*P**,*N*-Bidentate Amino Phosphoramidites: New Highly Effective Ligands for Pd-Catalysed Asymmetric Allylic Substitution

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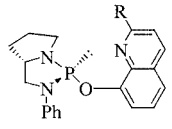
New chiral *P**,*N*-hybrid amino phosphoramidites have been obtained by one-step phosphorylation of amino alcohols. Complexation of the new ligands with $[Rh(CO)_2Cl]_2$ and $[Pd(allyl)Cl]_2$ gave the corresponding chelate complexes $[Rh(CO)Cl(\eta^2\text{-P,N})]$ and $[Pd(allyl)(\eta^2\text{-P,N})]^+BF_4^-$, which subsequently afforded up to 90% *ee* in the asymmetric Pd-catalysed sulfonylation of 1,3-diphenyl-2-propenyl acetate with sodium *p*-toluenesulfinate. In the enantioselective alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate, up to 98% enantioselectivity was achieved with $[Pd(allyl)(\eta^2\text{-P,N})]^+BF_4^-$ complexes as chiral catalysts.

Introduction

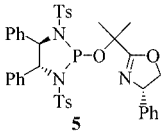
Chiral ligands with three P−O and/or P−N bonds have become increasingly important because of their synthetic availability, high π-acidity of the phosphorus atom, high resistance to oxidative destruction,[1−3] and their low cost. For example, BINOL-based monophosphites, which are highly efficient in asymmetric hydrogenation, are only 2% of the price of the well-known diphosphane BINAP.[4] Further modified heterobifunctional chiral phosphites, especially *P*,*N*-bidentate ones, have been applied to good effect in a wide range of catalytic processes, such as Cu-catalysed conjugate addition, Ir-catalysed hydrogenation and Rh-catalysed hydrosilylation.[1−3,5,6] In Pd-catalysed allylic substitution, work has concentrated mainly on nonsymmetric and sterically hindered substrates,[5−9] with only moderate results for the most common test substrate, 1,3-diphenyl-2-propenyl acetate (**1**, Scheme 1).[10]

Thus, pyridinophosphite ligands derived from (*S*)-BINOL provided product **2** with an enantioselectivity of up to 37%,[11,12] and phosphitooxazolines based on (*S*)- or (*R*)-BINOL afforded up to 43% *ee*.[13] Even more modest results − less than 31% *ee* − were delivered by the quinoline-derived phosphite ligands based on (*R*)-BINOL, (1*R*,2*R*)-*N*,*N*′-dimethyl-1,2-diphenylethylene-1,2-diamine, *N*-methylephedrine, (1*R*,2*R*)-1,2-bis(methylamino)cyclohexane, and (*S*)-prolinol.[14] The most effective *P*,*N*-bidentate ligands applied so far in the Pd-catalysed allylic substitution of **1** with dimethyl malonate are the compounds **4**−**6**.



4 QUIPHOS (R=H)

85% *ee*[14-16]



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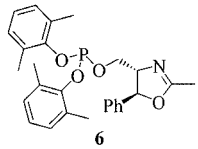
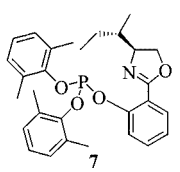
88% *ee*[7]



6

85% *ee*[17]

Notably, variation of R did not increase the enantioselectivity of ligand **4**.[14] Thus, more effective phosphite ligands are still needed. Indeed, the only phosphite ligands used in asymmetric allylic sulfonylation (Scheme 1) appear to be the phosphitooxazolines **7** and **8** recently reported by us.[18,19] They delivered up to 92% *ee* in the synthesis of **3**, which is very close to the efficiency of Helmchen's phosphanyloxazolines.[20]



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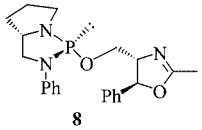

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Here we describe the synthesis of new P*-chiral amino phosphoramidites, their complexation with Rh^I and Pd^{II} and application in Pd-catalysed enantioselective allylic substitution.

