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Asymmetric allylation of aldehydes with chiral platinum phosphinite complexes

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Abstract—Platinum phosphinite complexes made from chiral diols catalyze the enantioselective allylation of cinnamaldehyde. This reaction proceeds with better yields at shorter reaction times in the presence of acetic acid. Enantiomeric excesses were greater when reactions were carried out with phosphinite ligands having hydrogen bond donors or acceptors.

1. Introduction

Enantioselective C–X (X = C, N, or O) bond formation is a key step in the synthesis of many pharmaceuticals. The development of chiral asymmetric catalysts for this step has become a challenging task.[1] The enantioselectivity achieved in a reaction for a particular substrate is often not transferable to a different substrate. Hartwig has elegantly demonstrated that what is desirable is a set of catalysts with similar reactivity, but editable stereochemical elements to fine tune enantioselectivity.[2] We wished to generate a set of ligands that could be readily modified for achieving selectivity.

Asymmetric allylation of the aldehyde is particularly difficult. Available methods utilizing chiral (acyloxy)boranes,[3] titanium,[4] zirconium,[5] indium,[6] and silver[7] complexes of BINAP/BINOL are quite cumbersome. An exception to this, is the report of Hall, which utilizes a diol–$SnCl_4$ complex at low temperatures with good selectivity.[8] Herein, we report a series of chiral platinum-phosphinite complexes (Fig. 1), readily synthesized from chiral diols. The efficiency of these catalysts is doubled in the presence of acetic acid. The use of Lewis acids and bases to promote allylation has been studied earlier,[9] however Lewis acid catalysis often requires anhydrous conditions while base catalysis is not compatible with aliphatic aldehydes.

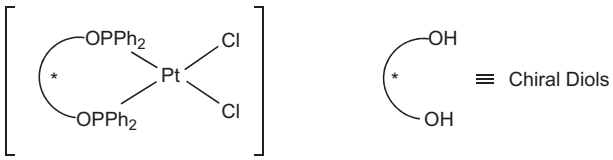
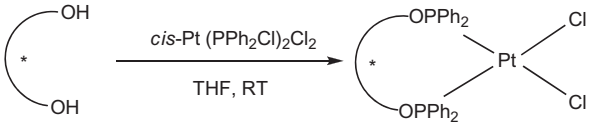


Figure 1.

2. Results and discussion

Phosphinites have been shown to be excellent ligands in a variety of reactions.[10] Our complexes have been synthesized by two different methods as outlined in Schemes 1 and 2. We refer to the procedure outlined in Scheme 1 as a templated synthesis[11] of the complex. The free ligands are not readily accessible using the procedure outlined in Scheme 2.



Scheme 1. Synthesis of platinum bisphosphinite complexes (template procedure).

The choice of phosphinites was based on the presence of hydrogen bond donors **8**, **10**–**12**, and **15** and hydrogen bond acceptors **3**, **4**, and **9** in different stereochemical sites. These were to be compared with chiral Pt complexes **1**, **2**, **5**,

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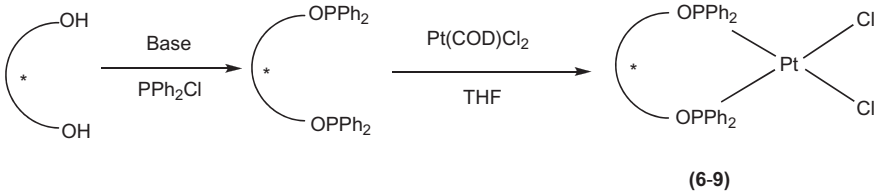
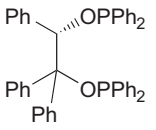
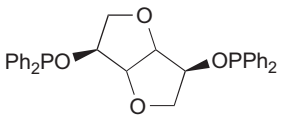


Scheme 2. Synthesis of platinum bisphosphinite complexes via the ligands **L6**–**L9**.

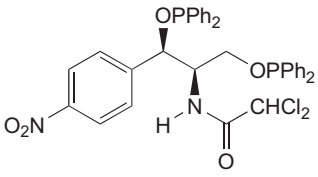
and **6** which did not have such functionalities. Pt complexes based on isoascorbic acid **14**–**16** could also be synthesized except when it was completely unfunctionalized. In this case alone, the Pt-complex made from isoascorbic acid decomposed during purification. Complexes **1**, **2**, **5**, and **7** could be characterized by X-ray diffraction studies (Figs. 2–5).



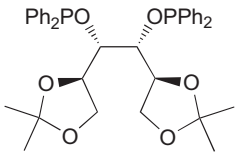
Ligand; **L6**



Ligand; **L7**



Ligand; **L8**



Ligand; **L9**

The allylation of aldehydes by allyltributyltin was attempted by using **1** as a catalyst. Complex **1** was found to be significantly more effective than *cis*-$Pt(PPh_3)_2Cl_2$ for the test reaction[12] (Scheme 3). Other aromatic aldehydes such as benzaldehyde and anisaldehyde gave reasonable

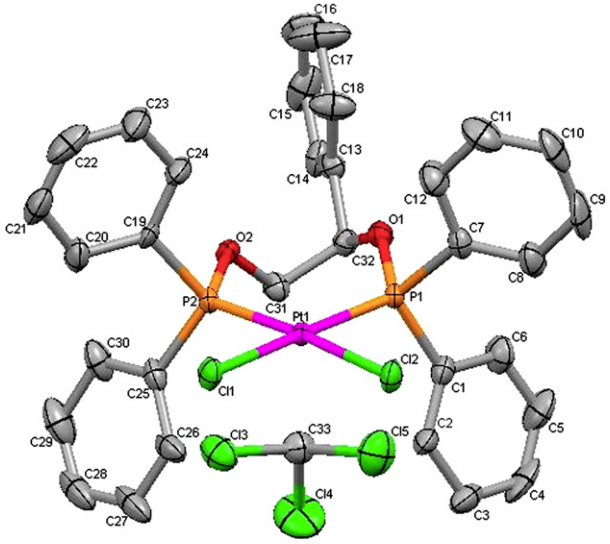


Figure 2. X-ray crystal structure of complex **1**. Ellipsoids set to 30% probability. Hydrogen atoms are omitted for clarity.

