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Construction of chiral Ti(IV)–Rh(I)–salenophos complexes and their application in the asymmetric hydroformylation of functionalised olefins

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Abstract

The synthesis of new chiral salenophos-type ligands bearing 'hard' and 'soft' coordination sites is described. The polyfunctionalised ligands are used for the construction of monometallic and early–late heterobimetallic complexes. In the reaction with titanium(IV) reagents the salen subunit selectively coordinated to the 'hard' metal. The phosphine groups in turn can be coordinated to rhodium(I). The coordination geometry of the diphosphine–Rh subunit is strongly influenced by the counter ligands COD or CO and Cl, respectively. In the asymmetric hydroformylation of vinyl acetate with one of the Rh–Ti-complexes, the branched aldehyde is predominantly formed with 30% ee.

1. Introduction

The development of highly efficient catalysts for asymmetric hydroformylation of prochiral olefins represents a challenging task in academic and industrial research.[1] Chiral aldehydes obtained as products have an enormous potential as building blocks in organic synthesis.[2] Hitherto, rhodium complexes based on chiral phosphorus ligands have been shown to be competent catalysts for highly regio- and stereoselective hydroformylation of a range of different olefinic substrates.[3]

As a part of our ongoing research concerned with the construction and application of bifunctional catalysts[4] we focused our attention on the use of chiral bimetallic complexes in asymmetric hydroformylation. Particularly attractive are heterobimetallic catalysts containing early as well as late transition metals.[5] The 'hard' metal could advantageously activate and adjust an appropriate bifunctional substrate while the second 'soft' metal is executing the hydroformylation. Such complexes showing cooperative effects in asymmetric catalysis[4,6] may have relevance as biomimetic models and synthetic

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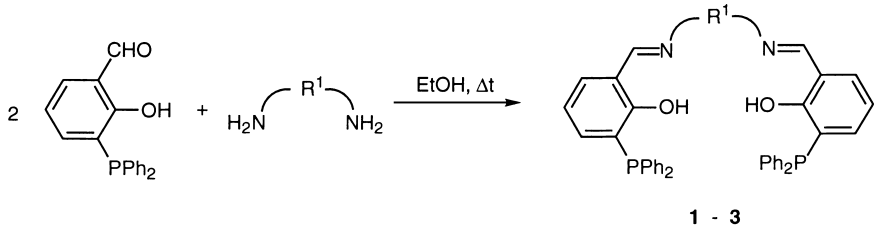
enzymes (chemzymes) and hold entirely new perspectives in the enantiofacial differentiation of prochiral substrates.[7]

In principle, the application of achiral bimetallic complexes with metals of d^0–d^8-electronic configuration (e.g. Ti(IV)–Rh(I) or Zr(IV)–Rh(I)) for hydroformylation was investigated by Choukroun and Ziolkowski.[8] In some instances they found that the hard metal increased the formation of the terminal aldehyde when 1-hexene was hydroformylated.[8c] However, to the best of our knowledge no asymmetric version of this particular reaction has been elucidated.

As a main requisite for each asymmetric heterobimetallic catalysis an appropriate ligand is required which is able to accommodate two different metals in a defined manner.[9] In particular, chiral hydroxy phosphines are useful hosts owing 'hard' (O) and 'soft' ligating atoms (P).[10] Recently, we described the synthesis of the polyfunctionalised chiral phosphine (*R*,*R*)-diph-salenophos[11] (**1**, Scheme 1) and its stepwise complexation to Ti(IV) and Pd(II).[12] Herein, we wish to report the synthesis of other salenophos-type ligands and the preparation of the corresponding mono- and heterobimetallic complexes. Subsequently, the first results of the application of the new complexes in asymmetric hydroformylation are discussed.