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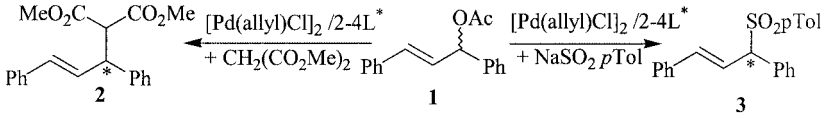
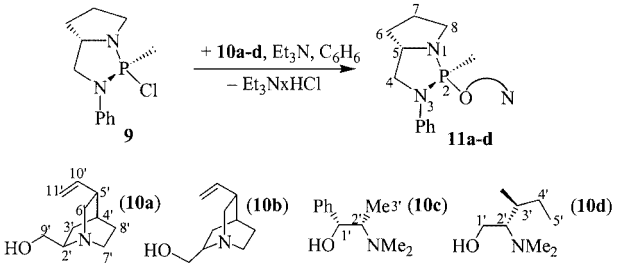
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.



Scheme 1

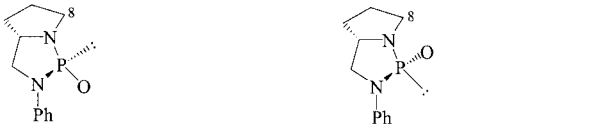
Results and Discussion

The novel *P*,*N*-ligands were synthesized through the one-step phosphorylation of appropriate amino alcohols **10a**−**d** with (2*R*,5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]octane (**9**) (Scheme 2).



Scheme 2

Compounds **11a**−**d** are both stable and very soluble in common organic solvents. The synthesis is highly stereoselective, yielding only epimers with exocyclic substituents at the phosphorus atom in a pseudo-equatorial location. Therefore, the *P**-stereocenter has an (*R*) absolute configuration, which is proved by the characteristic[16,19] $^2J_{C\text{-}8,P}$ coupling (34.3−38.5 Hz) in the ^{13}C NMR spectra of **11a**−**d** (see Table 2 and Exp. Sect.). The magnitude of $^2J_{C\text{-}8,P}$ seems to be strongly controlled by the dihedral angle associated with the lone-pair orbital of the phosphorus atom and C-8.[21]



cis-location of C(8) and phosphorus lone pair; $^2J_{C(8),P} \sim 40$ Hz

trans-location of C(8) and phosphorus lone pair; $^2J_{C(8),P} \sim 0$ Hz

The pseudo-equatorial location of exocyclic functions was previously found for ligands **4**,[16] **8**,[19] and for (*S*)-prolinol-based phosphacyclanes.[21,22] According to the ^{31}P NMR spectroscopic data (Table 1), from ligands **11a**−**d**, only **11d** contains some minor stereoisomer with an (*S*) configuration of the *P**-stereocenter.

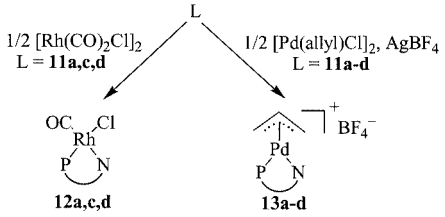
Complexation of **11a**−**d** with $[Rh(CO)_2Cl]_2$ and [Pd(allyl)Cl]$_2$ (in the presence of $AgBF_4$) produced neutral and cationic metal *cis*-chelates, respectively (Scheme 3).

Thus, the $^1J_{P,Rh}$, $^1J_{C,Rh}$, $^2J_{C,P}$ and ν(CO) data for complexes **12a**,**c**,**d** (Tables 1 and 2) agree well with the suggested structures (see ref.[8] and refs. cited therein); ν(CO) and $^1J_{P,Rh}$ are sensitive indicators that allow us to estimate the π-acceptor ability of the phosphorus center and the degree of electronic nonsymmetry of *P*,*N*-ligands.[8,9,23] Accordingly, amino phosphoramidites **11a**−**d** are intermediate between amino phosphanes and amino phosphites.[6,24]

Table 1. Selected spectroscopic data for **11a**−**d**, **12a**,**c**,**d**, and **13a**−**d** (in $CHCl_3$)

Compound	^{31}P NMR δ_P	^1J(P,Rh) [Hz]	IR ν(CO) [cm^{-1}]
11a	122.9		
11b	121.8		
11c	121.4		
11d	120.7 (98%), 114.4 (2%)[a]		
12a	129.4	235.3	2008
12c	128.0	232.4	2010
12d	124.7	234.0	2005
13a	126.9, 125.8		
13b	125.8		
13c	127.6, 125.6		
13d	124.9, 123.5		

[a] Percentage of each epimer.



