Hydridorhodium Diphosphite Catalysts in the Asymmetric Hydroformylation of Styrene†

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Chiral diphosphites based on (2*R*,3*R*)-butane-2,3-diol, (2*R*,4*R*)-pentane-2,4-diol, (2*S*,5*S*)-hexane-2,5-diol, (1*S*,3*S*)-diphenylpropane-1,3-diol and *N*-benzyltartarimide as chiral bridges have been used in the rhodium-catalysed asymmetric hydroformylation of styrene. Enantioselectivities up to 76% at 50% conversion have been obtained with stable hydridorhodium diphosphite catalysts. High regioselectivities (>95%) and high conversions (>99%) to 2-phenylpropanal were found under relatively mild reaction conditions [25–40 °C, 9 bar of CO–H_2 (1:1) pressure]. The solution structures of [RhH(L)$(CO)_2$] complexes (L = bidentate diphosphite) have been studied; NMR and IR spectroscopic data revealed fluxional behaviour. Depending on the structure of the bridge, the diphosphite adopts equatorial–equatorial or equatorial–axial co-ordination to the rhodium. The structure and the stability of the catalysts seems to play a fundamental role in the asymmetric induction.

Asymmetric hydroformylation is a convenient method for obtaining optically pure aldehydes, which for example can be used as starting materials for the synthesis of pharmaceuticals.[1,2] 2-Arylpropionic acids represent a class of antiinflammatory reagents which can be obtained by oxidation of the corresponding aldehydes. Since only one enantiomer is responsible for the biological activity, the preparation of optically pure products is desired. Asymmetric hydroformylation of functionalised alkenes followed by oxidation of the aldehydes can give 2-arylpropionic acids in only two steps. From the early seventies, transition-metal complexes based on rhodium and platinum have been used as catalysts in asymmetric hydroformylation.[3–11] With rhodium–diphosphine catalysts the regioselectivity is encouraging but the obtained enantioselectivity has been low up till now. With platinum–diphosphine catalysts high enantioselectivities have been reported but both the regioselectivity and the chemoselectivity to the branched aldehyde is generally low. It is assumed that both regio- and stereo-selectivity are determined by the structure of the catalyst and can be steered by choice of the ligand. Recently Casey *et al.*[12] published a correlation between the natural bite angle of chelating diphosphines and the regioselectivity in the rhodium-catalysed hydroformylation. Development of diphosphine ligands giving a P–Rh–P bond angle of approximately 120° has resulted in hydridorhodium diphosphine complexes with high selectivity to linear products. Since van Leeuwen and Roobeek[13,14] reported high activity of bulky phosphite ligands in rhodium-catalysed hydroformylation, there has been growing interest in the use of these ligands.[15–18] Generally phosphites and diphosphites can easily be synthesised from diols and phosphorochloridites in the presence of a base and are less prone to oxidation than are phosphines.[19–22] High regioselectivities with diphosphite ligands in the rhodium-catalysed hydroformylation of functionalised alkenes have been published by Kwok and Wink[23] and Cuny and Buchwald.[24] Chiral diphosphites are also of interest since they can serve as ligands in the asymmetric hydroformylation of alkenes which results in the formation of optically active aldehydes. The first reports on asymmetric hydroformylation revealed catalytic activity of the ligands but no asymmetric induction was obtained with chiral rhodium–(di)phosphite catalysts.[25,26] In a previous paper we reported[27] the use of chiral diphosphites based on commercially available optically active 1,2- and 1,4-diols in the asymmetric hydroformylation of styrene. Enantiomeric excesses (e.e.s) up to 20% and high regioselectivity to the branched aldehyde were obtained. Takaya and co-workers[28] published the results of the asymmetric hydroformylation of vinyl acetate (e.e. ≈50%) with chiral bis(triaryl phosphite)rhodium complexes. Highly enantioselective hydroformylation of functionalised alkenes with a rhodium–phosphine–phosphite catalyst has been reported recently.[29] At the same time workers at Union Carbide reported the asymmetric hydroformylation of various alkenes with e.e.s up to 90% using a rhodium–diphosphite catalyst based on (2*R*,4*R*)-pentane-2,4-diol.[30]

a **b**

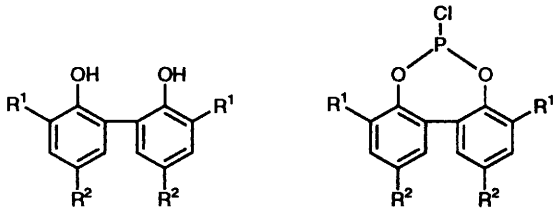
To our knowledge structural information about hydridorhodium disphosphite complexes is scarce, despite NMR and IR studies of them.[29,31–35] A structural similarity between diphosphines and diphosphites is expected which means that in hydridorhodium diphosphite complexes the diphosphite may co-ordinate in an equatorial–equatorial or an equatorial–axial fashion to the rhodium, structures **a** and **b** respectively.[36] We have synthesised a series of chiral diphosphites with C_2 symmetry and various bridges between the two phosphorus atoms in order to study the effect of the length of the bridge on the structure of the [RhH(L)$(CO)_2$] (L = diphosphite) complex. We report here the regio- and enantio-selectivity in the asymmetric hydroformylation of styrene with different rhodium catalysts based on chiral diphosphite ligands. The results of the hydroformylation experiments are discussed in relation to the solution structures and stability of the hydridorhodium diphosphite catalysts.

Results and Discussion

Synthesis.—The structurally related diols (2*R*,3*R*)-butane-2,3-diol, (2*R*,4*R*)-pentane-2,4-diol and (2*S*,5*S*)-hexane-2,5-diol

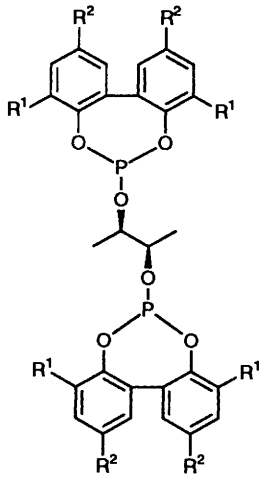
† *Non-SI unit employed:* bar = 10^5 Pa.

were used as starting materials for the synthesis of chiral diphosphite ligands. The phosphorochloridites **IIa–IIc** were all derived from 2,2'-bis(phenols), **Ia–Ic**. *tert*-Butyl and methoxy substituents were introduced at the *ortho* and *para* positions of the biaryl moiety to vary the properties of the diphosphite ligands. The alkanediols, with C_2 symmetry, react in moderate to good yields (35–92%) with **IIa–IIc** in the presence of pyridine to give the corresponding diphosphites L^1–L^7. Besides the diphosphites based on flexible alkanediols, two others have been synthesised to increase the steric bulk and rigidity, L^8 and L^9 respectively. Compound L^8 is based on (1*S*,3*S*)-diphenylpropane-1,3-diol and L^9 on *N*-benzyltartarimide. As a consequence of rapid ring inversion in the bis(phenol) phosphorus moiety no axial chirality (giving rise to diastereoisomers) has been found in the diphosphite compounds by ^{31}P NMR spectroscopy.[37] Hydrolysed phosphorochloridites were sometimes formed as side products during the synthesis of the diphosphites. The latter were all stable during purification on silica gel under an atmosphere of argon and were isolated as white solids.

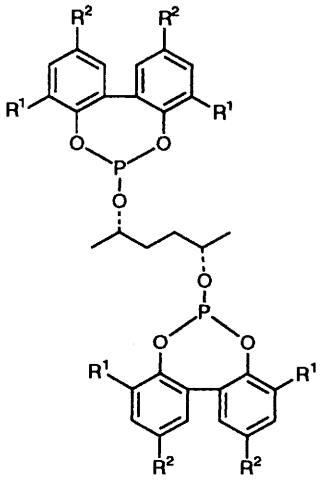


	R^1	R^2	
Ia	H	H	**IIa**
Ib	Bu^t	Bu^t	**IIb**
Ic	Bu^t	OMe	**IIc**

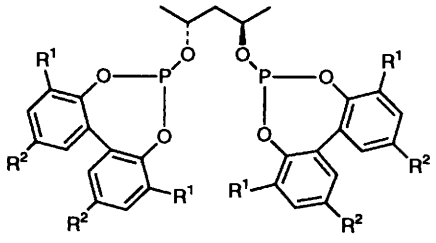
Catalysis.—The chiral diphosphites L^1–L^9 have been used in the rhodium-catalysed asymmetric hydroformylation of styrene. The catalysts were always prepared *in situ* by adding the diphosphite L to $[Rh(acac)(CO)_2]$ (acac = acetylacetonate) as a catalyst precursor. Under typical hydroformylation conditions the active catalyst $[RhH(L)(CO)_2]$ was formed. The results of the asymmetric hydroformylation of styrene with L^4 (first reported at Union Carbide[30]) are given in Table 1. Other C_2 symmetrical diphosphites give low e.e.s and therefore a more thorough study of these hydroformylation catalysts was performed. (Additional experiments with L^4 and L^5, under different reaction conditions, have been reported by Union Carbide, see ref. 30.)