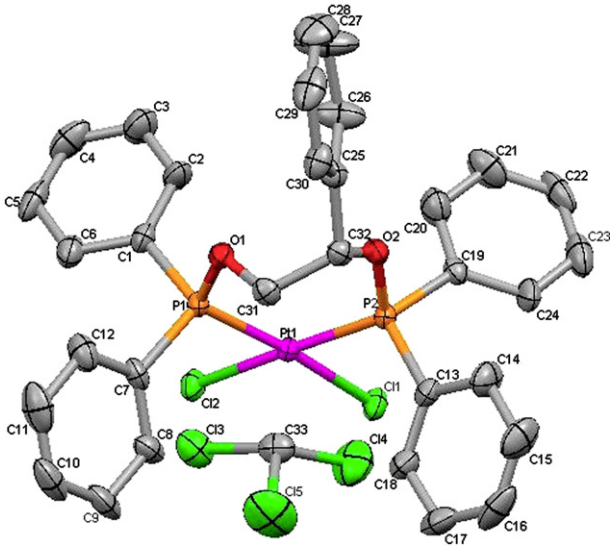


Figure 3. X-ray crystal structure of complex **2**. Ellipsoids set to 30% probability. Hydrogen atoms are omitted for clarity.

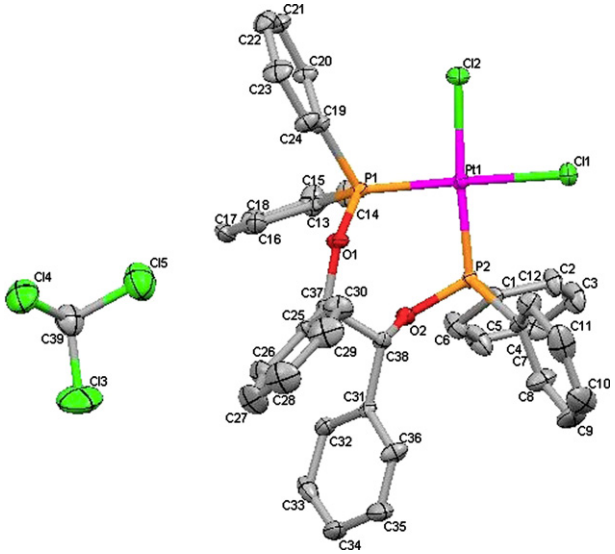


Figure 4. X-ray crystal structure of complex **5**. Ellipsoids set to 30% probability. Hydrogen atoms are omitted for clarity.

chemical yields (62% and 68%) and moderate enantioselectivities (benzaldehyde; 55% and anisaldehyde; 54%) with complex **8**. The allylation of aliphatic aldehydes however could not be carried out using the Pt complexes reported here and continue to be a challenge. The recently

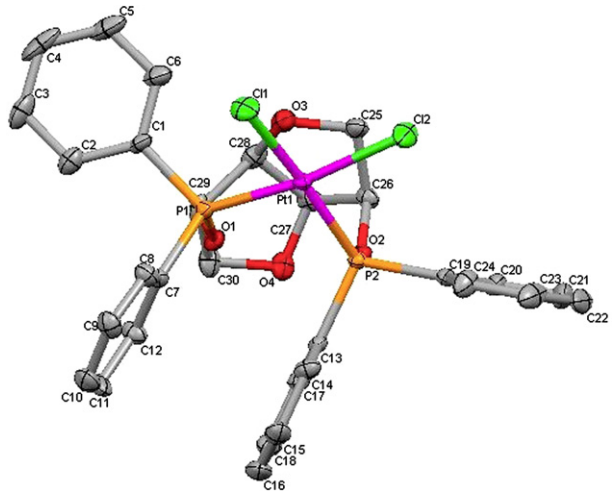
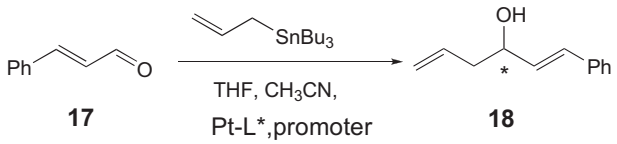


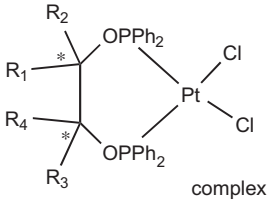
Figure 5. X-ray crystal structure of complex **7**. Ellipsoids set to 30% probability. Hydrogen atoms are omitted for clarity.



Scheme 3. Allylation of cinnamaldehyde by chiral platinum bisphosphinite complexes.

reported Pd complex for the same reaction needs to be heated to 50 °C to achieve significant yields[13] (see Tables 1 and 2).

