Abstract: Novel chiral P,N-bidentate arylphosphites have been prepared by a one-step phosphorylation of appropriate hydroxy ketimines based on (R)-(+)camphor. Metal chelate complexes [Rh(CO)(PN)Cl] and [Pd(PN)(allyl)]BF4 with the ligands were obtained and the new compounds were fully characterized by 1H, 13C and 31P NMR, IR, MS (EI, FAB and ESI techniques) and X-ray crystal structure analysis. Using these ligands, up to 73% ee has been achieved in the asymmetric palladium-catalyzed sulfonylation of 1,3-diphenyl-2-propenyl acetate with sodium p-toluenesulfinate.

Key words: allylations, asymmetric catalysis, chiral ketimines, palladium, P,N-ligands

Imino phosphines constitute an important group of chiral P,N-bidentate ligands for asymmetric catalysis by metal complexes.1–3 The vast majority of such compounds contain an aldimine fragment, whereas systems with ketimine units are fairly uncommon.4–6 Imino phosphites have been successfully used in enantioselective catalysis because of their high p-acidity, resistance to undesired oxidation, synthetic accessibility, and low cost.3,7,8 However, all these ligands contain a peripheral aldimine group; phosphites with a ketimine fragment were not known until recently. In 2004 we reported the synthesis of the first chiral aryl phosphite 2c, containing a ketimine substituent, based on (R)-(+)camphor and the results of its preliminary testing in palladium-catalyzed asymmetric allylation.9 Developing this topic further, in the present work we discuss the synthesis of a new series of such ligands and their application in palladium-catalyzed asymmetric allylation. Moreover, we will make a direct comparison of the new chiral iminophosphites with their phosphine analogues.

Novel P,N-bidentate chiral aryl phosphites were easily obtained by phosphorylation of appropriate iminoalcohols 2a and 2b or the iminophenol 2c with an easily accessible bis(2,6-dimethylphenyl)chlorophosphite (1; Scheme 1). Usually, this chlorophosphite is synthesized from 2,6-dimethylphenol and PCl3 in the presence of triethylamine in benzene.10,11 We have improved the procedure and developed a novel, versatile, solvent-free method for the synthesis of phosphorochloridite (1) through the use of a catalytic amount of 1-methylpyrrolidin-2-one. The reaction time is three-fold shorter and no solvent is required. Hence, this simple, economical and time-saving procedure represents a handy method for the synthesis of convenient and cheap phosphorylating reagents, based on substituted phenols.

Scheme 1 Synthesis of iminophosphites 2a–c

SYNTHESIS 2007, No. 11, pp 1717–1723
Advanced online publication: 11.05.2007
DOI: 10.1055/s-2007-96066; Art ID: Z26206SS
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The resulting iminophosphites \(3a-c\) are stable under dry conditions. For instance, the \(^{31}\text{P}\) NMR spectrum of compound \(3c\), recorded several months after its synthesis, showed no signals of any decomposition products. It is noteworthy that all starting reagents are inexpensive; iminooalcohols \(2a, 2b\) and iminophenol \(2c\) were obtained by one-pot synthesis from 2-aminoethanol, \((S)\)-isoleucinol or 2-aminophenol and \((R)\)-(+)camphor. In contrast to the use of hydrochloric acid\(^{12}\) in the synthesis of \(1c\) described previously,\(^9\) we applied anhydrous zinc(II) chloride\(^{13}\) as a catalyst in the synthesis of ketimines \(2a-c\). Despite moderate yields, this procedure has the advantage of avoiding a three-step synthesis through the \(N\)-nitroimine of \((R)\)-camphor.\(^{14}\)

As for complexation patterns, ligands \(3a-c\) represent typical chelating agents. Thus, their reactions with \([\text{Rh(CO)}_2\text{Cl}]_2\) and with \([\text{Pd(allyl)}\text{Cl}]_2\) in the presence of \(\text{AgBF}_4\) gave neutral \((4a-c)\) and cationic \((5a-c)\) metal chelates with a \(\text{cis}\)-orientation of the \(P\) and \(N\) donor atoms (Scheme 2). This is evident from the \(^{31}\text{P}\) NMR data for the complexes (Table 1).