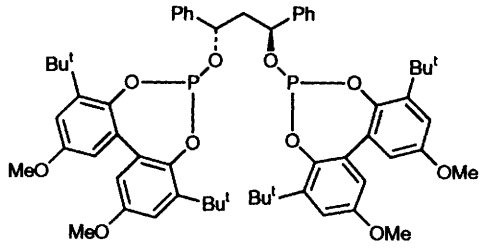
(2*R*, 3*R*) -L^1 R^1 = R^2 = Bu^t
(2*R*, 3*R*) -L^2 R^1 = Bu^t, R^2 = OMe



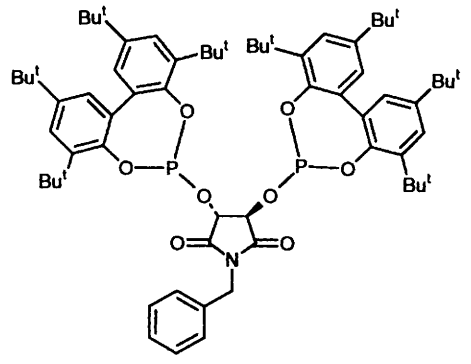
(2*S*, 5*S*) -L^6 R^1 = R^2 = Bu^t
(2*S*, 5*S*) -L^7 R^1 = Bu^t, R^2 = OMe



(2*R*, 4*R*) -L^3 R^1 = R^2 = H
(2*R*, 4*R*) -L^4 R^1 = R^2 = Bu^t
(2*R*, 4*R*) -L^5 R^1 = Bu^t, R^2 = OMe



(1*S*, 3*S*) -L^8



(3*R*, 4*R*) -L^9

Table 1 Hydroformylation of styrene with $[RhH(L^4)(CO)_2]$ as catalyst[a]

Entry	T/°C	P:Rh	p/bar	t/h	Turnover frequency[b]	% Conversion[c]	% Isoaldehyde[d]	% e.e[e]
1[f]	40	2.5	9	17	15	96	95	37
2[f]	40	8	9	17	11	95	95	48
3	40	8	9	5	166	99	95	40
4	25	8	9	5	16	21	96	68
5	40	2.5	9	5	113	89	96	50
6	40	2.5	18[g]	5	34	45	96	57
7	40	2.5	18[h]	5	145	78[i]	80	8
8	40	2.5	45[j]	5	73	63	96	63

[a] Styrene:catalyst molar ratio is 421:1; catalyst prepared *in situ* unless otherwise stated. [b] In mol styrene (mol Rh)$^{-1}$ h^{-1} determined after 2 h of reaction by GC. [c] Of styrene. [d] Regioslectivity. [e] Excess of the predominantly formed enantiomer (absolute configuration *s*). [f] Complex not prepared *in situ*. [g] $p(CO)/p(H_2) = 3$. [h] $p(CO)/p(H_2) = 0:33$. [i] 20% Hydrogenation to ethylbenzene. [j] $p(CO)/p(H_2) = 1$.

In all experiments an excess of diphosphite was used to exclude the formation of $[RhH(CO)_4]$ which is a highly active achiral hydroformylation catalyst with a predominant regioselectivity for linear aldehydes.[38] In the first two entries in Table 1 the substrate was immediately added after the autoclave had been heated to the desired reaction temperature. Since there is an incubation time for the formation of $[RhH(L)(CO)_2]$ from $[Rh(acac)(CO)_2]$ and the diphosphite, low initial turnover frequencies [11–15 mol styrene (mol Rh)$^{-1}$ h^{-1}] were found. To increase the reaction rate to more practical values, the catalyst was prepared overnight under typical hydroformylation conditions {25–40 °C, 9 bar of syn gas [CO–H_2 (1:1)], 15 h}. An approximately ten-fold increase in initial reaction rate was obtained by following this procedure. The initial turnover frequencies increased to 113–166 mol styrene (mol Rh)$^{-1}$ h^{-1} (entries 3 and 5). Except for entry 7 (for which an increased partial pressure of H_2 was used) the regioselectivity for branched (iso) aldehyde (2-phenylpropanal) always exceeds 90%. High regioselectivities for branched aldehyde in the hydroformylation of styrene and related substrates are ascribed to a preference for a branched alkylrhodium intermediate[39] or an electronically stabilised η^3-benzyl intermediate.[40] When the reaction temperature was decreased from 40 to 25 °C, lower rates were recorded, while the enantiomeric excesses increased considerably. Comparison of entry 3 with 4 shows an increase in e.e. from 40 to 68%. Asymmetric hydroformylation with L^5 resulted in enantioselectivities up to 76% at 25 °C (50% conversion). The partial pressures of CO and H_2 also influence the selectivity and the rate of the hydroformylation reaction. A three-fold increase in partial pressure of CO decreases the initial turnover frequency by the same factor (entry 5 *vs.* 6) which suggests a rate-determining step for the addition of substrate to rhodium. More detailed kinetic studies on hydroformylation with phosphites, in which a similar rate-determining step is found, have been reported.[17,41,42] A dramatic effect on chemo-, regio-and enantio-selectivity was observed at a three-fold increase in pressure of H_2 (entry 5 *vs.* 7). Hydrogenation to ethylbenzene occurred as a competing side reaction to an extent of 20%. The regioselectivity for branched aldehyde decreased to about 80% and the enantiomeric excess dropped to 8%. There is also a reaction rate dependency on hydrogen partial pressure since the initial turnover frequency increased to 145 mol styrene (mol Rh)$^{-1}$ h^{-1}. At 45 bar of syn gas an increased partial pressure of CO decreased the reaction rate but this was slightly compensated by the higher hydrogen partial pressure [entry 8, $p(CO) = p(H_2) = 22.5$ bar].

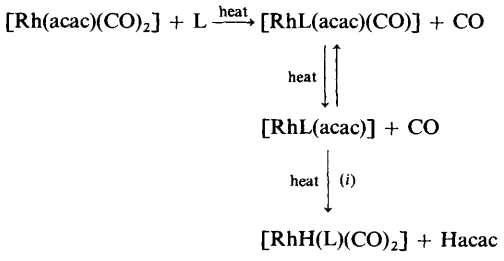
The encouraging enantiomeric excesses obtained with catalysts based on L^4 and L^5 led us to use structurally related diphosphite ligands in the asymmetric hydroformylation. A major difference between the $[RhH(L)(CO)_2]$ catalysts ($L = L^1$–L^9) is that the chelate ring size varies from seven- to nine-membered. Hydroformylation experiments with the catalyst $[RhH(L)(CO)_2]$ prepared *in situ* have been carried out for all L^1–L^9 under standard reaction conditions. The results are given in Table 2. Four experiments were done at 25 °C (entries 10, 12, 19 and 21) in order to improve the enantiomeric excesses. In all reactions (except 13) the obtained regioselectivity to branched aldehyde is very good (above 90%). At 40 °C the conversions determined after 5 h varied between 74 and 99%. Compounds L^6 and L^7 based on (2*S*,5*S*)-hexane-2,5-diol show a considerably lower catalytic activity (entries 16 and 17) than do the others. The initial turnover frequencies for entries 9–12 show that higher catalytic activities are obtained with L^2 compared to L^1 at both 25 and 40 °C. Furthermore the compound based on (2*R*,4*R*)-pentane-2,4-diol, in which the bis(phenol) moiety is substituted with methoxy groups at the *para* positions, shows the highest catalytic activity.

