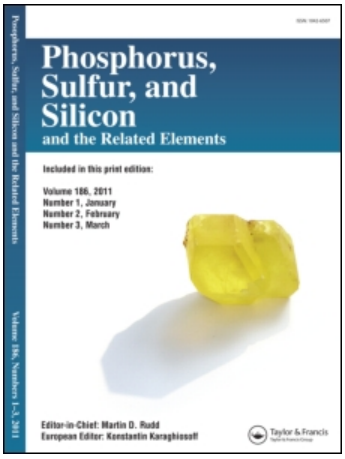

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The Reaction of the Bis-spirocyclic Phosphazene [N 3 P 3 (O 2 C 12 H 8) 2 Cl 2] (O 2 C 12 H 8 = 2,2'-Dioxybiphenyl) with Thiophenols, in the Presence of Alkali Carbonates

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THE REACTION OF THE BIS-SPIROCYCLIC PHOSPHAZENE $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ ($O_2C_{12}H_8 = 2,2'$-DIOXYBIPHENYL) WITH THIOPHENOLS, IN THE PRESENCE OF ALKALI CARBONATES

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*The reactions of the spirocyclic phosphazene $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ ($O_2C_{12}H_8 = 2,2'$-dioxybiphenyl) with the thiophenols HS—C_6H_4—R and M_2CO_3 (M = K or Cs) in refluxing acetone gave respectively the spirocyclic substituted derivatives $[N_3P_3(O_2C_{12}H_8)_2(SC_6H_4—R)_2]$ R = H (**2a**), Br (**2b**), OMe (**2c**), NO_2 (**2d**). The reaction is a two-step process the second of which is much faster than the first and the monosubstituted intermediate $[N_3P_3(O_2C_{12}H_8)_2(SC_6H_4—R)Cl]$ cannot be detected. By contrast, in the analogous reactions with the phenols HO—C_6H_4—R and M_2CO_3 (M = K or Cs) in acetone or THF, to give the known derivatives $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4—R)_2]$, the first step is faster although both are very dependent on R, M and the solvent. Thus, in the case of the phenol HO—C_6H_4—OMe the reaction conditions could be adjusted to give the useful synthetic intermediate monosubstituted derivative $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4—OMe)Cl]$ (**3**). The reaction of $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ with the bifunctional reagent mercaptophenol HS—C_6H_4—OH was not specific and led to mixtures of cyclic and oligomeric products.*

Keywords: Cyclothiophosphazenes; oligomers; phosphazenes

The spirocyclic phosphazenes[1] are an important class of cyclophosphazenes that have received much attention during the past years.[2,3] In particular, the bis-spiro dichloro derivative having 2,2′-dioxybiphenyl units $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ (**1**) is a useful synthetic intermediate for

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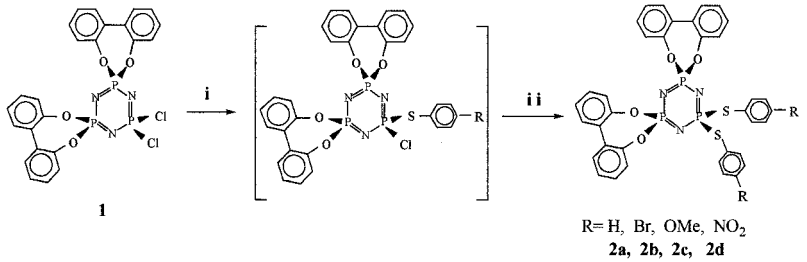
many aryloxy[4,5] or amino[4,6] derivatives, including stable radical reagents[7] and transition metal complexes[8] or NLO chromophores.[9] It also has been used to form polycondensation polymers with various bifunctional reagents.[10]

Most of the reactions carried out with this starting materials involve oxygen or nitrogen nucleophiles and there are no reports describing reactions with thiophenols. It is well known that the thiophenolates NaS—C_6H_4—R react with hexachlorocyclotriphosphazene [$N_3P_3Cl_6$] and that the direct use of the thiols HS—C_6H_4—R in the presence of Cs_2CO_3 in acetone at room temperature lead to the formation of the geminally substituted derivatives [$N_3P_3Cl_4$(S—C_6H_4—R)$_2$], [$N_3P_3Cl_2$(S—C_6H_4—R)$_4$] and the hexasubstituted product [N_3P_3(S—C_6H_4—R)$_6$] although in low yield.[11]

In this work we describe the results obtained studying the reactions of **1** with several thiophenols HS—C_6H_4—R including the bifunctional reagent HS—C_6H_4—OH.

