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Analogues of DIOP. Synthesis, reactivity, and NMR behaviour

Armin Börner [a], Renat Kadyrov [a], Manfred Michalik [b] and Detlef Heller [a]

[a] *Max-Planck-Gesellschaft, Arbeitsgruppe "Asymmetrische Katalyse" an der Universität Rostock, Buchbinderstrasse 5 / 6, 18055 Rostock (Germany)*
[b] *Institut für Organische Katalyseforschung e.V. an der Universität Rostock, Buchbinderstrasse 5 / 6, 18055 Rostock (Germany)*

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Abstract

The (4*R*,5*R*)-4,5-Bis(diphenylphosphinomethyl)-2-(α-naphthoxy)-1,3,2-dioxaphospholane (**1**) and (4*R*,5*R*)-4,5-bis(diphenylphosphinomethyl)-2-dimethylamino-2-oxo-1,3,2-dioxaphospholane (**2**), analogues of the chiral bisphosphine ligand DIOP, have been synthesized. Both compounds have a second phosphorus functionality in the backbone of the chiral bisphosphine. That the reactivities of the various phosphorus atoms in **1** are different was shown for the reaction with BH_3. The complexation behaviour of **1** towards Rh^I was studied with the aid of ^{31}P NMR spectroscopy.

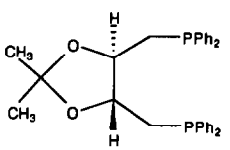
Key words: Phosphorus; Rhodium; Nuclear magnetic resonance

1. Introduction

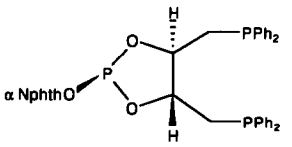
Homogeneous asymmetric hydrogenation by transition metal complexes with chelating bisphosphines has provided useful syntheses of many enantiomerically pure substances [1]. One of the most versatile ligands has proved to be DIOP [2], first described by Kagan. In connection with our particular interest in introducing second functionalities at defined distances in selected phosphine ligands [3], which can interact with a second metal or the substrate itself, we describe here two analogues of DIOP in which the chiral backbone involves an additional phosphorus functionality.

Our special interest in the synthesis of a ligand carrying a phosphite group arose from recent reports, in which chelating bisphosphites were shown to be effective catalysts for hydroformylation reactions [4,5]. A chiral platinum complex based on a chiral phosphite ligand with C_3 symmetry has been shown to be an interesting example of a Brønsted acid [6]. Therefore, chiral diphosphinophosphites like **1** appeared to us to be of interest as model compounds for binuclear catalysts. For the purpose of comparison we synthesized **2**. In complexes of **2**, coordination of the backbone-phosphorus to the metal is prevented, and so its complexation behaviour should be related to that of DIOP.

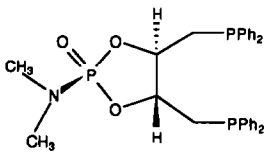
Having accomplished the synthesis of **1**, we had to consider which of the three phosphorus atoms would



DIOP



1



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Correspondence to: Dr. A. Börner.

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be involved in the complexation of rhodium. A simple rule attributes superior π-donor qualities to phosphites than to phosphines [7]. However, the reported differences are quite small, and variation in the substituents on the phosphorus, in conjunction with the contribution of the chelate effect, might change this sequence.

2. Results and discussion

The cyclic phosphite **1** was prepared by the reaction of (2 *R*,3 *R*)-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (**3**) [8,9] with α-naphthoxydichlorophosphine (**4**) in the presence of triethylamine (Scheme 1). The compound was purified by preparative thin layer chromatography, and proved to be stable for a short time in air, although decomposition occurred within a few hours.

The structure of **1** was deduced from spectroscopic data and mass spectrometry. Thus, the ^{1}H NMR spectrum of **1** in $CDCl_3$ shows two distinct multiplets due to the secondary protons at δ 4.12 and 4.37. This clearly indicates that the original C_2-symmetry of DIOP is broken by the non-planar phosphite in the backbone. This assumption is supported by the ^{13}C NMR spectrum, in which two sets of signals for the primary and secondary carbon atoms are observed. Selected chemical shifts and coupling constants are listed in Table 1.

