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Bisxantphos: Stereoselective synthesis and coordination behaviour of a new class of cyclic double bridged diphosphines

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ABSTRACT

A new class of cyclic double bridged diphosphine ligands was developed and the coordination properties are described. The reaction of 4,5-dilithioxanthene with dichlorophenylphosphine gave a cyclic double bridged diphosphine ligand based on two xanthene backbones (**4**) as a single stereoisomer. X-ray crystal structure determination revealed that the groups bridging the two phosphorus atoms are arranged in a *syn*-disposition. This new cyclic bisxantphos structure was modified with bulky residues at the third substituent of the phosphorus atoms, thus forming cavity-shaped ligands.

1. Introduction

As part of our continuous effort in search of new ligand systems with interesting properties in catalysis [1], we here report the synthesis of cyclic double bridged diphosphines based on two xanthene backbones. Implementing features of biological systems in transition metal catalysts [2], the ligand design aims to create metallo-cavitands. Enzymatic reactions typically impose selectivity by control of the geometry in the enzyme–substrate complex. In homogeneous catalysis sophisticated modular ligand systems have been designed using bioinspired supramolecular interactions [3] or by introducing bulky organic scaffolds, like cyclodextrins or calixarenes, for substrate encapsulation [4–6]. The environment of a bound substrate can be closely controlled by confinement of the metal centre, in particular enabling a catalytic reaction to be driven towards the product that best adapts to the steric restraints imposed by the confining structure.

Phosphorus-based calix[4]arenes [4] and calix[6]arenes [5] have been employed as scaffolds for the development of structurally well-defined pocket-shaped ligands. The combination of calixarene cavities with catalytic centres was shown to lead to shape-selective catalysts. Also the use of cyclodextrins as synthetic cavitands received much attention in recent years and there are numerous reports on their application in catalysis [6].

Cyclic double bridged diphosphines in which the two phosphine lone pairs are in *syn* orientation form another class of ligands in which the metal embracement is particularly effective. Each phosphorus atom has one substituent R forced to reside at the front side of the metal centre, and therefore, structural modulations are possible around the metal centre by varying R groups (Fig. 1). Substituents that provide large steric bulk can have a pronounced effect on substrate coordination to the metal centre. Synthetic routes to these cyclic diphosphines are relatively undeveloped and the compounds are usually obtained as mixtures of stereoisomers. Stereoselective synthetic methods have been developed for 1,*n*-diphosphacycloalkanes by Alder et al. [7], for 1,5-diaza-3,7-disphosphacyclooctane derivatives by Karasik et al. [8] and for phosphorus-bridged [1.1]ferrocenophanes by Mizuta and coworkers [9].

In this paper, we report the stereoselective synthesis of a new class of cyclic double bridged diphosphines based on two xanthene backbones, as well as its coordination behaviour to transition metals. The rigid ligand structure should not only determine the

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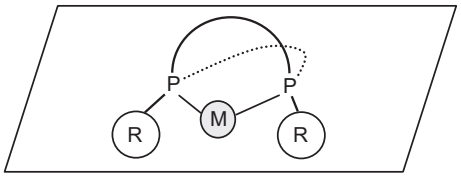


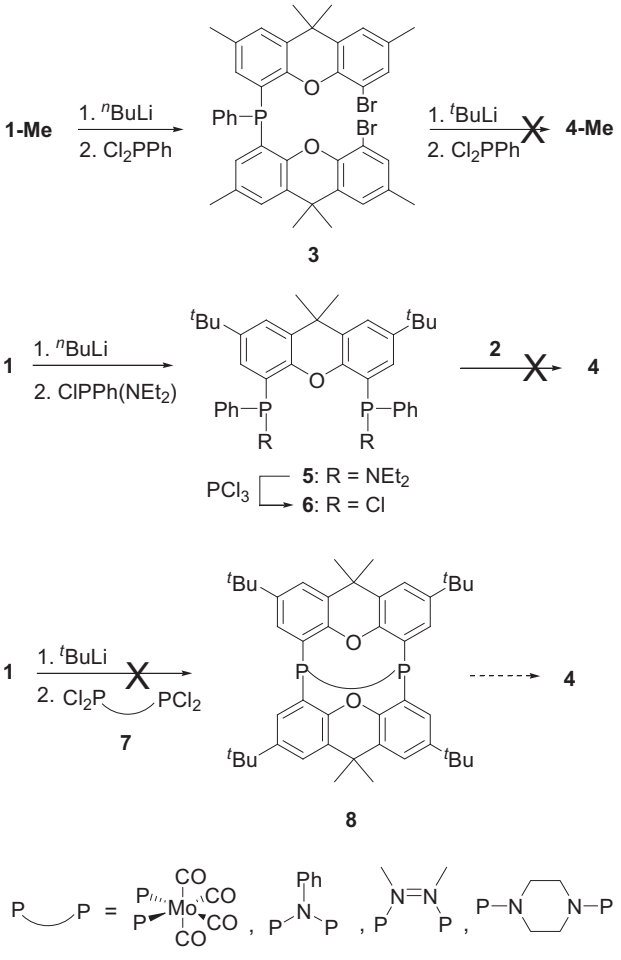
Fig. 1. Schematic representation of a cyclic double bridged diphosphine.

electronic properties of the metal, but also introduce geometrical effects that may determine the way the substrate interacts with the catalyst. In addition, cyclic bisxantphos ligands that are modified with residues that are sterically demanding were developed in order to create cavity-shaped ligands.

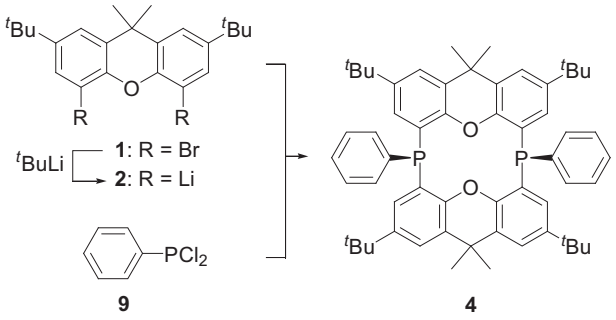
2. Results and discussion

As the preparation of target compound **4** (Scheme 2) inevitably involved a troublesome double cyclization, we studied stepwise synthesis procedures (Scheme 1). The reaction of $PhPCl_2$ with two equivalents of the monolithiated analogue of 4,5-dibromo-2,7,9,9-tetramethylxanthene (**1-Me**) gave the expected bisxantphos monophosphine derivative **3**.