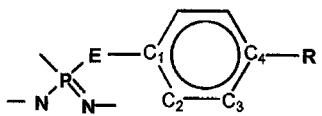
RESULTS AND DISCUSSION

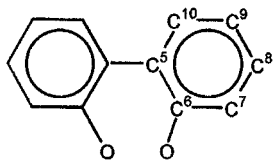
The reactions of the spirocyclic phosphazene [$N_3P_3(O_2C_{12}H_8)_2Cl_2$] (**1**) ($O_2C_{12}H_8$ = 2,2′-dioxybiphenyl) with the thiophenols HS—C_6H_4—R and M_2CO_3 (M = K or Cs) in acetone or THF gave respectively the spirocyclic substituted derivatives [$N_3P_3(O_2C_{12}H_8)_2(SC_6H_4$—R)$_2$] R = H (**2a**), Br (**2b**), OMe (**2c**), NO_2 (**2d**) (Scheme 1). From a synthetic point of view the best experimental procedure was the use of acetone and Cs_2CO_3 at the refluxing temperature, with a 1.25 mmol of thiol per chlorine (see Experimental part). All the analytical and spectroscopic data (Experimental part) were in accord with the proposed structure. Significantly, the ^{13}C NMR spectra (Table I) showed the expected[6] decrease (ca. 5 ppm) of the chemical shift of the aromatic carbon bonded to the S atom and the increase (ca. 5 ppm) of the one in the para-position after the transformation of the starting thiol into the phosphazene thiophenolate.



SCHEME 1 **i** and **ii** = HS—⬡—R, (M_2CO_3 M = K or Cs), acetone or THF.

TABLE I ^{13}C NMR (d8-THF) Data for the Cyclophosphazenes[a]





Compound	E	R	C_1	C_2	C_3	C_4	C^5	C^6	C^7	C^8	C^9	C^{10}
2a	S	H	130.1, d (3)	136.6, d (5)	129.9	129.8	129.7	149.3 t (4.5)	122.8	130.2	126.6	130.3
2b	S	Br	127.9	138.4	133.1	124.9	129.6	149.1 br	122.7	130.3	126.8	130.4
2c[b]	S	OMe	118.9	138.4, d (3)	115.4	162.0	129.8	149.4 br	122.8	130.2	126.6	130.3
2d	S	NO_2	137.4	137.3, d (5)	125.3, d (2)	149.5, d (3)	130.0	149.4 t (4.5)	123.0	131.0	127.5	131.1
3[c]	O	OMe	144.8	123.0	115.3	158.6	129.6	149.1, br	122.7	130.4, d (6)	127.0	130.5, d (6)

[a]The values given in brackets are the J_{PC} coupling constants in Hz.
[b]55.5 (O—CH_3).
[c]55.7 (O—CH_3).

Although the formation of the disubstituted products **2** obviously proceeds in two-steps, it was not possible to detect the monosubstituted intermediate during the monitoring by ^{31}P NMR. Moreover, the use of a thiol/chlorine ratio of 1:1 gave an equimolar mixture of **2** and the starting material. These facts show that the second step (ii in Scheme 1) is much faster than the first; in agreement with the geminal mechanism that is observed for the chlorine substitution reactions between chlorophosphazenes and thiols.[11] Therefore, the overall reaction time in the formation of the disubstituted derivatives is that of the slower first step (i in Scheme 1).

Various experiments show that this process was dependent on the R, M, and the solvent. Thus, the reaction was faster in the order of R: Br > H > OMe > NO_2. Apart from the latter, this order parallels the acidity of the thiols (R/pKa = Br/7.00; H/7.78; OMe/8.08; NO_2/4.99),[12] suggesting the intervention of the thiophenolate anion. In fact, the case of the nitro derivative is not directly comparable with the others due to the lower solubility of the thiol HS–C_6H_4–NO_2 and the product **2d** in acetone. Besides, although this latter compound was white when isolated, the reaction mixture was reddish and the final yield was much lower than in the other cases, suggesting other by-side processes.

