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New chiral phosphite ligands bearing sp^2-nitrogen: complexation properties and palladium(II)-catalysed enantioselective allylic alkylation

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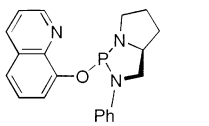
Abstract—New homochiral *P*,*N*-bidentate phosphite-type ligands containing sp^2-nitrogen were synthesised and their complexation with Rh(I) and Pd(II) atoms was investigated. The X-ray crystal structure of one of the chelate chlorocarbonyl rhodium complexes was obtained. E.e.s of up to 85% were attained in the Pd-catalysed allylic substitution reaction using the new *P*,*N*-ligands. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The largest and most effective group of known chiral *P*,*N*-bidentate ligands for metal complex catalysis consist of compounds with sp^2-hybridised nitrogen donor centres. These have provided substantial advances in most important enantioselective catalytic reactions including allylic substitution, the Heck reaction, conjugate addition to enones, hydrogenation, reduction of ketones, hydrosilylation–oxidation and hydroboration–oxidation of olefins (see Refs. 1–3 and references cited therein, and Refs. 4–12). The nature of the sp^2-*N* centres in these ligands was widely varied, but the phosphorus centre largely remained the same (a diphenylphosphine group). More recently some systems were designed that possess phosphite- or amidophosphite-type phosphorus centres. Such ligands exhibit some remarkable features. One of them is the enhanced π-acidity of the *P*-centre. A series of such catalysts has been successfully applied in the enantioselective conjugate addition of organozinc reagents to enones, the hydrosilylation of ketones, hydrogenation of vinylarenes, Diels–Alder reactions and allylic substitution reactions.[1–3,13–18] In particular, application of ligands **1**–**4** gave e.e.s of up to 88% in the model Pd-catalysed alkylation reaction of 1,3-diphenyl-2-propenyl acetate by dimethyl malonate.[16–18]

Herein, we report on the synthesis, complexation with Rh(I) and Pd(II) and the catalytic application of new homochiral *P*,*N*-phosphite ligands **5**–**7** bearing sp^2-nitrogen atoms. Chiral phosphite derivatives of Schiff



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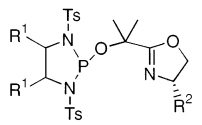
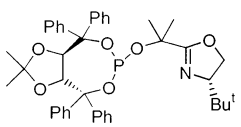


2a-2c

	R^1	R^2	
	Ph	Bu^t	(a)
	$(CH_2)_4$	Bu^t	(b)
	Ph	Ph	(c)



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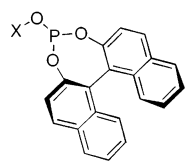

4a, 4b

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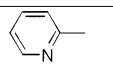
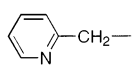
		(a)
		(b)

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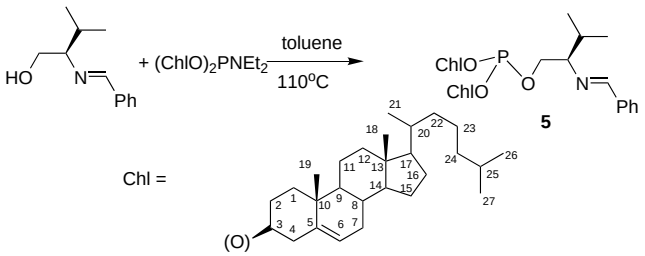
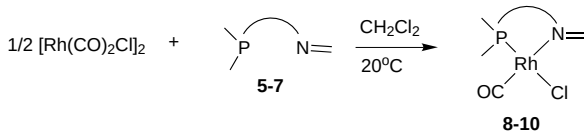
bases and phosphitooxazolines with an acyclic phosphorus centre have not been described before.

2. Results and discussion

Ligand **5** was prepared by reaction of (2*R*)-2-{*N*-(benzylideneamino)}-3-methylbutanol-1 with an equimolar amount of phosphorus amidite.



The syntheses of compounds **6** and **7** were carried out using the corresponding chlorophosphites. In the case of **6** the chlorophosphite was used without isolation. Compounds **5**–**7** were found to be stable under anhydrous conditions. The reaction of **5**–**7** with $[Rh(CO)_2Cl]_2$ gives the chelate complexes **8**–**10**, respectively.



Principal spectral data for these complexes are summarised in Table 1.

The values of ν(CO), ν(Rh–Cl) and ^1J(P,Rh) are characteristic for chlorocarbonyl rhodium(I) complexes with chelate *P*,*N*-phosphites.[19,20] The ^1J(C,Rh) values for **8**–**10** are within a 68–75 Hz interval typical for [Rh(CO)Cl(P^N)], where P^N is a *cis*-coordinated *P*,*N*-bidentate ligand.[19,21] As a result of the enhanced π-acidity of the phosphorus atoms, the values of ν(CO) and ^1J(P,Rh) for **8**–**10** are higher than those for