The second new DIOP analogue **2** was obtained by reaction of **3** with $Me_2NP(O)Cl_2$ (**5**) (Scheme 2). It was purified by preparative thin layer chromatography and subsequent flash chromatography.

The structure of **2** was established from the ^{1}H NMR spectrum, in which the compound shows two

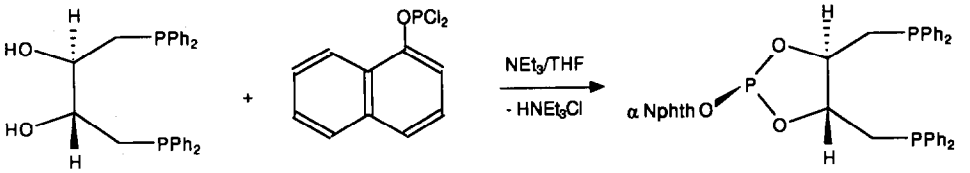
TABLE 1. ^{13}C chemical shifts and ^{13}C–^{31}P-coupling constants of **1** and **2**

Compound	Chemical shift (δ^{31}C)			
	$(CH_2)_A$	$(CH_2)_B$	$(CH)_A$	$(CH)_B$
1	33.4, m ^1J = 16.6 Hz	34.3, m ^1J = 15.9 Hz	80.2, m ^2J = 7.5 Hz	82.2, m ^2J = 8.3 Hz
2	33.3, ddd ^1J = 15.6 Hz ^3J = 12.2 Hz ^4J = 3.6 Hz	34.0, ddd ^1J = 15.4 Hz ^3J = 5.5 Hz ^4J = 2.9 Hz	80.2, ddd ^2J = 15.3 Hz $^2J'$ = 7.6 Hz ^3J = 2.7 Hz	82.3, ddd ^2J = 18.5 Hz $^2J'$ = 8.3 Hz

multiplets at δ 4.25 and 4.41 due to the non-equivalent protons on the heterocycle (*vide supra*). The two *N*-methyl groups are observed at δ 2.53 and 2.62 giving well separated doublets ($^3J(^{31}P-^1H)$ = 1 Hz). The ^{13}C NMR spectrum of **2** corresponds well to that of **1**. Selected chemical shifts and ^{13}C–^{31}P couplings are given in Table 1.

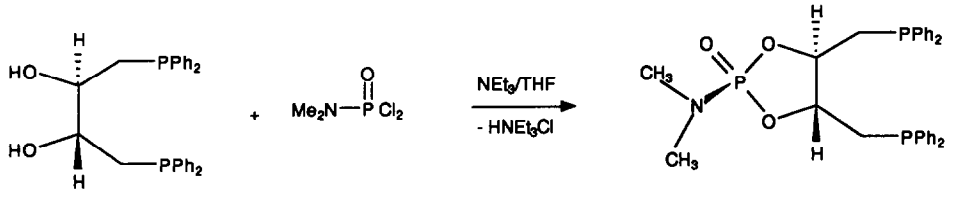
Initially, the reactivities of the three phosphorus atoms of **1** were investigated by stepwise reaction with BH_3 at −78°C in THF. Figure 1 shows the ^{31}P NMR spectra of **1** and its adducts with borane.

For **1** itself, two distinct phosphine signals appear, at δ −22.5 and −23.1, due to the non-symmetry of the molecule discussed above. As expected, the phosphite exhibits a single resonance at δ 135.0. The latter was split into four signals (δ 135.7, 135.3, 135.2, 135.0) when **1** was treated with one equivalent of BH_3 (Entry I), which indicates that four different compounds have been formed in the reaction. A broad signal at δ 16.0 indicates the formation of phosphine–borane adducts, and its shift agrees well with the values found for other



3 **4** **1**

Scheme 1.



3 **5** **2**

Scheme 2.