By changing the solvent and the alkali carbonate it was found that the reactions in Scheme 1 were faster in acetone than in THF and much faster with Cs than with K. The difference between the two extreme cases (acetone/Cs vs. THF/K) was measured semiquantitatively estimating the reaction times by ^{31}P NMR, and was found that, at the refluxing temperature, the rate of the overall reaction R_T(acetone/Cs) was nearly twenty times R_T(THF/K) (Table II).

We also checked that the compound **2c** was quantitatively recovered after being refluxed for 18 h in the presence of an excess of the thiol

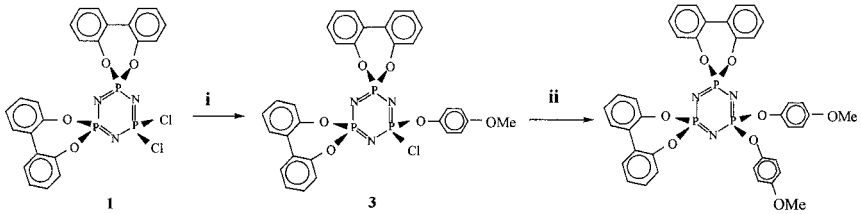
TABLE II Summary of the Relative Reactions Rates for Schemes 1 and 2

Scheme	Estimated ratio of rates
1	R_T(acetone/Cs) $\approx$ 20 R_T (THF/K)
2	R_1(acetone/Cs) $\approx$ 100 R_1 (THF/K)
2	R_T(acetone/Cs) $\gg$ 150 R_T (THF/K)
1 and 2	$R_{1(phenol)}$(acetone/Cs) $\approx$ 48 $R_{T(Thiol)}$ (acetone/Cs)
1 and 2	$R_{T(phenol)}$(acetone/Cs) $\approx$ 2 $R_{T(Thiol)}$ (acetone/Cs)
1 and 2	$R_{1(phenol)}$(THF/K) $\approx$ 6 $R_{T(Thiol)}$ (THF/K)
1 and 2	$R_{T(phenol)}$(THF/K) $\approx$ 0.25 $R_{T(Thiol)}$ (THF/K)

R_T = rate of the overall reaction.
R_1 = rate of the first step.

HS—C_6H_4—OMe, showing that no S—S coupling or other decomposition processes take place during the formation of **2**.

The process shown in Scheme 1 is comparable to the substitution reactions of **1** with the related phenols HO—C_6H_4—R,[5] that also are faster with the more acidic phenols, and with acetone/Cs_2CO_3. However, an study of this reaction with the phenol HO—C_6H_4—OMe (Scheme 2) revealed important differences with the analogous thiol. Thus, although the first step in Scheme 2 is also faster than the second, the actual difference is only moderate, and the monosubstituted derivative **3** clearly is observed as an intermediate. On the other hand, the effects of the solvent and the metal carbonate on both rates (also acetone > THF and Cs > K) are more marked than in the case of the thiols (Table II). In fact, this difference could be adjusted by changing the experimental conditions, and it was possible to obtain **3** in high yield and purity using either K_2CO_3 in refluxing THF or Cs_2CO_3 in THF at room temperature (the optimised procedure to obtain **3** pure in good yield is described in the Experimental part). The structure of **3** was undoubtedly established by the spectroscopic data (Experimental part). Most significant were the pseudosinglet (second order AB_2 spin system) observed in the ^{31}P NMR spectrum, (Table III) which is typical of this type of monosubstituted bis-spirophosphazene, and the ^{13}C NMR spectrum that showed the expected signals for the NP—OC_6H_4—OMe groups.[5]

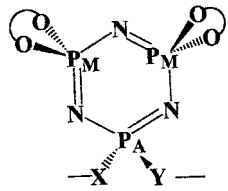


SCHEME 2 **i** and **ii** = HO—⬡—OMe, (M_2CO_3 M = K or Cs), acetone or THF.

The semiquantitative evaluation of the relative rates of steps 1 and 2 in Scheme 2 revealed that in the formation of **3** the R_1(acetone/Cs) was about 100 times the R_1(THF/K), but, the overall rate for the formation of the known[5] final product [$N_3P_3(O_2C_{12}H_8)_2(OC_6H_4$—$OMe)_2$] the R_T(acetone/Cs) was much more than 150 times the R_T(THF/K) (Table II).