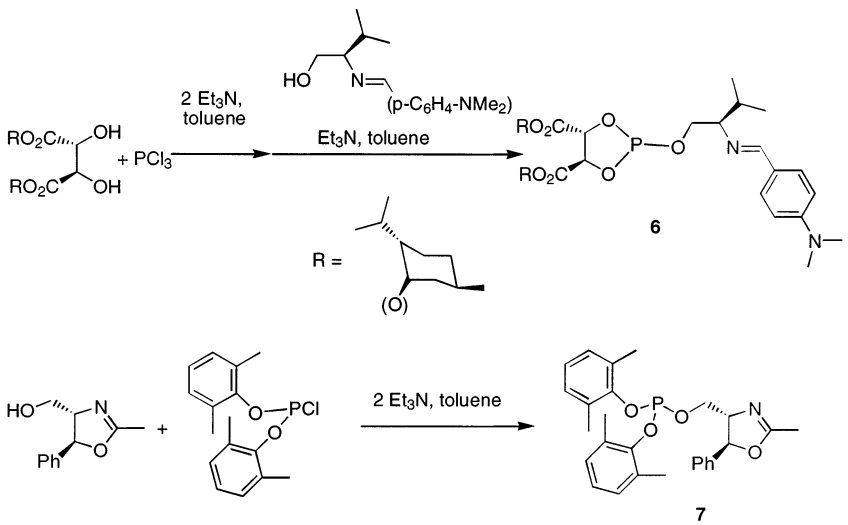


Table 1. Selected spectral data for compounds **8**–**10**

Compound	IR (cm^{-1})		NMR (in $CDCl_3$)				
	ν(CO), $CHCl_3$ (KBr)	ν(Rh–Cl), $CHCl_3$ (Nujol)	^{31}P		^{13}C		
			δ_P (ppm)	^1J(P,Rh) (Hz)	δ_{CO} (ppm)	^1J(C,Rh) (Hz)	^2J(C,P) (Hz)
8	2020 (2006)	293 (292)	129.73	251.6	187.29	75.1	19.5
9	2034 (2022)	304 (304)	147.23	277.5	186.24	69.7	18.3
10	2030 (2022)	292 (293)	124.53	276.8	186.11	72.4	18.9

Table 2. Selected ^{13}C NMR data for compounds **5**–**12**

Compound	**5**	**8**	**11**	**6**	**9**	**7**	**10**	**12**
δ_C (C=N) (ppm)	160.88	170.98	161.39	160.86	170.79	165.58	173.93	174.93
$\Delta\delta_C$[a]		10.10	0.51		9.93		8.35	9.07

[a] $\Delta\delta = \delta$(complex)$-\delta$(ligand).

analogous complexes with phosphine-type ligands. For example, chelate chlorocarbonyl rhodium(I) complexes with phosphinopyrazol derivatives of ferrocene show ν(CO) bands at 1980–2008 cm^{-1} in CH_2Cl_2 solution and ^1J(P,Rh) of 161–176 Hz.[22]

The ^{13}C NMR spectroscopic data for compounds **8**–**10** are in good agreement with the proposed structures. In particular, significant coordination shifts ($\Delta\delta$) of the azomethine-type carbons (Table 2) can serve as reliable spectral evidence for the coordination of sp^2-nitrogens to the metal atom.

Sedimentation analysis of complex **8** (1% $CHCl_3$ solution, 25°C), taken as an example, also supports its mononuclear nature. The obtained molecular mass value of $M_z = 1250 \pm 7\%$ Da is in good agreement with the calculated value $M_r = 1159$.

Monocrystals of compound **10** were obtained by slow evaporation of its solution in CH_2Cl_2/hexane mixture, and the molecular structure was determined by X-ray diffraction analysis (Fig. 1). The conformation of the oxazoline cycle is twisted with the deviations of C(2) and C(3) atoms of 0.33 and –0.17 Å, respectively. In spite of coordination to Rh(1) all the geometric parameters of this cycle are quite typical. The only exception is the slightly non-planar configuration of the N(1) atom (the sum of the bond angles involving N(1) is equal to 357.3(2)°). The six-membered metallacycle is characterised by the distorted boat conformation with the deviation of the Rh(1) and C(11) atoms by 0.82 and 0.66 Å. The phosphorus atom is characterised by the slightly distorted tetrahedral configuration with non-equal P–O distances. It is noteworthy that shortening of the P–O bond is observed in the case of P(1)–O(3), which lies in the OC–Rh(1)–Cl plane.

In contrast to the reaction with $[Rh(CO)_2Cl]_2$, reaction of **5** with $[PdCl_2(COD)]$ proceeds unselectively. Thus, the ^{31}P NMR spectra of both reaction solution in $CDCl_3$ (in situ) and solution of the product in $CDCl_3$ show δ_P resonances at 91.34 (35%) and 78.71 (65%). The latter resonance is characteristic of a chelate complex *cis*-$[PdCl_2(P\wedge N)]$,[23,24] whereas the downfield resonance is typical for a product of composition P/Pd = 2.[24] The product **11** has been also obtained in almost quantitative yield by carrying out the reaction with double the amount of the ligand.