Scheme 3

Table 2. ^{13}C NMR spectroscopic data for **11a** and **12a** (in $CDCl_3$; $J_{C,P}$ in Hz)

Carbon atom	Compound **11a**	**12a**
CO		184.9 ($^1J_{C,Rh}$ = 70.9, $^2J_{C,P}$ = 21.9)
C_{Ar}	145.5−114.5	142.3−116.6
10′	140.4	137.4
11′	114.0	115.6
5	63.0 (^2J = 8.8)	62.4 (^2J = 11.7)
9′	62.9 (^2J = 4.6)	66.5 (^2J = 2.8)
2′	55.5 (^3J = 2.3)	59.6
4	54.6 (^2J = 7.3)	52.8 (^2J = 4.0)
7′	48.9	50.7
8	48.4 (^2J = 38.5)	49.6 (^2J = 19.7)
6′	47.4	48.0
5′	39.6	38.6
6	31.9	30.9
4′	27.3	26.4
8′	26.5	25.5
7	25.9 (^3J = 3.8)	25.1 (^3J = 4.4)
3′	24.4	25.3

Besides chelate product **12d**, the reaction of **11d** with $[Rh(CO)_2Cl]_2$ afforded the *trans*-$[Rh(CO)Cl(\eta^1\text{-}L)_2]$ complex, where the ligands are coordinated in a *P*-monodentate manner. The complex clearly exhibits the characteristic doublet peak δ_P = 123.8 ppm, $^1J_{P,Rh}$ = 176.8 Hz (46%) in the ^{31}P NMR spectrum. Such side-products have been observed several times and arise from the sterically hindered nitrogen atom, which impedes chelation.[8,9,19]

In complex **12a**, the quinuclidine nitrogen atom is coordinated to the rhodium atom, as witnessed by the significant (up to 4 ppm) coordination shifts $\Delta\delta_C = \delta_C(\text{complex}) - \delta_C(\text{ligand})$ observed for C-2′, C-6′, and C-7′ (Table 2). Similar $\Delta\delta_C$ values have been observed for chelate Rh^I complexes with quincoridine-derived phosphites.[25] The large $^2J_{C\text{-}8,P}$ values in complex **12a** (19.7 Hz) clearly indicate that the quinuclidyl substituent is in a pseudo-equatorial position and, therefore, that the *P** atom had an (*R*) absolute configuration. This conclusion, and other findings on the structure of **12a**, agree well with the X-ray analysis data of its monocrystal. Thus, in the crystal of **12a** two independent molecules are characterized by (*S*) and (*R*) configurations of asymmetric N(1′) and P(2) atoms (without taking into account the formal priority of the metal atom). In one independent molecule, the phospholidine cycle has a twist conformation with deviations of C(4) and C(5) atoms of 0.27 and 0.20 Å, respectively, while in a second independent molecule this cycle is characterized by a slightly distorted envelope conformation with a deviation of N(3) of 0.29 Å. The pyrollidine cycles have envelope conformations [C(7) atoms deviate by 0.58 Å on average] with the phenyl substituent in a pseudo-equatorial position. The quincoridine substituent occupies a pseudo-equatorial position as related to the phospholidine cycle. In turn, the rhodium atom occupies an axial position.

Similarly to the compound described in ref.[16], the phosphorus atom in **12a** has a tetrahedral configuration (the sum basal N−P−O and N−P−N angles are 302 and 298°, respectively). The N(1)−P(2)−O(1) and N(3)−P(2)−O(1) angles are about 2−3° less than the analogous ones in ref.[16] The elongation of P−N bonds by up to 0.02 Å compared to those in ref.[16] may due to a *trans* effect of the chlorine substituent.

The rhodium atom has almost ideal square-planar coordination, with an average deviation from the mean plane of 0.02 Å. The bond lengths of coordination polyhedra of the rhodium atom are close to those in rhodium and palladium complexes with *P,N*-bidentate aryl phosphites[8] (Figure 1).

The principal structural difference between the two independent molecules is the geometry of the six-membered metallacycles, which are characterized by a distorted boat conformation. The C(2′) and P(2) atoms in the first molecule deviate from the basal plane by 0.62 and 0.50 Å, and C(2′A) and P(2A) in the second molecule deviate by 0.32 and 0.60 Å, respectively. Previously investigated rhodium and palladium complexes with the same type of coordination polyhedra have six-membered metallacycles with a chair conformation. However, the introduction of the bulky ferrocenyl moiety near the six-membered metallacycle[8] changed this conformation to a distorted boat. Thus, the distorted boat conformation of the metallacycles in **12a** can be attributed to steric overcrowding caused by the massive 1-azabicyclo[2.2.2]octane and 1,3-diaza-2-phosphabicyclo-[3.3.0]octane moieties.

