,**l** comprise two or more conformers by six-membered chelate ring (see Table 2) similar to cationic Rh and Ir complexes with (1*R*,2*R*)-$Ph_2PCH(Ph)CH(Me)NHMe$ [44]. In addition, the reaction of **5c** with $[Rh(CO)_2Cl]_2$ produces some amount of the *trans*-[Rh(P^N)$_2$Cl(CO)] complex, which is characterized by the doublet resonances δ_P 145.92 (^1J(P,Rh) 184.6 Hz) and δ_P 145.31 (^1J(P,Rh) 186.4 Hz) [37,45].

Such a conclusion was easily made from the ^{31}P-NMR and IR data for the products of complexation (Tables 1 and 2). Complexes (S^{ax})-**6n** (ν(CO) 2036 cm^{-1}, ^1J(P,Rh) 275.7 Hz) and (R^{ax})-**6n** (ν(CO) 2035 cm^{-1}, ^1J(P,Rh) 276.7 Hz) have spectral parameters typical for *cis*-location of P and N atoms; spectral data for (R^{ax})-**6n′** (ν(CO) 2020 cm^{-1}, ^1J(P,Rh) 262.0 Hz) are characteristic of *trans*-structure of the complex [37,47].

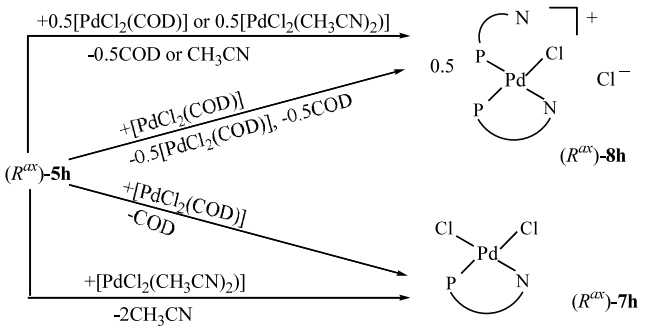
Table 4
^{31}P-NMR data for compounds (R^{ax})-**7h**, (R^{ax})-**8h**, (R^{ax})-**9h**, (S^{ax})-**7i**, (R^{ax})-**10j**, (S^{ax})-**9l** (in $CDCl_3$)

Compound	δ_P (^2J,(P,P′), Hz)
(R^{ax})-**7h**	103.20
(R^{ax})-**8h**	134.76 (97.2), 50.64 (97.2)
(R^{ax})-**9h**	144.80
(S^{ax})-**7i**	103.90
(R^{ax})-**10j**	139.76
(S^{ax})-**9l**	145.26, 144.12

This remarkable dependence of the products of complexation structure on the absolute configuration of the BINOL fragment and on the structure of the nitrogen-containing fragment must be taken into account when catalytically applying these ligands.