Bromide-lithium exchange of the two remaining bromide moieties using four equivalents of *t*-BuLi and subsequent reaction with a second equivalent of $PhPCl_2$ under high dilution (due to low solubility of the dilithio intermediate), resulted in the formation of merely traces of bisxantphos **4-Me**. Alternatively, 4,5-bis(chlorophenylphosphino)-2,7-di-*tert*-butyl-9,9-dimethylxanthene (**6**) was synthesized as a mixture of diastereomers by reacting compound **2** (Scheme 2) with two equivalents of $PPh(NEt_2)Cl$, followed by the exchange of the NEt_2 moieties by chlorides using PCl_3. This compound was highly insoluble, however, hampering the final ring closure with a second equivalent of dilithio compound **2**.



Scheme 1. Stepwise synthesis procedures towards bisxantphos **4**.



Scheme 2. Synthetic route to bisxantphos **4**.

We also explored the possibility of a templated synthesis of compound **4**. The transition metal template bis(dichlorophenylphosphino)tetracarbonyl-molybdenum and the P–N templates *N*,*N*-bis(dichlorophosphino)aniline, *N*,*N*-bis(dichlorophosphino) methylamine, 1,2-bis(dichlorophosphino)-1,2-dimethylhydrazine and 1,4-bis(dichlorophosphino)piperazine were reacted with dilithio compound **2** under high dilution, but in neither of these reactions a cyclization product was observed.

Finally, the successful synthetic route to cyclic bisxantphos is shown in Scheme 2. The commercially available 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (**1**) was again chosen as a starting material. Lithiation of **1** with four equivalents of *t*-BuLi provided compound **2**. Slow simultaneous addition of this compound and dichlorophenylphosphine (**9**) to a stirred ether solution using a double syringe pump gave cyclic diphosphine **4** in 10% yield. In addition to the cyclic bisxantphos **4**, the monophosphine derivative and oligomers were formed. The isolation of compound **4** from the reaction mixture was achieved by centrifugally accelerated, radial, thin-layer chromatography.

The yield of merely 10% is low and optimization attempts did not lead to yields exceeding 20% so far. It should be noted that such low yields are not uncommon in the synthesis of challenging structures such as cyclic double bridged disphosphines. Zabel et al. reported for the analogues reaction of 1,1′-dilithioferrocene with (−)-dichloromenthylphosphine to form a *trans*-phosphorus-bridged [1.1]ferrocenophane a yield of only 2% [10]. In addition, the overall yield of the laborious multistep synthesis of 1,*n*-diphosphacycloalkanes and *syn*-phosphorus-bridged [1.1]ferrocenophanes by, respectively, Karasik and Mizuta did not exceed 30% [8,9].

In the $^{31}P\{^{1}H\}$ NMR spectrum of **4**, one sharp signal was observed at $\delta = -37.9$ ppm, which is an upfield shift compared to the related acyclic 2,7-di-*tert*-butyl-9,9-dimethyl-4,5-bis(diphenylphosphino) xanthene ($\delta = -16.2$ ppm) [11]. The upfield shift can be attributed to a flattening of the phosphorus atoms, caused by the conformational constraints imposed by the cyclic structure [12]. The presence of only one phosphorus signal suggested that a single stereoisomer was formed [13]. From the ^{1}H NMR spectrum it was evident that compound **4** is highly symmetrical. The *tert*-butyl protons are observed as one sharp singlet and two distinct resonances corresponding to the methyl groups were found at $\delta = 1.73$ and 1.52 ppm.

Crystals suitable for X-ray diffraction were obtained by slow diffusion of methanol into a dichloromethane solution of

compound **4**. The structure is shown in Fig. 2 and selected angles and bond lengths are given in Table 1.

The crystal structure shows that the two bridging xanthene groups are arranged in a *syn*-disposition. The structure has C_S symmetry, with an exact, crystallographic mirrorplane passing through the two phosphorus atoms and the attached phenyl rings. There is no additional symmetry present in the molecule. P1 and P2 and their environments are thus independent. The potential C_{2v} symmetry of the molecule is broken by the different orientations of *tert*-butyl groups in the crystal structure. In solution, these groups can freely rotate and therefore the *tert*-butyl groups and the phosphorus atoms are equivalent according to the NMR observations. Here, the compound shows a time averaged C_{2v} symmetry.

The P···P distance is 4.2890(13) Å, significantly longer than the 4.080 Å observed for the Xantphos ligand [14]. In metal complexes of ligands of the Xantphos family, the P···P distance is even shorter [15], except in complexes where the ligand displays *trans*-coordination, in which case the distance is around 4.5 Å [16]. The increased rigidity of ligand **4** makes prediction of its coordination behaviour based on previous results with the Xantphos family difficult. On the one hand, the longer P···P distance results in a significantly larger bite-angle, and this disfavours *cis*-coordination of this ligand in square planar or octahedral complexes. On the other hand, the reduced flexibility of **4** could also hamper *trans*-coordination. Therefore, the formation of several transition metal complexes of bisxantphos **4** was examined.