Table 1 Selected Spectroscopic Data for Compounds \(4a-c\) and \(5a-c\)

| Compound | \(^{31}\text{P}\) NMR \(^*\) | IR
|----------|-----------------|-----------------
| \(4a\)   | 121.5           | 287.4 2028     |
| \(4b\)   | 119.7           | 281.3 2024     |
| \(4c\)   | 137.8           | 297.6 2026     |
| \(5a\)   | 127.1 (5%), 124.8 (95%) | – – |
| \(5b\)   | 120.9 (82%), 119.8 (18%) | – – |
| \(5c\)   | 143.5 (54%), 141.5 (46%) | – – |

\(^*\) Recorded in CHCl$_3$.

The \(^{31}\text{P}\) NMR and IR spectral data of compounds \(4a-c\) indicate features\(^{15}\) typical of aryl phosphites of the type \(3a-c\) which have pronounced \(\pi\)-electron-withdrawing ligands, and which have been shown to be important for attaining high chemical and optical yields in some areas of asymmetric catalysis.\(^2,3\) Interestingly, the spectral parameters of \(4a-c\) strongly depend on the structural features. Thus, the electron-donating \(\text{sec}\)-butyl substituent in \(4b\) causes an appropriate drop in the \(^1J_{\text{P-Rh}}\) and \(v(\text{CO})\) values.

In general, \(^{31}\text{P}\) NMR and IR spectral data indicate that ligands \(3a-c\) have rather similar electronic demands. Complex \(4a\) was characterized by X-ray diffraction (Figure 1).

**Scheme 2** Synthesis of complexes \(4a-c\) and \(5a-c\)

Figure 1 Molecular structure of complex \(4a\). Atoms are given by thermal ellipsoids at 50% probability. Principal bonds and angles averaged over two independent molecules (Å and °): Rh(1)–C(1K) 1.827(7), Rh(1)–N(1) 2.137(5), Rh(1)–P(1) 2.168(1), Rh(1)–Cl(1) 2.387(1), P(1)–O(1) 1.599(4), P(1)–O(2) 1.599(4), P(1)–O(3) 1.604(5), C(1K)–O(1K) 1.143(8); C(1K)–Rh(1)–N(1) 173.3(2), N(1)–Rh(1)–P(1) 87.9(1), P(1)–Rh(1)–Cl(1) 168.4(6), O–P(1)–O 100.7(2).

Compound \(4a\) crystallized in the chiral space group \(P2_1\), with two independent molecules per unit cell. Both of the independent molecules are characterized by the same \(R\) configuration of the \(C(1)\) and \(C(4)\) atoms. In both of the independent molecules, the conformation of metallocycles may be described as a distorted boat. In one of the two independent molecules, the deviation of the \(C(1)\) and \(N(1)\) atoms from the basal plane are equal to 0.99 and 1.53 Å, respectively, while in the second, the Rh(1A) and C(2A) atoms are deviated to 1.00 and 0.69 Å, respectively.

The Rh(1) atom has a distorted square-planar configuration. The deviation of the said atom from the plane of \(P(1)\), \(N(1)\), \(O(1K)\) and \(Cl(1)\) atoms is equal to 0.99 and 1.53 Å, respectively, while in the second, the Rh(1A) and C(2A) atoms are deviated to 1.00 and 0.69 Å, respectively.

The \(\text{Rh}(1)\) atom has a distorted square-planar configuration. The deviation of the said atom from the plane of \(P(1)\), \(N(1)\), \(O(1K)\) and \(Cl(1)\) atoms is equal to 0.18 Å (averaged value for the two independent molecules). Such a distortion of the \(\text{Rh}(1)\) coordination polyhedron may be ex-
plained by the high extent of steric overcrowding due to the presence of the bulky P,N-ligand.