Also useful was the comparison of the substitution rates of **1** with thiols and phenols (Schemes 1 and 2) that showed (Table II) that for the conditions acetone/Cs the R_1(phenol) was about 48 times R_T(thiol) and R_T(phenol) was about 2 R_T(thiol), while in the conditions THF/K

TABLE III ^{31}P NMR (d8-THF) Data for Cyclophosphazenes



Compound	X	Y	δ_A	δ_M	J_{AM}
2a	S—C_6H_5	S—C_6H_5	48.3	20.6	31.7
2b	S—C_6H_4—Br	S—C_6H_4—Br	47.3	20.3	31.7
2c	S—C_6H_4—OMe	S—C_6H_4—OMe	49.3	20.9	28.8
2d	S—C_6H_4—NO_2	S—C_6H_4—NO_2	50.7	23.9	34.2
3	O—C_6H_4—OMe	Cl	21.7[a]		
4[b]	O—C_6H_4—SH	Cl	23.7[a]		
5[c]	O—C_6H_4—SH	O—C_6H_4—SH	11.2	26.9	93
6[c]	S—C_6H_4—OH	S—C_6H_4—OH	52.7	24.1	26
7[c]	O—C_6H_4—S H	S—C_6H_4—OH	39.9	27.4	36

[a] It corresponds to the central peak of a multiplet arising from an AB_2 system.
[b] THF as solvent.
[c] Acetone as solvent.

the differences were R_1(phenol) $\approx$ 6 R_T(thiol) and R_T(phenol) $\approx$ 0.25 R_T(thiol).

The preparation of **3** is interesting because it is a synthetic useful reagent to obtain mixed substituted derivatives. However, we observed that the reaction of **3** with the thiol HS—C_6H_4—OMe was very dependent on the solvent and the metal carbonate. Thus, no reaction took place after 72 h in refluxing THF with K_2CO_3, but in refluxing acetone with Cs_2CO_3 a slow reaction occurred leading to various unidentified decomposition products. However, the ^{31}P NMR spectra of the reacting system showed the signals of a AM_2 spin system at 39.1(t, 1P), and 25.5(d, 2P) (J_{AM} = 58.6 Hz), that might be attributed to the mixed species $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4—OMe)(SC_6H_4—OMe)]$ (O/S) (ca. 56% of the total). Very similar results were observed in the reaction of **3** with the thiol HS—C_6H_4—Br.

We also checked that no changes were observed after refluxing in acetone the bis-thiophenolate cyclophosphazene **2c** with the phenol HO—C_6H_4—OMe, or the bis-aryloxy cyclophosphazene $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4—OMe)_2]$ with the thiol HS—C_6H_4—OMe in the presence of Cs_2CO_3, showing no replacements between thiophenolate and aryloxy groups in those spirocyclic phosphazenes.

4, O/Cl), $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4{-}SH)_2]$ (**5**, O/O), $[N_3P_3(O_2C_{12}H_8)_2(SC_6H_4{-}OH)_2]$ (**6**, S/S) and $[N_3P_3(O_2C_{12}H_8)_2(SC_6H_4{-}OH)(OC_6H_4{-}SH)]$ (**7**, O/S), together with condensation dimers, trimers and higher oligomers. Also consistently, no sign of the monosubstituted intermediate $[N_3P_3(O_2C_{12}H_8)_2(SC_6H_4{-}OH)Cl]$ (S/Cl) was detected. The final composition of the mixtures and the nature of the oligomers formed strongly depended on the molar ratio of the reactants, the metal carbonate, the solvent, the temperature and the reaction time.

In one extreme, the reaction with an excess of mercaptophenol, in refluxing acetone with Cs_2CO_3 gave in 2 h a mixture of **5** (O/O), **6** (S/S), and **7** (O/S) (**6** being much more abundant). After 35 h the spectrum showed a complex oligomers mixture that could not be fully characterized.