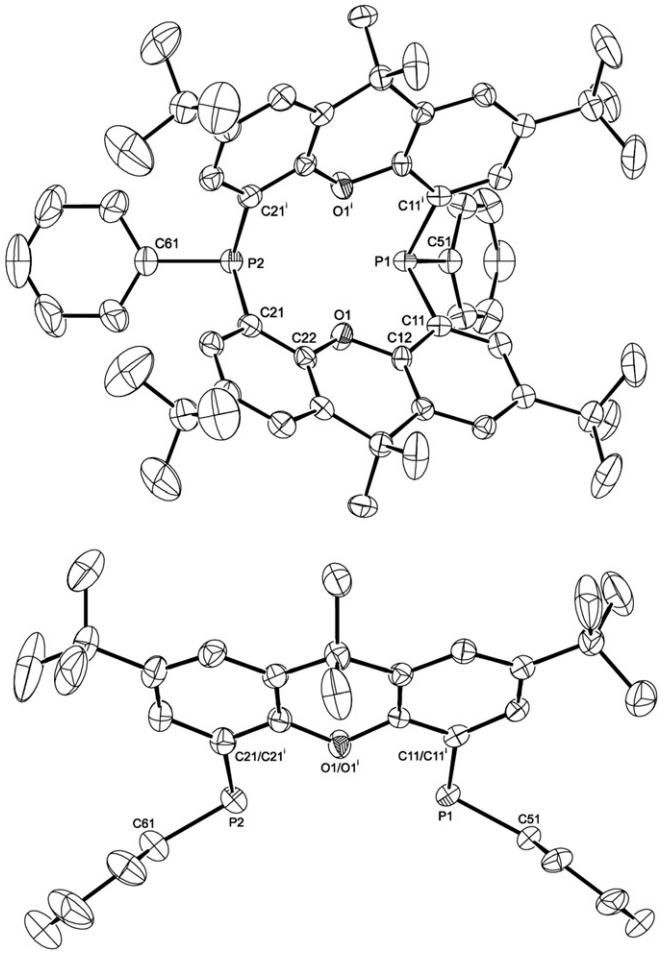


Fig. 2. Molecular structure of **4**, determined by X-ray crystallography. Displacement ellipsoids are drawn at the 50% probability level. Symmetry operation *i*: 2-x, y, z. Hydrogen atoms and solvent molecules are omitted for clarity. Top: view along the crystallographic [*0,0,1*] direction. Bottom: view along the crystallographic [*-1,0,0*] direction.

Table 1
Selected bond lengths and angles for compound **4**.

bond length (Å)		bond angle (°)	
C21–P2	1.843 (3)	C21–P2–C21^{i}	99.04 (16)
P2–C61	1.846 (4)	C21–P2–C61	102.52 (13)
C21–C22	1.401 (4)	P2–C21–C22	118.71 (19)
C21–C26	1.408 (4)	P2–C21–C26	123.4 (2)
C11–P1	1.847 (2)	C11–P1–C11^{i}	99.59 (15)
P1–C51	1.837 (3)	C11–P1–C51	102.67 (10)
C11–C12	1.399 (3)	P1–C11–C12	118.36 (18)
C11–C16	1.386 (3)	P1–C11–C16	123.67 (18)
P1···P2	4.2890 (13)		

When $[(PhCN)_2PtCl_2]$ was reacted with one equivalent of diphosphine **4** in methylene chloride, the resulting $^{31}P\{^1H\}$ NMR spectrum displayed one sharp signal at $\delta = -23.6$ ppm with a $^1J_{(Pt,P)}$ coupling constant of 1781 Hz. The value of the $^1J_{(Pt,P)}$ can be directly correlated to the coordination mode of the diphosphine. Values below 3000 Hz (usually around 2500 Hz) are encountered for *trans*-diphosphines, and higher values (around 3600 Hz) for complexes in which the phosphines occupy *cis*-positions. The low value of 1781 Hz is probably due to a distorted *trans* geometry [17]. The large deviation from the usual value around 2500 Hz for most *trans*-complexes is probably due to the strained structure of the double bridged diphosphine, which also causes an unusual chemical shift in the ^{31}P NMR of $\delta = -37$ ppm for the free ligand. The formation of *trans*-[(**4**)$PtCl_2$] is interesting since the development of only *trans*-coordinating diphosphine ligands is the subject of ongoing research [18]. We performed MM2 and PM3 analysis on [(**4**)$PtCl_2$] and the calculated bond lengths and angles are depicted in Tables 2 and 3. The P1–Pt–P2 bond angle is approximately 140°. Despite this small bite angle, a *trans*-complex can not be excluded. In *trans*-spanning Xantphos–Pd complexes, P1–Pd–P2 angles of 150° have previously been observed [16a,b]. A calculated optimized structure of [(**4**)$PtCl_2$] shows the bisxantphos ligand coordinated in a *trans*-fashion (Fig. 3).

The reaction of ligand **4** with $[Pd(cod)Cl_2]$ in methylene chloride at room temperature gave [(**4**)$PdCl_2$] as a yellow powder. A $^{31}P\{^1H\}$ NMR spectrum of this complex showed one sharp signal at $\delta = -14.5$ ppm. We also studied the formation of palladium–allyl complexes with bisxantphos **4**, but these were only analyzed *in situ*, because isolation of the complexes invariably led to product decomposition. When $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ was mixed with two equivalents of ligand **4** in CD_2Cl_2, the resulting ^{31}P NMR spectrum displayed one singlet at $\delta = -21.22$ ppm. The ^1H NMR spectrum was less clear. The terminal protons *syn* and *anti* to the central proton of the allyl group in complex [(**4**)$Pd(\eta^3\text{-}C_3H_5)$]Cl interconverted slowly on the NMR time scale and consequently two signals were observed in the ^1H NMR spectrum at $\delta = 3.23$ and 2.90 ppm. This *syn–anti* isomerization takes place via an $\eta^3–\eta^1–\eta^3$ rearrangment.

Table 2
Calculated bond lengths and angles (MM2) for [(**4**)$PtCl_2$].

bond length (Å)		bond angle (°)	
C21–P2	1.86	C21–P2–C21^{i}	106.1
P2–C61	1.84	C21–P2–C61	117.3
C21–C22	1.41	P2–C21–C22	121.8
C21–C26	1.40	P2–C21–C26	118.6
P1···P2	4.44	P1–Pt–P2	142.3
Pt–Cl	2.29	Cl–Pt–Cl	165.2

Table 3
Calculated bond lengths and angles (PM3) for [(**4**)$PtCl_2$].

bond length (Å)		bond angle (°)	
C21–P2	1.88	C21–P2–C21^{i}	99.2
P2–C61	1.82	C21–P2–C61	106.9
C21–C22	1.41	P2–C21–C22	121.5
C21–C26	1.39	P2–C21–C26	121.8
P1···P2	4.23	P1–Pt–P2	139.3
Pt–Cl	2.32	Cl–Pt–Cl	167.7

There were no signals observed of an olefinic CH_2-unit (typically two double doublets around δ = 5.0 ppm). This excludes the presence of an η^1-allyl complex and we can conclude that ligand **4** forms an η^3-allyl complex.