3.3. Complexation of the new P,N-hybride ligands with the Pd(II) precursors

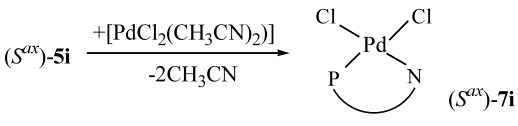
Also of great interest and practical importance is the reaction of the new *P*,*N*-ligands with Pd(II) complexes, for the latter are often used as the catalytic precursors in the Pd-catalyzed allylic alkylation reactions [13,40]. For studying of the complexation with Pd(II) were chosen aminophosphite **5b** and iminophosphites **5h**–**j**,**l**,**m**, which gave six-membered Rh chelates selectively and in high yields (see above). But their reactions with [$PdCl_2$(COD)] proceed not in the same way. Thus, the ^{31}P-NMR spectrum of the (R^{ax})-**5h**–[$PdCl_2$(COD)] (P–Pd = 1) reaction solution contains the signals of the neutral chelate complex (R^{ax})-**7h** (δ_P 103.2, s, 60%) and of the cationic complex (R^{ax})-**8h** (AX system: δ_P 50.64, d and δ_P 134.76, d, ^2J(P,P′) 97.2 Hz, 40%). When the reaction was performed at a lower concentration (starting with 0.5×10^{-4} mol of [$PdCl_2$(COD)] instead of 1×10^{-4} mol), the share of the (R^{ax})-**7h** product grew (up to 72%), as expected. Complex (R^{ax})-**7h** was obtained in a pure state by the reaction of (R^{ax})-**5h** with [$PdCl_2(CH_3CN)_2$] (P–Pd = 1); pure complex (R^{ax})-**8h** was synthesized by the reaction of (R^{ax})-**5h** with [$PdCl_2(CH_3CN)_2$] (P–Pd = 2) or with [$PdCl_2$(COD)] (P–Pd = 2). Both complexes were fully characterized by the usual spectral methods (see Section 2 and Table 4). Thus, the *cis*-positioning of the phosphorus atoms in complex (R^{ax})-**8h** is proved by the characteristic value of the ^2J(P,P′) parameter (97.2 Hz) and the only ν(Pd–Cl) band (298 cm^{-1}, CsI, Nujol) in its IR spectrum [15,48–50]. The results of cyclic voltammetry for the (R^{ax})-**8h** solution in DCM reveal the presence of Cl^- anions in its structure (E_{na} = +1.3 eV), for the peak grows upon adding of [Et_3NBz]$^+Cl^-$ into the solution. In general, complexation of ligand (R^{ax})-**5h** can be illustrated with the scheme:



Iminophosphite **5m** undergoes complexation in a similar way. Thus, in the reaction solution of the system **5m**–[$PdCl_2$(COD)] (P–Pd = 1) in $CDCl_3$ were detected two conformers of a neutral chelate (δ_P 113.34, s, 60% and δ_P 105.87, s, 25%; ν(Pd–Cl) 342, 297 cm^{-1}) and a neutral symmetric complex [Pd(η^1-P^N)$_2Cl_2$] (δ_P 117.00, s, 15%; ν(Pd–Cl) 322, 306 cm^{-1}) [31,51,52]. When the reaction was performed at the P–Pd = 2 molar ratio, besides the neutral product [Pd(η^1-P^N)$_2Cl_2$] (24%), a new cationic complex *cis*-[PdCl(η^2-P^N)(η^1-P^N)]$^+Cl^-$ (an analogue of (R^{ax})-**8h**) was detected. It consists of two conformers: (1) δ_P 63.50, d, ^2J(P,P′) 31.8 Hz and δ_P 123.35, d, ^2J(P,P′) 31.8 Hz (60%); (2) δ_P 64.37, d, ^2J(P,P′) 95.7 Hz and δ_P 127.80, d, ^2J(P,P′) 95.7 Hz (16%). Unfortunately, the attempt to isolate pure *cis*-[PdCl(η^2-P^N)(η^1-P^N)]$^+BF_4^-$ complex by adding a THF solution of $AgBF_4$ (Ag–Pd = 1) failed. Although the singlet resonance δ_P 117.00 of the neutral [Pd(η^1-P^N)$_2Cl_2$] complex vanished from the ^{31}P-NMR spectrum, there appeared a new set of the quartet signals of AX and AB systems in the 47.72–135.24 ppm range, which correspond to various cationic complexes of unknown structures [49,50].

Ligand **5b** does not produce cationic complexes when reacting with [$PdCl_2$(COD)]. Thus, at the P–Pd = 1 molar ratio, the reaction solution gives in the ^{31}P-NMR spectrum peaks at δ_P 90.63, 77.44 and 50.76 ppm. Their characteristic chemical shifts allowed to ascribe them to the complexes [Pd(η^1-P^N)$_2Cl_2$], [Pd(η^2-P^N)Cl_2] [19,27] and [Pd_2Cl_2(μ-Cl)$_2$(η^1-P^N)$_2$] [53,54], correspondingly. Indeed, when the reaction was performed at the P–Pd = 2 molar ratio, the only broaden singlet δ_P 90.63 was observed.