The P(1) atom has a distorted pyramidal configuration (the sum of the three O–P–Rh angles is equal to 352°). Due to the presence of bulky 1,7,7-trimethylbicyclo[2.2.1]heptane and 2,6-dimethylphenyl groups, the P(1)–Rh(1)–Cl(1) angle is noticeably distorted in comparison to those in previously investigated complexes with P,N-ligands.16–19 The Rh(1)–P(1) bond length is close to that found in complexes with the 1,3-diaza-2-phosphabicyclo[3.3.0]octane ligand.17 The configuration at the N(1) atom is planar (the sum of angles at this atom is 359.3, on average). The P(1)–N(1) distance is almost identical to those found in previously investigated complexes.

The 31P NMR spectra of complexes 5a–c contain two singlets (Table 1), assigned to their exo- and endo-isomers.15 The averaged coordination shifts [\( \Delta \delta_P = \delta_P(\text{complex}) - \delta_P(\text{ligand}) \)] for complexes 5a–c, are equal to −9.3, −13.9 and 2.7 ppm, respectively, and indicate the presence of a –P–Pd bond in all cases. Large coordination shifts \( \Delta \delta_C = \delta_C(\text{complex}) - \delta_C(\text{ligand}) \) of 14.6 and 13.5 ppm for the signals of the imino C-2 atoms in the 13C NMR spectra of complexes 5a and 5c, respectively, also suggest coordination of the peripheral imino group to palladium. ESI and FAB MS data are consistent with the mononuclear structures of complexes 5a–c.

Iminophosphites 3a–c (L), their complexes 5a–c, and systems [Pd(allyl)Cl]2/2L and [Pd(allyl)Cl]2/4L generated in situ, were used in the palladium-catalyzed reactions of enantioselective allylic substitution (Scheme 3). The results obtained are summarized in Tables 2 and Table 3. Particularly good chemical and optical yields (up to 80% and 73% ee, respectively; see Table 2, entry 5) were obtained using 3c in the sulfonylation of 1,3-diphenylallyl acetate (6) with sodium p-toluene sulfinate. Ligands 3a and 3b afforded essentially racemic product 7 (Table 2).

Still better results (up to 94% ee and a nearly stoichiometric conversion) were obtained with ligand 3c in the alkylation of allyl acetate 6 with dimethyl malonate (see Table 3, entry 15). The yields were found to be dependent on the nature of the nucleophile, the catalyst and on the solvent. For instance, in both catalytic reactions, the asymmetric induction increases significantly when passing from complex 5c to the catalytic system [Pd(allyl)Cl]2/2L (see Table 2, entries 5 and 6; Table 3, entries 13 and 16, 15 and 17). This favorable effect can be associated with the replacement of the outer-sphere BF4− anion by Cl−. Furthermore, the enantioselectivity of allylic alkylation in dichloromethane was found to be appreciably higher than in THF (see Table 3, entries 13, 15–17). As in the allylic sulfonylation, ligand 3a again showed low asymmetric induction (≤36% ee, Table 3). In contrast, 3b provided appreciable enantioselectivity of up to 82% ee (Table 3, entry 9). In this reaction, complex 5b and the catalytic system [Pd(allyl)Cl]2/2L gave almost identical optical yields of 8 (see Table 3, entries 9 and 12), dichloromethane being a solvent of choice. The dramatic superiority in asymmetric induction of 3b over 3a is due to the bulky sec-butyl substituent bearing an additional C-stereocenter. The highest enantioselectivities were obtained using iminophosphite 3c. The 2-aminophenol fragment in its structure reduces the degree of conformational freedom and leads to the high degree of rigidity necessary for efficient transfer of chirality during the catalytic process.

### Table 2 Enantioselective Allylic Sulfonylation of 6 with Sodium p-Toluene Sulfinate (in THF)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Ratio L/Pd</th>
<th>Isolated yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Pd(allyl)Cl]2/3a</td>
<td>1:1</td>
<td>31</td>
<td>7 (S)</td>
</tr>
<tr>
<td>2</td>
<td>[Pd(allyl)Cl]2/3a</td>
<td>2:1</td>
<td>25</td>
<td>3 (S)</td>
</tr>
<tr>
<td>3</td>
<td>[Pd(allyl)Cl]2/3b</td>
<td>1:1</td>
<td>29</td>
<td>6 (R)</td>
</tr>
<tr>
<td>4</td>
<td>[Pd(allyl)Cl]2/3b</td>
<td>2:1</td>
<td>42</td>
<td>12 (R)</td>
</tr>
<tr>
<td>5</td>
<td>[Pd(allyl)Cl]2/3c</td>
<td>1:1</td>
<td>80</td>
<td>73 (R)</td>
</tr>
<tr>
<td>6</td>
<td>5c</td>
<td>1:1</td>
<td>41</td>
<td>65 (R)</td>
</tr>
</tbody>
</table>