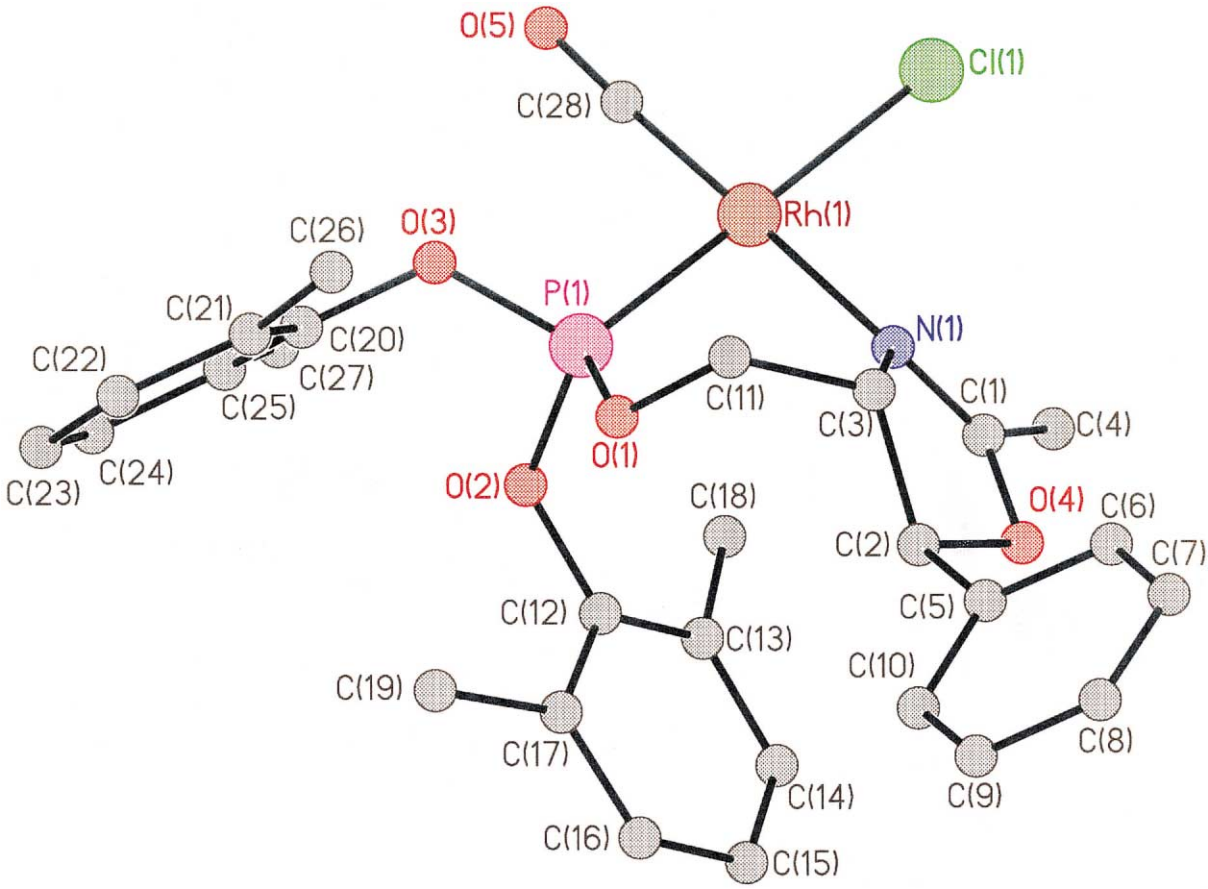
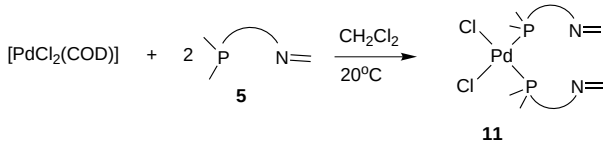
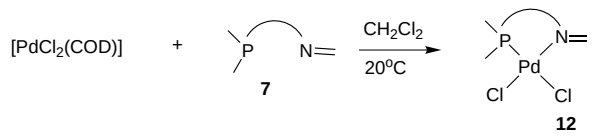


Figure 1. General view of **10**. Principal bond lengths (Å): Rh(1)–Cl(1) 2.3721(7), Rh(1)–P(1) 2.1727(7), Rh(1)–N(1) 2.118(2), Rh(1)–C(28) 1.827(2), P(1)–O(3) 1.600(2), P(1)–O(1) 1.610(2), P(1)–O(2) 1.615(2), O(4)–C(1) 1.337(3), O(4)–C(2) 1.475(3), O(5)–C(28) 1.145(3), N(1)–C(1) 1.286(3), N(1)–C(3) 1.499(3); bond angles (°): C(28)–Rh(1)–N(1) 178.1(1), C(28)–Rh(1)–P(1) 90.75(7), N(1)–Rh(1)–P(1) 87.62(6), C(28)–Rh(1)–Cl(1) 88.39(7), N(1)–Rh(1)–Cl(1) 93.24(6), P(1)–Rh(1)–Cl(1) 179.13(3), O(3)–P(1)–O(1) 108.01(10), O(3)–P(1)–O(2) 99.30(9), O(1)–P(1)–O(2) 98.20(9), O(3)–P(1)–Rh(1) 113.07(7), O(1)–P(1)–Rh(1) 113.62(7), O(2)–P(1)–Rh(1) 122.60(7), C(1)–N(1)–C(3) 105.1(2), C(1)–N(1)–Rh(1) 128.82(17), C(3)–N(1)–Rh(1) 123.36(15), O(5)–C(28)–Rh(1) 177.2(2).



