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Phosphide-Borane Complexes as Key Intermediates in the Synthesis of Optically Active 1,3-Oxaphospholanes

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ABSTRACT

The syntheses, from the triphenylphosphine-borane complex, of chiral 1,3-oxaphospholanes and optically active bis-1,3-oxaphospholanes, obtained by cleavage of a carbon–phosphorus bond with lithium, are described.

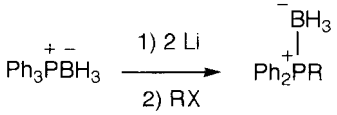
INTRODUCTION

Chiral phosphines are an important class of ligands for the preparation of transition metal complex catalysts [1]. The use of phosphine-borane complexes in the synthesis of chiral functional diphosphines has increased in organic synthesis over the past few years, and many articles have been published on the synthetic utility of these complexes [2]. To prepare a new diphosphine structure, we decided to synthesize diphosphines possessing a chiral phosphorus included in a heterocycle: the 1,3-oxaphospholanes. These compounds are scarce in the literature [3], and up to now they have not been obtained in optically active form. Their synthesis using phosphine-borane complexes as intermediates are described in this article.

RESULTS AND DISCUSSION

Recently, we reported the first example of a phosphide-borane complex, generated by cleavage of a carbon–phosphorus bond with lithium at room temperature as an intermediate [4] that underwent a subsequent reaction with an alkyl halide to form a phosphine–borane complex (Scheme 1).

From the triphenylphosphine-borane complex, this method allowed us to obtain the phosphine-borane complexes containing a chiral phosphorus atom by cleavage successively of two carbon–phosphorus bonds. As summarized in Scheme 2, the re-



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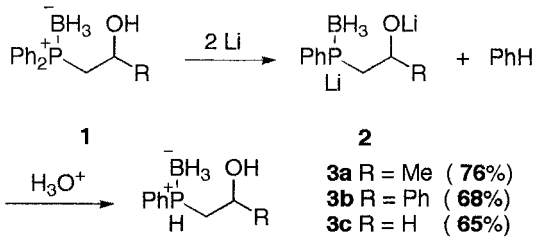

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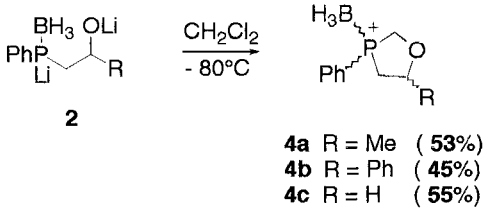

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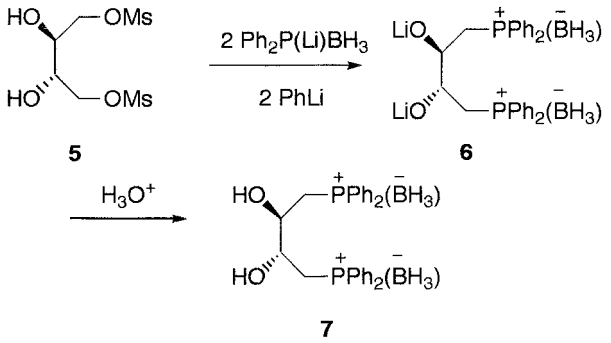

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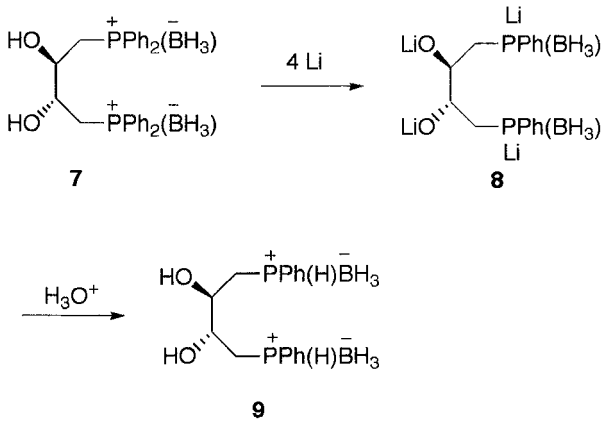
action of the hydroxyalkyldiphenylphosphine-borane complexes **1** with lithium, in THF, at room temperature, afforded directly the desired phosphine-borane complexes, without protection of the