**Scheme 3** Enantioselective palladium-catalyzed allylic sulfonylation and alkylation of 1,3-diphenylallyl acetate (6)
It is useful to compare the stereoselectivity of iminophosphites 3a–c to related iminophosphine ligands 9–11 (Figure 2). Under comparable conditions to the catalytic allylic alkylation described for compounds 3a–c, xanthene-containing ligand 920 yielded racemic 8, while phosphine 10, which is the closest analogue of phosphite 3c, gave up to 51% ee and noticeably lower conversion (74–80%).4 The highest enantioselectivity among ligands 9–11 was achieved with compound 11 (69%),21 however, this is still lower than those obtained with iminophosphites 3b and 3c. In addition, synthesis of ligands 9–11 is more complex and proceeds in significantly lower yields.4,20,21 Therefore, iminophosphites 3b and 3c are superior to phosphines 9–11. It should be noted that region- and enantioselectivities of phosphorus-containing oxazolines in the palladium-catalyzed allylic alkylation of cinnamyl acetate could be considerably improved by the introduction of a diarylphosphine group instead of a diarylphosphane fragment.22 Feringa et al. convincingly demonstrated that, compared to state of the art bidentate phosphines such as DuPhos, PhanePhos and JosiPhos, readily accessible and stable, monodentate BINOL-based phosphoramidites can lead to both higher rates and/or higher enantioselectivities in the asymmetric hydrogenation of α- and β-dehydroamino acid derivatives.23 These facts, when taken together, testify that highly diverse and extraordinarily inexpensive chiral phosphites represent a new generation of phosphorus-containing ligands for metal-complex asymmetric catalysis.2,3,24,25

In conclusion, a significant improvement in the general procedures used for the synthesis of both phosphorylation reagents and chiral ketimines has been developed. It allows the synthesis of chiral P,N-bidentate phosphite-type ligands to be performed faster and reduces the number of stages required for the synthesis of chiral ligand building blocks from cheap starting materials. Hence, the new procedure offers great opportunities for the convenient synthesis of a broad variety of structurally diverse bidentate ligands.

Taking the palladium-catalyzed allylic substitution of 1,3-diphenylallyl acetate as a test case, it has been demonstrated that the new ligands outperform their phosphine analogues and possess high potential for asymmetric catalysis. To this end, further tuning of the ketimino phosphites, and studies on their application in various transition-metal-catalyzed processes, are in progress in our laboratories.

IR spectra were recorded in CHCl₃ on a Specord M80 instrument (polyethylene cell). 31P, 13C and 1H NMR spectra were recorded on a Bruker AMX–400 instrument (162.0 MHz for 31P, 100.6 MHz for 13C and 400.13 MHz for 1H). The complete assignment of all the resonances in 13C NMR spectra was achieved using DEPT techniques. Chemical shifts (ppm) are given relative to TMS (1H and 13C