Scheme 1. Salenophos-type ligands. (*R*,*R*)-Diph-salenophos **1**: R^1=(*R*,*R*)-1,2-diphenyleth-1,2-diyl; (*R*,*R*)-cyc-salenophos **2**: R^1=(*R*,*R*)-cyclohex-1,2-diyl; (*R*,*R*)-bin-salenophos **3**: R^1=(*R*)-binaphth-1,1′-diyl

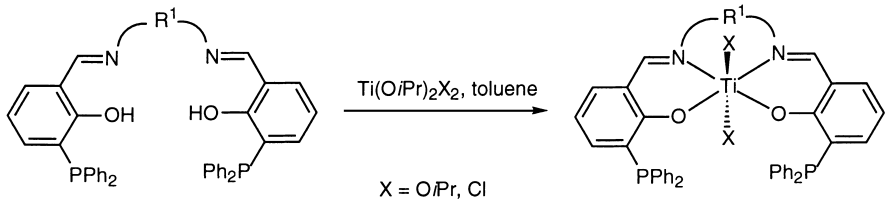
2. Results and discussion

2.1. Synthesis of the catalytic system

In general, chiral salenophos-type ligands are easily constructed by a modular approach reacting two equivalents of 3-diphenylphosphino-2-hydroxybenzaldehyde and the appropriate chiral diamine in boiling ethanol (Scheme 1). Besides the earlier described (*R*,*R*)-diph-salenophos **1**, we have now succeeded in the synthesis of the related hydroxy phosphines containing a cyclohexyl- **2** and a binaphthyldiimine backbone **3**, respectively.

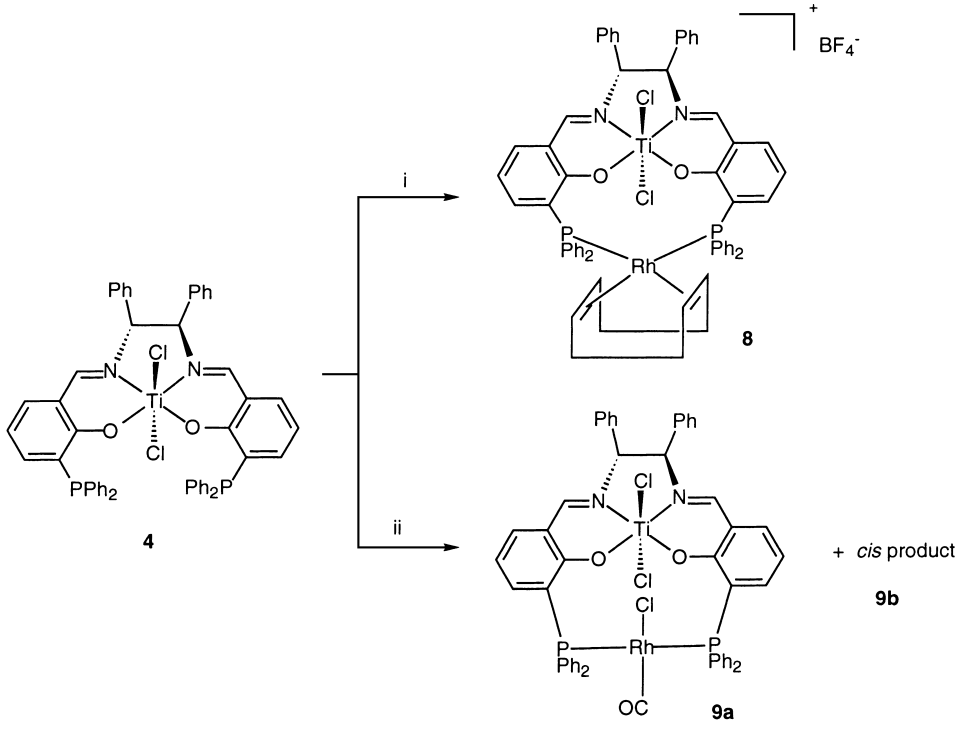
Salenophos-type ligands have a unique structure since they contain 'hard' as well as 'soft' ligating atoms. They are therefore suitable for the construction of early–late heterobimetallic complexes. For the synthesis of mononuclear titanium(IV) complexes, salenophos ligands were individually treated with Ti(O*i*Pr)$_4$ or Ti(O*i*Pr)$_2$Cl$_2$ (Scheme 2). After the reaction with ligands **1** and **2**, respectively, we were able to isolate uniform titanium complexes **4**–**6** bearing two isopropoxy or chlorine ligands in apical positions at the metal centre. Unfortunately, the synthesis of cyc-salenophos–Ti(O*i*Pr)$_2$ complex failed. In this reaction a number of products were yielded which could not be separated by crystallisation.