Table 1. Complexes synthesized by the template procedure



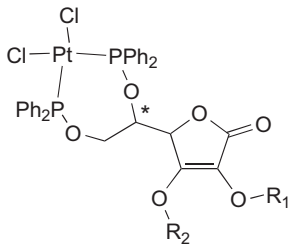
complex **1-5**

Entry	R1	R2	R3	R4	Complex ($LPtCl_2$)
1	H	H	H	Ph	(*R*)-**1**
2	H	H	H	Ph	(*S*)-**2**
3	H	COOEt	H	COOEt	(2*R*,3*R*)-**3**
4	H	COOEt	H	COOEt	(2*S*,3*S*)-**4**
5	H	Ph	H	Ph	(1*R*,2*R*)-**5**

In order to improve the reactivity, we tested the utility of acetic acid as a promoter and the use of different solvent mixtures. These results are summarized in Table 3. Although very good chemical yields were obtained, no enantioselectivity could be achieved under these conditions with catalyst **1**.

The enhancement achieved with the addition of acetic acid is presumably due to the protonation of cinnamaldehyde. The addition of water has a small effect but is significantly

Table 2. Complexes made from ascorbic acids (AA) **10**–**13** and isoascorbic acids (IAA) **14**–**16** using the template procedure



complexes **10-16**

Entry	R_1	R_2	Complex ($LPtCl_2$)
1	H	H	**10**
2	Bn	H	**11**
3	H	Bn	**12**
4	Bn	Bn	**13**
5	Bn	H	**14**
6	H	Bn	**15**
7	Bn	Bn	**16**

Table 3. Evaluation of the optimal reaction conditions for the allylation reaction using complex **1**

Entry	**1** (mol %)	Solvent	*T* (h)	Promoter (1 equiv)	Yield[a] (%)
1	10	THF	18	None	84
2	1	THF	22	None	48
3	1	THF	30	Water	62
4	1	THF	31	AcOH	90
5	1	CH_3CN	29	AcOH	90
6	1	CH_3CN/THF; 1:1	14	AcOH	90
7	1	CH_3CN/THF; 1:1	50	Excess AcOH	29
8	0.1	CH_3CN/THF; 1:1	45	AcOH	63
9[b]	1	CH_3CN/THF; 1:1	72	AcOH	0

[a] Isolated yield.
[b] No complex added.

less than that achieved with acid. This effect is different from what is observed in the Pd catalyzed allylation of imines where acid is detrimental and water was effective in bringing about complete conversion.[11]

Complexes **1**–**16** were then scanned for enantioselective catalysis using the best conditions achieved for the allylation of cinnamaldehyde. No attempts were made to optimize the reaction further and the reported yields are the average of three runs. These results are given in Table 4.

There are mechanistic studies by Zhao,[15] Greeves,[16] and Denmark,[17] on the Lewis acid promoted allylation reaction. However, the mechanism of allylation catalyzed by Pt is not well established. We carried out the activation of allytributyltin[18] as proposed by Yamamoto to generate a Pt allyl species. Subsequently, the allyl group was added to the protonated aldehyde. Examination of the observed ee suggests that the presence of a hydrogen bond donor/acceptor on the chiral ligand is essential for promoting enantioselectivity. Complexes **1**–**6** did not show any ee. A comparison of the crystal structures **1**, **2**, **5**, and **7** suggests

Table 4. Allylation of cinnamaldehyde with various platinum bisphosphinite complexes[a]

Entry	Complex	Time (h)	Yield (%)	ee[b] (%)
1	**1**	14	90	Nil
2	**2**	17	82	Nil
3	**3**	09	85	Nil
4	**4**	11	92	Nil
5	**5**	06	97	Nil
6	**6**	30	64	Nil
7	**7**	12	91	28 (*R*)
8	**8**	22	88	88 (*R*)
9	**9**	22	81	12 (*R*)
10	**10**	13	90	73 (*R*)
11	**11**	10	89	83 (*R*)
12	**12**	19	77	15 (*R*)
13	**13**	18	84	Nil
14	**14**	28	81	70 (*S*)
15	**15**	32	70	47 (*S*)
16	**16**	23	83	Nil
17[c]	**8**	72	59	41 (*R*)

[a] The optimized reaction condition found in entry 6 of Table 3 was utilized and the reaction was followed by TLC.
[b] Determined by chiral HPLC using Chiralcel OD column from Daicel.
[c] In the absence of acetic acid.

that the complex showing moderate ee has a pronounced asymmetry or a very bulky group at the asymmetric carbon, which bends over to the Pt–Cl side. Particularly interesting examples are **6**, **13**, and **16**, which all have bulky substituents, but no hydrogen bond donors and exhibit no enantioselectivity. Clearly, it is not only important to have a bulky substituent on the asymmetric carbon, but it is also important to have hydrogen bond donors/acceptors.

Given the importance of the acetic acid in promoting the reaction, it is not surprising that the hydrogen bond donor/acceptor sites on the ligand play a role in enhancing the enantioselectivity.[14] Complexes **7** and **8** were generated from readily available diols and tested for asymmetric induction, although they are not similar to the ascorbic acid complexes. Complex **8**, which has hydrogen bond donors and acceptors is exceptionally good in promoting a *re* face attack, thus supporting our hypothesis. The importance of acetic acid in achieving good enantioselectivity is evident from entry 17 in Table 4. Apart from the drastic decrease in the chemical yield (59%), the enantioselectivity also suffers a setback without the addition of acetic acid.