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Ratio L/Pd</th>
<th>Solvent</th>
<th>Conversion (%)</th>
<th>ee (%)</th>
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<tr>
<td>1</td>
<td>[Pd(allyl)Cl]₂/3a</td>
<td>1:1</td>
<td>THF</td>
<td>18</td>
<td>12 (S)</td>
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<tr>
<td>2</td>
<td>[Pd(allyl)Cl]₂/3a</td>
<td>2:1</td>
<td>THF</td>
<td>29</td>
<td>30 (S)</td>
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<td>CH₂Cl₂</td>
<td>93</td>
<td>15 (S)</td>
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<tr>
<td>4</td>
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<td>2:1</td>
<td>CH₂Cl₂</td>
<td>94</td>
<td>22 (S)</td>
</tr>
<tr>
<td>5</td>
<td>5a</td>
<td>1:1</td>
<td>THF</td>
<td>50</td>
<td>7 (S)</td>
</tr>
<tr>
<td>6</td>
<td>5a</td>
<td>1:1</td>
<td>CH₂Cl₂</td>
<td>65</td>
<td>36 (S)</td>
</tr>
<tr>
<td>7</td>
<td>[Pd(allyl)Cl]₂/3b</td>
<td>1:1</td>
<td>THF</td>
<td>36</td>
<td>2 (R)</td>
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<tr>
<td>8</td>
<td>[Pd(allyl)Cl]₂/3b</td>
<td>2:1</td>
<td>THF</td>
<td>14</td>
<td>21 (R)</td>
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<tr>
<td>9</td>
<td>[Pd(allyl)Cl]₂/3b</td>
<td>1:1</td>
<td>CH₂Cl₂</td>
<td>34</td>
<td>82 (R)</td>
</tr>
<tr>
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<td>[Pd(allyl)Cl]₂/3b</td>
<td>2:1</td>
<td>CH₂Cl₂</td>
<td>36</td>
<td>55 (R)</td>
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<tr>
<td>11</td>
<td>5b</td>
<td>1:1</td>
<td>THF</td>
<td>19</td>
<td>59 (R)</td>
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<tr>
<td>12</td>
<td>5b</td>
<td>1:1</td>
<td>CH₂Cl₂</td>
<td>65</td>
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<tr>
<td>13</td>
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<td>1:1</td>
<td>THF</td>
<td>98</td>
<td>82 (R)</td>
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<td>THF</td>
<td>97</td>
<td>92 (R)</td>
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<td>15</td>
<td>[Pd(allyl)Cl]₂/3c</td>
<td>1:1</td>
<td>CH₂Cl₂</td>
<td>99</td>
<td>94 (R)</td>
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<td>16</td>
<td>5c</td>
<td>1:1</td>
<td>THF</td>
<td>54</td>
<td>51 (R)</td>
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<tr>
<td>17</td>
<td>5c</td>
<td>1:1</td>
<td>CH₂Cl₂</td>
<td>43</td>
<td>78 (R)</td>
</tr>
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</table>
NMR) and 85% H₃PO₄ in D₂O (31P NMR). Mass spectra were recorded with an AMD 402 spectrometer (FAB) and a Finnigan LCQ Advantage spectrometer (electrospray ionization technique, ESI). Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow). Optical yields of product 7 were determined using HPLC [(R,R)-WHELK-01 column] according to the literature.²⁸ Conversion of substrate 8 was quantitatively determined by NMR spectroscopy (1H and 31P) ¹³C, and ¹⁹F NMR). Mass spectra were recorded with a Finnigan LCQ Advantage spectrometer (electrospray ionization technique, ESI).

Bis-(2,6-dimethylphenyl)chlorophosphite (1)

Bis(2,6-dimethylphenyl)chlorophosphite (1) was purchased from Aldrich and Acros Organics and used without further purification.

Yield: 4.63 g (75%); colorless oil; bp 133–135 °C/1 Torr.

The spectroscopic and physicochemical characteristics of this substance fully correspond to published data.¹⁰¹¹

Synthesis of Iminoalcohols 2a and 2b; General Procedure

A mixture of (R)-camphor (6.09 g, 40 mmol) and anhydrous ZnCl₂ (0.55 g, 4 mmol) in o-xylene (80 mL) was heated under reflux in a Dean–Stark apparatus for 25 h. The solvent was removed and the residue was stirred at 150 °C for 1.5 h. The dark-red paste obtained was cooled to r.t. and unreacted starting materials were removed under vacuum (aspirator) at temperatures <180 °C. The residue was then twice fractionally distilled under high vacuum.

Yield: 4.63 g (75%); colorless oil; bp 133–135 °C/1 Torr.

¹³P NMR (162 MHz, CDCl₃): 8 174.3.