In general, complexation of the new BINOL-based *P*,*N*-hybride phosphites with [$PdCl_2$(COD)] proceed not selectively. That must be taken into account when choosing starting metal precursors for catalytic reactions. On the other hand, using [$PdCl_2(CH_3CN)_2$] and [Pd(allyl)Cl]$_2$ leads to the neutral and cationic Pd chelates selectively and in high yields. The selective synthesis of complex (R^{ax})-**7h** has been already described (see above). Its homologue (S^{ax})-**7i** was obtained in a similar way:



The complex was characterized by usual spectral methods (see Section 2 and Table 4). It is notable that the ν(Pd–Cl) adsorption bands in the IR spectra of (S^{ax})-**7i**, (R^{ax})-**7h** and (R^{ax})-**8h** have maximums at about 300 cm^{-1}, which is characteristic of the Pd–Cl bonds *trans*-positioned to the BINOL-derived phosphite group [31]. Therefore, the *trans*-influence of the latter is lower in comparison with other phosphites, for which the

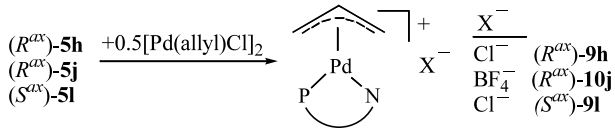
Table 5
Enantioselective allylic alkylation of 3-penten-2-yl ethyl carbonate with dimethyl malonate according to Scheme 1 (L*–Pd = 2)

Entry	L*	Solvent	T (°C)	Yield (%) [a]	% ee [b]
1	(R^{ax})-**5a**	THF	r.t.	30	2 (*S*)
2	(R^{ax})-**5a**	THF	−18	3	34 (*S*)
3	(R^{ax})-**5b**	THF	r.t.	50	26 (*R*)
4	(R^{ax})-**5b**	THF	5	45	21 (*R*)
5	(R^{ax})-**5b**	THF	−18	30	18 (*R*)
6	(S^{ax})-**5h**	THF	65	60	2 (*S*)
7	(S^{ax})-**5h** [c]	THF	r.t.	80	46 (*S*)
8	(S^{ax})-**5h** [d]	THF	r.t.	30	9 (*S*)
9	(S^{ax})-**5h**	THF	r.t.	90	58 (*S*)
10	(S^{ax})-**5h**	THF	5	70	43 (*S*)
11	(S^{ax})-**5h**	THF	−20	70	35 (*S*)
12	(S^{ax})-**5h**	DCM	r.t.	85	4 (*S*)
13	(S^{ax})-**5h**	Toluene	r.t.	0	–
14	(S^{ax})-**5h**	CH_3CN	r.t.	0	–
15	(R^{ax})-**5h**	THF	r.t.	95	5 (*S*)
16	(R^{ax})-**5h**	THF	5	65	11 (*S*)
17	(R^{ax})-**5h**	THF	−20	65	3 (*S*)
18	(R^{ax})-**5h**	DCM	r.t.	0	–
19	(S^{ax})-**5i**	THF	r.t.	90	41 (*R*)
20	(S^{ax})-**5i**	THF	−18	55	39 (*R*)
21	(R^{ax})-**5i**	THF	r.t.	95	48 (*R*)
22	(S^{ax})-**5j**	THF	r.t.	65	50 (*R*)
23	(S^{ax})-**5j**	DCM	r.t.	98	49 (*R*)
24	(R^{ax})-**5j**	THF	r.t.	25	74 (*R*)
25	(R^{ax})-**5j** [c]	THF	r.t.	55	76 (*R*)
26	(R^{ax})-**5j**	THF	5	86	81 (*R*)
27	(R^{ax})-**5j**	DCM	r.t.	93	19 (*R*)
28	(R^{ax})-**5j**	Toluene	r.t.	80	81 (*R*)
29	(S^{ax})-**5l**	THF	r.t.	20	7 (*S*)
30	(R^{ax})-**5n**	THF	r.t.	40	28 (*R*)
31	**11**	THF	r.t.	20	7 (*S*)

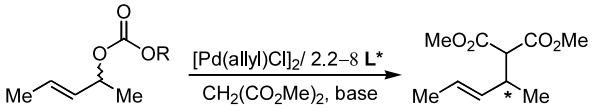
[a] Yield of analytically pure product after column chromatography.
[b] The enantiomeric excesses were determined by chiral GC (fused silica capillary column DP-TFA-γ-CD, 90 °C, He, 1.8 bar).
[c] L*–Pd = 1.
[d] L*–Pd = 4.