The palladium complex [(**4**)Pd(η^3-C_3H_5)]OTf was prepared *in situ* by addition of diphosphine **4** to [Pd(η^3-C_3H_5)Cl]$_2$, followed by two equivalents of silver triflate. One singlet at $\delta = -21.34$ ppm was observed in the ^{31}P NMR spectrum. Interestingly, the dynamics of the methyl and *tert*-butyl groups of the backbone varied with the counterion. A single resonance corresponding to the *tert*-butyl groups and two resonances for the backbone methyl groups were observed in [(**4**)Pd(η^3-C_3H_5)]Cl, whereas two resonances for the *tert*-butyl groups and four distinct resonances for the methyl groups were observed in complex [(**4**)Pd(η^3-C_3H_5)]OTf. Similar behaviour was previously observed for [(Xantphos)Pd(η^3-C_3H_5)]X complexes for which the interconvertion of the backbone substituents was ascribed to reversible dissociation of one-half of the bidentate ligand or pseudorotation via a pentacoordinate palladium complex formed by coordination of the counterion [19]. In the pentacoordinated [(**4**)Pd(η^3-C_3H_5)]Cl complex the chloro anion facilitates both the η^3–η^1–η^3 (or π–σ–π) rearrangment of the allyl moiety [20] and the *syn*–*syn*, *anti*–*anti* exchange (apparent rotation of the allyl group). The latter is a faster exchange process than the *syn*–*anti* isomerization. As a result an apparent high symmetry (C_{2v}) is obtained as indicated by one average resonance for the *tert*-butyl groups and two resonances for the methyl groups. In [(**4**)Pd(η^3-C_3H_5)]OTf, with the non-coordinating OTf anion, both processes are slower than in the Cl-complex. If these processes are slow on the NMR time scale, the symmetry of the complex is C_1, resulting in four methyl signals and two *tert*-butyl signals in the ^{1}H NMR spectrum of [(**4**)Pd(η^3-C_3H_5)]OTf.

2.1. Synthesis of functionalized bisxantphos derivatives

Next, sterically demanding residues were introduced in the cyclic bisxantphos structure in order to create a pocket around the transition metal. Structural modulations of bisxantphos **4** are possible by varying the aryldichlorophosphine species in the cyclization step. We chose to make use of arylbromides as third subsituent on the phosphorus atoms. After the cyclization step, the arylbromides were converted to benzaldehyde moieties to allow the elegant and mild introduction of *e.g.* bulky amino acid fragments via reductive amination.

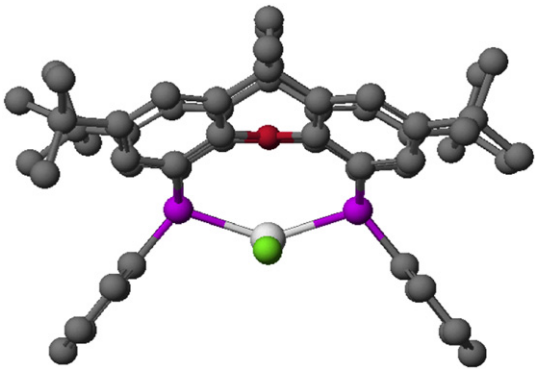
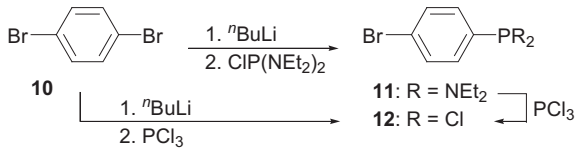


Fig. 3. Calculated optimized structure of [(**4**)$PtCl_2$] using PM3.



Scheme 3. Synthetic routes to compound **12**.

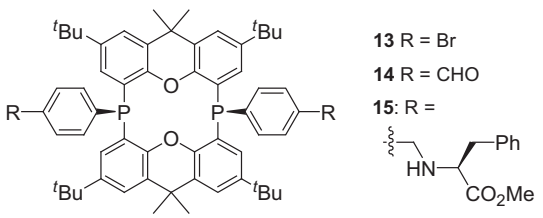
Therefore, the synthesis of aryldichlorophosphine **12** was explored. Arylbromide **12** has previously been synthesized using a Friedel–Crafts reaction between PCl_3 and bromobenzene, but the desired *para* substituted product could not be separated from its *ortho* and *meta* isomers [21]. A different approach starts with monolithiation of dibromobenzene **10**, followed by the addition of bis(diethylamino)chlorophosphine to yield the arylphosphorus diamide **11** (Scheme 3). Diethylamino phosphane **11** can be converted to dichloride **12** by treatment with PCl_3. However, the formed Et_2NPCl_2 reacted with **12** during work-up to generate $ArPCl(NEt_2)$ and this was difficult to separate from the desired product. In a shorter albeit less controllable route, compound **12** was obtained by reacting the monolithiated analogue of 1,4-dibromobenzene with PCl_3. The principal side-product encountered was Ar_2PCl and compound **12** was obtained by fractional distillation.

Following the same procedure as used for the synthesis of double bridged diphosphine **4**, aryldichlorophosphine **12** was employed to obtain cyclic bisxantphos **13** as an air-stable powder. Lithiation of **13** with *n*-BuLi/TMEDA in diethyl ether at −78 °C generated the dilithio derivative that was quenched with anhydrous DMF to afford the bisaldehyde **14** in high yield after acidic work-up (Scheme 4). The addition of TMEDA (*N*,*N*,*N*',*N*'-tetramethylethane-1,2-diamine) was required to prevent decomposition of the dilithiated intermediate. The formyl groups formed could be clearly identified by their NMR resonances (^{1}H NMR: δ = 10.05 ppm, ^{13}C {^{1}H} NMR: δ = 192.2 ppm).

Finally, as an example of sterically demanding residues, L-phenylalanine methyl ester moieties were introduced via reductive amination of bisaldehyde **14** using sodium triacetoxyborohydride giving bisxantphos **15**. Unfortunately we were unable to grow crystals suitable for X-ray diffraction, but the characterization of **15** was achieved by multinuclear NMR spectroscopy.

2.2. Catalysis

In the rhodium catalyzed hydroformylation of 1-octene ligand **4** gave very low activity and selectivity (conditions: 20 bar CO/H_2, 80 °C). The systems was 15 times less active than Xantphos based



Scheme 4. Bisxantphos with various substituents.

catalysts and gave a l/b ratio of only 3. Isomerization to internal alkenes took place (30%). Therefore no further hydroformylation reactions were pursued.