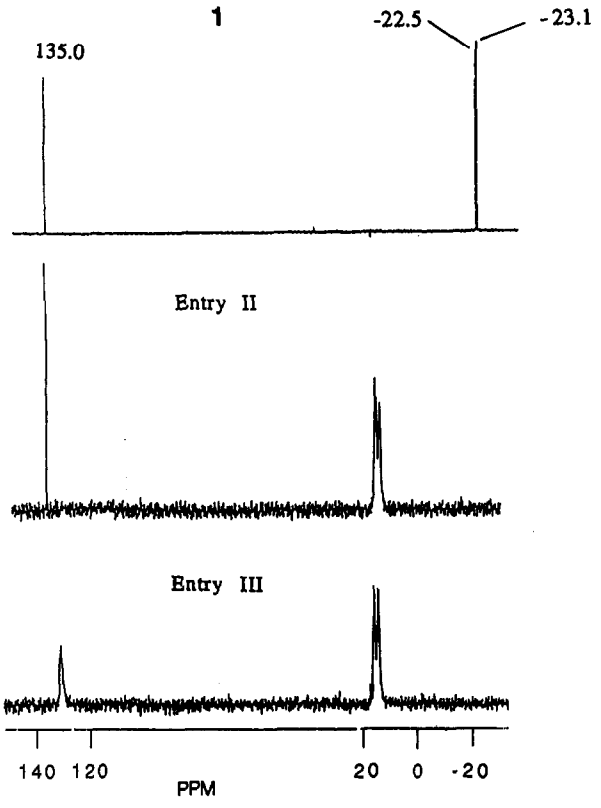


Fig. 1. ^{31}P NMR spectra of the reaction of **1** with BH_3 in benzene-d_6.

phosphine–boranes [10]. In the phosphine region, four lines are observed (δ −21.9, −22.1, −22.3, −22.5), and can be attributed to uncomplexed phosphine groups of **1** itself and the phosphine signals of two regioisomeric monoborane adducts. The spectrum obtained after addition of a second equivalent BH_3 (Entry II) provides clear evidence for this assumption. All the phosphine signals have disappeared and have been replaced by two now distinguishable signals of phosphine–boranes (δ 15.2, 13.7), indicating, as does the observation of a single phosphite resonance (δ 136.0), the formation of a single compound. Addition of a third equivalent of BH_3 converts the phosphite into the tris(borane) complex (Entry III: δ 130.1, 15.5, 14.0).

The results observed with BH_3 led us to believe that the reaction of **1** with Rh^I would give rise to a definite *cis*-complex, as is usually observed for chelating bisphosphines. Thus, **1** was treated with one or two equivalents of $[Rh(COD)_2]BF_4$ in two parallel experiments. The ^{31}P NMR spectra of both products isolated are very similar, and show a very complex pattern of lines, indicating the formation of oligomeric species that are only sparingly soluble in acetone (Fig. 2(a)). All attempts to isolate single complexes failed. Nevertheless, the careful interpretation of the spectra enabled the unambiguous assignment of all structures. A simple first-order analysis produces a range of ^{103}Rh–^{31}P and ^{31}P–^{103}Rh–^{31}P coupling constants, generally difficult to observe in such complexity, and they are discussed below in detail. The full list of the coupling constants is presented in Table 2.

At first sight, the signals of the free phosphine cannot be detected in the spectrum (region between 0 and −25 ppm). This means that both phosphine groups are involved in the formation of complexes.

Especially remarkable is the double doublet at δ 128.5, which can be attributed to complexed phosphite. The corresponding ^{31}P–^{103}Rh–^{31}P coupling constant of 61.0 Hz is also found in the double doublet at δ 2.3, and is in the range reported for other *cis*-complexes of Rh^I [11]. The correspondence of the vicinal coupling indicates that both resonances belong to a unique species. Because of the extreme chemical shift of both signals, we attribute this NMR pattern to structure A (COD is omitted for clarity). Additional proof for this assignment is provided by the proton-coupled ^{31}P spectrum (Fig. 2(b)). Measurable ^{31}P–^{1}H coupling constants ($^3J(^{31}P$–$^{1}H)$ approx. 20 Hz) can be observed only for the phosphite signal discussed. This observation indicates a rigid structure in which the favoured twist-envelope conformation of the 1,3,2-dioxaphospholane [12] is reinforced by intramolecular chelation, as in structure **A**.