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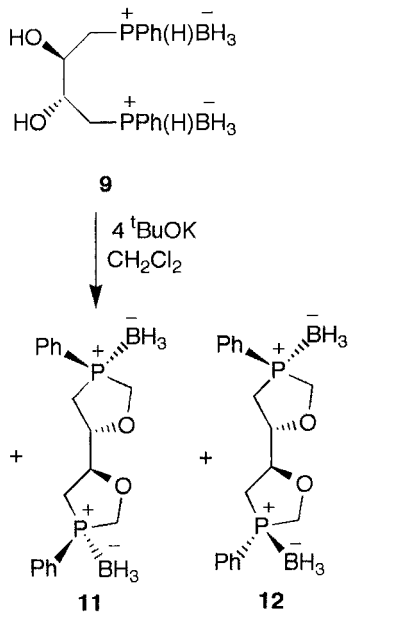

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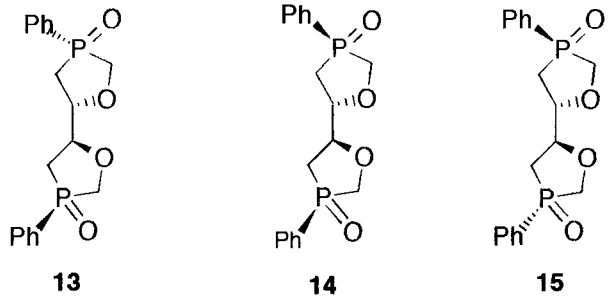

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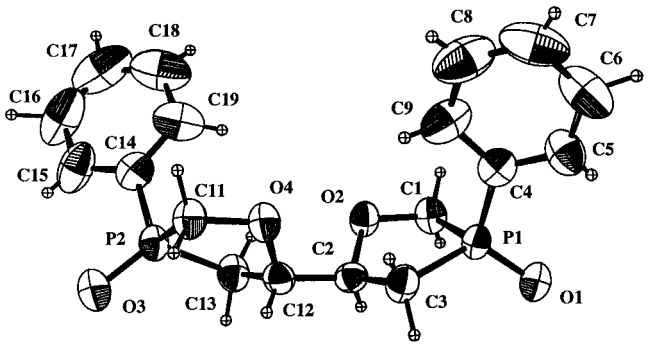

FIGURE 1 Molecular structure of the oxidized form of **13**.

hydroxy group. The phenyllithium formed by the cleavage of the phosphorus–carbon bond had reacted with the hydroxy group in each case, and the expected secondary phosphine-borane complexes **3** [5] were obtained after hydrolysis.

The bimetallic intermediate **2** is particularly in-

TABLE 1 Selected Bond Distances (Å) and Angles (°) for Compound **13**

Bond distances:	
P(1)–C(1): 1.830	P(2)–C(11): 1.833
P(1)–C(3): 1.812	P(2)–C(13): 1.814
O(2)–C(1): 1.418	O(4)–C(12): 1.416
O(2)–C(2): 1.422	O(4)–C(11): 1.422
C(2)–C(3): 1.529	C(12)–C(13): 1.532
C(2)–C(12): 1.490	
Bond angles:	
C(1)–P(1)–C(3): 92.7	C(11)–P(2)–C(13): 92.9
P(1)–C(3)–C(2): 104.6	P(2)–C(13)–C(12): 103.5
C(3)–C(2)–O(2): 107.8	C(13)–C(12)–O(4): 109.7
C(2)–O(2)–C(1): 109.5	C(12)–O(4)–C(11): 109.5
O(2)–C(1)–P(1): 105.2	O(4)–C(11)–P(2): 105.8
O(2)–C(2)–C(12): 108.9	
O(4)–C(12)–C(2): 109.3	

teresting since the presence of two nucleophilic sites allowed us to obtain a heterocycle by reaction with a compound bearing two leaving groups. In this way, we have prepared a new class of compounds, the 1,3-oxaphospholane borane complexes **4** (Scheme 3). These products were synthesized in one step, by reaction of dichloromethane with **2**, at −80°C. These compounds were obtained as a 50:50 mixture of diastereomers, easily separated by chromatography.

This key reaction sequence led us to investigate the synthesis of diphosphines with a new bis-1,3-oxaphospholane structure prepared by a series of reactions starting from (L)-tartaric acid. The first steps have already been described in the literature up to the compound **5** [6]. The mixture of lithium diphenylphosphine-borane and phenyllithium, obtained by reaction of lithium with triphenylphosphine-borane, has reacted with **5**, leading to **7** after hydrolysis (Scheme 4).