The spectroscopic and physicochemical characteristics of this substance fully correspond to published data.¹⁰¹¹

Synthesis of Ligands 3a–c; General Procedure

Bis(2,6-dimethylphenyl)chlorophosphite (0.83 g, 2.7 mmol) and Et₃N (0.4 mL, 2.7 mmol) were dissolved in benzene (20 mL) and the solution was cooled to 0 °C and stirred vigorously. The appropriate iminoalcohol 2a, 2b or iminophenol 2c (2.7 mmol) was added and the resulting mixture was stirred for 10 min at 0 °C and then heated to boiling point. After cooling to r.t., the Et₃N-HCl was filtered off and the residue was removed under vacuum (40 Torr). The residue was concentrated and dried under vacuum (1 Torr, 2 h).

Bis(2,6-dimethylphenyl) (E)-2′-((1R,4R)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)ethyl Phosphite (3a)

Yield: 1.01 g (95%); yellow oil.

¹³C NMR (100 MHz, CDCl₃): 8 11.1, 18.8, 19.5 (CH₃), 11.4 (C-5), 15.7 (CH₃, s Bu), 17.4, 17.5, 17.6, 17.7 (Ar-CH₂), 25.0 (C-4°), 27.2 (C-5), 32.1 (C-6), 35.9 (C-3), 36.7 (C-3°), 43.7 (C-4°), 46.8 (C-7), 53.6 (C-1), 64.3 (C-1'), 66.1 (d, 8 3.6 Hz, C-2°), 123.6 (Ar-CH₃), 128.6 (Ar-CH₂), 130.3 (d, 8 2.4 Hz, Ar-C), 148.9 (Ar-CO), 184.2 (C-2).

¹³P NMR (162 MHz, CDCl₃): 8 135.2.

MS (EI, 70 eV); m/z (%) = 524 (38) [M + H]⁺, 402 (100) [M – Me₂C₆H₃O]⁺, 234 (89) [CH₂CH₂N=C₁₀H₁₇ – H]⁺.


Bis(2,6-dimethylphenyl) (E)-2′-((1R,4R)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)ethyl Phosphite (3b)

Yield: 1.30 g (97%); yellow oil.

¹³C NMR (100 MHz, CDCl₃): 8 11.2, 18.7, 19.4 (CH₃), 17.5, 17.6 (Ar-CH₂), 27.2 (C-5), 31.9 (C-6), 35.6 (C-3), 43.6 (C-4), 46.8 (C-7), 52.7 (d, 8 3.4 Hz, CH₂N₂), 53.6 (C-1), 62.2 (CH₂O), 123.8 (Ar-CH₂), 128.6 (Ar-CH₂), 130.3 (d, 8 2.4 Hz, Ar-C), 148.9 (Ar-CO), 184.2 (C-2).

¹³P NMR (162 MHz, CDCl₃): 8 135.2.

MS (EI, 70 eV); m/z (%) = 546 (30) [M + H]⁺, 346 (100) [M – Me₂C₆H₃O]⁺, 178 (59) [CH₂CH₂N=C₁₀H₁₇ – H]⁺.

Anal. Calcd for C₂₈H₄₆NO₃P: C, 71.73; H, 8.28; N, 3.22.

Bis(2,6-dimethylphenyl) (E,2S,3’S,3’-Methyl-2’-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)pentyl Phosphite (3b)

Yield: 1.21 g (87%); pale-yellow oil.

¹³C NMR (100 MHz, CDCl₃): 8 10.8, 18.8, 19.5 (CH₃), 17.2, 17.4, 17.5, 17.6 (Ar-CH₂), 27.1 (C-5), 31.5 (C-6), 36.9 (C-3), 43.7 (C-4°), 47.4 (C-7), 54.2 (C-1), 121.1–148.5 (Ar-C), 186.8 (C-2).

¹³P NMR (162 MHz, CDCl₃): 8 134.2.

MS (EI, 70 eV); m/z (%) = 568 (48) [M + H]⁺, 402 (100) [M – Me₂C₆H₃O]⁺, 234 (89) [CH₂CH₂N=C₁₀H₁₇ – H]⁺.