3. Conclusion

In conclusion, we have discovered new bisphosphinite ligands from inexpensive starting materials and demonstrated that Pt complexes of these ligands can be readily synthesized. The ligands based on ascorbic acid provide an opportunity for editing the stereochemical elements with hydrogen bond donors and acceptors. They have exceptionally good potential for the catalytic enantioselective allylation of carbonyl compounds. High selectivity and turnover number are achieved in the presence of acetic acid as a promoter.

4. Experimental

4.1. General methods

All reactions and manipulations were routinely performed under nitrogen atmosphere by using standard Schlenk techniques in oven-dried glassware. Tetrahydrofuran and diethyl ether were doubly distilled over sodium/benzophenone and $LiAlH_4$. Dichloromethane was purified by distillation from P_2O_5. Triethylamine was distilled over KOH followed by $LiAlH_4$. Diphenylphosphine chloride was purified by distillation under nitrogen prior to use. Cinnamaldehyde was distilled before use. Analytical thin layer chromatography (TLC) was performed using Merck 60 F_{254} precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm). Further visualization was possible by staining with iodine or a basic solution of potassium permanganate, followed by heating on a hot plate. Column chromatography was performed using Merck silica gel 60–120 with freshly distilled solvents. Columns were typically packed as a slurry and equilibrated with the appropriate solvent system prior to use.

Nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker AMX 400 spectrometer operating at 400 MHz for ^{1}H and 162.02 MHz for ^{31}P ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.26, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); dddd (doublets of doublets of doublets of doublet); dt (doublets of triplet); or m (multiplets). The number of protons (*n*) for a given resonance is indicated by *n*H. Coupling constants are reported in Hz. Phosphorus nuclear magnetic resonance spectra (^{31}P NMR) are reported as δ in units of parts per million (ppm) relative to external H_3PO_4 (δ 0.0). HPLC-analysis was performed using Chiralcel OD column. Elemental analyses (C, H, N) were performed using Thermo Finnigan FLASH EA 1112 analyzer.

Literature methods were used for preparation of $[PtCl_2(1,5\text{-COD})]$,[19] derivatives of ascorbic and isoascorbic acid; 3-(benzyloxy)-5-(1,2-dihydroxyethyl)-4-hydroxyfuran-2(5*H*)-one,[20] 4-(benzyloxy)-5-(1,2-dihydroxyethyl)-3-hydroxyfuran-2(5*H*)-one,[21] 3,4-bis(benzyloxy)-5-(1,2-dihydroxyethyl)furan-2(5*H*)-one,[21] complexes **1** and **2**.[11]

4.2. Synthesis of complexes 3–5, 10–16[11]

4.2.1. [(2*R*,3*R*)-Diethyl 2,3-bis(diphenylphosphinooxy)succinate $PtCl_2$] 3. Colorless crystalline solid, yield 86%, $[\alpha]_D^{25} = +68.8$ (*c* 2.0, $CHCl_3$); ^{1}H NMR δ 7.77–7.69 (m, 8H, H_{arom}) 7.50–7.46 (m, 4H, H_{arom}) 7.37–7.31 (m, 8H, H_{arom}) 5.29 (dd, $J = 12.4$, 3.6 Hz, 2H, C*H*OP) 3.96 (m, 4H, CH_2CH_3) 1.13 (t, $J = 14.4$, 7.2 Hz, 6H, CH_2CH_3). ^{31}P NMR δ 93.3 (s) $J_{PPt} = 4014.8$. Anal. Calcd for $C_{32}H_{32}P_2O_6PtCl_2$: C, 45.73; H, 3.84. Found: C, 45.98; H, 4.40.

4.2.2. [(2*S*,3*S*)-Diethyl 2,3-bis(diphenylphosphinooxy)succinate $PtCl_2$] 4. Colorless crystalline solid, yield 75%, $[\alpha]_D^{25} = -61.1$ (*c* 2.0, $CHCl_3$); ^1H NMR; δ 7.79–7.69 (m, 10H, H_{arom}) 7.50–7.35 (m, 10H, H_{arom}) 5.28 (s, 2H, C*H*OP) 3.97 (m, 4H, CH_2CH_3) 1.14 (t, $J = 14.4$, 7.2 Hz, 6H, CH_2CH_3). ^{31}P NMR; δ 93.3 (s). Anal. Calcd for $C_{32}H_{32}P_2O_6PtCl_2$: C, 45.73; H, 3.84. Found: C, 45.90; H, 4.30.

4.2.3. [(1*R*,2*R*)-1,2-Bis(diphenylphosphinooxy)-1,2-diphenylethane $PtCl_2$] 5. Colorless crystalline solid, yield 88%, $[\alpha]_D^{25} = -12.3$ (*c* 1.2, $CHCl_3$); ^1H NMR; δ 8.01–6.62 (m, 30H, H_{arom}) 5.09 (t, $J = 12.0$, 5.2 Hz, 1H, C*H*OP) ^{31}P NMR; δ 96.1 (s) $J_{PPt} = 4236.8$ Hz. Anal. Calcd for $C_{38}H_{32}P_2O_6PtCl_2{\cdot}CHCl_3$: C, 48.39; H, 3.44. Found: C, 48.39; H, 3.59.