A characteristic feature of all titanium complexes was the essentially unchanged shift of resonances in the $^{31}P\{^1H\}$-NMR spectrum in comparison to the signals of the hydroxy phosphines **1**–**3**. This clearly indicated that the phosphine groups do not participate in the coordination of titanium.



Scheme 2. Salenophos–Ti(IV) complexes. (*R*,*R*)-Diph-salenophos–Ti(O*i*Pr)$_2$ **4**: R^1=(*R*,*R*)-1,2-diphenyleth-1,2-diyl, X=O*i*Pr; (*R*,*R*)-diph-salenophos–TiCl$_2$ **5**: R^1=(*R*,*R*)-1,2-diphenyleth-1,2-diyl, X=Cl; (*R*,*R*)-cyc-salenophos–TiCl$_2$ **6**: R^1=(*R*,*R*)-cyclohex-1,2-diyl, X=Cl; (*R*)-bin-salenophos–Ti(O*i*Pr)$_2$ **7**: R^1=(*R*)-binaphth-1,1′-diyl, X=O*i*Pr

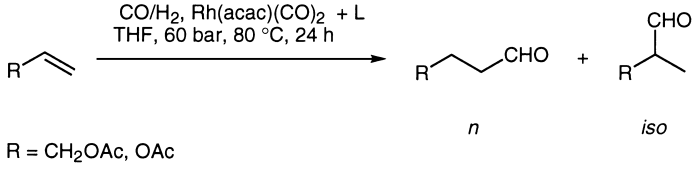
We next investigated the complexation of diph-salenophos–TiCl$_2$ **4** with different rhodium reagents (Scheme 3). Thus, in the reaction with [Rh(COD)$_2$]BF$_4$ in THF the asymmetric Ti–Rh complex **8** was observed lacking the C_2-symmetry of the precursor phosphine. The ^{31}P–^{31}P-coupling constant of 30.5 Hz (J_{RhP}=138.7 Hz and 144.3 Hz) derived from the ^{31}P{^{1}H}-NMR spectrum in CD_2Cl_2 provided unambiguous evidence for the *cis*-coordination of the phosphines to rhodium. Interestingly, the reaction of **4** with [RhCl(CO)$_2$]$_2$ in CD_2Cl_2 produced a mixture consisting of two Ti–Rh complexes in different ratios. The major product **9a** was characterised by a ^{31}P–^{31}P-coupling constant of 377.0 Hz (J_{RhP}=130.4 Hz, 133.2 Hz) indicating the *trans*-relationship of the phosphines. The minor product **9b** (C_2-symmetric species with J_{RhP}=127.6 Hz) was probably a dimeric μ-chloro-bridged complex with *cis*-coordination of the *P*-ligating atoms. Unfortunately, all attempts to separate the two complexes were unsuccessful.



Scheme 3. Reaction of (*R*,*R*)-diph-salenophos–TiCl$_2$ **4** with different rhodium precursors. (i) 1.0 equiv. [Rh(COD)$_2$]BF$_4$, THF, 30 min, rt, 45%; (ii) 0.5 equiv. [RhCl(CO)$_2$]$_2$, CD_2Cl_2, 10 min, rt

2.2. Application in asymmetric hydroformylation

The mono- and bimetallic precatalysts for hydroformylation of functionalised olefins (Scheme 4) were prepared in situ by mixing salenophos ligands **1**–**3** or the salenophos–Ti(IV) 'ligands' **4**–**6** with $Rh(acac)(CO)_2$ in a ligand:Rh ratio of 5:1. This procedure turned out to be more advantageous than the direct use of the rhodium complexes. An excess of the salenophos ligand prevents the formation of highly reactive but achiral complexes such as $HRh(CO)_3$. The hydroformylation was performed with a 1:1 mixture of H_2:CO at 60 bar and 80°C in THF as solvent.