We failed to obtain a heterocycle from **7** in one step using the intermediate **8** (Scheme 5). Therefore, we decided to synthesize the bis-1,3-oxaphospholane in two steps. First, the cleavage of a carbon–phosphorus bond with lithium led to the asymmetric phenylphosphine-borane **9**, obtained as a mixture of three diastereomers.

Then, the formation of the bis-heterocycle was realized using four equivalents of potassium tert-butoxide in dichloromethane (Scheme 6). The three diastereomeric forms **10**, **11**, and **12** were obtained and separated by chromatography on silica.

The X-ray and the elemental analysis characterizations of these compounds have been carried out on the corresponding phosphine oxides since a slow decomplexation of the phosphine-boranes was observed at room temperature. The diastereomers **10**, **11**, and **12** were treated successively with DABCO and hydrogen peroxide to furnish phosphine oxides **13**, **14**, and **15** (Scheme 7) [7].

The stereochemistry of **10** was established by the X-ray structure of the oxidized form **13** (Table 1, Figure 1) (As Imamoto was demonstrated, the conversion of the borane to the oxide form occurs with retention of configuration [8].) The stereochemistry of each of **11** and **12** was assigned by comparison with NMR spectra.

CONCLUSIONS

In summary, this work is a contribution to the study of the synthesis of 1,3-oxaphospholanes. Moreover, this is the first synthesis of optically active bis-1,3-oxaphospholanes. This new type of structure with a chiral phosphorus included in a heterocycle could be interesting as a ligand in enantioselective catalysis. Thus, our further investigations will be devoted to the determination of the efficiency of these new diphosphines in catalytic reactions.

EXPERIMENTAL

General

All reactions were carried out under a nitrogen atmosphere. Toluene and tetrahydrofuran were distilled over. Na before use and dichloromethane over CaO. ^{1}H, ^{13}C, and ^{31}P NMR investigations were performed on a Brucker AC 300 spectrometer, in deuteriochloroform, using the solvent as internal reference. Optical rotations were recorded on a Perkin Elmer 241 MC polarimeter. Melting points were determined on a Kofler hot stage apparatus. Silica gel (70–230 mesh) for column chromatography was purchased from Merck.

Synthesis of 1,3-Oxaphospholanes (**4a, 4b, 4c**)

To a magnetically stirred suspension of phosphine-borane complex (2 g, 7.7 mmol) in dry THF (5 mL) at 25°C were added thin, finely cut strips of lithium (0.106 g, 15.4 mmol). The mixture was stirred for 4 hours, during which time the colorless suspension turned into a red solution, and the lithium was consumed. The solution was then cooled to −80°C, and dry dichloromethane (5 mL, 77 mmol) was slowly added. The mixture was kept at this temperature for 1 hour and then allowed to come back gradually to room temperature. The reaction mixture was then stirred overnight, and a yellow suspension appeared.

The solution was hydrolyzed, and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were washed with water and dried (Na_2SO_4). The solvents were removed under reduced

pressure, the yellow residual oil was purified, and the diastereomers were separated by chromatography on silica gel with toluene as eluent leading to a yellow oil.

4a*: Yield: 53%*

1st Diastereomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.9 (m, 3H); 1.5 (d, $^{3}J_{HH}$ = 6.2 Hz, 3H); 1.9 (dt, $^{2}J_{HH}$ = 13.7 Hz, $^{2}J_{HP}$ = 13.7 Hz, $^{3}J_{HH}$ = 10.4 Hz, 1H); 2.5 (ddd, $^{2}J_{HH}$ = 13.7 Hz, $^{2}J_{HP}$ = 2.0 Hz, $^{3}J_{HH}$ = 5.4 Hz, 1H); 3.9 (dd, $^{2}J_{HH}$ = 12.0 Hz, $^{2}J_{HP}$ = 11.1 Hz, 1H); 4.0 (m, $^{3}J_{HH}$ = 10.4 Hz, $^{3}J_{HH}$ = 5.4 Hz, $^{3}J_{HH}$ = 6.2 Hz, 1H); 4.4 (dd, $^{2}J_{HH}$ = 12.0 Hz, $^{2}J_{HP}$ = 4.4 Hz, 1H); 7.1–7.8 (m, 5H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ: +29.7. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 20.9 ($^{3}J_{CP}$ = 5.0 Hz, CH_3); 35.1 ($^{1}J_{CP}$ = 38.0 Hz, CH_2); 68.7 ($^{1}J_{CP}$ = 31.3 Hz, CH_2); 78.2 ($^{2}J_{CP}$ = 3.5 Hz, CH); 128.0–132.7 ($C_{arom.}$).