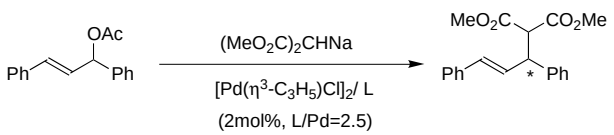
The ^{31}P NMR spectrum of **11** contains only one δ_P resonance at 91.34 ($CDCl_3$). The *cis*-orientation and terminal position of the chlorines in the coordination sphere of palladium is proved by IR spectral data: The ν(Pd–Cl) bands are at 316, 305 cm^{-1} ($CHCl_3$) and 316, 304 cm^{-1} (Nujol).[25] Analysis of ^{13}C NMR data shows that there is no binding of remote imino groups to metal in complex **11**. Particularly, coordination shifts $\Delta\delta_C$ for the resonances of azomethine carbon atoms were not observed (Table 2). Previously it has been shown that the structurally related ligand $(ChlO)_2PO(CH_2)_2NMe_2$ forms stable chelate complex *cis*-[$PdCl_2$(P^N)] if reacted with [$PdCl_2$(COD)].[23]

Complexation of the ligand **7** with [$PdCl_2$(COD)] is as follows.



^{31}P and ^{13}C NMR and IR analyses confirmed this mode of coordination. Thus, the resonance (δ_P 74.53) and the considerable coordination shift ($\Delta\delta_P$ −60.14) is observed in ^{31}P NMR spectra of **7** and **12** in $CDCl_3$. Two equally intensive ν(Pd–Cl) bands in the far IR region of **12** (291 and 345 cm^{-1}) result from the *cis*-configuration of the chlorine ligands under different *trans*-influence of phosphorus and nitrogen centres. The ^{13}C NMR spectra demonstrate considerable downfield coordination shifts $\Delta\delta_C$ for carbon atoms attached to the nitrogen (see Table 2), thus confirming coordination of the nitrogen atom of **7** to palladium.

Ligands **5**–**7** were tested in the Pd-catalysed enantioselective allylic substitution reaction.



The results (Table 3) show ligand **7** to be the most effective. In the case of **7** the reaction temperature and solvent can be varied without any loss of e.e. In contrast, the selectivity of allylation reactions using **5** and **6** depend heavily on the solvent used.

A number of chiral *P*,*N*-bidentate ligands giving almost quantitative optical yields have been described.[1–3] However, it is more correct to compare the effectiveness of **5**–**7** with *P*,*N*-bidentate derivatives of phosphorous acids **1**–**4** in the same type of reaction (**1**-85% e.e.,[16] **2a**-60% e.e.,[17] **2b**-52% e.e.,[17] **2c**-88% e.e.,[17] **3**-20% e.e.,[17] **4a** and **4b**-racemic[18]). So, our novel *P*,*N*-hybrid phosphite ligands lead to comparable e.e. values. Moreover, ligands **1**, **2a**–**c** and **3** possess additional stereogenic centres, some of which are in the phosphorus heterocycles. Ligand **7** has only one stereocentre in the oxazoline fragment. Other known hetero-bidentate phosphite ligands gave comparable results (68–71%[18] and 11–83% e.e.[26]). Further modifications of the most prominent structures **6** and **7** are in progress in our laboratories.

3. Experimental

3.1. General methods

All reactions were carried out under a dry argon atmosphere in freshly dried and distilled solvents. IR spectra were recorded on a Specord M80 or Nicolet 750 instrument. ^{31}P and ^{13}C NMR spectra were recorded on a Bruker AMX-400 instrument (162.0 MHz for ^{31}P; 100.6 MHz for ^{13}C). The complete assignment of all resonances in ^{13}C NMR spectra was achieved using DEPT technique. Chemical shifts (ppm) are quoted relative to $CDCl_3$ (^{13}C NMR, $\delta = 76.91$) and 85% H_3PO_4 (^{31}P NMR). Mass spectra (EI) were recorded on a Kratos MS 890 spectrometer and on a MSVKh TOF spectrometer with ionisation by californium-252 fission fragments (plasma desorption technique). Sedimentation analyses were performed on a MOM-3180 analytical ultracentrifuge according to published techniques.[27–29] Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow). Optical rotations were measured on a Perkin–Elmer 141 polarimeter.

Crystallographic data for **10**: At 110 K crystals of $C_{28}H_{30}ClNO_5PRh$ are monoclinic, space group $P2_1$, $a = 8.135(2)$, $b = 18.894(5)$, $c = 9.183(2)$ Å, $\beta =$

Table 3. Enantioselective Pd-catalysed allylic substitution of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate sodium salt using ligands **5**–**7**

Entry	Ligand	Temp.	Solvent	Time (h)	Yield (%)[a]	% e.e. (conf.)[b]
1	**5**	rt	THF	3	58	33 (*S*)
2	**5**	rt	CH_2Cl_2	3	57	13 (*S*)
3	**6**	rt	THF	48	10	76 (*S*)
4	**6**	rt	CH_2Cl_2	48	5	36 (*S*)
5	**7**	rt	THF	3	75	85 (*R*)
6	**7**	rt	CH_2Cl_2	3	83	85 (*R*)
7	**7**	0°C	THF	48	21	85 (*R*)

[a] Isolated yield.
[b] E.e. measured by HPLC (Chiracel OD).