Scheme 4. Hydroformylation of allyl acetate and vinyl acetate

We first investigated the salenophos ligands and salenophos–Ti complexes, respectively, in the hydroformylation of allyl acetate. Representative results are listed in Table 1. For runs 1, 4 and 6 monometallic Rh complexes were employed. Diph-salenophos– and cyc-salenophos–rhodium complexes were active catalysts whereas the bin-salenophos–rhodium performed rather sluggishly. In all trials, predominant formation of the linear aldehyde was observed. This result may be attributed to the large bite angle of salenophos ligands. According to mechanistic studies of Casey[13] and van Leeuwen[14] a large bite angle of the diphosphine ligand favoured the *n*-selectivity of the hydroformylation. Unfortunately, the branched aldehyde that we obtained as a minor product was racemic.

By application of heterobimetallic Ti–Rh complexes (runs 2, 5 and 7) we noted that only those Ti complexes bearing isopropoxy ligands were active. $TiCl_2$ complexes displayed no activity in the hydroformylation; presumably, due to the rapid formation of the catalytically inactive μ-chloro-bridged Ti–Rh species. The linear carbaldehyde was again predominantly formed. However, in comparison to the monometallic catalysts and in contrast to the reports of Choukroun and Ziolkowski[8] a significant increase in the formation of the branched product was caused by the titanium. Unfortunately, in these trials also only the formation of racemic product was observed.

Table 1
Hydroformylation of allyl acetate[a]

Run	Ligand	Conversion [%][b]	*iso*/*n* [b]	ee [%][b]
1	(*R*,*R*)-Diph-salenophos	98	4/96	*rac*
2	(*R*,*R*)-Diph-salenophos-Ti(O*i*Pr)$_2$	26	26/74	*rac*
3	(*R*,*R*)-Diph-salenophos-$TiCl_2$	-	-	-
4	(*R*)-Bin-salenophos	6	20/80	*rac*
5	(*R*)-Bin-salenophos-Ti(O*i*Pr)$_2$	16	40/60	*rac*
6	(*R*,*R*)-Cyc-salenophos	70	1/99	*rac*
7	(*R*,*R*)-Cyc-salenophos-$TiCl_2$	-	-	-

[a] Reaction conditions: 0.05 mmol Ligand, 0.01 mmol $Rh(acac)(CO)_2$, 1 mmol allyl acetate, 15 ml THF, $p(CO/H_2)$ = 60 bar ($CO:H_2$ = 1:1), time: 24 h. [b] determined by GC (see Experimental Section).

Table 2
Hydroformylation of vinyl acetate[a]

Run	Ligand	Conversion [%][b]	iso/n [b]	ee [%][b]
1	(*R*,*R*)-Diph-salenophos	93	99/1	*rac*
2	(*R*,*R*)-Diph-salenophos-Ti(O*i*Pr)$_2$	21	77/23	**30**
3	(*R*,*R*)-Diph-salenophos-TiCl$_2$	-	-	-
4	(*R*)-Bin-salenophos	5	99/1	-
5	(*R*)-Bin-salenophos-Ti(O*i*Pr)$_2$	35	99/1	6
6	(*R*,*R*)-Cyc-salenophos	30	99/1	6
7	(*R*,*R*)-Cyc-salenophos-TiCl$_2$	-	-	-

[a] Reaction condtions: 0.05 mmol ligand, 0.01 mmol Rh(acac)(CO)$_2$, 1 mmol vinyl acetate, 15 ml THF, p(CO/H$_2$) = 60 bar (CO:H$_2$ = 1:1), time: 24 h. [b] determined by GC (see Experimental section).