2nd Diastereomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.9 (m, 3H); 1.4 (d, $^{3}J_{HH}$ = 6.2 Hz, 3H); 2.0 (ddd, $^{2}J_{HH}$ = 14.3 Hz, $^{2}J_{HP}$ = 2.0 Hz, $^{3}J_{HH}$ = 7.8 Hz, 1H); 2.4 (ddd, $^{2}J_{HH}$ = 14.3 Hz, $^{2}J_{HP}$ = 9.6 Hz, $^{3}J_{HH}$ = 6.0 Hz, 1H); 4.2 (dd, $^{2}J_{HH}$ = 11.9 Hz, $^{2}J_{HP}$ = 4.6 Hz, 1H); 4.4 (dd, $^{2}J_{HH}$ = 11.9 Hz, $^{2}J_{HP}$ = 7.4 Hz, 1H); 4.5 (m, $^{3}J_{HH}$ = 7.8 Hz, $^{3}J_{HH}$ = 6.2 Hz, $^{3}J_{HH}$ = 6.2 Hz, $^{2}J_{HP}$ = 6.2 Hz, 1H); 7.2–7.8 (m, 5H). ^{31}P NMR (75.5 MHz, $CDCl_3$) δ: +26.8. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 20.7 ($^{3}J_{CP}$ = 7.3 Hz, CH_3); 36.5 ($^{1}J_{CP}$ = 38.5 Hz, CH_2); 70.7 ($^{1}J_{CP}$ = 31.7 Hz, CH_2); 77.8 ($^{2}J_{CP}$ = 2.6 Hz, CH); 125.2–132.0 ($C_{arom.}$).

4b*: Yield: 45%*

1st Diastereomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.7 (m, 3H); 2.3 (dt, $^{2}J_{HH}$ = 13.7 Hz, $^{2}J_{HP}$ = 13.7 Hz, $^{3}J_{HH}$ = 10.5 Hz, 1H); 2.9 (ddd, $^{2}J_{HH}$ = 13.7 Hz, $^{2}J_{HP}$ = 2.6 Hz, $^{3}J_{HH}$ = 5.5 Hz, 1H); 4.2 (dd, $^{2}J_{HH}$ = 12.2 Hz, $^{2}J_{HP}$ = 11.0 Hz, 1H); 4.7 (dd, $^{2}J_{HH}$ = 12.2 Hz, $^{2}J_{HP}$ = 4.5 Hz, 1H); 4.9 (m, $^{3}J_{HH}$ = 10.5 Hz, $^{3}J_{HH}$ = 5.5 Hz, $^{3}J_{HP}$ = 3.6 Hz, 1H); 7.2–8.0 (m, 10H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ: +28.3. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 37.1 ($^{1}J_{CP}$ = 36.6 Hz, CH_2); 70.6 ($^{1}J_{CP}$ = 31.0 Hz, CH_2); 82.7 ($^{2}J_{CP}$ = 1.7 Hz, CH); 128.2–132.0 ($C_{arom.}$).

2nd Diastereomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.7 (m, 3H); 2.5 (ddd, $^{2}J_{HH}$ = 14.6 Hz, $^{2}J_{HP}$ = 2.5 Hz, $^{3}J_{HH}$ = 9.1 Hz, 1H); 2.7 (ddd, $^{2}J_{HH}$ = 14.6 Hz, $^{2}J_{HP}$ = 8.5 Hz, $^{3}J_{HH}$ = 6.0 Hz, 1H); 4.3 (dd, $^{2}J_{HH}$ = 11.9 Hz, $^{2}J_{HP}$ = 4.4 Hz, 1H); 4.6 (dd, $^{2}J_{HH}$ = 11.9 Hz, $^{2}J_{HP}$ = 6.6 Hz, 1H); 5.3 (m, $^{3}J_{HH}$ = 9.1 Hz, $^{3}J_{HH}$ = 6.0 Hz, $^{3}J_{HP}$ = 5.8 Hz, 1H); 7.1–8.0 (m, 10H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ: +26.5. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 35.2 ($^{1}J_{CP}$ = 36.4 Hz, CH_2); 69.1 ($^{1}J_{CP}$ = 30.5 Hz, CH_2); 83.3 ($^{2}J_{CP}$ = 3.1 Hz, CH); 128.6–132.1 ($C_{arom.}$).