ν(Pd–Cl) bands are normally observed at 280–290 cm^{-1} [19,27,46,55].

Reactions of [Pd(allyl)Cl]$_2$ with ligands (R^{ax})-**5h**, (R^{ax})-**5j** and (S^{ax})-**5l** lead to cationic chelate complexes (R^{ax})-**9h**, (R^{ax})-**10j** and (S^{ax})-**9l** (complex **10j** was obtained by the ion exchange reaction with $AgBF_4$):



The products were characterized by the standard physical methods (see Section 2 and Table 4) and, in addition, complex (R^{ax})-**9h** was analyzed by cyclic voltammetry (in CH_3OH, $E_{na} = +1.29$ eV). It should be noted that there are two sets of peaks in the ^{31}P- and ^{13}C-NMR spectra of (S^{ax})-**9l**, which indicates the existence of the *exo*- and *endo*-isomers of the compound. It is not observed for complexes (R^{ax})-**9h** and (R^{ax})-**10j** either because of the fast interconversion of the isomers or because of the absence of one of the isomers (see [40] and references cited therein, [56,57]).

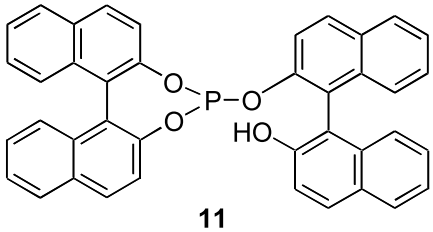


Scheme 1.

3.4. Pd-catalyzed allylic substitution reactions

Several of the new *P*,*N*-ligands based on optically active BINOLs were tested in the Pd-catalyzed allylic alkylation of 3-penten-2-yl carbonate with dimethyl malonate (Scheme 1, R = Et, base = BSA, KOAc).

The obtained results are summed up in Table 5. The following conclusions can be made from them: (1) the derivatives of the well-known chiral inductors–aminoalcohols Chirald ((R^{ax})-**5a**) and *N*-methylephedrine ((R^{ax})-**5b**) gave poor results (less than 34% ee), as well as oxazolinephosphite (R^{ax})-**5n** (entry 30); (2) the best results were shown by ligands bearing imino groups—(S^{ax})-**5h** and (R^{ax})-**5j** (up to 81% ee). The C*-stereocenters in the nitrogen-containing fragments are crucial, for ligand (S^{ax})-**5l**, which does not have one, gave only 7% ee (entry 29). Notably, ligands **2a**–**d**, which, similar to (S^{ax})-**5l**, are only of axial chirality, also shown low enantioselectivity (see Section 1); (3) presence of a nitrogen donor atom is crucial, because the previously obtained by us *P*-monodentate



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phosphite (**11**) [58] is ineffective (entry 31); (4) the optical yields are strongly dependent on the optical configuration of the BINOL fragment (compare entries 9 and 15, 23 and 27) and, sometimes, on the solvent used (compare, for example, entries 9 and 12); (5) changing of the L*–Pd ratio from 2 to 1 slightly improves the catalytic results (compare entries 24 and 25), but if the ratio is increased up to L*–Pd = 4, the results become much worse (compare entries 7 and 8).

It must be noted that ligands (S^{ax})-**5j** and (R^{ax})-**5j** gave generally higher results than very similar to them ligands (S^{ax})-**5i** and (R^{ax})-**5i**. The electronic properties (including a degree of electronic non-symmetry) of ligands **5i** and **5j** are very close, since the values of the ν(CO) and ^1J(P,Rh) parameters in their corresponding

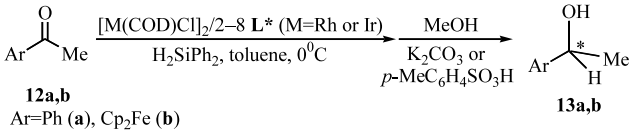
Table 6
Enantioselective hydrosilylation of ketones **12a,b** (see Scheme 2 M = Rh)