An almost complete conversion into aldehydes (98%) was obtained at 40 °C (entry 15). Compound L^8 also shows a relatively high catalytic activity. A conversion of 99% was found within 5 h (entry 18). General trends in reaction temperature *versus* selectivity are in agreement with those in Table 1. On going from 40 to 25 °C the reaction rate always decreased, while the regio- and enantio-selectivity increased. A close inspection of the temperature effect on the enantiomeric excess reveals an increase varying from 7 to 15% (entry 20 *vs.* 21 and 18 *vs.* 21, respectively) by lowering the temperature from 40 to 25 °C. An interesting trend is found between the enantiomeric excess and the structure of the diphosphite. The highest enantiomeric excesses at 40 °C are found with the L^4, L^5 and L^8 (entries 14, 15 and 18, Table 2). These backbones give rise to eight-membered rings in the catalyst. Compounds L^1 and L^2, based on (2*R*,3*R*)-butane-2,3-diol, gave moderate e.e.s between 19 and 30% (entries 9–11). Low enantiomeric excesses (1–7%, entries 16 and 17) have been obtained with L^6 and L^7, based on (2*S*,5*S*)-hexane-2,5-diol. Compound, L^9 which contains a relatively rigid tartarimide backbone, gave low enantiomeric excesses (entries 20 and 21). From the results in Table 2 it becomes clear that predominantly the (*S*)-aldehyde is formed when ligands based on (*R*,*R*)-diols are used.* Inversion of configuration at the chiral carbon atoms [C(2) and C(5)] in (2*S*,5*S*)-hexane-2,5-diol results in an inversion to predominantly (*R*)-aldehyde (entries 16 and 17). The results obtained with L^3 are in contradiction with this trend (entry 13). The absence of bulky substituents at the *ortho* and *para* positions of the bis(phenol) groups may give rise to a deviant structure of the catalyst and so lead to an inverted absolute configuration of the predominantly formed enantiomer.

Catalyst Preparation.—Hydridorhodium diphosphite complexes are generally considered as the active catalysts in the

* Compound L^8 has the same 'absolute' configuration at C(1) and C(3) in comparison to L^1–L^5 but the opposite *R*/*S* indicator results from the Cahn, Ingold and Prelog rules.

asymmetric hydroformylation but structural information is scarce.[29,31–35] The active catalyst can be formed from a starting rhodium precursor such as [Rh(acac)(CO)$_2$]. Under typical hydroformylation conditions, [RhL(acac)] (L = diphosphite) complexes undergo transformation to trigonal-bipyramidal hydridorhodium diphosphites (Scheme 1).



Scheme 1 Formation of [RhH(L)(CO)$_2$] from [Rh(acac)(CO)$_2$] and the diphosphite L. (*i*) CO–H_2

The [Rh(L)(acac)] complexes were prepared by adding 1 equivalent of the rhodium precursor [Rh(acac)(CO)$_2$] to the diphosphite L (L = L^1–L^9). In all cases displacement of CO was observed immediately and yellow-green solutions were formed.[28] Infrared and ^{31}P NMR spectroscopy showed that the ease of replacement of CO by diphosphite strongly depends on the structure of the latter. When ligands L^1, L^2 and L^9 were added to [Rh(acac)(CO)$_2$] two doublets were found in the ^{31}P NMR spectra with phosphorus–rhodium coupling constants close to 300 Hz.[28] Stirring for longer periods at 80 °C had some influence on the ratio between these doublets but did not result in one of the doublets exclusively (see Table 3). The existence of a [RhL(acac)(CO)] species in which the ligand L co-ordinates in a monodentate fashion can be excluded since no signals were observed at the chemical shift of the free diphosphite. It seems that co-ordination of the diphosphite in a bidentate fashion takes place immediately.[27,28] Infrared spectra for mixtures of [RhL(acac)] and [RhL(acac)(CO)] complexes showed an absorption near 2006 cm^{-1} which is indicative of a Rh(CO) species. The exact structure of [RhL(acac)(CO)] could not be determined but preliminary spectroscopic data indicate the existence of a fluxional trigonal-bipyramidal complex. Two additional IR absorptions are found at 1581 and 1523 cm^{-1} which can be ascribed to two carbonyls of acetylacetonate. The low-temperature ^{31}P NMR spectrum for RhL^1(acac)(CO)] revealed a rapid exchange of both phosphorus atoms. The complex was formed exclusively by stirring [Rh(acac)(CO)$_2$] and 1 equivalent of L^1 for 1 h at room temperature. At 193 K the exchange still took place and revealed two incompletely resolved phosphorus chemical shifts indicating both phosphorus atoms to be inequivalent (δ 140.0, $^1J_{Rh-P}$ = 285; δ 127.2, $^1J_{Rh-P}$ = 313 Hz). Adding 1 equivalent of L^3 to [Rh(acac)-(CO)$_2$] gives only one doublet in the ^{31}P NMR spectrum. An intense vibration was found in the IR spectrum at 2009 cm^{-1} which suggests exclusive formation of [RhL(acac)(CO)]. With L^4–L^8, [RhL(acac)] complexes can be formed exclusively. With L^5 one IR vibration was found at 1516 cm^{-1} for the carbonyls of acetylacetonate co-ordinated to rhodium. The low-temperature ^{31}P NMR spectrum showed one doublet (203 K, δ 147.7, $^1J_{Rh-P}$ = 305 Hz).

Characterisation of [RhH(L)(CO)$_2$] *Complexes.*—The [RhH(L)(CO)$_2$] complexes were prepared under hydroformylation conditions by adding 1 equivalent of diphosphite to the

Table 2 Hydroformylation of styrene with chiral rhodium–diphosphite catalysts[a]

Entry	Diphoshite	*T*/°C	Turnover frequency[b]	% Conversion[c]	% Isoaldehyde[d]	% e.e.	Absolute configuration[e]
9	L^1	40	66	74	93	19	(*S*)
10	L^1	25	15	18	95	30	(*S*)
11	L^2	40	177[f]	99	92	25	(*S*)
12	L^2	25	31	40	93	34	(*S*)
13	L^3	40	117	81	80	11	(*R*)
14	L^4	40	113	89	96	50	(*S*)
15	L^5	40	207[f]	98	94	67	(*S*)
16	L^6	40	19	26	93	1	(*R*)
17	L^7	40	19	26	92	7	(*R*)
18	L^8	40	165	99	90	47	(*S*)
19	L^8	25	40	45	95	62	(*S*)
20	L^9	40	106	81	92	3	(*S*)
21	L^9	25	26	27	95	10	(*S*)

[a] All reactions were carried out with 13.1 mmol styrene. Styrene:catalyst molar ratio is 421:1, P:Rh molar ratio is 2.5:1. [b] In mol styrene (mol Rh)$^{-1}$ h^{-1} determined after 2 h at reaction by GC. [c] Of styrene after 5 h. [d] Regioselectivity. [e] Absolute configuration of the predominantly formed isomer. [f] After 1 h of reaction.

Table 3 ^{31}P NMR and IR data for complexes [RhL(acac)(CO)] and [RhL(acac)][a]

L	[RhL(acac)(CO)]	[RhL(acac)]	Ratio[c]	Conditions[d]	Rh–CO band (cm^{-1})
L^1	134.9 (296)	139.7 (317)	0.38	2 h, 80 °C	2008
L^2	135.5 (294)	139.6 (316)	0.43	2 h, 80 °C	2006
L^3	147.3 (286)	—	—	1 h, r.t.	2009
L^4	—	146.0 (306)	—	1 h, r.t.	—
L^5	—	146.1 (306)	—	1 h, r.t.	—
L^6	—	137.2 (320)	—	1 h, 80 °C	—
L^7	—	137.9 (318)	—	1 h, 80 °C	—
L^8	—	137.4 (319)	—	1 h, 80 °C	—
L^9	146.7 (294)	136.1 (299)	0.13	1 h, 80 °C	2013

[a] In [$^2H_8$]toluene under an atmosphere of argon starting from 0.0194 mmol of [Rh(acac)(CO)$_2$]. ^{31}P-{^{1}H} NMR spectra recorded in the same solvent under an argon atmosphere at room temperature. [b] Chemical shifts (δ) in ppm. Coupling constants ($^1J_{Rh-P}$)/Hz in parentheses. [c] ^{31}P NMR integral ratio [RhL(acac)]:[RhL(acac)(CO)]. [d] r.t. = room temperature.