4.3. Synthesis of (*S*)-1,2-bis(diphenylphosphinooxy)-1,1,2-triphenylethane L6

(*S*)-1,1,2-Triphenylethane-1,2-diol (0.1 g, 0.344 mmol) was dissolved in THF (10 ml) and cooled to −40 °C, and *n*-butyllithium in hexane (0.98 M, 0.575 mmol) was added. Freshly distilled PPh_2Cl (0.575 mmol) was added to this cooled solution, and the reaction mixture was allowed to warm up to room temperature and stirred for 14 h. The solvent and other volatile components were removed under a reduced pressure. The colorless residue was dissolved in dry degassed toluene and passed through activated basic alumina under nitrogen. The toluene solution was washed with degassed water and dried over anhydrous K_2CO_3, filtered, and toluene was removed in vacuum. Compound **L6** was obtained as a white semisolid (0.148 g, 65% yield). ^1H NMR; δ 7.11–6.45 (m, 35H, Ph) 5.99 (s, 1H, C*H*OP). ^{31}P NMR; δ 114.8 (s) and 111.1 (s).

4.4. General procedure for the synthesis of bisphosphinite ligands L7–L9

4.4.1. (3*S*,6*S*)-3,6-Bis(diphenylphosphinooxy)-hexahydrofuro[3,2-*b*]furan L7. Isomannide (0.342 mmol) was dried azeotropically and dissolved in a dried and degassed mixture of dichloromethane (1 ml), triethylamine (5 ml), and 4-dimethylaminopyridine (0.342 mmol). This solution was cooled to 0 °C and PPh_2Cl was added dropwise. When the addition was complete, the ice bath was removed and stirring was continued for 15 h. The solvent was removed under reduced pressure, and the residue dissolved in dry toluene and passed through a basic alumina column under nitrogen. Toluene was removed under reduced pressure. Ligand **L6** was obtained as a light yellow oil and, was used for complexation without further purification, yield 68%. ^1H NMR; δ 6.90–6.84 (m, 9H, H_{arom}) 6.83–6.69 (m, 11H, H_{arom}) 4.65 (dd, $J = 12.0$, 9.6 Hz, 1H, C*H*OP). ^{31}P NMR; δ 114.4 (s).

4.4.2. *N*-((1*R*,2*R*)-1,3-Bis(benzhydryloxy)-1-(4-nitrophenyl) propan-2-yl)-2,2-dichloroacetamide L8. Yellow semisolid, yield 51%, ^1H NMR; δ 6.98–8.10 (m, 24H, H_{arom}) 6.26 (s, 1H, C*H*Cl_2) 5.63 (d, 1H, $J = 6.4$ Hz, C*H*OP) 5.25 (m, 2H, C*HH*OP) 4.93 (m, 1H, C*H*N) ^{31}P NMR; δ 117.6 (s) and 116.5 (s).

4.4.3. (*R*)-4-((1*S*,2*R*)-2-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-1,2-bis(diphenylphosphinooxy)ethyl)-2,2-dimethyl-1,3-dioxolane L9. Colorless semisolid, yield 52%. ^1H NMR; δ 7.22–7.57 (m, 20H, H_{arom}) 4.14 (dd, 2H, $J = 12.0$, 11.6 Hz, C*H*$_2$C) 3.97 (dd, 1H, $J = 8.8$, 8.4 Hz, C*H*OC) 3.75 (d, 1H, $J = 6.0$ Hz, C*H*OP) 1.41 (s, 3H, CH_3) 1.35 (s, 3H, CH_3) ^{31}P NMR; δ 117.6 (s) and 116.7 (s).

4.5. General procedure for the synthesis of bisphosphinite complexes (6–9)

4.5.1. [(*S*)-1,2-Bis(diphenylphosphinooxy)-1,1,2-triphenylethane $PtCl_2$] 6. Bisphosphinite ligand **L6** (0.157 mmol) was dissolved in 1 ml dry THF and added to a solution of $Pt(COD)Cl_2$ (0.157 mmol) in THF (5 ml) under a dry nitrogen atmosphere. The solution was stirred until it became a clear yellow solution (5 h). After 2 h a yellow precipitate appeared that was filtered and washed with cold THF (5 ml) and diethyl ether (5 ml) to give a light yellow powder **6**, 77% yield, $[\alpha]_D^{25} = +9.6$ (*c* 0.5, $CHCl_3$); ^1H NMR; δ 7.74–6.33 (m, 35H, Ph) 6.33 (d, $J = 15.6$ Hz, 1H, C*H*OP). ^{31}P NMR; δ 134.9 (d) $J_{PP} = 38.8$ Hz and 108.1 (d) $J_{PP} = 40.5$ Hz. Anal. Calcd for $C_{44}H_{36}P_2O_2PtCl_2$: C, 57.15; H, 3.92. Found: C, 57.33; H, 3.83.

4.5.2. [(3*S*,6*S*)-3,6-Bis(diphenylphosphinooxy)-hexahydrofuro[3,2-*b*]furan $PtCl_2$] 7. Colorless crystalline solid, yield 85%, $[\alpha]_D^{25} = +16.2$ (*c* 0.5, CH_2Cl_2); ^1H NMR; δ 7.89–7.22 (m, 20H, H_{arom}) 5.30 (d, $J = 11.6$ Hz, 2H, C*H*OP) 4.58 (s, 2H, C*H*OC) 4.07 (s, 2H, C*H*HO) 3.95 (d, $J = 12$ Hz, 2H, CH*H*O). ^{31}P NMR;δ 76.9 (s) $J_{PtP} = 4280.5$ Hz. Anal. Calcd for $C_{30}H_{28}P_2O_4PtCl_2$: C, 46.17; H, 3.62. Found: C, 45.79; H, 3.82.