4c*: Yield: 55%*

^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.8 (m, 3H); 2.3 (qt, $^{2}J_{HH}$ = 14.0 Hz, $^{2}J_{HP}$ = 12.0 Hz, $^{3}J_{HH}$ = 8.7 Hz, $^{3}J_{HH}$ = 9.0 Hz, 1H); 2.4 (ddd, $^{2}J_{HH}$ = 14.0 Hz, $^{2}J_{HP} < 1$ Hz, $^{3}J_{HH}$ = 3.4 Hz, $^{3}J_{HH}$ = 6.6 Hz, 1H); 3.8 (tt, $^{2}J_{HH}$ = 9.6 Hz, $^{3}J_{HH}$ = 9.0 Hz, $^{3}J_{HH}$ = 6.6 Hz, $^{3}J_{HP}$ = 6.6 Hz, 1H); 3.9 (dd, $^{2}J_{HH}$ = 12.0 Hz, $^{2}J_{HP}$ = 10.0 Hz, 1H); 4.37 (dd, $^{2}J_{HH}$ = 12.0 Hz, $^{2}J_{HP}$ = 3.8 Hz, 1H); 4.4 (m, $^{2}J_{HH}$ = 9.6 Hz, $^{3}J_{HH}$ = 8.7 Hz, $^{3}J_{HH}$ = 3.4 Hz, 1H) 7.3–8.0 (m, 5H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ: +24.9. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 29.1 ($^{1}J_{CP}$ = 37.9 Hz, CH_2); 69.7 ($^{2}J_{CP}$ = 3.8 Hz, CH_2); 70.6 ($^{1}J_{CP}$ = 31.4 Hz, CH_2); 129.0–132.1 ($C_{arom.}$).

Synthesis of 1,4-bis(Diphenylphosphino)butane-2,3-diol-diborane (**7**)

To triphenylphosphine-borane complex (3.1 g, 11 mmol) and finely cut strips of lithium (0.180 g, 26 mmol) was added 25 mL of dry THF. The mixture was vigorously stirred at room temperature during 6 hours. The dark solution was cooled to 0°C, and the 1,4-dimethanesulfonylbutane-2,3-diol (1.5 g, 5.3 mmol) was introduced into the reaction flask. After having been stirred at room temperature during 12 hours, the mixture was hydrolyzed with a solution of 2N HCl, and extracted with CH_2Cl_2. The aqueous layer was extracted twice, the combined layer extracts were washed with water (in small quantities) and dried (Na_2SO_4). The product was purified by recrystallization from a mixture of MeOH/H_2O. White crystals: mp = 98–100°C, yield: 70%.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.1 (m, 6H); 2.3–2.8 (m, 4H); 3.1 (s, 2H); 3.9 (m, 2H); 7.2–7.9 (m, 20H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ: +12.3 (m). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 29.7 ($^{1}J_{CP}$ = 37.2 Hz, CH_2); 69.6 ($^{2}J_{CP}$ = 10.9 Hz, CH); 133.3–127.7 ($C_{arom.}$).

Preparation of 1,4-di(Phenylphosphino)butane-2,3-diol-diborane (**9**)

To a mixture of borane complex **7** (3.6 g, 7.7 mmol) and thin, finely cut strips of lithium (0.242 g, 34.6 mmol) was added 18 mL of dry THF. The mixture was stirred vigorously during one night. The colorless suspension turned quickly into a dark-red solution, and the lithium was consumed. The reaction mixture was hydrolyzed with H_2O and extracted with CH_2Cl_2. The aqueous layer was extracted twice; the combined extracts were washed with H_2O (in small quantities) and dried (Na_2SO_4). The solvent was

evaporated under reduced pressure, and the residue was subjected to chromatography on silica gel (gradient elution: toluene, toluene/ethyl acetate: 9/1). A mixture of three diastereomers was obtained.

White crystals: yield: 66.4%. ^{1}H NMR (300 MHz, acetone D_6) δ: 1.0 (m, 6H); 2.2–2.6 (m, 4H); 3.6–4.2 (m, 4H); 5.8 (dm, $^1J_{PH}$ = 377.5 Hz, 2H); 7.5–8.1 (m, 10H). ^{13}C NMR (75.5 MHz, acetone D_6) δ: 28.8–29.1 (CH_2); 70.7–71.3 (CH), 126–135 ($C_{arom.}$).