Table 4 NMR and IR data for $[RhH(L)(CO)_2]$ complexes[a]

L	$\delta(^{31}P)$[b]	$\delta(^1H)$[b]	$^1J_{Rh-P}$[c]	$^1J_{Rh-H}$[c]	$^2J_{P-H}$[c]	IR (cm^{-1}) Rh–(CO)	IR (cm^{-1}) Rh–H
L^1	154.1	−10.08	|210|	7.2	|99.9|	2029, 1988	*d*
L^2	156.1	−10.05	|209|	7.2	|96.0|	2029, 1987	*d*
L^4	158.5	−10.25	237	3.0	< 3.0	2073, 2015	1985
L^5	159.6	−10.26	233	6.0	< 3.0	2070, 2011	1982
L^6	157.7	−10.07	234	6.0	< 3.0	2068, 2011	1984
L^7	159.6	−10.04	233	< 3.0	< 3.0	2069, 2012	1983
L^8	160.1	−9.97	231	< 3.0	< 3.0	2076, 2018	1990
L^9	158.7	−10.43	237	3.0	12.0	2082, 2024	1997

[a] Prepared in $[^2H_8]$toluene starting from 0.0194 mmol $[Rh(acac)(CO)_2]$, 40 °C, 8 h under 15–20 bar of syn gas. [b] $^{31}P-\{^1H\}$, ^{31}P and ^1H NMR spectra recorded in $[^2H_8]$toluene under atmospheric conditions at r.t. Chemical shifts (δ) in ppm. [c] Coupling constants in Hz. [d] Not found.

catalyst precursor $[Rh(acac)(CO)_2]$. Relatively long reaction times (8 h, 15–20 bar of syn gas) were needed for a complete conversion into $[RhH(L)(CO)_2]$ which explains the relatively long incubation times in hydroformulation experiments (Table 1). Shorter reaction times resulted, depending on the diphosphite chosen, in incomplete reactions. Intermediate [RhL(acac)(CO)] and [RhL(acac)] species were observed as side products in the ^{31}P NMR spectra. Compounds L^1–L^9 were used for the formation of $[RhH(L)(CO)_2]$ complexes. With the non-bulky L^3 the hydridorhodium diphosphite complex was not stable under the operating conditions. The complexes formed have been characterised by ^{31}P and ^1H NMR and IR spectroscopy (Table 4).

The complexes showed somewhat broadened doublets at room temperature in the $^{31}P-\{^1H\}$ NMR spectra. These are caused by a rhodium–phosphorus coupling in the range 231–237 Hz in the case of L^4–L^9. In two cases (L^1 and L^2) relatively small $^1J_{Rh-P}$ coupling constants (about 210 Hz) were found. Furthermore, both ^{31}P and ^1H NMR spectra showed a considerably large $^2J_{P-H}$ coupling constant (about 100 Hz) which suggests a time-averaged *cis,trans* relationship between the phosphorus and the hydrogen atom bonded to the rhodium. Large $^2J_{P_{ax}-H}$ coupling constants (≈160 Hz) for phosphorus and hydrogen atoms bonded *trans* to rhodium have been reported.[28,31–33] The smaller values found for our complexes suggest rapid exchange of a phosphorus-donor atom bonded in an equatorial or axial manner to the rhodium centre. The complexes with L^1 or L^2 showed double triplets for the hydride in the ^1H NMR spectrum caused by coupling with rhodium and two (averaged) phosphorus atoms. When L = L^4–L^9 small $^2J_{P-H}$ coupling constants (< 3 Hz) were found which are indicative of a *cis* relationship between the phosphorus and the hydrogen atom bonded to the rhodium.[26,28,29,31] As a consequence of the C_2 symmetry, the phosphorus atoms are equivalent in the free diphosphites. However, this is not the case in hydridorhodium diphosphite complexes. Even in the case when both phosphorus atoms are co-ordinated in an equatorial fashion to the rhodium, both have a different orientation towards the hydrogen atom and the axial carbon monoxide molecule. A difference in chemical shift for the phosphorus atoms could not be observed at room temperature since fluxionality makes both atoms indistinguishable. In the complexes of L^1 and L^2 the fluxionality is not halted completely at 193 K which suggests low-energy-barrier pseudo-Berry rearrangements (see Table 5). The low-temperature hydride region of the ^1H NMR spectrum appeared as a broad doublet since the small *cis* $^2J_{P_{eq}-H}$ and the $^1J_{Rh-H}$ coupling constants were not resolved completely at 193 K. As expected the low-temperature $^2J_{P_{ax}-H}$ coupling constants are quite large. For L^1, a $^2J_{P_{ax}-H}$ coupling constant close to 220 Hz was observed. Furthermore a small rhodium–hydride coupling of about 8 Hz was found. Comparable data were obtained for L^2 (213 K, $^2J_{P_{ax}-H}$ = 211, $^1J_{Rh-H}$ = 9 Hz). From these results it can be concluded that one phosphorus-donor atom occupies an axial position and exhibits a large $^2J_{P-H}$ coupling constant, the other one an equatorial position with a small coupling constant (structure **b**).[35]

Table 5 Phosphorus-31 and ^1H NMR data of complexes $[RhH(L)(CO)_2]$ at low temperature[a]

L	$\delta(^{31}P)$[b]	$\delta(^1H)$[b]	$^1J_{Rh-P}$[c]	$^2J_{P^1-P^2}$[c]	T/K
L^1	Unresolved	Unresolved	|210|	—	193
L^2	Unresolved	Unresolved	|209|	—	193
L^4	164.1, 154.8	−9.88	234	242	213
L^5	165.3, 155.7	−9.93	233	236	213
L^6	162.1, 158.6	−10.00	234	259	208
L^7	165.2, 160.1	−9.98	233	261	213
L^8	164.9, 156.9	−9.73	240	241	213
L^9	164.6, 157.5	−10.19	236	327	213

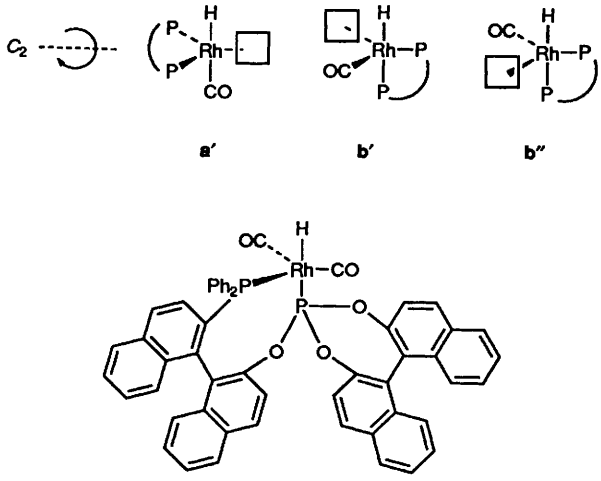
[a] In $[^2H_8]$toluene starting from 0.0194 mmol $[Rh(acac)(CO)_2]$, 8 h at 40 °C, 15–20 bar of syn gas. [b] $^{31}P-\{^1H\}$ and ^1H NMR spectra recorded in $[^2H_8]$toluene under atmospheric conditions. Chemical shifts (δ) in ppm. [c] Coupling constants in Hz.

The fluxionality of $[RhH(L)(CO)_2]$ complexes of L^4–L^9 can be completely frozen out at 213–208 K. Indeed two ^{31}P chemical shifts are observed with accidentally equivalent $^1J_{Rh-P}$ coupling constants close to 235 Hz. For these complexes small (< 3 Hz) $^1J_{Rh-H}$ and small $^2J_{P-H}$ coupling constants (< 3 Hz) were found which suggest an equatorial co-ordination of both phosphorus donor atoms.[31–33,35] Large $^2J_{P_{eq}-P_{eq}}$ coupling constants (between 236 and 327 Hz) have been observed at low temperature which we think is typical of an equatorial relationship of the phosphorus-donor atoms bonded to the rhodium (structure **a**). From the results in Table 5 it becomes clear that a suitable bridge between the two phosphorus atoms leads to formation of one of the two possible trigonal-bipyramidal $[RhH(L)(CO)_2]$ complexes (structure **a** or **b**). It seemed that diphosphite ligands based on (2*R*,3*R*)-butane-2,3-diol (L^1 and L^2), giving rise to a seven-membered chelate ring, lead to stabilisation of structure **b**. Interestingly, the rigid tartarimide backbone of L^9 with a chelate ring size of seven results in formation of structure **a**. Compounds L^4–L^8 which form eight- and nine-membered rings with rhodium, also lead to formation of structure **a**.