3. Conclusions

In summary, we have described a stereoselective route to cyclic double bridged diphosphine ligands based on two xanthene backbones. The reaction of dilithio-xanthene with dichlorophenylphosphine gave cyclic bisxantphos (**4**) as a single stereoisomer. X-ray crystal structure determination revealed that the phosphorus bridging groups are arranged in a *syn*-disposition. Double bridged cyclic diphosphines in which the two phosphorus lone pairs are *cis* oriented are useful chelates in transition metal catalysts. The coordination behaviour of the new ligand to several transition metals was investigated. The route is flexible in the choice of aryldichlorophosphine and should permit a range of substituents to be introduced on the phosphorus atoms. The new bisxantphos structure was modified with sterically demanding residues on the third substituent of the phosphorus atoms which opens the way to create a shape-selective pocket upon coordination of the ligands to a metal centre.

4. Experimental section

4.1. General remarks

Unless stated otherwise, reactions were carried out under an atmosphere of argon using standard Schlenk techniques. THF and diethyl ether were distilled from sodium/benzophenone. Tertiary amines, CH_2Cl_2 and methanol were distilled from CaH_2 and toluene was distilled from sodium. Deuterated solvents were distilled from the appropriate drying agents. Unless stated otherwise, all chemicals were obtained from commercial suppliers and used as received. Bis(diethylamino)chlorophosphine was synthesized according a published procedure [22]. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. NMR spectra were recorded on a Varian Mercury 300, a Varian Inova 500 or a Bruker Avance DRX-300 spectrometer. Chemical shifts are reported in ppm and are given relative to tetramethylsilane (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P). High Resolution Mass Spectra were recorded at the Department of Mass Spectrometry at the University of Amsterdam using Fast Atom Bombardment (FAB) ionization on a JOEL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. Samples were loaded in a matrix solution (3-nitrobenzyl alcohol) on to a stainless steel probe and bombarded with xenon atoms with an energy of 3 KeV. Elemental analyses were carried out by Kolbe Mikroanalytisch Labor, Mülheim an der Ruhr (Germany).

4.2. Synthesis and coordination behaviour of **4**

4.2.1. Cyclic bisxantphos **4**

To a solution of 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimeth ylxanthene (2.50 g, 5.2 mmol) in diethyl ether (36.4 mL) was added dropwise *t*-BuLi (1.5 M in pentane, 13.6 mL, 20.8 mmol) at −78 °C. The reaction mixture was allowed to reach room temperature overnight. The resulting yellow solution was transferred into a 50 mL gastight glass syringe. A second gastight syringe was filled with a solution of dichlorophenylphosphine (0.93 g, 5.2 mmol) in diethyl ether (50 mL). Both solutions were added simultaneously to a flask charged with diethyl ether (50 mL) using a syringe pump at a rate of 0.2 mL min^{-1}. After the addition was completed, the reaction mixture was allowed to stir for another 2 h. The mixture was washed with water (100 mL) and the organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 and purified by silica gel circular column chromatography (20% CH_2Cl_2 in hexanes). Finally, recrystallization from CH_2Cl_2/MeOH yielded **4** as a white powder (0.22 g, 10%). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): $\delta = 1.19$ (s, 36H, $C(CH_3)_3$), 1.52 (s, 6H, CH_3), 1.73 (s, 6H, CH_3), 7.27–7.32 (m, 10H, H-arom), 7.46–7.50 (m, 8H, H-arom); ^{13}C {^1H} NMR (75 MHz, CD_2Cl_2, 293 K): $\delta = 30.8$, 34.0, 34.2, 34.9, 123.1, 125.3 (t, $J = 12.8$ Hz), 126.3, 127.3, 127.8, 129.5 (t, $J = 4.0$ Hz), 132.0 (t, $J = 15.7$ Hz), 138,6 (t, $J = 12.1$ Hz), 145.3, 151.7 (t, $J = 23.3$ Hz); ^{31}P {^1H} NMR (121 MHz, CD_2Cl_2, 293 K): $\delta = -37.90$; HRMS (FAB+): *m*/*z* calcd. for $C_{58}H_{67}O_2P_2$ ($M+H^+$): 857.4616; found: 857.4622.

4.2.2. X-ray crystal structure determination of **4**

Crystals of **4** suitable for X-ray diffraction were grown by slow diffusion of methanol into a solution of compound **4** in methylene chloride. $C_{58}H_{66}O_2P_2 \cdot CH_2Cl_2$ + disordered solvent, Fw = 941.97[*], colourless block, 0.50 × 0.50 × 0.30 mm^3, orthorhombic, $Cmc2_1$ (no. 36), a = 19.4478(2), *b* = 18.7047(1), *c* = 16.9358(1) Å, V = 6160.66(8) $Å^3$, *Z* = 4, D_x = 1.016 g/cm^3[*], μ = 0.19 mm^{-1}[*]. 57324 Reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, $\lambda = 0.71073$ Å) up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ $Å^{-1}$ at a temperature of 150(2) K. Intensity integration was performed with EvalCCD [23]. The SADABS [24] program was used for absorption correction and scaling based on multiple measured reflections (0.83–0.94 transmission range). After merging the Friedel pairs, 3768 Reflections were unique ($R_{int} = 0.0365$), of which 3240 were observed [$I > 2\sigma(I)$]. The structure was solved with Direct Methods using the program SHELXS-97 [25]. The structure was refined with SHELXL-97 [25] against F^2 of all reflections. The crystal structure contained solvent accessible voids (1269 $Å^3$/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON [26] resulting in 411 e^-/unit cell. Non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. 315 Parameters were refined with one restraint. R1/wR2 [$I > 2\sigma(I)$]: 0.0420/0.1133. R1/wR2 [all refl.]: 0.0509/0.1174. *S* = 1.047. Residual electron density between −0.24 and 0.40 e/$Å^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program [26]. [*] derived quantities do not contain the contribution of the disordered solvent.