We then studied the hydroformylation of vinyl acetate. With this substrate the formation of the branched aldehyde is generally more favoured. This phenomenon is caused by the heteroatom adjacent to the olefin which stabilises the intermediate isoalkylmetal species better than the isomeric *n*-alkylmetal complex. Insertion of CO occurs predominantly at the 1-position of the olefin. Chiral 2-acetoxypropanal formed is a valuable precursor of threonine and a source of 2-hydroxypropanal being a useful building block for the synthesis of steroids, antibiotics and peptides.

The hydroformylation was carried out under the conditions described for allyl acetate. In Table 2 relevant results are recorded. As anticipated, all active catalysts preferentially produced the branched aldehyde. Similar to the reaction with allyl acetate in the series of monometallic catalysts the Rh–(*R*,*R*)-diph-salenophos complex provided the highest conversion (run 1). Poor reactivity was obtained with the catalyst based on (*R*)-bin-salenophos (run 4). Although the conversion with cyc-salenophos–rhodium was low, asymmetric induction (6% ee) was observed. Similar to the reaction with allyl acetate, only Ti–Rh complexes with isopropoxy as co-ligand catalysed the hydroformylation of vinyl acetate (runs 2 and 5). The use of diph-salenophos–Ti(O*i*Pr)$_2$–rhodium diminished the *iso*/*n*-selectivity, however, 2-acetoxypropanal was obtained in 77% chemical yield and 30% ee. This represents the first example of the successful application of a chiral early–late heterobimetallic catalyst in asymmetric hydroformylation.

Although the enantioselectivity is only moderate, this example provides evidence that transfer of chirality from the backbone to the catalytically active metal mediated by a second metal is possible.[15] Our preliminary results make salenophos-bimetallic complexes attractive catalysts for further investigations with the potential for additional synthetic power and the impetus for mechanistic information arising from the role of the second metal. Currently, work is in progress to test other functionalised olefins in this reaction.

3. Experimental

3.1. General procedures

All solvents were dried and distilled under argon. Reactions involving phosphines and organometallic compounds were performed under an Ar atmosphere by using standard Schlenk techniques. Tetrahydro-

furan (THF), Et_2O and toluene were distilled from sodium/benzophenone ketyl, CH_2Cl_2 was distilled from CaH_2. Commercial reagents were used without further purification. Thin-layer chromatography was performed on precoated TLC plates (silica gel 60 F_{254}, Merck). Flash chromatography was carried out with silica gel 60 (particle size 0.040–0.063 mm, Merck). Melting points are corrected. The optical rotation was measured on a 'gyromat-HP' instrument (Fa. Dr. Kernchen). NMR spectra were recorded on a Bruker ARX 400 instrument at 303 K. Spectra were obtained at the following frequencies: 400.13 (^{1}H), 100.63 (^{13}C), 161.98 (^{31}P). Chemical shifts of ^{1}H and ^{13}C NMR spectra are given relative to the residual solvent peak (δ). Chemical shifts of ^{31}P NMR spectra are reported in ppm referred to H_3PO_4 as external standard. The mass spectra were recorded on an AMD 402 instrument (Fa. Intectra).

3.2. General procedure for the synthesis of salenophos ligands

A Schlenk tube was charged with 17.3 mmol (5.29 g) of 3-diphenylphosphino-2-hydroxybenzaldehyde[11,12] and ethanol (120 ml) and heated to 70°C. After the aldehyde was completely dissolved, a solution of the appropriate diamine (8.64 mmol) in ethanol (20 ml) was added dropwise. The reaction mixture was kept for a further 1 h at this temperature and then cooled to room temperature. After addition of water (30 ml) a precipitate was formed. Stirring was continued for 20 min. The product was allowed to settle, filtered and dried in vacuo. If necessary, the crude product was purified by flash chromatography.