Besides differences in co-ordination of the diphosphites to the rhodium, also differences in stability of $[RhH(L)(CO)_2]$ complexes have been observed. The complexes of L^1, L^2, L^6, L^7 and L^9 showed orange-brown reaction mixtures after 8 h at 40 °C under 15–20 bar of syn gas. The ^{31}P NMR spectra always show additional chemical shifts around δ 10 which can be ascribed to hydrolysis of the diphosphite ligands to phosphonates. The complex of L^2 showed an additional chemical shift in the ^{31}P NMR spectrum. Isolation of this side product by precipitation in acetonitrile gave an orange powder which was characterised as a carbonyl-bridged dimeric rhodium

species $[Rh_2L^2_2(CO)_2]$ (^{31}P NMR δ 154.9, $^1J_{Rh-P}$ = 336 Hz; IR 1818 cm^{-1}; positive-ion FAB mass spectrum *m/z* 1986). During *in situ* preparation of $[RhH(L)(CO)_2]$ complexes, degradation of ligand could result in the formation of other rhodium species under hydroformylation conditions. Infrared experiments have been carried out on the complexes in solution to find out whether other rhodium species were formed. Table 4 shows IR absorptions obtained for $[RhH(L)(CO)_2]$ complexes where L = L^1–L^9. In all cases two absorptions are ascribed to two terminal rhodium–carbonyl vibrations and one to a rhodium–hydride vibration. With L^1 and L^2 the rhodium–hydride absorption could not be found. Probably this band is hidden under one of the two rhodium–carbonyl vibrations. Additional bands are often observed for $[RhH(L)(CO)_2]$ complexes of L^1, L^2, L^6, L^7 and L^9 around 2080, 2050 and 1860 cm^{-1} which become more intense when the corresponding ^{31}P NMR spectra show an increased degradation of ligand. This can be explained by displacement of ligand resulting in the formation of rhodium carbonyl clusters. Infrared spectroscopic studies on rhodium carbonyl compounds like $[Rh_4(CO)_{12}]$ has revealed bands at around 2080, 2050 and 1860 cm^{-1}.[38,43] Remarkable results from NMR and IR spectroscopy were found with $[RhH(L)(CO)_2]$ complexes of L^4, L^5 and L^8. Solutions of these complexes were yellow and showed considerably less hydrolysis of the ligands compared to complexes of L^1, L^2, L^6, L^7 and L^9. Absorptions in the IR spectra originating from rhodium carbonyl clusters were almost absent. These results suggest rather stable $[RhH(L)(CO)_2]$ complexes of L^4, L^5 and L^8. Deuteridorhodium complexes have been prepared starting from $[Rh(acac)(CO)_2]$ and diphosphite under an atmosphere of D_2 and CO. In all cases the rhodium–hydride vibration disappeared completely. The $[RhD(L)(CO)_2]$ complexes of L^1 and L^2 gave terminal rhodium–carbonyl vibrations at the same wavenumbers as those observed for the analogous $[RhH(L)(CO)_2]$ complexes. These results are in full agreement with the proposed structure **b** for $[RhH(L)(CO)_2]$ complexes of L^1 and L^2. Replacement of hydrogen by deuterium in $[RhH(L)(CO)_2]$ complexes for *e.g.* L^4, L^6 and L^7 gives somewhat shifted terminal rhodium–carbonyl vibrations in agreement with deuterium and carbonyl being *trans* to one another as in structure **a**: L^4, 2081, 2008; L^6, 2054, 2005; and L^7, 2052, 2004 cm^{-1}. It is obvious that structurally related diphosphite ligands cause considerable differences in co-ordination and stability of $[RhH(L)(CO)_2]$ complexes.

$[RhH(L)(CO)_2]$: *Structure* versus *Stability and Enantioselectivity*.—We propose that the highest enantioselectivities in the hydroformylation reaction will be obtained with ligands co-ordinating in an equatorial–equatorial fashion to the rhodium with retention of C_2 symmetry in the catalysts. Co-ordination of styrene to a vacant equatorial position with the diphosphite ligand co-ordinating in the same plane (along the pseudo-C_2 axis, structure **a'**) will give rise to the most effective interaction between substrate and ligand (see below). The highest enantiomeric excesses are indeed observed with the relatively stable $[RhH(L)(CO)_2]$ complexes of L^4, L^5 and L^8 in which the phosphorus-donor atoms co-ordinate equatorially to the rhodium resulting in eight-membered rings (Table 2). The rather unstable complexes of L^6, L^7 and L^9, in which the diphosphite ligands co-ordinate in an equatorial–equatorial manner give disappointing enantioselectivities (Table 2). An explanation for these low enantioselectivities might be an ineffective C_2 symmetry of the $[RhH(L)(CO)_2]$ complex after co-ordination of the diphosphite. At this point we cannot exclude low enantioselectivities originating from instability of the catalysts. The low enantiomeric excesses (Table 2) obtained with the fluxional $[RhH(L)(CO)_2]$ complexes of L^1 and L^2 can be explained by structures **b'** and **b''**. Co-ordination in an equatorial–axial manner to give rise to two competing intermediate species **b'** and **b''** which most likely lead to products



with opposite absolute configurations. Equatorially–axially co-ordinating ligands forming eight-membered hydridorhodium phosphine–phosphite catalysts as reported by Takaya and co-workers.[29] give, by contrast, high enantioselectivities (< 95%) in the asymmetric hydroformylation of various substrates. The ^{31}P and ^1H NMR spectra of the catalyst revealed no fluxional behaviour or indications of the occurrence of equatorially–equatorially co-ordinating species. Hence, these systems do not require equatorial–equatorial co-ordination in order to give high enantioselectivities.

Conclusion

Structurally related chiral diphosphites based on (2*R*,3*R*)-butane-2,3-diol, (2*R*,4*R*)-pentane-2,4-diol and (2*S*,5*S*)-hexane-2,5-diol can be used as ligands in the asymmetric hydroformylation of styrene. High conversions (up to 99%) and high regioselectivities (up to 96%) for branched aldehyde were obtained under relatively mild reaction conditions (25–40 °C, 9 bar syn gas). The NMR and IR spectroscopic studies on hydridorhodium diphosphite complexes revealed both equatorial–equatorial and equatorial–axial co-ordinated diphosphites. The actual structure of the hydridorhodium diphosphite complex has a strong influence on the selectivity of the hydroformylation reaction which is also observed for rhodium diphosphine complexes.[12,36] It seemed that relatively stable $[RhH(L)(CO)_2]$ complexes are formed with diphosphites L^4, L^5 and L^8 leading to eight-membered rings. Enantioselectivities up to 76% have been found with these complexes. Rather disappointing enantioselectivities have been observed with diphosphites based on (2*R*,3*R*)-butane-2,3-diol (L^1 and L^2) and (2*S*,5*S*)-hexane-2,5-diol (L^6 and L^7). Both the stability and the structure of the hydridorhodium diphosphite catalysts play a fundamental role in the asymmetric induction. Spectroscopic studies have revealed different solution structures for the complexes. The highest enantioselectivities are obtained with diphosphites co-ordinating in an equatorial–equatorial manner to the rhodium. Small structural changes in the backbone of the ligand probably cause a dramatic effect on asymmetric induction. In conclusion, stable C_2 symmetrical hydridorhodium complexes can serve as a promising group of catalysts in the asymmetric hydroformylation of styrene.