4.2.3. Preparation of [(**4**)$PdCl_2$]

Ligand **4** (10.0 mg, 11.7 μmol) and [Pd(cod)Cl_2] (3.7 mg, 11.7 μmol) were placed in a Schlenk flask. Methylene chloride (2 mL) was added and the reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure. The resulting yellow powder was washed with diethyl ether and dried *in vacuo* (11.6 mg, 96%). ^1H NMR (500 MHz, CD_2Cl_2, 293 K): $\delta = 1.19$ (s, 36H, $C(CH_3)_3$), 1.45 (s, 6H, CH_3), 1.75 (s, 6H, CH_3), 7.32 (m, 4H, H-arom), 7.48–7.52 (m, 10H, H-arom), 7.85 (m, 4H, H-arom); ^{13}C {^1H} NMR (125 MHz, CD_2Cl_2, 293 K): $\delta = 26.7$, 27.3, 28.2, 31.1, 31.2, 35.0, 37.9, 124.4, 127.2 (t, $J = 11.3$ Hz), 128.0, 129.9, 135.0 (t, $J = 9.3$ Hz), 135,8 (t, $J = 5.0$ Hz), 147.2 (t, $J = 5.7$ Hz), 154.0 (t, $J = 7.7$ Hz); ^{31}P {^1H} NMR (202 MHz, CD_2Cl_2, 293 K): $\delta = -14.48$; HRMS (FAB+): *m*/*z* calcd. for $C_{58}H_{66}O_2P_2Pd$ ($M-Cl_2$): 962.3593; found: 962.3599.

4.2.4. Preparation of [(**4**)$PtCl_2$]

Ligand **4** (10.0 mg, 11.7 μmol) and [$(PhCN)_2PtCl_2$] (5.5 mg, 11.7 μmol) were placed in a Schlenk flask. Acetonitrile (2 mL) was added and the reaction mixture was stirred overnight at room

temperature. The solvent was removed under reduced pressure. The resulting white solid was washed with hexanes and dried *in vacuo* (12.5 mg, 95%). ^{1}H NMR (500 MHz, CD_2Cl_2, 293 K): $\delta = 1.19$ (s, 36H, $C(CH_3)_3$), 1.46 (s, 6H, CH_3), 1.75 (s, 6H, CH_3), 7.33 (m, 4H, H-arom), 7.50 (m, 10H, H-arom), 7.62 (m,4H, H-arom); ^{13}C {^{1}H} NMR (125 MHz, CD_2Cl_2, 293 K): $\delta = 28.1, 31.3, 34.6, 34.8, 35.5, 123.7, 125.9$ (dd, $J = 12.7$ Hz, $J = 9.3$ Hz), 126.9, 127.8, 129.8, 130.2 (t, $J = 4.0$ Hz), 132.6 (t, $J = 16.1$ Hz), 139,3 (t, $J = 12.2$ Hz), 145.9, 152.3 (t, $J = 24.3$ Hz); ^{31}P {^{1}H} NMR (202 MHz, CD_2Cl_2, 293 K): $\delta = -23.56$ ($^1J_{Pt-P} = 1781$ Hz); HRMS (FAB+): *m/z* calcd. for $C_{58}H_{66}O_2P_2Pt$ ($M-Cl_2$): 1051.4191; found: 1051.4216.

4.2.5. Computational details

Molecular mechanics calculations were performed using the Cache WorkSystem (Fujitsu Ltd.) Pro Version 7.5.0.85, using the MM2 and PM3 programs without changing parameters.

4.2.6. In situ preparation of [(**4**)Pd(η^3-C_3H_5)]Cl

Ligand **4** (10.0 mg, 11.7 μmol) and [Pd(η^3-C_3H_5)Cl]$_2$ (2.2 mg, 5.9 μmol) were placed in a Schlenk flask. CD_2Cl_2 (1 mL) was added and the mixture was stirred for 1 h before analyzed by NMR spectroscopy. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): $\delta = 1.17$ (s, 36H, $C(CH_3)_3$), 1.57 (s, 6H, CH_3), 1.66 (s, 6H, CH_3), 2.90 (m, 2H), 3.23 (m, 2H), 5.56 (m, 1H, H_{meso}), 7.18–7.22 (m, 8H, H-arom), 7.49–7.56 (m, 10H, H-arom); ^{31}P {^{1}H} NMR (121 MHz, CD_2Cl_2, 293 K): $\delta = -21.11$.

4.2.7. In situ preparation of [(**4**)Pd(η^3-C_3H_5)]OTf

Ligand **4** (10.0 mg, 11.7 μmol) and [Pd(η^3-C_3H_5)Cl]$_2$ (2.2 mg, 5.9 μmol) were placed in a Schlenk flask. CD_2Cl_2 (1 mL) was added and the reaction mixture was stirred for 1 h. Next AgOTf (2.8 mg, 11 μmol) was added and the mixture was filtered before analyzed by NMR spectroscopy. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): $\delta = 1.18$ (s, 18H, $C(CH_3)_3$), 1.19 (s, 18H, $C(CH_3)_3$), 1.54 (s, 3H, CH_3), 1.64 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.69 (s, 3H, CH_3), 2.90 (m, 2H), 3.23 (m, 2H), 5.51 (m, 1H, H_{meso}), 7.17–7.33 (m, 8H, H-arom), 7.50–7.58 (m, 10H, H-arom); ^{31}P {^{1}H} NMR (121 MHz, CD_2Cl_2, 293 K): $\delta = -21.34$.

4.3. Stepwise synthesis procedures towards **4**

4.3.1. Bis-(5-bromo-2,7,9,9-tetramethyl-9H-xanthen-4-yl)-phenylphosphine (**3**)

To a solution of 4,5-dibromo-2,7-dimethyl-9,9-dimeth ylxanthene (2.0 g, 5.0 mmol) in THF (50 mL), *n*-butyllithium (2.4 M in hexanes, 2.0 mL, 4.9 mmol) was added dropwise at −78 °C. The solution was stirred for 1.5 h. Then, a solution of dichlorophenylphosphine (0.35 mL, 2.6 mmol) in pentane (10 mL) was slowly added to the solution. The resulting mixture was stirred at −78 °C for 2 h and was subsequently allowed to warm to room temperature overnight. The mixture was hydrolyzed using a 1.0 M solution of HCl in water and extracted with methylene chloride (3 × 20 mL). The combined organic layers were dried over $MgSO_4$. Removal of the solvent *in vacuo* yielded a light yellow solid. The product was recrystallized from methylene chloride/methanol, yielding 1.4 g of colourless needles (74%). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): $\delta = 1.66$ (s, 6H, CH_3), 1.69 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 2.27 (s, 6H, CH_3), 6.61 (bs, 2H, H-arom), 7.20 (m, 5H, H-arom), 7.36 (bs, 4H, H-arom), 7.63 (bs, 2H, H-arom); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta = 21.0, 21.5, 32.0, 32.4, 35.2, 111.0, 125.3, 127.0, 128.6, 129.1, 129.3, 131.8, 132.4, 132.7, 133.2, 135.3$ (d, $J = 22$ Hz), 135.8 (d, $J = 12$ Hz), 145.8, 150.4, 150.6; ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$, 293 K): $\delta = -24.7$.