*3.3. (*R,R*)*-N,N-*Bis(3-diphenylphosphino-2-hydroxybenzylidene)-cyclohexan-1,2-diamine*

*3.3.1. Cyc-salenophos **2***

Following the general procedure for the synthesis of salenophos ligands, 9.56 mmol (2.93 g) 3-diphenylphosphino-2-hydroxybenzaldehyde were treated with 4.78 mmol (0.55 g) (*R*,*R*)-1,2-diaminocyclohexane. The obtained crude product was already analytically pure. Yield 2.9 g (90%); mp 118–121°C; $[\alpha]_D^{25}$=−527.3 (*c* 1.01, $CHCl_3$); ^{31}P NMR ($CDCl_3$) δ=−16.0 (s, P, PPh); ^{1}H NMR ($CDCl_3$) δ=12.50 (s, 2H, OH), 8.13 (s, 2H, CH=N), 7.30–6.35 (m, 26H, Ph), 2.95 (m, 2H, CHN), 1.92–1.35 (m, 8H, CH_2); ^{13}C NMR ($CDCl_3$) δ=164.7 (CH=N), 163.4 (d, $^2J_{PC}$=18.2 Hz, CO), 136.4–117.5 (Ph), 72.3 (CHN), 32.9 (CH_2), 24.1 (CH_2); IR (Nujol) $\tilde{\nu}$=1624 (s), 1597 (m), 1432 (s, P–C), 1294, 1266, 1148, 1094, 1070, 1027, 954 (w), 744, 696 (s, C–H_{arom}); MS (EI, 70 eV) [*m/z*] (rel. int. %): 690 [M^+] (100), 385 (48), 304 (50), 183 (28); calcd $C_{44}H_{40}N_2O_2P_2$ (690.76): C, 76.51; H, 5.84; N, 4.06; P, 8.97; found: C, 75.70; H, 5.92; N, 4.02; P, 8.63.

*3.4. (*R*)*-N,N-*Bis(3-diphenylphosphino-2-hydroxybenzylidene)-[1,1′]binaphthalenyl-2,2′-diamine*

*3.4.1. Bin-salenophos **3***

Following the general procedure for the synthesis of salenophos ligands, 3.80 mmol (1.16 g) 3-diphenylphosphino-2-hydroxybenzaldehyde were treated with 1.90 mmol (0.54 g) (*R*)-2,2′-diamino-1,1′-binaphthalene. The crude product was purified by flash chromatography (*n*-hexane:EtOAc, 4:1). Yield 1.4 g (86%); mp 102–110°C; $[\alpha]_D^{25}$=−317.7 (*c* 0.9, $CHCl_3$); ^{31}P NMR ($CDCl_3$) δ=−16.3 (s, P, PPh); ^{1}H NMR ($CDCl_3$) δ=12.61 (s, 2H, OH), 8.25 (s, 2H, CH=N), 7.77–6.50 (m, 38H, Ph); ^{13}C NMR ($CDCl_3$) δ=162.3 (d, $^2J_{PC}$=16.2 Hz, CO), 156.0 (CH=N), 144.1–117.2 (Ph); IR (Nujol) $\tilde{\nu}$=1600, 1583, 1558 (m), 1433 (m, P–C), 1292, 1262, 1204, 1144 (w), 741, 694 (m, C–H_{arom}); MS (EI, 70 eV) [*m/z*] (rel. int. %): 860 [M^+] (83), 676 (10), 572 (92), 556 (100), 539 (13), 478 (32), 430 (28); calcd $C_{58}H_{42}N_2O_2P_2$ (860.93): C, 80.92; H, 4.92; N, 3.25; P, 7.20; found: C, 80.11; H, 5.12; N, 3.66; P, 6.81.