Experimental

General.—All reactions were carried out in oven-dried glassware using Schlenk techniques under an atmosphere of argon. Toluene was distilled from sodium–benzophenone, pyridine from CaH_2 and stored under an atmosphere of argon; PCl_3 was distilled before use and stored under an atmosphere of argon. Dichloromethane was dried over P_2O_5 and distilled

from CaH_2. Chemicals were obtained from Janssen Chimica and Aldrich Chemical Co. Compounds **Ib**, **Ic**, and **IIa**–**IIc** were prepared according to literature procedures.[18,27,44,45] For column chromatography silica gel 60 (230–400 mesh) from Merck was used. Infrared spectra were recorded on a Nicolet 510 FT-IR spectrophotometer. Melting points were determined on a Gallenkamp MFB-595 apparatus in open capillaries and are uncorrected. The NMR spectra were obtained on a Bruker AMX 300 spectrometer the ^{31}P and ^{13}C spectra being ^{1}H decoupled unless otherwise stated. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Gas chromatographic analysis were run on a Carlo Erba GC 6000 Vega Series apparatus (split/splitless injector, J&W Scientific, DB1 30 m column, film thickness 3.0 μm, carrier gas 70 kPa He, flame ionisation detector) equipped with a Hewlett-Packard HP 3396 integrator. Enantiomeric excesses were measured after reduction of the aldehydes with $NaBH_4$ to the corresponding alcohols on a Carlo Erba Vega 6000 gas chromatograph with split/splitless injector, SGE 50 m chiral β-cyclodextrin column, flame ionisation detector, and Shimadzu C-R 5A integrator. Absolute configurations were determined by comparison of the retention times with that of optically pure (*R*)-(+)-2-phenylpropanol. Hydroformylation reactions were carried out in a laboratory-made stainless-steel autoclave (200 cm^3). Syn gas 3.0 was obtained from Praxair. Elemental analyses were performed by the Department of Micro-Analyses at the University of Groningen.

Catalysis.—In a typical experiment the autoclave was dried under reduced pressure at 80 °C for 1 h, filled with [Rh(acac)$(CO)_2$] (0.031 mmol), diphosphite (0.039 mmol, P:Rh ratio of 2.5:1) and toluene (15 cm^3). It was then purged three times with syn gas [CO–H_2 (1:1)] and pressurised to the appropriate initial pressure with syn gas. After heating the autoclave at the reaction temperature, the reaction mixture was stirred for 15 h to form the active catalyst. Styrene (1.5 cm^3, filtered on neutral activated aluminium oxide) and decane (5 mmol, dried on magnesium sulfate) were placed in the autoclave. During the reaction several samples were taken from the autoclave. After a desired reaction time the autoclave was cooled, depressurised and vented with nitrogen. The reaction mixture was directly vacuum distilled to remove the catalyst and analysed by gas chromatography. A sample of the reaction mixture (containing about 6 mmol of aldehydes) was dissolved in ethanol (20 cm^3). Sodium tetrahydroborate (12 mmol) was added and the reaction mixture stirred for 90 min at room temperature. After quenching the mixture with water, it was extracted two times with ethyl acetate–hexane (1:1). The organic layers were combined and dried on magnesium sulfate. About 20 μl of the reduced reaction mixture were dissolved in ethanol (10 cm^3) and analysed by GC for determination of the enantiomeric excess.

Preparation of [RhH(L)$(CO)_2$] *Complexes*.—In a typical experiment a vessel (5 cm^3) was filled with [Rh(acac)$(CO)_2$] (0.0194 mmol), diphosphite (0.0194 mmol) and [$^2H_8$]toluene (1–2 cm^3) and placed in the autoclave. The autoclave was purged three times with syn gas and pressurised (15–20 bar). After reaction for 8 h at 40 °C the autoclave was cooled and depressurised. Under atmospheric conditions, NMR tubes were filled and immediately analysed. No decomposition of [RhH(L)$(CO)_2$] was observed during analysis.

Preparation of Diphosphites.—L^1. 4,4',6,6'-Tetra-*tert*-butyl-2,2'-bis(phenol) **Ib** (7.0 mmol, 3.32 g) azeotropically dried with toluene (3 × 5 cm^3), was dissolved in toluene (25 cm^3) and pyridine (25 mmol, 2.0 cm^3). This solution was added dropwise to a cooled solution (0 °C) of PCl_3 (8.0 mmol, 0.70 cm^3) and pyridine (25 mmol, 2.0 cm^3). The reaction mixture was refluxed for 2 h. The solvent and excess of PCl_3 were removed under vacuum and compound **IIb** formed *in situ* was dissolved in toluene (20 cm^3) and pyridine (20 mmol, 1.62 cm^3). (2*R*,3*R*)-Butane-2,3-diol (3.0 mmol, 0.27 g) was dissolved in toluene (30 cm^3) and added dropwise to the solution of **IIb** at 0 °C. The reaction mixture was stirred overnight at room temperature. The pyridine salts formed were filtered off. Evaporation of the solvent gave a white foam which was purified twice by flash column chromatography [eluent: 5% ethylacetate–light petroleum (b.p. 60–80 °C)], R_f 0.57. Yield 1.45 g (50%, 1.50 mmol) of a white powder, m.p. 116–118 °C, $\alpha_D^{22} = 16.4°$ (c = 0.50 g per 100 cm^3, CH_2Cl_2) (Found: C, 76.75; H, 9.85. $C_{60}H_{88}O_6P_2$ requires C, 74.50; H, 9.20%). NMR ($CDCl_3$): ^{31}P, δ 145.6 (s); ^{13}C, δ 150.3 (s, aromatic C), 146.8 (d, J_{PC} = 4.5), 143.5 (s, aromatic C), 140.5 (d, aromatic, J_{PC} = 5.3), 136.8 (s, aromatic C), 133.2 (d, aromatic C, J_{PC} = 2.0), 127.2 (s, aromatic CH), 127.0 (s, aromatic CH), 125.9 (s, aromatic CH), 125.4 (s, aromatic CH), 124.6 (s, aromatic CH), 122.9 (s, aromatic CH), 73.7 [dd, CH(O), $^2J_{PC}$ = 15.2, $^3J_{PC}$ = 7.3], 36.0 [s, $C(CH_3)_3$], 35.9 [s, $C(CH_3)_3$], 35.2 [s, $C(CH_3)_3$], 35.1 [s, $C(CH_3)_3$], 32.3 [s, $C(CH_3)_3$], 32.1 [s, $C(CH_3)_3$], 31.9 [s, $C(CH_3)_3$], 30.3 [s, $C(CH_3)_3$] and 15.9 (s, CH_3); ^{1}H, δ 7.49–7.47 (m, 4 H, aromatic), 7.24–7.22 (m, 2 H, aromatic), 7.19 (s, 2 H, aromatic, J = 2.3), 4.70 (m, 2 H, CH), 1.54 (s, 9 H, *o*-Bu^t), 1.53 (s, 9 H, *o*-Bu^t), 1.41 (s, 9 H, *p*-Bu^t), 1.40 (s, 9 H, *p*-Bu^t) and 1.19 (d, 6 H, CH_3, J = 5.4 Hz].

L^2. 6,6'-Di-*tert*-butyl-4,4'-dimethoxy-2,2'-bis(phenol) **Ic** (5.0 mmol, 1.79 g), azeotropically dried with toluene (3 × 5 cm^3), was dissolved in toluene (20 cm^3) and pyridine (10 mmol, 0.81 cm^3). This solution was added dropwise to a cooled solution (0 °C) of PCl_3 (6.0 mmol, 0.52 cm^3) and pyridine (10 mmol, 0.81 cm^3). The reaction mixture was stirred for 2 h at reflux temperature. The solvent and excess of PCl_3 were removed under vacuum and compound **IIc** formed *in situ* was dissolved in toluene (10 cm^3) and pyridine (20 mmol, 1.62 cm^3). (2*R*,3*R*-Butane-2,3-diol (2.0 mmol, 0.180 g) was dissolved in toluene (30 cm^3) and added dropwise to the cooled (0 °C) solution of **IIc**. The reaction mixture was stirred overnight at room temperature and then refluxed for 1 h. The pyridine salts formed were filtered off. Evaporation of the solvent gave a white foam which was purified twice by flash column chromatography (eluent 10% ethyl acetate–light petroleum, R_f 0.22; eluent 2.5% ethyl acetate–toluene, R_f 0.30). Yield 0.60 g (35%, 0.70 mmol) of a white powder, m.p. 107–109 °C, $\alpha_D^{22} = 17.7°$ (c = 0.30, CH_2Cl_2) (Found: C, 66.90; H, 7.65. $C_{48}H_{64}O_6P_2$ requires C, 66.80; H, 7.50%), NMR ($CDCl_3$): ^{31}P-(^{1}H coupled), δ 145.8 (d, $^3J_{PH}$ = 7.3); ^{13}C, δ 156.0 (s, aromatic C), 143.0 (d, aromatic C, J_{PC} = 3.8), 142.3 (d, aromatic C, J_{PC} = 6.8), 142.2 (d, aromatic C, J_{PC} = 6.8), 134.2 (d, aromatic C, J_{PC} = 3.8), 114.8 (s, aromatic CH), 113.5 (s, aromatic CH), 133.3 (s, aromatic CH), 7.37 [dd, CH(O), $^2J_{PC}$ = 13.4, $^3J_{PC}$ = 4.4], 56.1 (s, OCH_3), 35.9 [s, $C(CH_3)_3$], 31.6 [$C(CH_3)_3$] and 15.9 (s, CH_3); ^{1}H, δ 6.97 (d, 2 H, aromatic, J = 2.6), 6.96 (d, 2 H, aromatic, J = 2.6), 6.70 (d, 2 H, aromatic, J = 2.7), 6.69 (d, 2 H, aromatic, J = 2.7), 4.59 (m, 2 H, CH), 3.81 (s, 6 H, OCH_3), 3.79 (s, 6 H, OCH_3), 1.44 (s, 18 H, Bu^t), 1.42 (s, 18 H, Bu^t) and 1.18 (d, 6 H, CH_3, J = 6.1 Hz).