In the other extreme (1:1 ratio, K_2CO_3, in THF under reflux) the reaction gave first **4**(Cl/O) and proceeded very slowly forming again a complex mixture of oligomers that could not be unambiguously characterized. It was however interesting that, in spite of the low molecular weight (Mw = 1800), the DSC curve of the final solid exhibited a well defined glass transition temperature (Tg = 194°C).

CONCLUSION

The cyclic phosphazene $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ reacts with thiols $HS{-}C_6H_4{-}R$ and M_2CO_3 (M = K or Cs) to yield only the disubstituted products $[N_3P_3(O_2C_{12}H_8)_2(SC_6H_4{-}R)_2]$. However, with the phenol $HO{-}C_6H_4{-}OMe$ the reaction conditions could be adjusted to obtained the useful monosubstituted intermediate $[N_3P_3(O_2C_{12}H_8)_2(O{-}C_6H_4{-}OMe)Cl]$.

The reaction with the bifunctional mercaptophenol $HS{-}C_6H_4{-}OH$ was not regiospecific and gave mixtures of low Mw not well defined oligomers, having a surprising high Tg (194°C).

Experimental

All the reactions were carried out under dry nitrogen. K_2CO_3 and Cs_2CO_3 were dried at 140°C prior to use. The acetone used as solvent

was distilled twice from anhydrous $CaSO_4$. The THF was treated with KOH and distilled twice from Na in the presence of benzophenone. The phenols and thiophenols were used as purchased (Aldrich), the mercaptophenol used had a high level of purity (97%). The cyclic $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ was prepared as described elsewhere.[5]

The IR spectra were recorded with a Perkin-Elmer FT Paragon 1000 spectrometer. NMR spectra were recorded on Bruker AC-200, AC-300 and DPX 300 instruments, using $d_{8\text{-THF}}$ as solvent. ^1H and $^{13}C\{^1H\}$ NMR are given in δ relative to TMS. $^{31}P\{^1H\}$ NMR are given in δ relative to external 85% aqueous H_3PO_4. Coupling constants are in Hz. C, H, N, S analyses were performed by Centro de Apoyo Científico-Tecnológico a la Investigación of the Universidad de Vigo (Spain). GPC were measured with a Perkin Elmer equipment with a Model LC 250 pump, a Model LC 290 UV, and a Model LC 30 refractive index detector. The samples were eluted with a 0.1% by weight solution of tetra-n-butylammonium bromide in THF through Perkin Elmer PLGel (Guard, 10^5, 10^4, and 10^3 Å) at 30°C. Approximate molecular weight calibration were obtained using narrow molecular weight distribution polystyrene standards. Tg values were measured with a Mettler DSC 300 differential scanning calorimeter equipped with a TA 1100 computer, at 10°C/min.

Synthesis of $[N_3P_3(O_2C_{12}H_8)_2(SC_6H_4\text{-}R)_2]$ R = H(2a), Br(2b), OMe(2c), NO_2(2d)

A mixture of $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ (0.5 g, 0.87 mmol), the thiophenol HS—C_6H_5 (0.224 mL, 2.18 mmol), and Cs_2CO_3 (1.06 g, 3.25 mmol) in acetone (30 mL) was refluxed for 2 h. The volatiles were evaporated in vacuo and the residue was washed with water (30 mL) and filtered. The crude product was washed with water (50 mL), isopropanol (2 × 20 mL) and diethyl ether (2 × 20 mL) to give **2a** as a white microcrystalline powder (0.55 g, 88% yield).

The other compounds (all white solids) were prepared following exactly the same procedure with the following amounts of the corresponding thiophenols, refluxing times and yields: **2b)** 0.41 g, 1 h, 88%; **2c)** 0.268 g, 4 h, 75%; **2d)** 0.34 gr, 5 h, 53% (see text). This latter product was washed with acetone (2 × 15 mL) before the other washings.

2a) $C_{36}H_{26}O_4S_2N_3P_3$ (721.66): calcd. C 59.9, H 3.63, N 5.82, S 8.89; found C 59.6, H3.6, N 5.83, S 8.30. IR (KBr, cm^{-1}): 3064w [ν(CH-aromatic)]; 1499m, 1475m, 1438m [ν(C=C) dioxybiphenyl]; 1268m [ν(PO—C)]; 1221s, 1176vs [ν(PN)]; 1094s [ν(P—OC)]; 720m, 686m [δ-(CH out of plane, aromatic monosubstitution)]. ^{31}P NMR: see Table III.