Synthesis of 5,5′-bis(3-Phenyl-1,3-Oxaphospholane) (**10, 11, 12**)

A mixture of **9** (1.7 g, 5.08 mmol) in 17 mL of dry CH_2Cl_2 was cooled to −30°C, and potassium tert-butoxide (2.39 g, 21.0 mmol) was added rapidly. The mixture was kept at this temperature during 20 minutes, and then it was allowed to come back gradually to room temperature. The colorless solution took on a dark-red coloration. After the mixture had been stirred during 2 hours and 30 minutes, the solution was hydrolyzed at 0°C with 1N HCl and extracted by CH_2Cl_2. The organic layers were washed with H_2O and dried (Na_2SO_4). The solvent was removed under reduced pressure, and the three diastereomers were separated by chromatography on silica gel with cyclohexane/ethyl acetate (9/1) as eluent. White crystals: yield: 60% (**10**: 1/4, **11**: 1/2, **12**: 1/4).

10: mp = 131–132°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.0 (m, 6H); 2.4 (m, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 9.9 Hz, $^2J_{HP}$ = 13.7 Hz, 2H); 2.5 (m, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 5.2 Hz, 2H); 4.0 (dd, $^2J_{HH}$ = 12.2 Hz, $^2J_{HP}$ = 11.1 Hz, 2H); 4.1–4.2 (m, 2H); 4.6 (dd, $^2J_{HH}$ = 12.2 Hz, $^2J_{HP}$ = 4.5 Hz, 2H); 7.4–7.8 (m, 10H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ: +28.9. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 31.3 ($^1J_{CP}$ = 37.5 Hz, CH_2); 70.9 ($^1J_{CP}$ = 30.6 Hz, CH_2); 82.0 (CH); 129.1–131.2 ($C_{arom.}$).

11: mp = 135–136°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.9 (m, 6H); 2.3–2.5 (m, 4H); 4.0 (dd, $^2J_{HH}$ = 12.2 Hz, $^2J_{HP}$ < 1 Hz, 1H); 4.0–4.1 (m, 1H); 4.3–4.5 (m, $^2J_{HH}$ = 12.0 Hz, $^2J_{HP}$ = 6.3 Hz, $^2J_{HP}$ = 3.3 Hz, 2H); 4.5 (dd, $^2J_{HH}$ = 12.2 Hz, $^2J_{HP}$ = 4.4 Hz, 1H); 4.5–4.6 (m, 1H); 7.4–8.9 ($C_{arom.}$, 10H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ: +29.5. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 30.0 ($^1J_{CP}$ = 35.4 Hz, CH_2); 30.9 ($^1J_{CP}$ = 37.9 Hz, CH_2); 69.8 ($^1J_{CP}$ = 29.3 Hz, CH_2); 70.9 ($^1J_{CP}$ = 31.3 Hz, CH_2); 81.2 ($^1J_{CP}$ = 6.9 Hz, $^3J_{CP}$ = 3.9 Hz, CH); 82.8 ($^1J_{CP}$ = 2.9 Hz, $^3J_{CP}$ = 2.9 Hz, CH); 125.3–137.8 ($C_{arom.}$).

12: mp = 138–139°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.1 (m, 6H); 2.3–2.4 (m, $^2J_{H\text{-}H}$ = 14.6 Hz, $^3J_{HH}$ = 6.5 Hz, $^2J_{HP}$ = 9.4 Hz, $^3J_{HH}$ = 7.6 Hz, $^2J_{PH}$ = 3.7 Hz, 4H); 4.3 (dd, $^2J_{HH}$ = 12.1 Hz, $^2J_{HP}$ = 4.4 Hz, 2H); 4.4–4.5 (m, 2H); 4.5 (dd,$^2J_{HH}$ = 12.1 Hz, $^2J_{HP}$ = 7.3 Hz, 2H); 7.5–7.8 (m, 10H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ: +28.2. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 30.7 ($^1J_{CP}$ = 35.7 Hz, CH_2); 69.5 ($^1J_{CP}$ = 30.1 Hz, CH_2); 82.5 (CH); 127.5–133.3 ($C_{arom.}$).

Decomplexed Forms: For General Procedure, See Ref. [6]

From **10**: mp = 119–120°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.7–1.9 (m, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 2.5 Hz, $^2J_{HP}$ = 6.5 Hz, 2H); 2.5 (ddd, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 6.2 Hz, $^2J_{HP}$ = 26.4 Hz, 2H); 3.8–3.9 (m, 2H); 4.0 (dd, $^2J_{HH}$ = 12.1 Hz, $^2J_{HP}$ = 28.8 Hz, 2H); 4.7 (dd, $^2J_{HH}$ = 12.1 Hz, $^2J_{HP}$ = 1.2 Hz, 2H); 7.1–7.6 (m, 10H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ: −20.9. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 33.3 ($^1J_{CP}$ = 15.6 Hz, CH_2); 73.1 ($^1J_{CP}$ = 18.7 Hz, CH_2); 84.0 (CH); 128.3–140.1 ($C_{arom.}$).