Entry	L*	Ketone	L*–M	Yield (%) [a]	% ee
1	(R^{ax})-**5a**	**12a**	1	60	19 (*R*)
2	(R^{ax})-**5a**	**12a**	2	65	17 (*S*)
3	(S^{ax})-**5h**	**12a**	1	54	8 (*R*)
4	(S^{ax})-**5h**	**12a**	2	73	13 (*R*)
5	(S^{ax})-**5i**	**12a**	1	44	10 (*R*)
6	(S^{ax})-**5i**	**12a**	2	56	15 (*R*)
7	(R^{ax})-**5i**	**12a**	1	57	19 (*S*)
8	(R^{ax})-**5i**	**12a**	2	61	23 (*S*)
9	(R^{ax})-**5j**	**12a**	1	3	11 (R)
10	(R^{ax})-**5j**	**12a**	2	19	20 (S)
11	(R^{ax})-**5j**	**12a**	3	20	16 (S)
12	(S^{ax})-**5j**	**12a**	1	43	0
13	(S^{ax})-**5j**	**12a**	2	13	1 (R)
14	(S^{ax})-**5j**	**12a**	3	11	1 (R)
15	(S^{ax})-**5l**	**12a**	1	45	2 (R)
16	(S^{ax})-**5l**	**12a**	2	11	3 (R)
17	(R^{ax})-**5n**	**12a**	1	58	18 (*S*)
18	(R^{ax})-**5n**	**12a**	2	30	43 (*S*)
19	(R^{ax})-**5n**	**12a**	3	74	58 (*S*)
20	(R^{ax})-**5n**	**12a**	4	1	19 (*S*)
21	(R^{ax})-**5n** [b]	**12a**	1	97	11 (*S*)
22	(R^{ax})-**5n** [b]	**12a**	2	49	38 (*S*)
23	(R^{ax})-**5n** [b]	**12a**	3	1	5 (*R*)
24	(R^{ax})-**5n**	**12b**	1	90	2
25	(R^{ax})-**5n**	**12b**	2	35	55
26	(R^{ax})-**5n**	**12b**	3	40	60
27	(S^{ax})-**5n**	**12a**	1	64	1 (*R*)
28	(S^{ax})-**5n**	**12a**	2	69	4 (*R*)
29	(S^{ax})-**5n** [b]	**12a**	1	91	8 (*R*)
30	(S^{ax})-**5n** [b]	**12a**	2	24	14 (*R*)
31	(S^{ax})-**5n** [b]	**12a**	3	1	2 (*R*)
32	**11**	**12a**	1	69	7 (*S*)
33	**11**	**12a**	2	73	16 (*S*)
34	**11**	**12a**	3	56	21 (*S*)
35	**11** [b]	**12a**	1	78	0
36	**11** [b]	**12a**	2	96	3 (*S*)

[a] The yield of **13a** after distillation and **13b** after purification [34].
[b] $[Ir(COD)Cl]_2$ was used as a catalyst precursor.

[Rh(CO)Cl(P^N)] complexes are almost the same (Tables 1 and 2). So, it is the steric properties of the ligands **5i** and **5j** what is responsible for the difference in their enantioselectivity. Ligands **5i** and **5j** are of similar structures and only –N=CHR fragments are different. To estimate the bulkiness of the substituents, the cone angles θ_R for the *p*-$C_6H_4NMe_2$ and Cp_2Fe fragments have been calculated mathematically by constructing the corresponding computer models. The calculated cone angle for the Cp_2Fe fragment ($\theta_R = 159$) is significantly larger then the angle for the *p*-$C_6H_4NMe_2$ fragment ($\theta_R = 133$). Hence, bulky substituents attached to the imine group of the *P*,*N*-iminophosphite ligands are likely to lead to higher optical yields in the catalytic reaction.