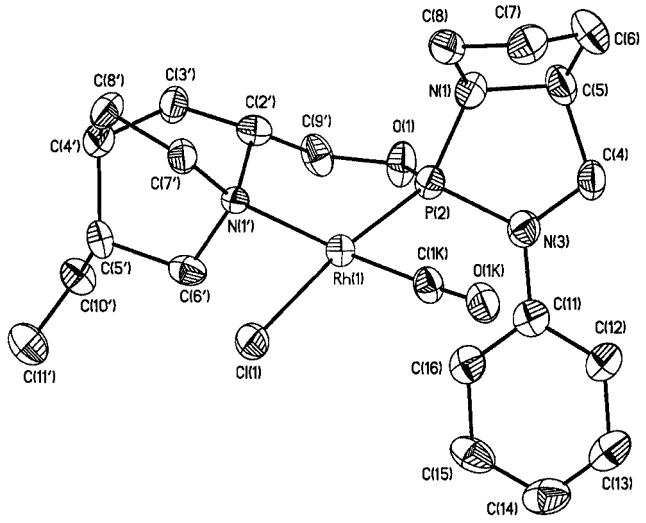


Figure 1. General view of one of the two independent molecules of **12a**; atoms are presented as thermal ellipsoids drawn at 50% probability level; selected averaged bond lengths [Å] and angles [°]: Rh(1)−P(2) 2.176(2), Rh(1)−Cl(1) 2.408(2), Rh(1)−N(1′) 2.174(6), Rh(1A)−C(1 K) 1.826(9), C(1 K)−O(1 K), O(1 K)−C(1 K) 1.11(1), P(2)−N(1) 1.656(8), P(2)−N(3) 1.706(7); P(2)−Rh(1)−C(1 K) 85.5(3), Cl(1)−Rh(1)−C(1 K) 89.4(3), Cl(1)−Rh(1)−N(1 K) 90.7(2), Cl(1)−Rh(1)−P(2) 172.29(8), N(1′)−Rh(1)−C(1 K) 176.0(3), N(1)−P(2)−N(3) 93.0(4)

Cationic palladium chelates **13a**−**d** are stable in air and very soluble in common organic media. There are two sets of peaks in the ^{31}P NMR spectra of **13a**, **13c**, and **13d** (Table 1), which indicate the existence of the *exo* and *endo* isomers of the compounds. Two peak sets are not seen for complex **13b**, because of either the fast interconversion of isomers or the absence of one of them (see refs.[8,9] and references cited therein).

Amino amidophosphites **12a**−**d** and the isolated complexes **13a**−**d** were tested in asymmetric Pd-catalysed allylic substitution processes (Scheme 1). For allylic sulfonylation (Table 3) moderate chemical (up to 66%) and good optical (up to 90% *ee*) yields of product **3** were achieved. For ligand **11a**, the enantioselectivity does not depend on the L*/[Pd] ratio (Entries 1−3). We suppose that the active catalytic particle here is represented by a cationic chelate $[Pd(allyl)(\eta^2\text{-}P,N)]^+X^-$ (X^- = Cl^-, BF_4^-). Indeed, its singlet peak δ_P = 125.0 ppm (28%) was found in the ^{31}P NMR spectrum of the $[Pd(allyl)Cl]_2$/4L* (L* = **11a**) solution in $CHCl_3$, together with signals of uncoordinated **11a** (δ_P = 122.9 ppm) and $[Pd(allyl)(\eta^1\text{-}P,N)(\eta^2\text{-}P,N)]^+Cl^-$ (AX system: δ_P = 100.3 ppm and δ_P = 61.4 ppm, $^2J_{P,P}$ = 87.7 Hz). With ligand **11d**, the L*/[Pd] ratio also did not influence the catalytic outcome (Entries 12,13,15). In contrast, when the ratio **11b**/[Pd] was increased from 1:1 to 2:1, the enantioselectivity improved sharply from 39 to 76% *ee* (Entries 4, 5). Most probably, here the palladium complex containing two molecules of the ligand possesses high catalytic activity

Table 3. Enantioselective allylic sulfonylation of **1** with $NaSO_2pTol$ (in THF)