4.3.2. 4,5-Bis-(N,N-diethylaminophenylphosphino)-2,7-di-tert-butyl-9,9-dimethylxanthene (**5**)

To a solution of 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimet hylxanthene (2.5 g, 5.2 mmol) in diethyl ether (80 mL), *n*-butyllithium (2.4 M in hexanes, 2.2 mL, 5.3 mmol) was added slowly at −78 °C. The solution was stirred for 2 h. Then, a solution of chloro(diethylamino)phenylphosphine (1.21 g. 5.6 mmol) in pentane (20 mL) was slowly added to the solution. The resulting mixture was stirred at −78 °C for 1 h and was subsequently allowed to warm to room temperature overnight. The mixture was filtered over basic alumina under argon atmosphere and the filter material was rinsed twice using methylene chloride (20 mL). The combined solvents were removed *in vacuo*, yielding **5** as an off-white solid (3.2 g, 89%, as a 2:1 mixture of rac- and mesodiastereomers). The air and moisture sensitive product was used without further purification. Major rac-isomer: ^{1}H NMR (300 MHz, C_6D_6, 293 K): $\delta = 0.89$ (t, $J = 9.3$ Hz, 12H, CH_3), 1.38 (s, 18H, $C(CH_3)_3$), 1.73 (s, 6H, CH_3), 3.07 (m, 8H, CH_2), 7.12–7.30 (m, 6H, H-arom), 7.35–7.60 (m, 8H, H-arom); ^{31}P {^{1}H} NMR (121 MHz, C_6D_6, 293 K): $\delta = 55.98$; Minor meso-isomer: ^{1}H NMR (300 MHz, C_6D_6, 293 K): $\delta = 0.98$ (t, $J = 9.8$ Hz, 12H, CH_3), 1.35 (s, 18H, $C(CH_3)_3$), 1.66 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 3.25 (m, 8H, CH_2), 7.0–7.12 (m, 6H, H-arom), 7.35–7.60 (m, 8H, H-arom); ^{31}P {^{1}H} NMR (121 MHz, C_6D_6, 293 K): $\delta = 53.64$; The ^{13}C {^{1}H} NMR spectrum was highly complex, and the signals could not be assigned to the individual isomers. Therefore all observed resonances are listed. ^{13}C {^{1}H} NMR (75 MHz, C_6D_6, 293 K): $\delta = 14.74, 31.78, 32.28, 32.52, 34.70, 34.92, 44.77, 122.48, 127.59, 127.86, 128.09, 128.87, 128.29, 129.19, 129.53, 131.86, 131.99, 132.13, 132.52, 132.67, 132.81, 140.53, 141.07, 145.11, 149.90, 150.73$.

4.3.3. 4,5-Bis(chlorophenylphosphino)-2,7-di-tert-butyl-9,9-dimethylxanthene (**6**)

1.0 g of **5** (1.47 mmol) was dissolved at 0 °C in 10 mL of freshly distilled PCl_3. The mixture was heated to 50 °C and stirred at that temperature for 2 h. After cooling the mixture to room temperature, the solvents were removed using high vacuum and the remaining solid was washed using hexanes (2 × 10 mL). This yielded 0.89 g of **6** as a 1:1 mixture of diastereomers (1.44 mmol, 98%). This air and moisture sensitive mixture was used without further purification. ^{1}H NMR (300 MHz, C_6D_6, 293 K): $\delta = 1,26$ (s, 18H, $C(CH_3)_3$), 1.40 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.43 (s, 6H, CH_3), 6,94 (m, 3H, H-arom), 7.0–7.18 (m, 4H, H-arom), 7.47 (dd, $J = 7.1$ Hz, $J = 3.2$ Hz, 2H, H-arom), 7.55–7.70 (m, 2H, H-arom), 7.85 (bs, 1H, H-arom), 7.91 (bs, 2H, H-arom); ^{31}P {^{1}H} NMR (121 MHz, C_6D_6, 293 K): $\delta = 76.9, 77.1$.

4.4. Synthesis of functionalized bisxantphos derivatives

4.4.1. 4-Bromophenyl-bis(diethylamino)phosphine (**11**)

To a solution of 1,4-dibromobenzene **10** (11.8 g, 50.0 mmol) in diethyl ether (125 mL) was added dropwise *n*-BuLi (2.5 M in hexanes, 20.0 mL, 50.0 mmol) at −78 °C. After stirring for 1 h at that temperature, bis(diethylamino)chlorophosphine **A** (10.5 g, 50.0 mmol) was added and the solution was allowed to warm to room temperature over a 16 h period. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. Flash column chromatography (neutral Al_2O_3, light petroleum) afforded **11** (11.7 g, 71%) as a white solid. ^{1}H NMR (500 MHz, C_6D_6, 293 K): $\delta = 0.97$ (t, $J = 7.1$ Hz, 12H, CH_3), 2.90–2.97 (m, 8H, CH_2), 7.24–7.27 (m, 2H, H-arom), 7.35–7.37 (m, 2H, H-arom); ^{13}C {^{1}H} NMR (125 MHz, C_6D_6, 293 K): $\delta = 15.1$ (d, $J = 3.5$ Hz), 43.4 (d, $J = 17.2$ Hz), 121.5, 122.4, 132.0 (d, $J = 2.9$ Hz), 133.5 (d, $J = 16.5$ Hz); ^{31}P {^{1}H} NMR (121 MHz, C_6D_6, 293 K): $\delta = 96.59$; HRMS (FAB+): *m/z* calcd. for $C_{14}H_{25}N_2PBr$ ($M+H^+$): 331.0939; found: 331.0945.