From **11**: mp = 102–103°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.9 (ddd, $^2J_{HH}$ = 6.5 Hz, $^3J_{HH}$ = 9.7 Hz, $^2J_{HP}$ = 20.9 Hz, 1H); 2.0 (ddd, $^2J_{HH}$ = 14.2 Hz, $^3J_{HH}$ = 9.1 Hz, $^2J_{HP}$ = 17.7 Hz, 1H); 2.2 (ddd, $^2J_{HH}$ = 14.2 Hz, $^3J_{HH}$ = 5.8 Hz, $^2J_{HP}$ = 1.58 Hz, 1H); 2.4 (ddd, $^2J_{HH}$ = 6.5 Hz, $^3J_{HH}$ = 13.5 Hz, $^2J_{HP}$ = 26.7 Hz, 1H); 3.6–3.7 (m, 1H); 4.0 (dd, $^2J_{HH}$ = 12.0 Hz, $^2J_{HP}$ = 23.6 Hz, 1H); 4.1–4.2 (m, 1H), 4.4 (m, $^2J_{HH}$ = 11.6 Hz, $^2J_{HP}$ = 23.4 Hz, 1H); 4.5 (m, $^2J_{HH}$ = 11.6 Hz, $^2J_{HP}$ < 1 Hz, 1H); 4.6 (dd, $^2J_{HH}$ = 12.0 Hz, $^2J_{HP}$ = 1.6 Hz, 1H); 7.2–7.7 ($C_{arom.}$, 10H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ: −20.2, −20.4. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 31.2 ($^1J_{CP}$ = 15.0 Hz, CH_2); 32.6 ($^1J_{CP}$ = 15.3 Hz, CH_2); 71.6 ($^1J_{CP}$ = 20.8 Hz, CH_2); 73.1 ($^1J_{CP}$ = 18.5 Hz, CH_2); 82.2 ($^1J_{CP}$ = 4.2 Hz, $^3J_{CP}$ = 1.6 Hz, CH); 84.3 ($^1J_{CP}$ = 3.0 Hz, $^3J_{CP}$ = 1.4 Hz, CH); 128.5–140.1 ($C_{arom.}$).

From **12**: mp = 138–139°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.9–2.0 (ddd, $^2J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 8.9 Hz, $^2J_{HP}$ = 17.3 Hz, 2H); 2.2 (dd, $^2J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 4.4 Hz, 2H); 4.0–4.1 (m, 2H); 4.4 (dd, $^2J_{HH}$ = 11.8 Hz, $^2J_{HP}$ = 23.4 Hz, 2H); 4.4–4.5 (dd, $^2J_{HH}$ = 11.8 Hz, $^2J_{HP}$ = 1.5 Hz, 2H); 7.3–7.6 (m, 10H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ: −19.6. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 30.8 ($^1J_{CP}$ = 15.2 Hz, CH_2); 71.4 ($^1J_{CP}$ = 21.3 Hz, CH_2); 82.7 (CH); 129.1–138.0 ($C_{arom.}$).

Oxidized Forms: For General Procedure, See Reference [6] (**13, 14, 15**)

13 (from **10**): mp = 176–177°C. $[\alpha]_D^{20}$ − 9.38 (c, 0.18, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.3–2.4 (m, 4H); 3.9 (dd, $^2J_{HH}$ = 13.0, $^2J_{HP}$ = 5.6 Hz, 2H); 4.3 (d, $^2J_{HH}$ = 13.0 Hz, 2H); 4.3–4.5 (m, 2H); 7.3–7.9 (m, 10H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ: +51.7. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 30.7 ($^1J_{CP}$ = 71.5 Hz, CH_2); 69.6 ($^1J_{CP}$ = 67.8 Hz, CH_2); 81.2 (CH); 128.8–132.6 ($C_{arom.}$).