Similarly, with the aid of vicinal ^{31}P–^{31}P couplings other fragments can be identified. Thus, in the overcrowded region at δ 15 the alliance of two doublets is revealed by their identical vicinal ^{31}P–^{31}P coupling constants of 35.4 Hz. The value of their ^{31}P–^{103}Rh coupling constant of 146.0 Hz and the slight difference in the chemical shift can best be interpreted by assuming the *cis*-structure **B** as usually observed for a chelating bisphosphine.

TABLE 2. Characteristic coupling constants (J) of fragments and complexes of the type $[(COD)Rh(P–P)]BF_4$

Fragment/ complex	Coupling constants (Hz)			
	O_3P–Rh	Ph_2P–Rh	O_3P–Rh –PPh_2	Ph_2P– Rh–PPh_2
	^1J	^1J	^2J	^2J
A	256.6	140.5	61.0	–
B	–	146.0	–	35.4
C	262.0	142.0	43.5	–
D	245.1	–	–	–
E/E'	–	141.9/ 142.6	–	–
F	–	146.4	–	–
1–$(BH_3)_2$	240.0	–	–	–
2	–	144.5/ 146.7	–	36.6

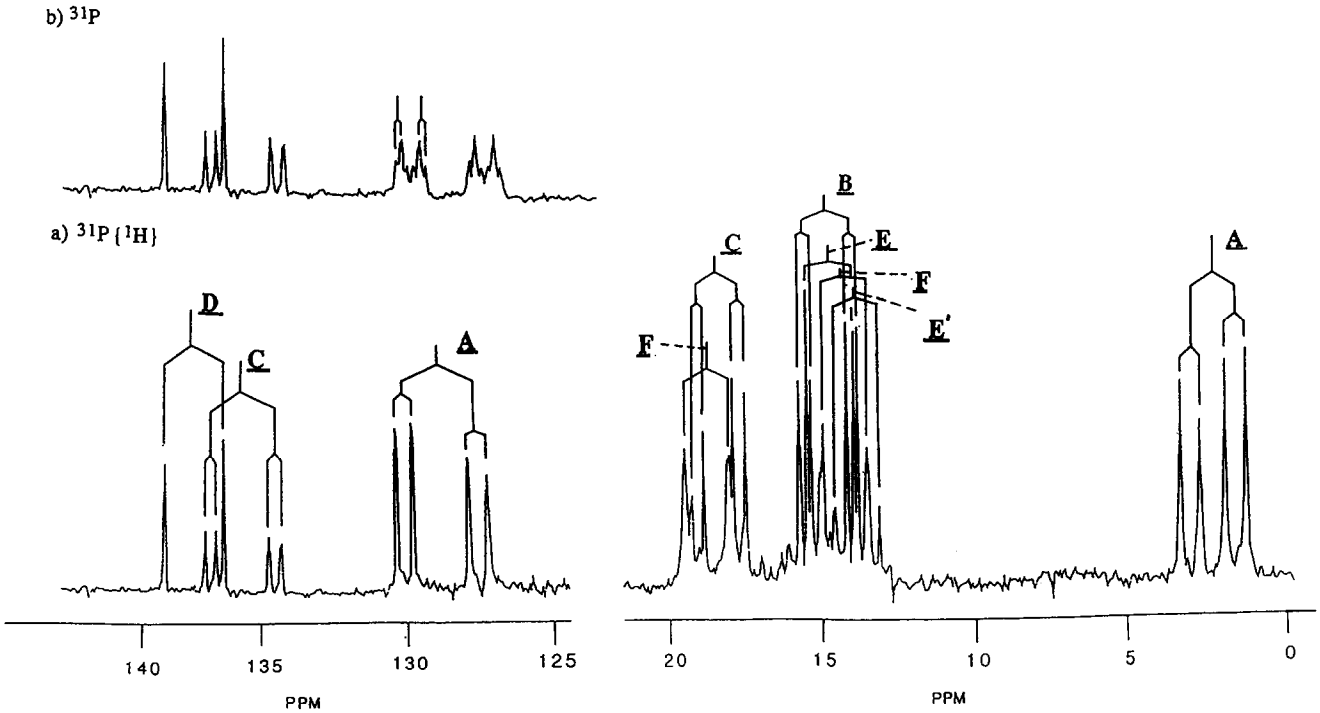
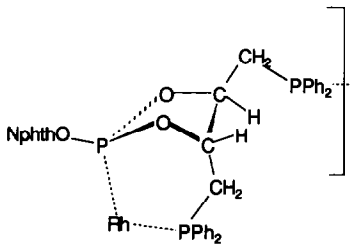
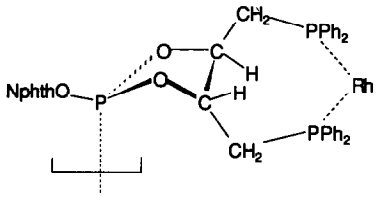