*3.4.2. (*R,R*)-Diph-salenophos–TiCl$_2$* ***4***

To a stirred solution of 1.74 mmol (1.37 g) (*R*,*R*)-diph-salenophos **1** in CH_2Cl_2 (10 ml) was added dropwise via syringe a 0.5 M solution of Ti(O*i*Pr)$_2$Cl$_2$ (3.5 ml) in CH_2Cl_2. During the addition the colour of the reaction mixture changed from yellow to deep red. After stirring overnight at room temperature Et_2O (20 ml) was added. The precipitated complex was filtered off, washed with Et_2O (2×10 ml) and dried in vacuo to yield the deep red complex **4**. Yield: 1.4 g (89%); mp >300°C; ^{31}P NMR (CD_2Cl_2) δ=−16.7 (s, P, PPh); ^{1}H NMR (CD_2Cl_2) δ=7.70 (s, 2H, CH=N), 7.41–6.80 (m, 36H, Ph), 5.45 (s, 2H, CHN); ^{13}C NMR (CD_2Cl_2) δ=163.4 (d, $^2J_{PC}$=9.1 Hz, CO), 162.9 (CH=N), 139.7–122.5 (Ph), 76.7 (CHN); IR (Nujol) $\tilde{\nu}$=1615, 1578 (m), 1549 (w), 1419 (w, P–C), 1379, 1263, 877 (m), 749 (w), 716 (m), 695 (w), 676 (m), 581 (m); MS (EI, 70 eV) [*m*/*z*] (rel. int. %): 905 [M$^+$] (71), 868 [M$^+$−H−HCl] (71), 44 (100); calcd $C_{52}H_{40}Cl_2N_2O_2P_2Ti$ (905.64): C, 68.97; H, 4.45; N, 3.09; found: C, 68.50; H, 4.20; N, 3.23.

*3.4.3. (*R,R*)-Cyc-salenophos–TiCl$_2$* ***5***

To a stirred solution of 0.26 mmol (0.18 g) (*R*,*R*)-cyc-salenophos **2** in toluene (5 mL) was added dropwise via syringe a solution of Ti(O*i*Pr)$_2$Cl$_2$ (0.05 g) in toluene (4 ml) at −50°C. During the addition the colour of the reaction mixture changed from yellow to brown. After stirring overnight at room temperature half of the solvent was removed by distillation whilst the complex started precipitating. The product was allowed to settle, filtered and dried in vacuo to yield the dark brown complex **5**. Yield: 0.1 g (48%); mp >300°C; ^{31}P NMR (CD_2Cl_2) δ=−16.7 (s, P, PPh); ^{1}H NMR (CD_2Cl_2) δ=8.32 (s, 2H, CH=N); 7.59–7.01 (m, 26H, Ph), 3.95 (d, ^3J=6.4 Hz, 2H, CHN), 2.55 (d, *J*=11.1 Hz, 2H, CH_2), 2.55 (d, *J*=7.6 Hz, 2H, CH_2), 2.05 (m, 2H, CH_2), 1.49 (m, 4H, CH_2); ^{13}C NMR (CD_2Cl_2) δ=163.6 (d, $^2J_{PC}$=19.1 Hz, CO), 159.3 (CH=N), 139.4–122.4 (Ph), 67.9 (CHN), 28.8 (CH_2), 24.1 (CH_2); IR (Nujol) $\tilde{\nu}$=1616, 1576 (m), 1547 (w), 1421 (w, P–C), 1386, 1265, 871 (m), 751 (w), 718 (m), 692 (w), 678 (m); MS (FAB pos., NBA) [*m*/*z*] (rel. int. %): 889 [M$^+$−2Cl+NBA] (100); calcd $C_{44}H_{38}Cl_2N_2O_2P_2Ti$ (807.53): C, 65.44; H, 4.74; N, 3.47; found: C, 65.06; H, 4.62; N, 3.44.