4.5.3. [*N*-((1*R*,2*R*)-1,3-Bis(benzhydryloxy)-1-(4-nitrophenyl)-propan-2-yl)-2,2-dichloroacetamide $PtCl_2$] 8. Colorless crystalline solid, yield 82%, $[\alpha]_D^{25} = +49.4$ (*c* 1.0, CH_2Cl_2); ^1H NMR; δ 7.98–7.03 (m, 24H, H_{arom}) 6.01 (s, 1H, C*H*Cl_2) 5.59 (d, $J = 14$ Hz, 1H, C*H*OP) 4.53 (t, $J = 24.8$, 12.4 Hz, 1H, C*H*HOP) 4.32 (d, $J = 8.0$ Hz, 1H, CH*H*OP) 3.78 (m, 1H, C*H*N) ^{31}P NMR (162.02 MHz, $CDCl_3$) δ 94.0 (d) and 92.7 (d) $J_{PP} = 6.4$, 8.1 Hz. $J_{PtP} = 4144.4$, 4099 Hz. Anal. Calcd for $C_{35}H_{30}P_2N_2O_5PtCl_4$: C, 43.91; H, 3.16; N, 2.93. Found: C, 43.86; H, 3.67; N, 3.55.

4.5.4. [(*R*)-4-((1*S*,2*R*)-2-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-1,2-bis(diphenylphosphinooxy)ethyl)-2,2-dimethyl-1,3-dioxolane $PtCl_2$] 9. Colorless crystalline solid, yield 86%; $[\alpha]_D^{25} = +23.1$ (*c* 0.2, $CHCl_3$); ^1H NMR; δ 8.11–7.45 (m, 20H, H_{arom}) 4.17 (d, $J = 9.2$ Hz, 1H, C*H*HC) 4.05 (d, $J = 4.8$ Hz, 1H, CH*H*C) 3.70 (dd, 1H, $J = 7.2$, 8.8 Hz, 2H, C*H*OC) 3.57 (dd, 1H, $J = 5.6$, 8.4 Hz, C*H*OP) 1.19 (s, 3H, CH_3) 1.05 (s, 3H, CH_3) ^{31}P NMR; δ 95.4 (s), $J_{PPt} = 4180$ Hz. Anal. Calcd for $C_{36}H_{40}P_2O_6PtCl_2$: C, 48.22; H, 4.50. Found: C, 47.32; H, 4.89.

4.6. Synthesis of bisphosphinite complexes, derived from ascorbic and isoascorbic acid

4.6.1. [(*R*)-5-((*S*)-1,2-Bis(diphenylphosphinooxy)ethyl)-3,4-dihydroxyfuran-2(5*H*)-one $PtCl_2$] 10. L-Ascorbic acid (0.009 g, 0.053 mmol) was dissolved in dry degassed THF

(2 ml), DMF (0.1 ml), and HMPA (0.1 ml) and added dropwise to a stirred solution of $[Pt(PPh_2Cl)_2Cl_2]$ (0.053 mmol) under nitrogen for 13 h at room temperature. The solvent was removed under vacuum and ether (10 ml) was added to the residue, which resulted in a gummy solid. Addition of warm toluene gave a hazy solution that gradually precipitated complex **10**, which was filtered and washed with cold toluene and diethyl ether to give a white powder 0.018 g, yield 43%; $[\alpha]_D^{25} = +29.6$ (*c* 1.1, DMSO); ^{1}H NMR; δ 7.85–7.28 (m, 20H, H_{arom}) 5.58 (br s, 1H, C*H*OP) 4.68 (s, 1H, C*H*OC) 4.40 (m, 1H, C*H*HOP) 3.91 (m, 1H, CH*H*OP) ^{31}P NMR; δ 93.7 (s) and 82.2 (s) $J_{PPt} = 4183.3$ Hz. Anal. Calcd for $C_{30}H_{26}P_2O_6PtCl_2$: C, 44.46; H, 3.23. Found: C, 45.41; H, 3.12.

4.6.2. [(*R*)-5-((*S*)-1,2-Bis(diphenylphosphinooxy)ethyl)-3-(benzyloxy)-4-hydroxyfuran-2(5*H*)-one $PtCl_2$] 11. White powder, yield 61%; $[\alpha]_D^{25} = +18.1$ (*c* 1.7, $CHCl_3$); ^{1}H NMR; δ 7.80–7.11 (m, 25H, H_{arom}) 5.47 (br s, 1H, C*H*OP) 4.90 (d, $J = 10.8$ Hz, 1H, C*H*OC) 4.72 (d, $J = 10.8$ Hz, 1H, C*H*HPh) 4.63 (s, 1H, CH*H*Ph) 4.38 (m, 1H, C*H*HOP) 3.86 (m, 1H, CH*H*OP) ^{31}P NMR; δ 95.45 (s) and 84.19 (s) $J_{PPt} = 4102.2$ Hz. Anal. Calcd for $C_{37}H_{32}P_2O_6PtCl_2$: C, 49.34; H, 3.58. Found: C, 49.32; H, 4.10.