L^3. This compound was prepared according to a modified literature procedure.[30] (2*R*,4*R*)-Pentane-2,4-diol (2.0 mmol, 0.208 g) was azeotropically dried with toluene (3 × 1 cm^3), dissolved in toluene (15 cm^3) and pyridine (20 mmol, 1.62 cm^3). A stock solution of **IIa** in benzene (4.5 cm^3, 1 mol dm^{-3}) was added. The reaction mixture was stirred overnight at room temperature and the pyridine salts formed were filtered off. Evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent 20% NEt_3–32% ethyl acetate–48% hexane, R_f 0.7). Yield 0.76 g, (71%, 1.43 mmol) of a white powder, m.p. 112–113 °C, $\alpha_D^{22} = -58.8°$ (c = 0.50, CH_2Cl_2). NMR ($CDCl_3$): ^{31}P, δ 148.7 (s); ^{13}C, δ 150.1 (s, aromatic C), 130.6 (s, aromatic C), 130.5 (s, aromatic CH), 129.8 (s, aromatic CH), 125.7 (s, aromatic CH), 122.9 (s, aromatic CH), 122.7 (s, aromatic CH), 68.7 (m, CHO), 46.9 (s, CH_2) and 24.2 (s, CH_3); ^{1}H NMR, δ 7.47–7.05 (m, 16 H,

aromatic), 4.76 (m, 2 H, CH), 1.79 (t, 2 H, CH_2, J = 6.1) and 1.38 (d, 6 H, CH_3, J = 6.2 Hz).

L^4. This compound was prepared according to a modified literature procedure.[30] Compound **IIb** formed *in situ* (5.0 mmol, prepared as described for L^1) was dissolved in toluene (10 cm^3) and pyridine (20 mmol, 1.62 cm^3). (2*R*,4*R*)-Pentane-2,4-diol (2.0 mmol, 0.208 g) was azeotropically dried with toluene (3 × 1 cm^3) and dissolved in toluene (15 cm^3). At 0 °C the pentanediol solution in toluene was added in 30 min to the solution of **IIb**. The reaction mixture was stirred overnight at room temperature and the pyridine salts formed filtered off. Evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent: 5% ethyl acetate–hexane, R_f 0.46). Yield 1.76 g (90%, 1.80 mmol) of a white powder, m.p. 128–129 °C, α_D^{22} = 35.6° (c = 0.50, CH_2Cl_2) (Found: C, 74.85; H, 9.30. $C_{61}H_{90}O_6P_2$ requires C, 74.65; H, 9.25%). NMR ($CDCl_3$): ^{31}P, δ 145.5 (s); ^{13}C, δ 146.8 (s, aromatic C), 146.7 (t, aromatic C, J_{PC} = 4.5), 146.5 (s, aromatic C), 146.1 (t, aromatic C, J_{PC} = 3.2), 140.6 (s, aromatic C), 140.3 (s, aromatic C), 133.6 (s, aromatic C), 133.1 (s, aromatic C), 127.2 (s, aromatic CH), 127.0 (s, aromatic CH), 124.7 (s, aromatic CH), 70.8 (t, CH, J_{PC} = 7.2), 47.3 (t, CH_2, $^3J_{PC}$ = 4.1), 35.9 [s, $C(CH_3)_3$], 35.1 [s, $C(CH_3)_3$], 32.1 [s, $C(CH_3)_3$], 31.8 [s, $CCH_3)_3$] and 23.4 (s, CH_3); ^1H, δ 7.42 (d, 2 H aromatic, J = 2.2), 7.41 (d, 2, H, aromatic, J = 2.2), 7.17 (d, 2 H, aromatic, J = 2.4), 7.16 (d, 2 H, aromatic, J = 2.4), 4.55 (m, 2 H, CH), 1.88 (t, 2 H, CH_2, J = 6.2), 1.47 (s, 18 H, *o*-Bu^t), 1.46 (s, 18 H, *o*-Bu^t), 1.34 (s, 18 H, *p*-Bu^t), 1.33 (s, 18 H, *p*-Bu^t) and 1.21 (d, 6 H, CH_3, J = 6.2 Hz).

L^5. This compound was prepared according to a modified literature procedure.[30] Compound **IIc** formed *in situ* (5.0 mmol, prepared as described for L^2) was dissolved in toluene (10 cm^3) and pyridine (20 mmol, 1.62 cm^3). (2*R*,4*R*)-Pentane-2,4-diol (2.0 mmol, 0.208 g) was azeotropically dried with toluene (3 × 1 cm^3) and dissolved in toluene (15 cm^3). The pentanediol solution in toluene was added in 30 min to the solution of **IIc** at room temperature. The reaction mixture was stirred overnight and the pyridine salts formed were filtered off. Evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent: 10% ethyl acetate–toluene, R_f 0.75). Yield 0.77 g (44%, 0.88 mmol) of a white powder, m.p. 104–106 °C, α_D^{22} = 36.7° (c = 0.30, CH_2Cl_2) (Found: C, 67.25; H, 7.70. $C_{49}H_{66}O_{10}P_2$ requires C, 67.10; H, 7.60%). NMR ($CDCl_3$): ^{31}P, δ 146.4 (s); ^{13}C, δ 156.1 (s, aromatic C), 155.9 (s, aromatic C), 143.1 (s, aromatic C), 142.9 (s, aromatic C), 142.7 (t, aromatic C, J_{PC} = 3.8), 142.1 (t, aromatic C, J_{PC} = 2.5), 134.5 (s, aromatic C), 134.0 (s, aromatic C), 114.8 (s, aromatic CH), 113.3 (s, aromatic CH), 70.6 (m, CH), 56.1 (s, OCH_3), 47.4 (t, CH_2, $^3J_{PC}$ = 2.1), 35.91 [s, $C(CH_3)_3$], 35.90 [s, $C(CH_3)_3$], 31.6 [s, $C(CH_3)_3$] and 23.5 (s, CH_3); ^1H, δ 6.97 (m, 4 H, aromatic), 6.71 (m, 4 H, aromatic), 4.55 (m, 2 H, CH), 3.81 (s, 6 H, OCH_3), 3.80 (s, 6 H, OCH_3), 1.87 (t, 2 H, CH_2, J = 6.6), 1.44 (s, 36 H, Bu^t) and 1.25 (d, 6 H, CH_3, J = 6.3 Hz).