Entry	Catalyst precursor	Ligand	L*/[Pd]	Isolated yield [%]	*ee* [%][a]
1	$[Pd(allyl)Cl]_2$	**11a**	1:1	56	77 (*S*)
2	$[Pd(allyl)Cl]_2$	**11a**	2:1	50	73 (*S*)
3	**13a**		1:1	24	76 (*S*)
4	$[Pd(allyl)Cl]_2$	**11b**	1:1	45	39 (*S*)
5	$[Pd(allyl)Cl]_2$	**11b**	2:1	65	76 (*S*)
6	$[Pd_2(dba)_3] \times CHCl_3$	**11b**	1:1	57	67 (*S*)
7	**13b**		1:1	41	60 (*S*)
8	$[Pd(allyl)Cl]_2$	**11c**	1:1	13	74 (*S*)
9	$[Pd(allyl)Cl]_2$	**11c**	2:1	25	61 (*S*)
10	$[Pd_2(dba)_3] \times CHCl_3$	**11c**	1:1	17	10 (*R*)
11	**13c**		1:1	66	80 (*S*)
12	$[Pd(allyl)Cl]_2$	**11d**	1:1	39	87 (*S*)
13	**$[Pd(allyl)Cl]_2$**	**11d**	**2:1**	**40**	**90 (*S*)**
14	$[Pd_2(dba)_3] \times CHCl_3$	**11d**	1:1	15	20 (*S*)
15	**13d**		1:1	40	83 (*S*)

[a] Measured by HPLC [(*R*,*R*)-Whelk-01].

and is very stereoselective. In addition, a considerable counterion effect was observed for complexes with ligand **11b** (Entries 4, 7).[26]

As all the variations in the structures of both the N-containing fragment and the carbon bridge between the P and N atoms did not cause considerable changes in enantioselectivity, the catalytic performance of ligands **11a−d** is mostly determined by the bicyclic chiral phosphorus block.

With $[Pd_2(dba)_3] \times CHCl_3$ as a catalytic precursor, generally inferior results were obtained. For ligands **11c** and **11d** the enantioselectivity dropped very sharply (Entries 10, 14), and even a product with reversed absolute configuration was produced in one case (Entry 10).

Application of pre-formed palladium complexes **13a−d** in asymmetric allylic alkylation resulted in excellent chemical and optical yields (Table 4). The enantioselectivity of the reaction demonstrates a strong dependence on both the solvent (Entries 3 and 4) and the structure of the amino alcohol block (Entries 1 and 3). Comparison of the results (under identical reaction conditions) for sulfonylation (Table 3, Entries 3, 7, 11, 15) and for alkylation (Table 4, Entries 1, 3, 5, 7) reveals that the right choice of nucleophile is important in achieving high level of enantioselectivity in allylic substitution reactions.

Table 4. Enantioselective allylic alkylation of **1** with dimethyl malonate

Entry	Catalyst precursor	Solvent	Conv. [%][a]	*ee* [%][b]
1	**13a**	THF	> 99	95 (*S*)
2	**13a**	CH_2Cl_2	99	97 (*S*)
3	**13b**	THF	98	91 (*R*)
4	**13b**	CH_2Cl_2	72	52 (*R*)
5	**13c**	THF	83	89 (*S*)
6	**13c**	CH_2Cl_2	88	79 (*S*)
7	**13d**	THF	> 99	92 (*S*)
8	**13d**	**CH_2Cl_2**	**92**	**98 (*S*)**

[a] Measured by HPLC. [b] Determined by HPLC analysis using a Daicel Chiralcel OD-H column.

The enantioselectivity obtained with ligands **11a−d** in the Pd-catalysed allylic alkylation of **1** with dimethyl malonate (98% *ee*) is the highest reported for chiral phosphite ligands and approaches the best overall results.[5,6,10]