4.6.3. [(*R*)-5-((*S*)-1,2-Bis(diphenylphosphinooxy)ethyl)-4-(benzyloxy)-4-hydroxyfuran-2(5*H*)-one $PtCl_2$] 12. White powder, yield 82%. $[\alpha]_D^{25} = +26.7$ (*c* 1.3, $CHCl_3$); ^{1}H NMR; δ 7.89–7.42 (m, 25H, H_{arom}) 5.43 (d, $J = 11.6$ Hz, 1H, C*H*HOPh) 5.28 (d, $J = 11.2$ Hz, 1H, CH*H*OPh) 4.86 (m, 1H, C*H*OP) 4.50 (s, 1H, C*H*OC) 4.29 (m, 1H, C*H*HOP) 4.24 (m, 1H, CH*H*OP) ^{31}P NMR; δ 93.9 (d) and 90.2 (d) $J_{PP} = 11.3$, $J_{PtP} = 4082.9$ Hz. Anal. Calcd for $C_{37}H_{32}P_2O_6PtCl_2$: C, 49.34; H, 3.58. Found: C, 49.75; H, 4.09.

4.6.4. [(*R*)-5-((*S*)-1,2-Bis(diphenylphosphinooxy)ethyl)-3,4-bis(benzyloxy)furan-2(5*H*)-one $PtCl_2$] 13. White powder, 83% yield; $[\alpha]_D^{25} = +31.5$ (*c* 1.0, $CHCl_3$); ^{1}H NMR; δ 7.80–7.18 (m, 30H, H_{arom}) 5.23 (d, $J = 11.6$ Hz, 2H, CH_2OPh) 5.14 (d, $J = 11.6$ Hz, 1H, C*H*HOPh) 5.04 (br s, 1H, CH*H*OPh) 4.72 (d, $J = 11.2$ Hz, 1H, C*H*OP) 4.48 (s, 1H, C*H*OC) 4.18 (m, 1H, C*H*HOP) 4.08 (m, 1H, C*H*HOP) ^{31}P NMR; δ 94.3 (s) $J = 4084.5$ Hz and 90.3 (s) $J_{PPt} = 3917.6$ Hz. Anal. Calcd for $C_{44}H_{38}P_2O_6PtCl_2$: C, 53.34; H, 3.86. Found: C, 53.21; H, 4.22.

4.6.5. [(*R*)-5-((*R*)-1,2-Bis(diphenylphosphinooxy)ethyl)-3-(benzyloxy)-4-hydroxyfuran-2(5*H*)-one $PtCl_2$] 14. White powder, yield 64%; $[\alpha]_D^{25} = -20.1$ (*c* 1.0, $CHCl_3$); ^{1}H NMR; δ 7.72–6.95 (m, 25H, H_{arom}) 5.86 (br s, 1H, C*H*OP) 5.27 (s, 1H, C*H*OC) 5.03 (d, $J = 10.0$ Hz, 1H, C*H*HPh) 4.92 (d, $J = 11.6$ Hz, 1H, CH*H*Ph) 3.92 (m, 1H, C*H*HOP) 3.11 (d, $J = 10.4$ Hz, 1H, CH*H*OP) ^{31}P NMR; δ 98.3 (s) $J_{PPt} = 3870.6$ Hz and 83.5 (s) $J_{PPt} = 4113.6$ Hz. Anal. Calcd for $C_{37}H_{32}P_2O_6PtCl_2$: C, 49.34; H, 3.58. Found: C, 49.29; H, 4.06.

4.6.6. [(*R*)-5-((*R*)-1,2-Bis(diphenylphosphinooxy)ethyl)-4-(benzyloxy)-4-hydroxyfuran-2(5*H*)-one $PtCl_2$] 15. White powder, yield 69%; $[\alpha]_D^{25} = -16.2$ (*c* 1.0, $CHCl_3$); ^{1}H NMR; δ 7.85–7.12 (m, 25H, H_{arom}) 5.30 (d, $J = 11.6$ Hz, 1H, C*H*HOP) 5.28 (d, 1H, $J = 11.8$ Hz, CH*H*OP) 4.88 (m, 1H, C*H*OP) 4.66 (d, $J = 4.0$ Hz, 1H, C*H*OC) 4.14 (m, 1H, C*H*HOP) 4.00 (m, 1H, CH*H*OP) ^{31}P NMR; δ 94.9 (s) $J_{PPt} = 4064.7$ Hz and 90.3 (s) $J_{PPt} = 3965.4$ Hz. Anal. Calcd for $C_{37}H_{32}P_2O_6PtCl_2$: C, 49.34; H, 3.58. Found: C, 50.75; H, 3.69. (HRMS in CH_3CN, sens = 4.37e^4): found 865.1082 $[M-Cl]^+$ ($C_{37}H_{32}P_2O_6PtCl$ requires 865.0962).

4.6.7. [(*R*)-5-((*R*)-1,2-Bis(diphenylphosphinooxy)ethyl)-3,4-bis(benzyloxy)furan-2(5*H*)-one $PtCl_2$] 16. White powder, 87% yield; $[\alpha]_D^{25} = +27.7$ (*c* 2.0, $CHCl_3$); ^{1}H NMR; δ 7.79–7.03 (m, 30H, H_{arom}) 5.11–4.86 (m, 4H, 2CH_2OPh) 4.63 (d, $J = 3.2$ Hz, 1H, C*H*OP) 4.09 (m, 1H, C*H*HOP) 3.70 (m, 1H, CH*H*OP) ^{31}P NMR; δ 96.3 (d), $J_{PPt} = 4081.2$, $J = 11.3$ Hz and 87.5 (d) $J_{PtP} = 4081.2$, $J_{PP} = 9.7$ Hz. Anal. Calcd for $C_{44}H_{38}P_2O_6PtCl_2$: C, 53.34; H, 3.86. Found: C, 53.18; H, 3.74. (HRMS in CH_3CN, sens = 7.21e^3): found 955.1322 $[M-Cl]^+$ ($C_{44}H_{38}P_2O_6PtCl$ requires 955.1431).