2b) $C_{36}H_{24}O_4Br_2S_2N_3P_3$ (879.45): calcd. C 49.2, H 2.75, N 4.80, S 7.29; found C 47.8, H 2.67, N 4.62, S 6.80. IR (KBr, cm^{-1}): 3062w [ν(CH-aromatic)]; 1500m, 1470m, 1436m [ν(C=C) dioxybiphenyl]; 1270m [ν(PO–C)]; 1226s, 1172vs [ν(PN)]; 1092s [ν(P–OC)]; 811m (out of plane δ-CH, aromatic *para*-disubstitution). ^{31}P NMR: see Table III. ^1H NMR (d_8-THF): 7.62–7.32 (m, $C_{12}H_8$), 7.35, 7.20 (d.d, C_6H_4, $J_{AB} = 7.9$). ^{13}C NMR: see Table I.

2c) $C_{38}H_{30}O_6S_2N_3P_3$ (781.71): calcd. C 58.4, H 3.87, N 5.38, S 8.20; found C 57.2, H 3.80, N 5.23, S 7.86. IR (cm^{-1} in KBr): 3067w [ν(CH-aromatic)]; 2940w, 2839w [ν(CH), CH_3] 1493m, 1476m, 1438m [ν(C=C) dioxybiphenyl]; 1292m [ν(PO–C)]; 1226s, 1171vs [ν(PN)]; 1093s [ν(PO–C)]; 827m (out of plane δ-CH, aromatic *para*-disubstitution). ^{31}P NMR: see Table III. ^1H NMR (d_8-THF): 7.60–7.27 (m, $C_{12}H_8$); 7.19, 6.93 (d.d, C_6H_4, $J_{AB} = 8.0$); 3.76 (s, CH_3). ^{13}C NMR: see Table I.

2d) $C_{36}H_{24}O_8S_2N_5P_3$ (811.66): calcd. C 53.3, H 2.98, N 8.63, S 7.90; found C 52.9, H 2.90, N 8.45, S 7.57. IR (cm^{-1} in KBr): 3063w [ν(CH-aromatic)]; 1497m, 1476m, 1437m [ν(C–C) dioxybiphenyl]; 1514s, 1344s [ν(NO)]; 1269m [ν(PO–C)]; 1226s, 1172vs (ν-PN); 1091s [ν(PO–C)]; 849 m (out of plane δ-CH, aromatic *para*-disubstitution). ^{31}P NMR: see table 3. ^1H NMR (d_8-THF): 7.62–7.20 (m, $C_{12}H_8$), 8.25, 7.93 (d.d, C_6H_4, $J_{AB} = 8.9$). ^{13}C NMR: see Table I.

Synthesis of $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4–OMe)Cl]$ (3)

A mixture of $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ (1.5 g, 2.61 mmol), the phenol HO–C_6H_4–OMe (0.32 g, 2.61 mmol), and Cs_2CO_3 (1.28 g, 3.92 mmol) in THF (40 mL) was stirred at room temperature for 21 h. The volatiles were evaporated in vacuo and the residue was extracted with CH_2Cl_2 (5 × 25 mL), evaporating the solvent and washing the product with diethyl ether (2 × 30 mL) to give **3** as a white microcrystalline powder (1.31 g., 81% yield).

$C_{31}H_{23}O_6ClN_3P_3$ (661.90): calcd. C 56.2, H 3.50, N 6.35; found C 56.2, H 3.57, N 6.33.

IR (cm^{-1} in KBr): 3066w [ν(CH-aromatic)]; 2996w, 2836w [ν(CH-methyl)] 1496m, 1477m, 1433m [ν(C=C), dioxybiphenyl]; 1274m [ν(PO–C)]; 1229s, 1170vs [ν(PN)]; 1092s [ν(P–OC)]; 832m (out of plane δ-CH, aromatic *para*-disubstitution). ^{31}P NMR see Table III. ^1H NMR (d_8-THF): 7.62–7.2 (m, $C_{12}H_8$), **7**.23, 6.93 (d.d, C_6H_4, $J_{AB} = 9.0$); 3.76 (s, CH_3). ^{13}C NMR: see Table I.

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