Experimental Section

General Remarks: All reactions were performed under argon in dehydrated solvents. IR spectra were recorded with a Specord M80 or Nicolet 750 instrument. ^{31}P and ^{13}C NMR spectra were recorded with a Bruker AMX 400 instrument (162.0 MHz for ^{31}P, 100.6 MHz for ^{13}C). Complete assignment of all the resonances in ^{13}C NMR spectra was achieved with DEPT techniques. Chemical shifts (ppm) are given relative to Me_4Si (^{13}C NMR) and 85% H_3PO_4 (^{31}P NMR). Mass spectra were recorded with a Kratos MS890 spectrometer (EI), an MSVKh TOF spectrometer with ionization by Cf-252 fission fragments (plasma desorption technique, PD), and an AMD 402 spectrometer (FAB). Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow). $[Rh(CO)_2Cl]_2$,[27] $[Pd(allyl)Cl]_2$,[28] $[Pd_2(dba)_3] \times CHCl_3$,[29] amino alcohol **10d**,[30] and (2*R*,5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane (**9**)[19] were synthesized by published procedures. Complexes **12a** and **13a−d** were synthesized by techniques similar to that reported.[9] Rhodium complexes **12c**,**d** were synthesized for the ^{31}P NMR and IR experiments in $CHCl_3$ medium analogously to the known procedures.[8] Compound **10c** was purchased from Aldrich and dried in vacuo (2 Torr, 3 h) immediately before use. Amino alcohols **10a**,**b** (quincoridine and quincorine, Buchler GmbH) and **10d** were azeotropically dried with benzene and distilled before use.

Synthesis and Characterization

Preparation of Ligands. General Technique: A solution of (2*R*,5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**9**) (1 g, 4.2×10^{-3} mol) in benzene (15 mL) was added dropwise to a stirred solution of the appropriate amino alcohol **10a−d** (4.2×10^{-3} mol) and Et_3N (0.6 mL, 4.2×10^{-3} mol) in the same solvent (15 mL) at 0 °C. The reaction mixture was then heated to boiling point, allowed to cool, stirred at 50 °C for 1 h, allowed to cool to room temperature and then filtered. The solvent was removed in vacuo (40 Torr), and the residue was dissolved in hexane (25 mL), filtered, concentrated and dried in vacuo (1 Torr, 2 h).

(2*R*,5*S*,2′*R*,4′*S*,5′*R*)-3-Phenyl-2-[(5′-vinyl-2′-quinuclidyl)methoxy]-1,3-diaza-2-phosphabicyclo[3.3.0]octane (11a): Colourless oil, 1.41 g (91% yield). MS (EI, 70 eV): *m*/*z* (%) = 371 (29) $[M]^+$, 289 (50), 221 (34), 205 (100), 197 (72), 136 (91). $C_{21}H_{30}N_3OP$ (371.2): calcd. C 67.90, H 8.14, N 11.31; found C 68.24, H 8.35, N 11.17.

(2*R*,5*S*,2′*S*,4′*S*,5′*R*)-3-Phenyl-2-[(5′-vinyl-2′-quinuclidyl)methoxy]-1,3-diaza-2-phosphabicyclo[3.3.0]octane (11b): Colourless oil, 1.391 g (90% yield). MS (EI, 70 eV): *m*/*z* (%) = 371 (30) $[M]^+$, 289 (48), 221 (34), 205 (100). $C_{21}H_{30}N_3OP$ (371.2): calcd. C 67.90, H 8.14, N 11.31; found C 68.17, H 8.28, N 11.20.

(2*R*,5*S*,1′*R*,2′*S*)-2-(2′-Dimethylamino-1′-phenylpropoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (11c): Colourless oil, 1.466 g (92% yield). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 7.8 (s, C-3′), 26.5 (d, ^3J = 4.5 Hz, C-7), 31.4 (s, C-6), 40.6 (s, NMe_2), 46.7 (d, ^2J = 34.3 Hz, C-8), 53.7 (d, ^2J = 7.5 Hz, C-4), 62.3 (d, ^2J = 9.0 Hz, C-5), 64.8 (d, ^3J = 2.4 Hz, C-2′), 76.7 (s, C-1′),

114.5−145.6 (C_{Ar}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 312 (2), 222 (67), 205 (12), 117 (100). MS (PD): *m*/*z* (%) = 383 (10) $[M]^+$, 205 (60), 162 (85), 72 (100). $C_{22}H_{30}N_3OP$ (383.2): calcd. C 68.91, H 7.89, N 10.96; found C 69.13, H 8.00, N 11.18.