4.7. 1-Phenylhexa-1,5-dien-3-ol 18

Optimized method for the asymmetric allylation of cinammaldehyde (Tables 3 and 4, entry 6). To an oven-dried 5 ml round-bottom side arm flask equipped with a magnetic stirring bar, was added **1** (570 μg, 0.756 μmol) and cinnamaldehyde **17** (9.5 μl, 75.6 μmol) in 0.5 ml acetonitrile. Allyltributyl stannane (28 μl, 90.7 μmol) was dissolved in 0.5 ml THF and added to the resulting mixture, which was then stirred for 10 min, followed by addition of the promotor AcOH (4.5 μl, 75.6 μmol). The reaction mixture was stirred for the required time at room temperature and then extracted with ether (5 × 10 ml). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The residual crude product was purified via silica gel chromatography to afford homoallylic alcohol **18** (phenylhexa-1,5-dien-3-ol) as a colorless oil. ^{1}H NMR; δ 7.40–7.21 (m, 5H_{arom}), 6.60 (d, $J = 15.9$ Hz, 1H, PhC*H*=CH), 6.25 (dd, $J = 15.9$, 6.3 Hz, 1H, PhCH=C*H*), 5.93–5.79 (m, 1H, CH_2CH=CH_2), 5.21–5.15 (m, 2H, CH_2CH=CH_2), 4.37–4.35 (m, 1H, CH_2CHOH), 2.48–2.33 (m, 2H, CH_2CH=CH_2). The enantiomeric excess was determined by HPLC analysis employing a Chiralcel OD column from Daicel [hexane/*i*-propanol 90:10, 1.0 ml/min, $\lambda = 220$ nm, $t_1 = 7.79$ min for the (*R*)-enantiomer, $t_2 = 11.44$ min for the (*S*)-enantiomer]. It has been established that the (*R*)-enantiomer elutes first.[22]

4.8. Crystal data

Suitable single crystals were mounted and X-ray diffraction data were collected on a SMART APEX CCD diffractometer (graphite-monochromated Mo-Ka radiation, Π–ω-scan technique, $\lambda = 0.71073$ Å). The intensity data were integrated by means of the SAINT program.[23] SADABS[24] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined against F^2 using all reflections with the aid of the SHELXTL package.[25] All non-hydrogen atoms were refined anisotropically. The H atoms were included in calculated positions with isotropic thermal parameters

related to those of the supporting carbon atoms but were not included in the refinement. All non-hydrogen atoms were found from the difference Fourier syntheses. All calculations were performed using the BRUKER SMART program.

4.8.1. Complex 1. (CCDC 648572): $PtCl_2(C_{32}H_{28}O_2P_2)\cdot CHCl_3$, $M = 891.84$; monoclinic, space group $P2_1$, $a = 9.472(6)$, $b = 17.526(10)$, $c = 11.041(7)$ Å, $\beta = 110.225(8)°$, $V = 1719.92(57)$ Å^3, $T = 293(2)$ K, $Z = 2$, $\mu = 4.590$ mm^{-1}, $R_{int} = 0.0290$ (for 12,358 measured reflections), $R_1 = 0.0339$ [for 5837 unique reflections with $I > 2\sigma(I)$], $wR_2 = 0.0908$ (for all 6029 unique reflections).

4.8.2. Complex 2. (CCDC 648573): $PtCl_2(C_{32}H_{28}O_2P_2)\cdot CHCl_3$, $M = 891.84$, monoclinic, space group $P2_1$, $a = 9.470(5)$, $b = 17.555(5)$, $c = 11.046(5)$ Å, $\beta = 110.041(5)°$, $V = 1725.2(13)$ Å^3, $T = 293(2)$ K, $Z = 2$, $\mu = 4.576$ mm^{-1}, $R_{int} = 0.0207$ (for 12,587 measured reflections), $R_1 = 0.0209$ [for 5852 unique reflections with $I > 2\sigma(I)$], $wR_2 = 0.0493$ (for all 6228 unique reflections).

4.8.3. Complex 5. (CCDC 648574): $PtCl_2(C_{38}H_{32}O_2P_2)\cdot CHCl_3$, $M = 967.93$; monoclinic, space group $P2_1$, $a = 9.891(3)$, $b = 17.537(5)$, $c = 11.225(3)$ Å, $\beta = 92.302(4)°$, $V = 1945.6(9)$ Å^3, $T = 293(2)$ K, $Z = 2$; $\mu = 4.056$ mm^{-1}, $R_{int} = 0.1711$ (for 22,406 measured reflections), $R_1 = 0.0613$ [for 7656 unique reflections with $I > 2\sigma(I)$], $wR_2 = 0.1469$ (for all 8967 unique reflections).

4.8.4. Complex 7. (CCDC 648575): $PtCl_2(C_{30}H_{28}O_4P_2)$, $M = 780.45$; monoclinic, space group $P2_1$, $a = 9.659(5)$, $b = 16.265(5)$, $c = 9.863(5)$ Å, $\beta = 111.761(5)°$, $V = 1435.2(11)$ Å^3, $T = 293(2)$ K, $Z = 2$, $\mu = 5.222$ mm^{-1}, $R_{int} = 0.0299$ (for 12,480 measured reflections), $R_1 = 0.0274$ [for 5787 unique reflections with $I > 2\sigma(I)$] $wR_2 = 0.0586$ (for all 6361 unique reflections).

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