Fig. 2. ^{31}P NMR spectra of the reaction of **1** with two equivalents $[Rh(COD)_2BF_4]$ in acetone-d_6.

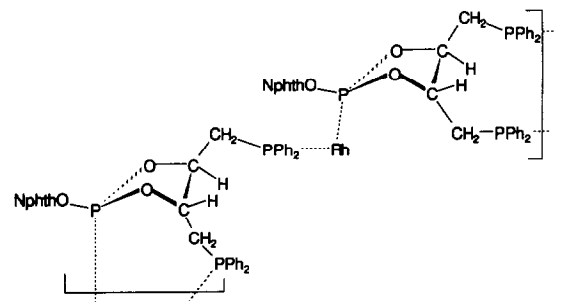


A



B

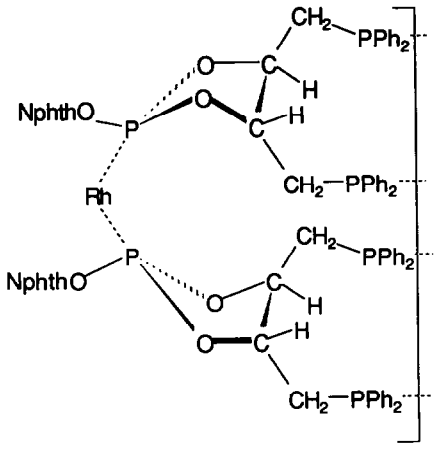
A set of signals similar to that discussed above for fragment **A** can be constructed by combination of the double doublet at δ 136 ($J(^{31}P-^{103}Rh) = 262.0$ Hz) and those at δ 18 ($J(^{31}P-^{103}Rh) = 142.0$ Hz). (The latter is superimposed upon the doublet of a hypothetic structure **F** which is discussed below.) Both show a unique vicinal coupling constant of $J(^{31}P-^{103}Rh-^{31}P) = 43.5$ Hz. Since intramolecular complexation has always been proposed for fragment **A**, it follows that the monodentate species has formula **C**.



C

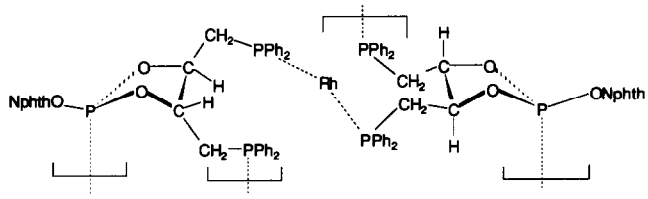
Of course, the existence of a symmetric bis(phosphinite) fragment like **D** should also be taken into consideration. Its presence can be readily deduced from the appearance of the doublet at δ 138. Both complexing phosphorus atoms are fully identical, and so only the $^{31}P-^{103}Rh$ coupling ($J(^{31}P-^{103}Rh) = 245.1$ Hz) can be observed.