103.027(5)°, $V=1375.2(6)$ Å^3, $Z=2$, $M=629.86$, $D_{calcd}=1.521$ g cm^{-3}, μ(Mo Kα)$=8.15$?m^{-1}, $F(000)=644$. The intensities of 33088 reflections were measured with a Smart 1000 CCD diffractometer at 110 K (λ(Mo Kα)$=0.71072$ Å, ω-scans with a 0.3° step in ω and 10 s per frame exposure, $2\theta<63°$), and 8165 independent reflections ($R_{int}=0.0270$) were used in a further refinement. The absorption correction was carried out semi-empirically from equivalents. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The absolute configuration of C(2) and C(3) atoms was estimated by mean of the Flack parameter, which was equal to 0.000(18) in the case of the *S* configuration. The refinement converged to $wR_2=0.0732$ and GOF $=1.049$ for all independent reflections ($R_1=0.0297$ was calculated against *F* for 7989 observed reflections with $I>2\sigma(I)$). All calculations were performed using the SHELXTL PLUS 5.0 program package on an IBM PC AT.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary nos. CCDC-164528 (structure **10**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK [Fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]

3.2. Synthesis

$[Rh(CO)_2Cl]_2$,[30] $[PdCl_2(COD)]$[31] and dicholesteryl-*N*,*N*-diethylphosphoramidite[24] were synthesised as published. PCl_3, NEt_3, 2,6-dimethylphenol were distilled before use. (4*S*,5*S*)-(−)-2-Methyl-5-phenyl-2-oxazoline-4-methanol (Fluka) was dried for 3 h over P_2O_5 in vacuum (1 mmHg) before use.

3.3. (2*R*)-2-{*N*-(Benzylideneamino)}-3-methylbutanol-1

The known iminoalcohol[32] was synthesised as published,[33] azeotropically dried with benzene and distilled before use.

3.4. (2*R*)-2-{*N*-(*p*-Dimethylaminobenzylideneamino)}-3-methylbutanol-1

The iminoalcohol was synthesised as published,[33] azeotropically dried with benzene and distilled before use. Yellow crystals (84%); mp 90–91°C; $[\alpha]_D^{19}=+9.8$ (*c* 10, CH_2Cl_2); $n_D^{20}=1.4411$. ^{13}C NMR ($CDCl_3$), δ_C: CH_3 19.51, 20.23; CH 29.85; $N(CH_3)_2$ 39.96; CH_2O 64.33; CHN 76.59; CH_{Ar} 111.24, 129.61; C_{Ar} 123.88, 151.75; CH= 161.76. ^{1}H NMR ($CDCl_3$), δ_H (*J*(H,H)/Hz): 7.98 (s, 1H, CH=); 7.51 (d, 2H, ^3J 8.8, H_{Ar}); 6.63 (d, 2H, ^3J 8.8, H_{Ar}); 3.84 (m, 1H, J_{gem} 11.2 CH_2O); 3.73 (m, 1H, J_{gem} 11.2, ^3J 3.2, CH_2O); 2.98 (s, 6H, $N(CH_3)_2$); 2.84 (m, 1H, ^3J 3.2, NCH); 3.43 (s, br., 1H, OH); 1.90 (m, 1H, ^3J6.8, CH); 0.92 (d, 3H, ^3J 6.8, CH_3); 0.84 (d, 3H, ^3J 6.8, CH_3). Anal. calcd for $C_{14}H_{22}N_2O$: C, 71.76; H, 9.46. Found: C, 71.98; H, 9.70%.

3.5. Di(2,6-dimethylphenyl) chlorophosphite

A solution of 2,6-dimethylphenol (4.80 g, 4×10^{-2} mol) and NEt_3 (5.80 mL, 4×10^{-2} mol) in benzene (30 mL) was added dropwise to a stirred solution of PCl_3 (1.80 mL, 2×10^{-2} mol) in the same solvent (120 mL) for 1 h at 0°C. The reaction mixture was heated to its boiling point, cooled and filtered. The solvent was removed from the filtrate in vacuo (40 mmHg). The residue was dried in vacuo (2 mmHg) and distilled; colourless oil (4.621 g, 75%); bp 133–135°C (1 mmHg); $n_D^{20}=1.5682$. ^{31}P NMR ($CDCl_3$), δ_P: 174.31. ^{13}C NMR ($CDCl_3$), δ_C (*J*(C,P)/Hz): $CH_{3(Ar)}$ 17.90, 17.96; $C_{p(Me_2PhO)}$ 124.96, 124.98; $C_{m(Me_2PhO)}$ 128.98, 128.99; $C_{o(Me_2PhO)}$ 130.21, 130.24; OC_{Ar} 148.68. Anal. calcd for $C_{16}H_{18}ClO_2P$: C, 61.34; H, 5.15; P, 10.55. Found: C, 61.59; H, 5.47; P, 10.30%.