4.4.2. (4-Bromophenyl)dichlorophosphine (**12**)

A solution of 1,4-dibromobenzene (14.2 g, 60.0 mmol) in 200 mL of THF was cooled to −78 °C *n*-BuLi (2.5 M in hexanes, 24.0 mL, 60.0 mmol) was added dropwise and the reaction mixture was

stirred for 1 h keeping the temperature at −78 °C. The resulting white, cloudy solution was added via a cannula to a solution of PCl_3 (32.9 g, 240 mmol) in THF (50 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. The precipitation was filtered off and solvent and excess PCl_3 were removed under reduced pressure. Purification by fractional distillation (135–140 °C, 14 mbar) yielded **12** (5.83 g, 37%) as a colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ = 7.61–7.64 (m, 2H, H-arom), 7.71–7.76 (m, 2H, H-arom); ^{13}C {^{1}H} NMR (125 MHz, C_6D_6, 293 K): δ = 121.5, 132.0 (d, J = 32.1 Hz), 132.5 (d, J = 7.9 Hz), 133.6, 139.7 (d, J = 53.5 Hz); ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$, 293 K): δ = 158.59.

*4.4.3. Cyclic bisxantphos **13***

Following the procedure as described for the synthesis of compound **4**, bisxantphos **13** was obtained starting from xanthene **1** (2.50 g, 5.2 mmol) and dichlorophosphine **12** (1.34 g, 5.2 mmol) in 10% yield (0.26 g) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ = 1.21 (s, 36H, $C(CH_3)_3$), 1.53 (s, 6H, CH_3), 1.74 (s, 6H, CH_3), 7.33–7.35 (m, 8H, H-arom), 7.43–7.47 (m, 8H, H-arom); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 293 K): δ = 31.7, 34.8, 34.9, 35.6, 121.2, 123.7, 125.6 (t, J = 19.6 Hz), 129.7, 130.3, 130.8, 134.5 (t, J = 16.1 Hz), 138.6 (dd, J = 7.5 Hz, J = 5.0 Hz), 146.0, 152.6 (t, J = 24.8 Hz); ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$, 293 K): δ = −37.15; HRMS (FAB+): m/z calcd. for $C_{59}H_{65}Br_2O_2P_2$ (M+H$^+$): 1015.2815; found: 1015.2813. Anal. calcd. for $C_{58}H_{64}Br_2O_2P_2$: C, 68.64; H, 6.36; Found: C, 68.39; H, 6.45.

*4.4.4. Cyclic bisxantphos **14***

At −78 °C, *n*-butyllithium (2.5 M in hexanes, 0.8 mL, 2.0 mmol) was added dropwise to a stirred solution of **13** (0.23 g, 0.2 mmol) and TMEDA (0.3 mL, 2.0 mmol) in diethyl ether (10 mL). The reaction mixture was stirred for 30 min at −78 °C. Then, DMF (0.15 mL, 2.0 mmol) was added and the reaction mixture was stirred for another 30 min allowing to warm to room temperature. The solution was washed with 2 M aqueous HCl (10 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Purification by silica gel column chromatography (10% ethyl acetate in light petroleum) yielded **14** (0.17 g, 95%) as a white powder. ^{1}H NMR (500 MHz, CD_2Cl_2, 293 K): δ = 1.24 (s, 36H, $C(CH_3)_3$), 1.58 (s, 6H, CH_3), 1.76 (s, 6H, CH_3), 7.44–7.45 (m, 4H, H-arom), 7.48–7.49 (m, 4H, H-arom), 7.69–7.71 (m, 4H, H-arom), 7.85–7.86 (m, 4H, H-arom), 10.05 (s, 2H, CHO); ^{13}C {^{1}H} NMR (125 MHz, CD_2Cl_2, 293 K): δ = 31.3, 34.8, 34.9, 35.6, 124.3, 124.9 (t, J = 18.9 Hz), 128.7, 129.7, 130.3, 132.9 (t, J = 16.2 Hz), 135.2, 146.5, 149.1 (t, J = 15.0 Hz), 152.2 (t, J = 24.1 Hz), 192.2; ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$, 293 K): δ = −34.71; HRMS (FAB+): m/z calcd. for $C_{60}H_{67}O_4P_2$ (M+H$^+$): 913.4515; found: 913.4490. Anal. calc. for $C_{60}H_{66}O_4P_2$: C, 78.92; H, 7.29; Found: C, 78.62; H, 7.61.

*4.4.5. Cyclic bisxantphos **15***

A mixture of L-phenylalanine methyl ester hydrochloride (8.6 mg, 0.04 mmol) and bisaldehyde **14** (18.3 mg, 0.02 mmol) in methylene chloride (2 mL) was treated with sodium acetate (6.6 mg, 0.08 mmol). After stirring for 3 h at room temperature, the reaction mixture was cooled to 0 °C and sodium triacetoxyborohydride (17.0 mg, 0.08 mmol) was added. The suspension was warmed to room temperature and stirred for another 3 h. Brine (3 mL) was added, and the mixture was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Purification by silica gel column chromatography (30% EtOAc in light petroleum) yielded **15** (20.8 mg, 84%) as a white powder. $[a]_D^{20}$ = −12.1° (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ = 1.20 (s, 36H, $C(CH_3)_3$), 1.52 (s, 6H, CH_3), 1.72 (s, 6H, CH_3), 2.99 (m, 4H, Hβ), 3.57 (m, 2H, Hα), 3.66 (d, J = 14.0 Hz, 2H, CH_2), 3.67 (s, 6H, OCH_3), 3.85 (d, J = 15.0 Hz, 2H, CH_2), 7.14–7.35 (m, 18H, H-arom), 7.43–7.48 (m, 8H, H-arom); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): δ = 31.6, 32.5, 34.8, 35.1, 38.8, 51.6, 52.5, 65.5, 123.4, 124.3 (t, J = 18.1 Hz), 126.3, 126.4, 126.5, 128.9, 129.2, 129.6, 130.0, 134.2 (t, J = 20.3 Hz), 137.7, 138.0, 139.1 (t, J = 13.5 Hz), 145.6, 150.7 (t, J = 19.5 Hz), 175.6; ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$, 293 K): δ = −36.95; HRMS (FAB+): m/z calcd. for $C_{80}H_{93}N_2O_6P_2$ (M+H$^+$): 1239.6509; found: 1239.6434.

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Appendix. Supplementary data

CCDC 789421 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.06.019.

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