A similar pattern may be attributed to the monodentate bisphosphine complex **E**. Owing to the chemical equivalence of the two participating phosphines only one doublet at 14.8 ($J(^{31}P-^{103}Rh) = 141.9$ Hz), is observed. The remaining two phosphine groups of this



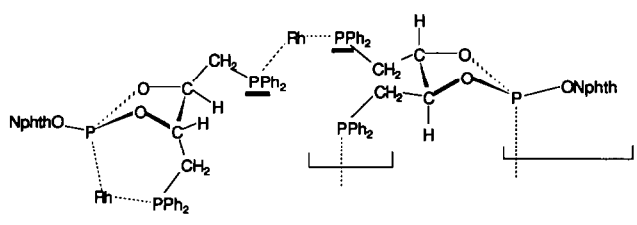
D

fragment must also be involved in complexation. The presence of such complexation may be indicated by the doublet at δ 14 ($J(^{31}P-^{103}Rh) = 142.6$ Hz), indicated in Fig. 2(a) as **E'**. However, these structures are rather speculative, since three different possible ways in which phosphine groups participate in the intermolecular complexation have to be taken into consideration.



E

The remaining hypothetical fragment **F** can be associated with the set of two lines at δ 18 and 14. The absence of the $^{31}P-^{31}P$ couplings implies the approximate equivalence of the two participating phosphorus atoms. The slight shift of one phosphine signal to lower field can be understood by consideration of fragment **A**. The remaining phosphine group of this structure must also be engaged in complexation, since no uncomplexed phosphine was detected. This complexation is present in the proposed binuclear species **F**.



F

It should be noted that all signals of the spectrum have been considered in the foregoing discussion.

To provide independent support for our analysis we treated $\mathbf{1}(BH_3)_2$, which was obtained in the reactivity studies above (Entry II), with $[Rh(COD)_2]BF_4$. The ^{31}P NMR spectrum of the complex shows a doublet at δ 141 with the characteristic $^{31}P-^{103}Rh$ coupling of 240.0 Hz. This confirms the identity of fragment **D**.

An initially puzzling result came from the reaction of **2** with $[Rh(COD)_2]BF_4$. The Rh-complex obtained is characterized in the ^{31}P NMR spectrum by a superimposed double-set of four lines at δ 15.0. Besides a vicinal $^{31}P-^{31}P$ coupling of 36.6 Hz, slightly differing metal–phosphorus couplings of 144.5 Hz and 146.7 Hz, respectively, are observed. This is in contrast to the resonances that were attributed to the closely related fragment **B** of the series **1**. Only a single $^{31}P-^{103}Rh$ coupling was found for the latter. An explanation for this result may come from the comparison of the ^{31}P NMR spectra of **1** and **2**. For **1** only a small difference in the chemical shift of both phosphines is observed ($\Delta\delta = 0.6$ ppm). In the case of **2** this difference is significantly larger ($\Delta\delta = 1.6$ ppm), implying that in **2** there is a more pronounced difference in the chemical environment of the two phosphine groups. Thus, we observed two $^{31}P-^{103}Rh$ couplings, for the **2**–Rh complex, whereas in the case of the corresponding **1**–Rh structure under our conditions only a single value, which must represent an average, can be detected.

As expected, the rhodium complex of **2** showed similar properties to DIOP in selected hydrogenation reaction. Thus with **2** we observed a very fast hydrogenation of α-methyl cinnamic acid, with 61% ee. Because of its irregular complexation behaviour, **1** was not tested as a catalyst.