3.6. (2′*R*)-2-(*N*′-Benzylideneamino)-3′-methylbutyldicholesterylphosphite 5

The published procedure[24] was followed, using dicholesteryl *N*,*N*-diethylphosphoramidite (0.874 g, 1×10^{-3} mol) and (2*R*)-2-{*N*-(benzylideneamino)}-3-methylbutanol-1 (0.191 g, 1×10^{-3} mol); white solid (0.834 g, 84%); mp 142–143°C; $[\alpha]_D^{20}=-25.0$ (*c* 1, CH_2Cl_2). ^{31}P NMR ($CDCl_3$), δ_P: 138.82. ^{13}C NMR ($CDCl_3$), δ_C (*J*(C,P)/Hz): CH_3 18.59; CH 30.14; OCH_2 62.90 (^2J 5.6); NCH 76.98 (^3J 4.3); $C_{o(Ar)}$ 128.18; $C_{m(Ar)}$ 128.25; $C_{p(Ar)}$ 130.12; $C_{(Ar)}$ 136.31; C_1 36.05; C_2 30.43 30.46; C_3 73.06 (^2J 12.6), 72.89 (^2J 13.6); C_4 40.99; C_5 140.35, 140.38; C_6 121.70; C_7 31.76; C_8 31.69; C_9 49.87; C_{10} 36.98; C_{11} 20.86; C_{12} 39.63; C_{13} 42.15; C_{14} 56.60; C_{15} 24.14; C_{16} 28.10; C_{17} 56.00; C_{18} 11.71; C_{19} 19.83; C_{20} 35.64; C_{21} 19.83; C_{22} 36.31; C_{23} 23.69; C_{24} 39.38; C_{25} 27.86; C_{26} and C_{27} 22.45 and 22.70. MS (EI, 70 eV), *m*/*z* (I, %): 404 (5), 369 (100); MS (PD), *m*/*z* (I, %): 625 (2), 548 (3), 386 (10), 222 (21), 161 (100). Anal. calcd for $C_{66}H_{106}NO_3P$: C, 79.87; H, 10.67; P, 3.12. Found: C, 80.23; H, 10.42; P, 3.46%.

3.7. (2′*R*,4*R*,5*R*)-2-{2′[*N*-(*p*-Dimethylaminobenzylideneamino)]-3′-methylbutoxy}-4,5-dicarmentoxy-1,3,2-dioxaphospholane 6

A solution of dimenthyl tartrate (1.00 g, 2.3×10^{-3} mol) and NEt_3 (0.65 mL, 4.6×10^{-3} mol) in toluene (10 mL) was added dropwise to a solution of PCl_3 (0.2 mL, 2.3×10^{-3} mol) in the same solvent at 0°C over 20 min. The reaction mixture was heated to 110°C and cooled to 0°C. A solution of (2*R*)-2-{*N*-(*p*-dimethylaminobenzylideneamino)}-3-methylbutanol-1 (0.54 g, 2.3×10^{-3} mol) and NEt_3 (0.33 mL, 2.3×10^{-3} mol) in toluene (10 mL) was then added dropwise to the obtained solution of chlorophosphite in situ at 0°C with stirring. The reaction mixture was heated to 110°C, then cooled to 20°C and filtered. The toluene was removed in vacuo (40 mmHg) and the residue was dried in vacuo (10 mmHg). Colourless oil (1.347 g, 85%); $[\alpha]_D^{24}=+120.65$ (*c* 10, $CHCl_3$). ^{31}P NMR ($CDCl_3$), δ_P: 144.35. ^{13}C NMR ($CDCl_3$), δ_C (*J*(C,P)/Hz): CH_3 17.98, 19.34; CH 29.33; $N(CH_3)_2$ 39.55; OCH_2 65.19 (^2J 5.4); OCH 75.22 (^2J 9.3); NCH 76.44 (^3J 9.0); $C_{o(Ar)}$ 129.13; $C_{m(Ar)}$ 110.89; $C_{p(Ar)}$ 151.33; C_{Ar} 124.07; C_1 25.47, 25.51; C_2 39.88, 40.00; C_3 75.46; C_4 46.16, 46.23; C_5 22.57; C_6 33.51; C_7 21.41, 21.46; C_8 30.75; C_9 20.26, 20.30; C_{10}

15.48, 15.51. MS (EI, 70 eV), m/z (I, %): 618 (1), 480 (3), 234 (5), 147 (26), 95 (100). Anal. calcd for $C_{38}H_{61}N_2O_7P$: C, 66.25; H, 8.93; P, 4.50. Found: C, 67.01; H, 9.06; P, 4.39%.

3.8. (4′*S*,5′*S*)-(2′-Methyl-5′-phenyl-2′-oxazolino-4′)-methyldi(*o*,*o*′-dimethyl)phenylphosphite 7

A solution of di(2,6-dimethylphenyl) chlorophosphite (0.842 g, 2.7×10^{-3} mol) in benzene (8 mL) was added dropwise to a stirred solution of (4*S*,5*S*)-(−)-2-methyl-5-phenyl-2-oxazoline-4-methanol (0.516 g, 2.7×10^{-3} mol) and NEt_3 (0.40 mL, 2.7×10^{-3} mol) in benzene (25 mL) at 0°C. Then the reaction mixture was heated to boiling point, cooled and filtered. The solvent was removed in vacuo (40 mmHg). The residue was dissolved in hexane (20 mL), filtered and the solvent was removed in vacuo (40 mmHg). The final residue was dried in vacuo (1 mmHg). Colourless oil (1.080 g, 86%); $[\alpha]_D^{27}=-78.6$ (c 1.24, $CHCl_3$). ^{31}P NMR ($CDCl_3$), δ_P: 134.67. ^{13}C NMR ($CDCl_3$), δ_C (J(C,P)/Hz): CH_3 13.77; $CH_{3(Ar)}$ 17.38, 17.41, 17.44, 17.47; OCH_2 63.25; NCH 74.67 (^3J 3.9); OCH 83.23; $C_{o(Ph)}$ 125.14; $C_{p(Ph)}$ 127.90; $C_{m(Ph)}$ 128.47; C_{Ph} 140.36; $C_{p(Me_2PhO)}$ 123.87; $C_{m(Me_2PhO)}$ 128.65; $C_{o(Me_2PhO)}$ 130.11 (^3J 2.8); OC_{Ar} 148.61. MS (EI, 70 eV), m/z (I, %): 463 (1, $[M]^+$), 342 (100), 300 (40), 174 (10), 132 (70), 177 (20), 125 (34). Anal. calcd for $C_{27}H_{30}NO_4P$: C, 69.97; H, 6.65; P, 6.68. Found: C, 70.22; H, 6.48; P, 6.86%.