14 (from **11**): mp = 208–209°C. $[\alpha]_D^{20}$ + 25.6 (c, 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.3–2.7 (m, 4H); 3.9–4.1 (2dd, $^2J_{HH}$ = 12.9 Hz, $^2J_{HP}$ = 3.1 Hz, $^2J_{HH}$

= 9.4 Hz, $^2J_{HP}$ = 12.9 Hz, 2H); 4.3 (dd, $^2J_{HH}$ = 12.9 Hz, $^2J_{HP}$ = 8.0 Hz, 1H); 4.4 (d, $^2J_{HH}$ = 12.9 Hz, 1H); 4.4–4.5 (2m, 2H); 7.5–8.0 ($C_{arom.}$, 10H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ: +52.1. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 30.5 ($^1J_{CP}$ = 21.2 Hz, CH_2); 31.4 ($^1J_{CP}$ = 24.8 Hz, CH_2); 67.8 ($^1J_{CP}$ = 68.0 Hz, CH_2); 69.8 ($^1J_{CP}$ = 68.4 Hz, CH_2); 79.5 (CH); 81.0 (CH); 129.1–133.0 ($C_{arom.}$).

15 (from **12**): mp = 223–224°C. $[\alpha]_D^{20}$ + 42.6 (c, 0.6, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.3–2.5 (m, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 7.3 Hz, $^2J_{HP}$ = 15.3 Hz, $^3J_{HH}$ = 6.7 Hz, $^2J_{HP}$ = 4.7 Hz, 4H); 4.0 (dd, $^2J_{HH}$ = 13.2 Hz, $^2J_{HP}$ = 4.5 Hz, 2H); 4.3 (dd, $^2J_{HH}$ = 13.2 Hz, $^2J_{HP}$ = 8.0 Hz, 2H); 4.4–4.5 (m, 2H); 7.4–7.9 (m, 10H). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ: +52.3. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 31.6 ($^1J_{CP}$ = 69.3 Hz, CH_2); 68.2 ($^1J_{CP}$ = 67.9 Hz, CH_2); 80.7 (CH); 129.1–132.7 ($C_{arom.}$). Anal. calcd for, $P_2C_{18}H_{20}O_4$ (mixture of the three stereomers: **13, 14, 15**): C, 59.67; H, 5.56; P, 17.01. Found: C, 59.21; H, 5.51; P, 16.67.

X-ray Crystallographic Analysis of Compound **13**

An orthorombic crystal of compound **13** was obtained by precipitation from acetonitrile; $P_2C_{18}H_{20}O_4$, H_2O: Mr = 392.33, $P2_12_12_1$, a = 5.982(7), b = 13.520(5), c = 23.832(4) Å, V = 1927(2) Å^{-3}, Z = 4, D_X = 1.352 Mg.m^{-3}, $\lambda(M_oK_\alpha)$ = 0.70926 Å, μ = 2.45 cm^{-1}, $F(000)$ = 824, T = 294 K, final R = 0.0394 for 1463 observations. The sample (0.22*0.24*0.45 mm) was studied on an automatic diffractometer CAD4 ENRAF-NONIUS with graphite monochromatized M_oK_α radiation. The cell parameters were obtained by fitting a set of 25 high-theta reflections. The data collection ($2\theta_{max}$ = 50°, scan $\omega/2\theta$ = 1, t_{max} = 60 seconds, range HKL: H 0,7 K 0,16 L 0,28), intensity controls without appreciable decay (0.3%) gives 2004 reflections from which 1463 with $I > 1.5\sigma(I)$.

After Lorenz and polarization corrections, the structure was solved with direct methods that revealed many nonhydrogen atoms of the molecule. The remaining ones were found after successive scale factor and Fourier-difference calculations. After isotropic (R = 0.092), then anisotropic refinement (R = 0.066), the hydrogen atoms were found with a Fourier difference (between 0.49 and 0.21 eÅ^{-3}). The whole structure was refined by the full-matrix least-squares techniques (use of F magnitude; x, y, z, βij for P and C atoms and x, y, z for H atoms; 287 variables and 1463 observations; $w = 1/\sigma(Fo)^2 = [\sigma^2(I) + (0.04Fo^2)^2]^{-1/2}$) with the resulting R = 0.0394, Rw = 0.0399, and Sw = 0.932 (residual $\Delta\rho \leq 0.27$ eÅ^{-3}).

Absolute structure from refinement of the η parameter [9], to 1.00 (2). As a check, a refinement fixed as the opposite absolute structure gave R = 0.0414, Rw = 0.0422, and Sw = 0.968.

Atomic scattering factors were from International Tables for X-ray Crystallography [10]. All the calculations were performed on a Digital MicroV AX 3100 computer with the MOLEN package (Enraf-Nonius, 1990).

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