L^6. Compound **IIb** formed *in situ* (7.0 mmol, prepared as described for L^1) was dissolved in toluene (10 cm^3) and pyridine (30 mmol, 2.43 cm^3). (2*S*,5*S*)-Hexane-2,5-diol (3.0 mmol, 0.354 g) prepared according to a literature procedure[46,47] was azeotropically dried with toluene (3 × 1 cm^3) and dissolved in toluene (15 cm^3). The hexanediol solution in toluene was added in 30 min to the solution of **IIb** at room temperature. The reaction mixture was stirred overnight and the pyridine salts formed were filtered off. Evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent: 10% ethyl acetate–light petroleum, R_f 0.76). Yield 2.75 g (92%, 2.77 mmol) of a white powder, m.p. 80–82 °C, α_D^{22} = 0.6° (c = 0.50, CH_2Cl_2) (Found: C, 75.15; H, 9.25. $C_{62}H_{92}O_6P_2$ requires C, 74.80; H, 9.30%). NMR ($CDCl_3$); ^{31}P-(^1H coupled), δ 146.0 (d, J_{PH} = 8.5); ^{13}C, δ 146.7 (d, aromatic C, J_{PC} = 3.8), 146.6 (d, aromatic C, J_{PC} = 5.3), 146.5 (d, aromatic C, J_{PC} = 5.3), 140.5 (d, aromatic C, J_{PC} = 3.8), 127.1 (s, aromatic CH), 124.7 (s, aromatic CH), 73.2 (d, CH_2, $^2J_{PC}$ = 12.8), 36.0 [s, $C(CH_3)_3$], 35.2 [s, $C(CH_3)_3$], 34.1 (s, CH_2), 32.1 [s, $C(CH_3)_3$], 31.9 [s, $C(CH_3)_3$] and 22.6 (s, CH_3); ^1H, δ 7.44 (m, 4 H, aromatic), 7.20 (m, 4 H, aromatic), 4.44 (m, 2 H, CH), 1.65 (m, 2 H, CH_2), 1.50 (s, 18 H, *o*-Bu^t), 1.49 (s, 18 H, *o*-Bu^t), 1.37 (s, 36 H, *p*-Bu^t) and 1.22 (d, 6 H, CH_3, J = 6.2 Hz).

L^7. Compound **IIc** formed *in situ* (7.0 mmol, prepared as described for L^2) was dissolved in toluene (10 cm^3) and pyridine (30 mmol, 2.43 cm^3). (2*S*,5*S*)-Hexane-2,5-diol[46,47] (3.0 mmol, 0.354 g) was azeotropically dried with toluene (3 × 1 cm^3) and dissolved in toluene (15 cm^3). The hexanediol solution in toluene was added in 30 min to the solution of **IIc** at room temperature. The reaction mixture was stirred overnight and the pyridine salts formed were filtered off. Evaporation of the solvent gave a white foam which was purified by flash column chromatography (eluent: 20% ethyl acetate–light petroleum, R_f 0.52). Yield 1.56 g, (58%, 1.75 mmol) of a white powder, m.p. 93–95 °C, α_D^{22} = 5.6° (c = 0.50, CH_2Cl_2) (Found: C, 67.70; H, 7.65. $C_{50}H_{68}O_{10}P_2$ requires C, 67.40; H, 7.70%). NMR ($CDCl_3$): ^{31}P-(^1H coupled), δ 146.7 (d, J_{PH} = 7.3); ^{13}C, δ 156.1 (s, aromatic C), 143.0 (d, aromatic C, J_{PC} = 4.5), 142.6 (d, aromatic C, J_{PC} = 6.0), 142.5 (d, aromatic C, J_{PC} = 6.0), 134.3 (d, aromatic C, J_{PC} = 3.8), 114.8 (s, aromatic CH), 113.4 (s, aromatic CH), 73.2 (d, CH, $^2J_{PC}$ = 13.5), 56.1 (s, OCH_3), 36.0 [s, $C(CH_3)_3$], 34.1 (s, CH_2), 31.7 [s, $C(CH_3)_3$] and 22.8 (s, CH_3); ^1H, δ 6.97 (d, 4 H, aromatic, J = 2.9), 6.71 (m, 4 H, aromatic), 4.41 (m, 2 H, CH), 3.81 (s, 12 H, OCH_3), 1.64 (m, 2 H, CH_2), 1.45 (s, 18 H, Bu^t), 1.44 (s, 18 H, Bu^t) and 1.23 (d, 6 H, CH_3, J = 6.2 Hz).

L^8. Compound **IIc** formed *in situ* (1.5 mmol, prepared as described for L^2) was dissolved in toluene (10 cm^3) and pyridine (10 mmol, 0.81 cm^3). (1*R*,3*R*)-Diphenylpropane-1,3-diol (0.57 mmol, 0.13 g) prepared according to a literature procedure[48–50] was azeotropically dried with toluene (3 × 1 cm^3) and dissolved in toluene (10 cm^3) and pyridine (10 mmol, 0.81 cm^3). The solution was added at room temperature to the solution of **IIc** and refluxed for 2 h. The pyridine salts formed were filtered off. Evaporation of the solvent gave a white foam which was purified by flash column chromatography [eluent: 10% ethyl acetate–toluene (v/v), R_f 0.66]. Yield 0.25 g, (44%, 0.25 mmol) of a white powder, m.p. 110–112 °C, α_D^{22} = 66.0° (c = 0.10, CH_2Cl_2). NMR ($CDCl_3$): ^{31}P, δ 145.7 (s); ^1H, δ 7.32–7.15 (m, 6 H, aromatic), 7.09–6.98 (m, 4 H, aromatic), 6.89 (d, 2 H, aromatic, J = 3.2), 6.88 (d, 2 H, aromatic, J = 3.9), 6.61 (d, 2 H, aromatic, J = 2.9), 6.56 (d, 2 H, aromatic, J = 3.0), 4.60 (m, 2 H, CHO), 3.81 (s, 6 H, OCH_3), 3.79 (s, 6 H, OCH_3), 2.64 (t, CH_2, J = 7.2 Hz), 1.24 (s, 18 H, Bu^t) and 1.23 (s, 18 H, Bu^t).

L^9. Compound **IIb** formed *in situ* (7.5 mmol, prepared as described for L^1) was dissolved in toluene (20 cm^3) and pyridine (30 mmol, 2.43 cm^3). *N*-Benzyltartarimide prepared according to a literature procedure[51] (3.0 mmol, 0.66 g) was azeotropically dried with toluene (3 × 2 cm^3) and dissolved in tetrahydrofuran (20 cm^3). This solution was added in 1 h at room temperature to the solution of **IIb** and the reaction mixture was stirred for 4 h. The pyridine salts formed were filtered off. Evaporation of the solvent gave a white foam which was purified by flash column chromatography under an atmosphere of argon (eluent: 20% ethyl acetate–hexane, R_f 0.73). Yield 60% (1.79 mmol, 1.96 g) of a white powder, m.p. 134–136 °C, α_D^{22} = 8.2° (c = 0.50, CH_2Cl_2) (Found: C, 73.80; H, 8.40; N, 1.20. $C_{67}H_{89}NO_8P_2$ requires C, 73.25; H, 8.15; N, 1.30%). NMR ($CDCl_3$): ^{31}P, δ 147.34 (s); ^{13}C, δ 171.0 [C(O)], 147.4 (aromatic C), 147.1 (aromatic C), 146.0 (aromatic C), 145.5 (aromatic C), 141.2 (aromatic C), 140.6 (aromatic C), 135.1 (aromatic C), 133.6 (aromatic C), 133.0 (aromatic C), 129.8 (aromatic CH), 129.3 (aromatic CH), 128.8 (aromatic CH), 127.1 (aromatic CH), 124.8 (aromatic CH), 76.1 [CH(O)], 43.6 (CH_2), 36.0 [$C(CH_3)_3$], 35.3 [s, $C(CH_3)_3$], 35.2 [$C(CH_3)_3$], 32.1 [$C(CH_3)_3$], 32.0 [$C(CH_3)_3$], 31.6 [$C(CH_3)_3$] and 15.9 (s, CH_3); ^1H, δ 7.45 (d, 2 H, aromatic, J = 2.37), 7.39 (d, 2 H, aromatic, J = 2.37), 7.37 (approximate dd, 2 H, aromatic), 7.28–7.24 (m, 3 H,

aromatic), 7.17 (d, 2 H, aromatic, J = 2.19), 7.16 (d, 2 H, aromatic, J = 2.19), 5.16 (approximate d, 2 CH, J_{PH} = 6.36), 4.68 (approximate d, CH_2, J = 1.59 Hz), 1.50 (s, o-Bu^t), 1.40 (s, o-Bu^t), 1.36 (s, p-Bu^t) and 1.34 (s, p-Bu^t).

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