3.9. Preparation of rhodium complexes: general technique

A solution of a 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 solvent was then removed in vacuum (40 mmHg), and hexane (10 mL) was added to the residue. The precipitate obtained was separated by centrifugation, washed with hexane (2×10 mL) and dried in vacuum (2 mmHg).

3.9.1. ((2′*R*)-2-(*N*′-Benzylideneamino)-3′-methylbutyldicholesterylphosphite-*P*,*N*)chlorocarbonyl rhodium(I) 8. Yellow solid (0.375 g, 90%); mp 125–126°C (dec.). ^{13}C NMR ($CDCl_3$), δ_C (J(C,P)/Hz): CH_3 18.50; CH 31.21; OCH_2 67.86; NCH 76.46 (^3J 6.6); $C_{o(Ar)}$ 128.16; $C_{m(Ar)}$ 132.23; $C_{p(Ar)}$ 132.95; $C_{(Ar)}$ 131.93; C_1 36.95; C_2 29.76; C_3 76.69, 80.43; C_4 39.70 (^3J 4.7), 40.18 (^3J 2.6); C_5 138.74, 139.35; C_6 122.28, 122.67; C_7 31.67; C_8 31.50, 31.60; C_9 49.67, 49.81; C_{10} 36.67, 36.87; C_{11} 20.75, 20.83; C_{12} 39.48; C_{13} 42.06; C_{14} 56.44; C_{15} 24.05; C_{16} 28.00; C_{17} 55.86; C_{18} 11.60, 11.63; C_{19} 20.10; C_{20} 35.54; C_{21} 18.93, 19.09; C_{22} 36.23; C_{23} 23.57; C_{24} 39.29; C_{25} 27.77; C_{26} and C_{27} 22.36 and 22.62. Anal. calcd for $C_{67}H_{106}ClNO_4PRh$: C, 69.44; H, 9.22; N, 1.21; P, 2.67. Found: C, 69.82; H, 9.02; N, 1.26; P, 2.55%.

3.9.2. ((2′*R*,4*R*,5*R*)-2-{2′[*N*-(*n*-Dimethylaminobenzylideneamino)]-3′-methylbutoxy}-4,5-dicarmentoxy-1,3,2-dioxaphospholane-*P*,*N*)chlorocarbonyl rhodium(I) 9. Yellow solid (0.264 g, 86%); mp 112–114°C (dec.). ^{13}C NMR ($CDCl_3$), δ_C (J(C,P)/Hz): CH_3 18.28, 20.19; CH 31.80; $N(CH_3)_2$ 39.75; OCH_2 68.15; OCH 75.64 (^2J 7.6); NCH 76.03 (^3J 6.2); $C_{o(Ar)}$ 134.33; $C_{m(Ar)}$ 110.57; $C_{p(Ar)}$ 153.39; C_{Ar} 119.14; C_1 25.94, 26.06; C_2 40.19, 40.36; C_3 76.79; C_4 46.49, 46.56; C_5 22.47, 22.96; C_6 33.82; C_7 21.72, 21.77; C_8 31.16; C_9 20.58; C_{10} 15.89, 16.02. Anal. calcd for $C_{39}H_{61}ClN_2O_8PRh$: C, 54.77; H, 7.19; N, 3.28; P, 3.62. Found: C, 54.89; H, 7.33; N, 3.09; P, 3.80%.

3.9.3. ((4′*S*,5′*S*)-(2′-Methyl-5′-phenyl-2′-oxazolino-4′)-methyldi(*o*,*o*′-dimethyl)phenylphosphite-*P*,*N*)chlorocarbonyl rhodium(I) 10. Yellow solid (0.202 g, 89%); mp 153–154°C (dec.). ^{13}C NMR ($CDCl_3$), δ_C (J(C,P)/Hz): CH_3 14.88; $CH_{3(Ar)}$ 17.87, 18.57; OCH_2 62.53; NCH 69.15; OCH 84.86; $C_{o(Ph)}$ 126.30; $C_{p(Ph)}$ 128.76; $C_{m(Ph)}$ 129.00; C_{Ph} 134.16; $C_{p(Me_2PhO)}$ 124.98, 125.21; $C_{m(Me_2PhO)}$ 129.09, 129.69; $C_{o(Me_2PhO)}$ 129.90 (^3J 2.9), 130.62 (^3J 2.8); OC_{Ar} 147.40 (^2J 6.2), 148.61 (^2J 16.2). Anal. calcd for $C_{28}H_{30}ClNO_5PRh$: C, 53.39; H, 4.80; P, 4.92. Found: C, 53.31; H, 5.00; P, 5.17%.

3.10. Preparation of palladium complexes

The palladium complex of **5** (L/Pd = 1) for NMR experiment was obtained as follows: a solution of **5** (0.298 g, 3×10^{-4} mol) in $CDCl_3$ (1.5 mL) was added dropwise to a stirred solution of $[PdCl_2(COD)]$ (0.086 g, 3×10^{-4} mol) in the same solvent (1.5 mL). A 1 mL sample of the obtained solution was then transferred to a NMR tube and NMR experiments were carried out.