3. Experimental details

NMR spectra were recorded on a Bruker AC 250 instrument at 303 K. Spectra were obtained at the following frequencies: 250.1 MHz (^1H), 62.9 MHz (^{13}C), 101.3 MHz (^{31}P). Optical rotations were measured on a "gyromat-HP" (Firma Dr. Kernchen). Preparative thin-layer chromatography was performed on precoated TLC plates (silica gel 60 F_{254}, layer thickness 2 mm, Merck). Flash chromatography was carried out with silica gel 60 (particle size 0.040–0.063 mm, Merck). The mass spectrum of **1** was recorded on an AMD 402 (Firma AMD Intectra) at 70 eV. All reactions were carried out under argon by standard Schlenk techniques. Tetrahydrofuran (THF) was purified by distillation from sodium/benzophenone ketyl. α-Naphthoxy dichlorophosphine was prepared by the reaction of

PCl_3 with α-naphthol in the presence of a catalytic amount of KI [13]. (Dimethylamino)dichlorophosphine oxide was prepared by a known method [14]. For the reaction with BH_3 a 1.0 M solution of BH_3–THF complex in THF was used. Rhodium complexes were prepared in THF by standard methods [15]. The hydrogenation was carried out at 0.1 MPa at 25°C.

3.1. (4R,5R)-4,5-Bis(diphenylphosphinomethyl)-2-(α-naphthoxy)-1,3,2-dioxaphospholane (1)

A solution of 0.21 g (0.872 mmol) of α-naphthoxydichlorophosphine in 10 ml of ether was added to a stirred solution of 0.4 g (0.872 mmol) of **3** and 0.5 ml of triethylamine in 40 ml of ether at 0°C. After overnight stirring at room temperature the solvent was evaporated and the remaining oil subjected to preparative thin-layer chromatography (eluent hexane/AcOEt 7:3) to give 250 mg (45.5%) of a colorless syrup: $[\alpha]_D = -63.7$ ($c = 1.4$, $CHCl_3$). Anal. Found: C 72.71; H, 5.30. $C_{38}H_{33}O_3P_3$ calc.: C, 72.37; H: 5.27%. ^1H NMR ($CDCl_3$): δ 2.30 (1H, dd, $J = 13.9$, 5.9 Hz); 2.38–2.50 (3H, m), 4.08–4.21 (1H, m); 4.28–4.43 (1H, m); 6.80–8.10 (27H, aromat). ^{31}P NMR (benzene): δ −23.1; −22.5; 135.0. IR (Nujol): 3057, 1600, 1660, 1440, 1434, 1390, 1260, 1232, 1082, 958, 892, 800, 740, 714, 696, 684 cm^{-1}. MS: *m/e* 630 ($M^{+\cdot}$, 4), 553 (M^+ − Ph, 1.7), 503 (M^+ − naphthyl, 1.8), 487 (M^+ − naphthoxy, 100), 445 (M^+ − PPh2), 423 (18), 301 (4), 262 (4), 239 ($PPh_2CH_2CH{=}CH{-}CH_2^+$, 20), 185 ($PPh_2^+$, 28), 144 (naphthol$^+$, 8).

3.2. (4R,5R)-4,5-Bis(diphenylphosphinomethyl)-2-dimethylamino-2-oxo-1,3,2-dioxaphospholane (2)

A solution of 0.13 g (0.55 mmol) of (dimethylamino)dichlorophosphine oxide in 10 ml of ether was added to a stirred solution of 0.25 g (0.55 mmol) of **3** and 2 ml of triethylamine in 30 ml of ether at 0°C. After overnight stirring at room temperature the precipitate was filtered off and the solvent removed. The remaining oil was purified by preparative thin-layer chromatography (eluent toluene/acetone 9:1) and subsequent flash chromatography (eluent toluene/acetone 4:1) to give 44 mg (15%) of a colorless syrup: $[\alpha]_D = -30.0$ ($c = 0.7$, $CHCl_3$). Anal. Found: C 69.63; H, 6.09. $C_{30}H_{32}NO_3P_3$ calc.: C, 69.93; H: 6.26%. ^1H NMR ($CDCl_3$): δ 2.10–2.52 (4H, m); 2.53 (3H, d, $J = 1$ Hz); 2.62 (3H, d, $J = 1$ Hz), 4.18–4.28 (1H, m); 4.37–4.48 (1H, m); 6.80–8.10 (20H, aromat). ^{31}P NMR ($CDCl_3$): δ −24.7; −23.1; 24.0.

Acknowledgments

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