*3.4.4. (*R*)-Bin-salenophos–Ti(O*i*Pr)$_2$* ***6***

To a stirred solution of 1.62 mmol (1.39 g) (*R*)-bin-salenophos in toluene (35 ml) 1.60 mmol (0.46 g) freshly distilled Ti(O*i*Pr)$_4$ was slowly added at room temperature. Stirring was continued overnight and then the volatiles were removed by distillation. The yellow residue was dried in vacuo to give the analytically pure titanium complex. Yield: 1.6 g (98%); mp 180°C (dec.); ^{31}P NMR ($CDCl_3$) δ=−16.3 (s, P, PPh); ^{1}H NMR ($CDCl_3$) δ=7.80–6.40 (m, 40H, Ph, CH=N), 4.57 (sept, ^3J=6.1 Hz, 2H, CHO), 0.92 (d, ^3J=6.1 Hz, 6H, CH_3), 0.86 (d, ^3J=6.1 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ=168.1 (d, $^2J_{PC}$=19.1 Hz, CO), 164.9 (CH=N), 149.7–116.4 (Ph), 78.9 (s, CHO), 25.5 (s, CH_3), 25.4 (s, CH_3); IR (Nujol) $\tilde{\nu}$=1608, 1583, 1536 (m), 1433 (m, P–C), 1410 (m), 1292, 1214, 1143, 1123 (w), 850, 744, 695, 621 (w, C–H$_{arom}$); MS (EI, 70 eV) [*m*/*z*] (rel. int. %): 906 [M$^+$−2O*i*Pr] (100); calcd $C_{64}H_{54}N_2O_4P_2Ti$ (1024.97): C, 75.00; H, 5.31; N, 2.73; found: C, 74.51; H, 5.41; N, 2.68.

*3.4.5. (*R,R*)-[Diph-salenophos–TiCl$_2$–Rh(COD)]BF$_4$* ***8***

A Schlenk tube was charged with 0.56 mmol (0.51 g) diph-salenophos–$TiCl_2$ **3** and THF (10 ml). After the complex was completely dissolved 0.56 mmol (0.23 g) [Rh(COD)$_2$]BF_4 were added in one portion. Stirring was continued for 30 min at room temperature, followed by the addition of Et_2O (50 ml). The product was allowed to settle, filtered and dried in vacuo yielding the brown complex **8**. Yield: 0.30 g (45%); mp >230°C, ^{31}P NMR (CD_2Cl_2) δ=25.3 (dd, J_{PP}=30.5 Hz, J_{RhP}=144.3 Hz), 13.7 (dd, J_{PP}=30.5 Hz, J_{RhP}=138.7 Hz); ^{1}H NMR (CD_2Cl_2) δ=8.0–6.5 (m, 38H, Ph, CH=N), 5.49 (m, 2H, CHN),

5.02 (m, 1H, CH), 4.64 (m, 1H, CH), 4.16 (m, 1H, CH), 3.79 (m, 1H, CH), 2.5–1.5 (m, 8H, CH_2); calcd $C_{60}H_{52}BCl_2F_4N_2O_2P_2RhTi$ (1203.53): C, 59.88; H, 4.35; N, 2.33; found: C, 59.65; H, 4.30; N, 2.35.

4. Hydroformylations

Hydroformylation reactions were performed in a 40 ml stainless steel autoclave (Fa. E. Haage) containing a glass beaker and a magnetic stirring bar. The beaker was charged with 0.01 mmol $Rh(acac)(CO)_2$. Subsequently, 0.05 mmol ligand and 1 mmol substrate dissolved in tetrahydrofuran (15 ml) were added under anaerobic conditions. The autoclave was closed, purged with 60 bar of syn-gas ($CO:H_2$=1:1) followed by heating the reaction mixture to 80°C. The gas pressure was set at 60 bar and reactions were conducted with vigorous stirring. After 24 h the autoclave was cooled to room temperature and depressurised. Analyses of samples were performed by gas chromatography.

4.1. GC conditions

Substrate: allyl acetate; determination of *n*/*iso*: HP 101, 25 m: t_R/min=15.4 (*iso*), 16.9 (*n*); determination of ee: Lipodex E, 25 m, 85°C; t_R/min=10.7, t_R/min=11.1.

Substrate: vinyl acetate; determination of *n*/*iso*: HP 5, 30 m: t_R/min=12.9 (*iso*), 13.8 (*n*); determination of ee: Lipodex E, 25 m, 100°C; t_R/min=1.7, t_R/min=2.3.

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15. It has to be taken into consideration that the chiral subunit is more than 10 Å away from the reaction centre (see Ref. 12).