(2*R*,5*S*,2′*S*,3′*S*)-2-(2′-Dimethylamino-3′-methylpentyloxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (11d): Colourless oil, 1.291 g (89% yield). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ = 11.0 (s, C-5′), 15.3 (s, CH_3), 26.0 (d, ^3J = 3.4 Hz, C-7), 26.5 (s, C-4′), 32.1 (s, C-6), 33.3 (s, C-3′), 41.9 (s, NMe_2), 48.4 (d, ^2J = 38.5 Hz, C-8), 54. 7 (d, ^2J = 7.2 Hz, C-4), 58.5 (s, C-1′), 63.4 (d, ^2J = 8.8 Hz, C-5), 67.5 (d, ^3J = 1.9 Hz, C-2′), 114.6−145.8 (C_{Ar}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 334 (1), 205 (66), 114 (100). MS (PD): *m*/*z* (%) = 349 (15) $[M]^+$, 319 (27), 221 (34), 114 (100). $C_{19}H_{32}N_3OP$ (349.2): calcd. C 65.30, H 9.23, N 12.02; found C 65.54, H 9.35, N 11.88.

Rhodium(I) and Palladium(II) Complexes

[Rh(CO)Cl(11a−P⌒N)] (12a): Pale yellow solid, 0.180 g (93% yield). IR (Nujol): $\tilde{\nu}$ = 296 [ν(Rh−Cl)] cm^{-1}. $C_{22}H_{30}ClN_3O_2PRh$ (537.1): calcd. C 49.13, H 5.62, Cl 6.59, N 7.81; found C 49.40, H 5.78, Cl 6.82, N 8.03.

[Pd(allyl)(11a−P⌒N)]$^+BF_4^-$ (13a): Pale yellow solid, 0.232 g (96% yield). MS (FAB): *m*/*z* (%) = 518 (100) $[M - BF_4]^+$, 477 (21), 311 (42), 205 (96). $C_{24}H_{35}BF_4N_3OPPd$ (605.2): calcd. C 47.59, H 5.82, N 6.94; found C 47.33, H 5.98, N 7.16.

[Pd(allyl)(11b−P⌒N)]$^+BF_4^-$ (13b): Yellow solid, 0.213 g (88% yield). MS (FAB): *m*/*z* (%): 518 (100) $[M - BF_4]^+$, 477 (15), 311 (29), 205 (30). $C_{24}H_{35}BF_4N_3OPPd$ (605.2): calcd. C 47.59, H 5.82, N 6.94; found C 47.44, H 6.03, N 6.89.

[Pd(allyl)(11c−P⌒N)]$^+BF_4^-$ (13c): White solid, 0.222 g (90% yield). MS (FAB): *m*/*z* (%): 530 (32) $[M - BF_4]^+$, 489 (12), 162 (100). $C_{25}H_{35}BF_4N_3OPPd$ (617.2): calcd. C 48.61, H 5.71, N 6.80; found C 48.37, H 5.84, N 6.93.

[Pd(allyl)(11d−P⌒N)]$^+BF_4^-$ (13d): Beige solid, 0.220 g (94% yield). MS (FAB): *m*/*z* (%): 496 (8) $[M - BF_4]^+$, 455 (5), 128 (100). $C_{22}H_{37}BF_4N_3OPPd$ (583.2): calcd. C 45.27, H 6.39, N 7.20; found C 45.51, H 6.23, N 7.33.

Crystallographic Data for 12a: Crystals of $C_{22}H_{30}ClN_3O_2PRh$ are monoclinic, space group $P2_1$, *a* = 8.410(3) Å, *b* = 11.557(4) Å, *c* = 23.267(8) Å, *V* = 2261.1(14) $Å^3$, *Z* = 4, *M* = 537.82, $d_{calcd.}$ = 1.580 $g·cm^{-3}$, μ(Mo-K_α) = 9.68 cm^{-1}, *F*(000) = 1104. Intensities of 13120 reflections were collected at 120 K with a SMART CCD 1000 diffractometer using Mo-K_α radiation (λ = 0.71072 Å, ω-scans with 0.3° step and 10 s exposure for each frame) and 8058 independent reflections (R_{int} = 0.0365) were used in further refinement. An absorption correction was applied semi-empirically from equivalents. The structure of **12a** was solved by direct methods and refined by a full-matrix techniques against F^2 in anisotropic approximation using the SHELXTL-97 5.1 program package[31]. The positions of hydrogen atoms were calculated geometrically and included in the refinement using the rigid body approximation. The refinement converged to wR_2 = 0.1238 and *GOF* = 1.020 for all independent reflections [R_1 = 0.0567 was calculated for 6829 observed reflections with $I > 2\sigma(I)$]. The absolute configuration was determined by use of the Flack parameter. CCDC-215598 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information: ^1H NMR spectroscopic data for compounds **11a−d** and the catalytic experimental procedures are provided (see also footnote on the first page of this article).

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