To study an isolated product of complexation of **5** with $[PdCl_2(COD)]$, the excess solvent was removed in vacuum (40 mmHg) and ether (10 mL) was added to the residue. The precipitate obtained was separated by centrifugation, washed with ether (2×10 mL), and dried in vacuum (1 mmHg).

3.10.1. *cis*-Dichloro[bis-((2′*R*)-2-(*N*′-benzylideneamino)-3′-methylbutyldicholesterylphosphite)] palladium 11. A solution of **5** (0.298 g, 3×10^{-4} mol) in CH_2Cl_2 (15 mL) was added dropwise to a solution of $[PdCl_2(COD)]$ (0.043 g, 1.5×10^{-4} mol) in the same solvent (15 mL) at 20°C, and the solution was stirred for 15 min. The excess solvent was removed in vacuum (40 mmHg) and ether (10 mL) was added to the residue. The precipitate obtained was separated by centrifugation, washed with ether (2×10 mL), and dried in vacuum (1 mmHg) to afford a yellow powder (0.314 g, 92%); mp 109–111°C (dec.). ^{13}C NMR ($CDCl_3$), δ_C (J(C,P)/Hz): CH_3 18.53; CH 30.13; OCH_2 69.64; NCH 75.71 (^3J 2.9); $C_{o(Ar)}$ 128.19; $C_{m(Ar)}$ 128.32; $C_{p(Ar)}$ 130.36; $C_{(Ar)}$ 136.00; C_1 35.99; C_2 28.74, 29.85; C_3 78.72, 79.24; C_4 39.95, 40.15; C_5 138.87, 139.06; C_6 122.94, 123.02; C_7 31.69; C_8 31.56; C_9 49.49, 49.63; C_{10} 36.52, 36.60; C_{11} 20.76; C_{12} 39.51; C_{13} 42.09; C_{14} 56.47; C_{15} 24.08; C_{16} 28.05; C_{17} 55.93; C_{18} 11.67; C_{19} 19.79; C_{20} 35.59, 35.63; C_{21} 19.07; C_{22} 36.18; C_{23} 23.61, 23.68; C_{24} 39.31; C_{25} 27.83; C_{26} and C_{27} 22.40 and 22.67. Anal. calcd for $C_{132}H_{212}N_2O_6P_2PdCl_2$: C, 73.32; H, 9.88; N, 1.30; P, 2.86. Found: C, 73.70; H, 10.25; N, 1.48; P, 2.55%.

3.10.2. *cis*-Dichloro[(4′*S*,5′*S*)-(2′-methyl-5′-phenyl-2′-oxazolino-4′)methyldi(*o*,*o*′-dimethyl)phenylphosphite] palladium 12. A solution of **7** (0.139 g, 3×10^{-4} mol) in CH_2Cl_2 (15 mL) was added dropwise to a solution of $[PdCl_2(COD)]$ (0.086 g, 3×10^{-4} mol) in the same solvent (15 mL) at 20°C, and the solution was stirred for 15 min. The excess solvent was removed in vacuum (40 mmHg) and ethyl ether (10 mL) was added to the residue. The precipitate obtained was separated by centrifugation, washed with ether (2×10 mL), and dried in vacuum (1 mmHg) to afford a yellow powder (0.154 g, 80%); mp 152–154°C (dec.). ^{13}C NMR ($CDCl_3$), δ_C (J(C,P)/Hz): CH_3 15.14; $CH_{3(Ar)}$ 17.54, 17.74; OCH_2 65.06; NCH 67.03; OCH 84.46; $C_{o(Ph)}$ 126.14; $C_{p(Ph)}$ 125.28, 125.93; $C_{m(Ph)}$ 128.85; C_{Ph} 133.66; $C_{p(Me_2PhO)}$ 125.28, 125.93; $C_{m(Me_2PhO)}$ 129.27, 129.76; $C_{o(Me_2PhO)}$ 129.62 (^3J 3.0), 130.04 (^3J 3.1); OC_{Ar} 146.67 (^2J 7.3), 148.22 (^2J 18.3). Anal. calcd for $C_{27}H_{30}NO_4PPdCl_2$: C, 50.60; H, 4.72; N, 2.19; P, 4.83. Found: C, 50.88; H, 4.94; N, 2.02; P, 4.59%.

3.11. Catalytic experiments

Dimethyl malonate (0.145 g, 1.1 mmol, 2.1 equiv.) was dissolved in anhydrous solvent (CH_2Cl_2 or THF, 2 mL). Sodium hydride (0.042 g, 1.06 mmol, 2 equiv.) was then added portionwise and the anion was allowed to form over ca. 30 min. The catalysts were pre-formed by dissolving $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.1 mg, 5.7 μmol, 1 mol%) and a corresponding ligand (28.5 μmol, 5 mol%) in the solvent (2 mL) and stirring the mixture for ca. 40 min. Then 1,3-diphenyl-2-propenyl acetate (0.133 g, 0.53 mmol) in the solvent (0.5 mL and 2×0.25 mL rinse) was added dropwise via a Teflon® cannula to the sodium salt of dimethyl malonate, followed by addition of the catalyst solution. The bright yellow solution was stirred until the reaction was complete (as monitored by TLC). The brownish yellow reaction mixture was then poured into 1N aq. NaOH and extracted with ether. The combined organic phases were washed with satd aq. NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to give a crude oil. Purification by flash chromatography (eluting with 10–20% gradient of ethylacetate/hexane) gave the allylic alkylation product as white crystals.

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