It should be noted that the catalytic system based on (R^{ax})-**5j** allows reaching a very high enantioselectivity. The matter is that 1,3-dimethyl-substituted allyl substrates are referred to as unmanageable ones [59] and it is rather difficult to reach high stereoselectivity in that case. To the best of our knowledge, only two *P*,*N*-hybrid ligands gave in the mentioned above allylation process an enantioselectivity higher than 80%: one of the new generation phosphinooxazolines (70–90% ee) [33] and a 2-(phosphinoaryl)pyridine derived ligand (Scheme 1, R = Me, ^{i}Pr, Ph, 78–93% ee) [59]. And these high results were achieved by thorough optimization of the reaction conditions at a low temperature (−25–−40 °C) and, in the latter case, by addition of crown ethers. So, compound (R^{ax})-**5j** holds a worthy of note position, surpassing many well-known *P*,*N*-bidentate ligands [60–62].



Scheme 2.

3.5. Rh-catalyzed hydrosilylation reactions

Some of the new *P*,*N*-hybride phosphites were also tested in the asymmetric reduction of prochiral ketones with diphenylsilane (Scheme 2).

The obtained results are summed up in Table 6. As in the Pd-catalyzed allylation, ligands (R^{ax})-**5a**, (S^{ax})-**5l** and **11** are not effective (entries 1–2, 15–16, 32–36). Rather low results were also shown by iminophosphites (entries 3–14). The best results were obtained with ligand (R^{ax})-**5n** (up to 58% ee for **13a** and up to 60% ee for **13b**), the absolute configuration of the BINOL fragment being a crucial factor for the optical yields (compare with the results given by (S^{ax})-**5n**, Table 6). The L*–M ratio and solvent also deeply influence the catalytic results (Table 6).

Despite some known *P*,*N*-bidentate ligands give more than 90% ee in the reaction (see [13,40] and references cited therein), the obtained results hold a worthy of note position. Especially important is obtaining of enantiomerically enriched 1-ferrocenylethanol (**13b**), which is a valuable chiral synthon in the synthesis of some anticancer drugs [63]. Besides, the ^{31}P-NMR spectral monitoring of the $[Rh(COD)Cl]_2$–(R^{ax})-**5n** reaction mixture (in d_8-toluene) revealed the presence of several complex products. Thus, when the L*–Rh ratio varied in the 1–3 range, a set of doublet signals δ_P 128.94–156.83 (^1J(P,Rh) 259.3–311.0 Hz) were detected. So, it is an actual task to prepare a real catalyst selectively, free of the by-products of complexation. Such experiments are in progress in our group.

4. Conclusion

A series of novel chiral *P*,*N*-hybrid phosphite ligands was prepared. They bear the identical BINOL-derived phosphorus fragment and widely vary in the structure of the amino alcohol part. Most of the ligands react with $[Rh(CO)_2Cl]_2$ highly selectively giving stable chelate complexes [Rh(CO)Cl(P^N)]. The only exception is phosphitooxazoline (**5n**), which leads to the dimeric product $[Rh(CO)Cl(P\hat{}N)]_2$ of the 'head-to-tail' type. In contrast, complexation with $[PdCl_2(COD)]$ gives mixtures of the chelates $[PdCl_2(P\hat{}N)]$ and products containing two coordinated ligand molecules: *cis*-$[PdCl_2(\eta^1\text{-}P\hat{}N)_2]$ or *cis*-$[PdCl(\eta^2\text{-}P\hat{}N)(\eta^1\text{-}P\hat{}N)]^+Cl^-$. But the chelate complexes $[PdCl_2(\eta^2\text{-}P\hat{}N)]$ and $[Pd(allyl)(\eta^2\text{-}P\hat{}N)]^+X^-$ ($X = Cl$, BF_4) can be obtained starting from the other metal precursors—$[PdCl_2(CH_3CN)_2]$ and $[Pd(allyl)Cl]_2$, correspondingly. The new *P*,*N*-hybrid ligands gave up to 60% ee in the Rh-catalyzed hydrosilylation of acetophenone and acetylferrocene by diphenylsilane, the phosphitooxazoline ligand **5n** being the most effective one. In the Pd-catalyzed allylic alkylation of 3-pentene-2-yl carbonate by dimethyl malonate enantioselectivity up to 81% ee was observed, which is one of the highest known results among *P*,*N*-hybrid ligands for such an 'unmanageable' substrate. In this reaction better results were shown by iminophosphites rather than aminophosphites.

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