Anal. Calcd for C₂₉H₄₂NO₃P: C, 73.39; H, 8.85; N, 2.67. Found: C, 73.64; H, 8.98; N, 2.53.

Bis(2,6-dimethylphenyl) (E)-2′-((1R,4R)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)phenyl Phosphite (3c)

Yield: 1.21 g (87%); pale-yellow oil.

¹³C NMR (100 MHz, CDCl₃): 8 10.8, 18.8, 19.5 (CH₃), 17.2, 17.4, 17.5, 17.6 (Ar-CH₂), 27.1 (C-5), 31.5 (C-6), 36.9 (C-3), 43.7 (C-4°), 47.4 (C-7), 54.2 (C-1), 121.1–148.5 (Ar-C), 186.8 (C-2).

¹³P NMR (162 MHz, CDCl₃): 8 134.8.

MS (FAB); m/z (%) = 515 (7) [M⁺], 394 (10) [M – Me₂C₆H₃O]⁺, 290 (24) [(Me₂C₆H₃O)POH]⁺, 243 (27) [Me₂C₆H₃O]⁺ + H⁺, 122 (100) [Me₆C₆H₄OH]⁺.

Anal. Calcd for C₃₂H₄₆O₃P: C, 74.54; H, 7.43; N, 2.72. Found: C, 74.33; H, 7.58; N, 2.54.

Synthesis of Rhodium Complexes 4a and 4b for NMR and IR Experiments; General Procedure

Rhodium complexes with ligands 3b and 3c were synthesized as follows: a solution of the ligand (0.36 mmol) in CHCl₃ (0.5 mL) was added dropwise to a stirred solution of [Rh(CO)₂Cl]₂ (0.18 mmol) in CHCl₃ (0.5 mL). A sample of the resulting solution (0.5 mL) was transferred to a NMR tube or IR cuvette and spectral experiments were carried out.

Synthesis 2007, No. 11, 1717–1723 © Thieme Stuttgart · New York
An A solution of the corresponding ligand (0.4 mmol) in CHCl₃ (5 mL) was added to the solution and the reaction mixture was stirred for 30 min then the excess solvent was removed under vacuum (40 Torr) and hexane (10 mL) was added to the residue. The precipitate obtained was separated by centrifugation, washed with hexane (2 × 10 mL) and dried under vacuum (1 Torr).

Yield: 0.22 g (96%); colorless solid; mp 182–184 °C (dec.).

Anal. Calcd for C₃₅H₅₁BF₄NO₃PPd: C, 55.46; H, 6.78; N, 1.85. Found: C, 55.61; H, 6.71; N, 2.01.

13C NMR (100 MHz, CDCl₃): δ = 13.8284(17) Å, b = 14.1591(17), c = 11.7577(18) Å, β = 0.98693(3); V = 2859.8(6) Å³; Z = 4; D (calculated) = 1.472 gcm⁻³; μ (MoKα) = 7.81 cm⁻¹; F(000) = 1312. Reflections collected 22794; independent reflections 13624 (R(int) = 0.0177). Collected with a SMART CCD 1000 diffractometer using MoKα radiation (λ = 0.71072 Å, o-scans with 0.3° step and 10 s exposure for each frame). Absorption correction was applied semi-empirically to differences with I>2σ(I). The absolute configuration of 4a was determined by use of the Flack parameter. Crystallographic data (excluding structure factors) for 4a have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-295731. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: +44(1223)336033; E-mail: deposit@ccdc.cam.ac.uk].

**Acknowledgment**

The authors thank Dr. A. V. Korostylev (Leibniz-Institut für Organische Katalyse an der Universität Rostock, Germany) for his assistance in preparing the manuscript. The authors gratefully acknowledge receiving the chiral HPLC columns: (R,R)-WHELK-01 from Regis Technologies (USA) and the ChiralCel OD-H from Daicel Chemical Industries, Ltd. (Japan). This work was partially supported by the Russian Foundation for Basic Research (Grant No. 06-03-90898-Mol-a).
References

(32) Sheldrick G. M. SADABS, v 2.01, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA