A New Performance of the Reaction of $PCl_3/AlCl_3$ with Anisoles − One-Pot and Multi-Step Syntheses of a New Fused-Ring System [1,2,3]Benzoxadiphospholo[2,3-*b*][1,2,3]benzoxadiphosphole

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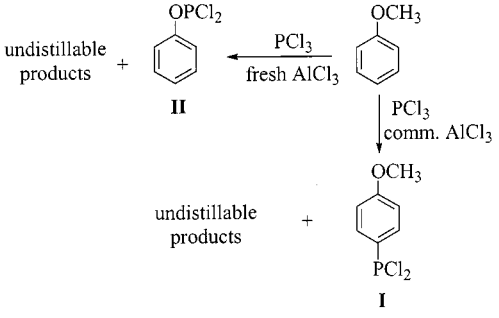
Anisoles **4** react with $AlCl_3$ and PCl_3 to yield the new fused bicyclic system derivatives **5** and **6** as major products in a one-pot procedure. An alternative multi-step synthesis of this system is also reported in which bis(*o*-methoxyaryl)phosphane oxides **11** are treated with $AlCl_3$ and PCl_3; the diarylphosphane oxides **11** are obtained by a new simple method.

Introduction

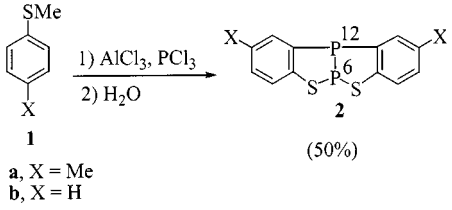
Since the last century the Friedel−Crafts-type reaction using PCl_3 and $AlCl_3$ has been an excellent method for the direct attachment of a phosphorus atom to an aromatic ring to give aryldichlorophosphanes or diarylchlorophosphanes. However, this reaction is very sensitive to the type of substituents present on the aromatic ring[1,2] and the literature often gives conflicting results.[3,4] In particular, it is reported[4a] that anisole upon treatment with phosphorus trichloride and aluminium chloride, afforded *p*-anisylphosphonous dichloride (**I**) but in very poor yields and with large amounts of undistillable residues, while in some cases it gave phenylphosphorodichloridite (**II**) but always in poor yields. In addition, it is reported[4a,4b] that this phosphonation reaction fails completely when thioanisoles are used (Scheme 1).



Scheme 1. Literature-known results from the reaction between anisole or thioanisole and $AlCl_3/PCl_3$

To increase the yield and the selectivity of this phosphonation reaction on anisoles and thioanisoles, the $AlCl_3$ catalyst has been replaced[4a] by $SnCl_4$ and, very recently,[4b] by $BiCl_3$.

In contrast to these reported results, in recent years, we discovered[5] that the reaction of PCl_3 and $AlCl_3$ with thioanisoles **1** gave, unexpectedly, the new fused bicyclic system[6] **2** (fused 1,2,3-benzothiadiphosphole) in good yields (see Scheme 2). In addition, we found that the reaction is very dependent on the ratio of the reagents and on the quality of the $AlCl_3$, which, in this reaction, is not a catalyst, but a reagent. The best yields of **2** were obtained with freshly sublimed $AlCl_3$ and a ratio 1:0.6:2−4 of thioanisole **1**/$AlCl_3/PCl_3$ and final quenching with water.



Scheme 2. One-pot synthesis of **2**

The molecular structure of **2** was determined[5a] by X-ray analysis with the molecule adopting a butterfly-like structure with the phosphorus electron lone pairs in a *cis* configuration and in an eclipsed conformation. Recently, the course of this anomalous reaction has been studied[5c] by ^1H and ^{31}P NMR and it was seen that the benzothiadiphosphole system is formed by a "domino reaction" as reported in Scheme 3. Probably, because of the relative complexity of the structure of **2**, its formation from this simple and well-known reaction was never observed. It should be noted that the final phosphonium salt **G** does not give, after treatment with water, the expected product of hydrolysis **3**, but gives **2a** as a product of reduction. At that time, this result was unexplained.

Results and Discussion

On analysis of the data on anisoles reported[4] above and our results[5] on thioanisoles, we decided to reinvestigate the reaction of anisoles **4** with the couple $PCl_3/AlCl_3$, in order

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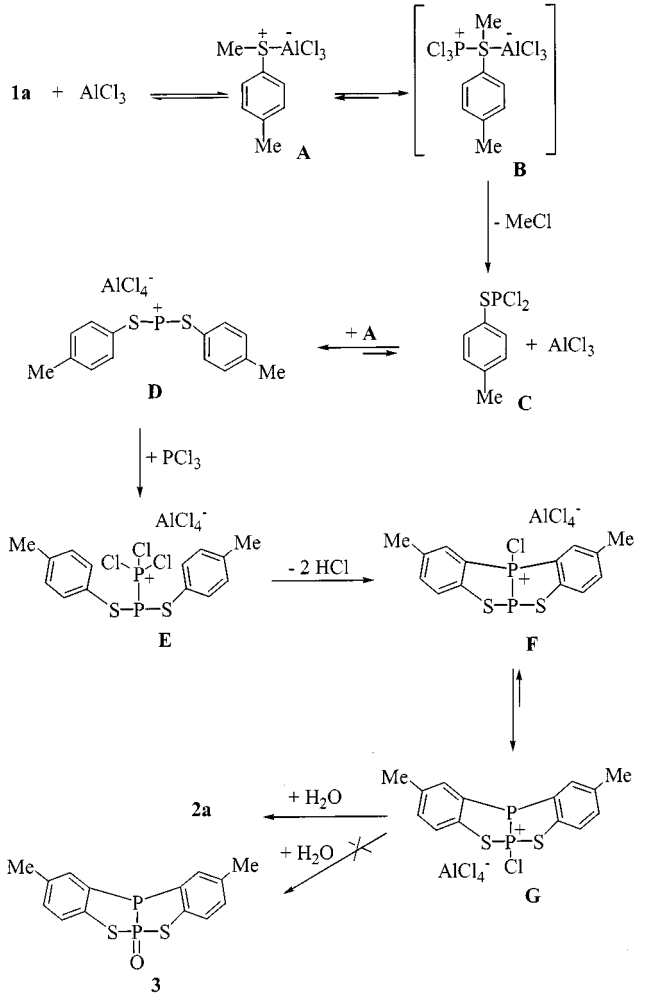
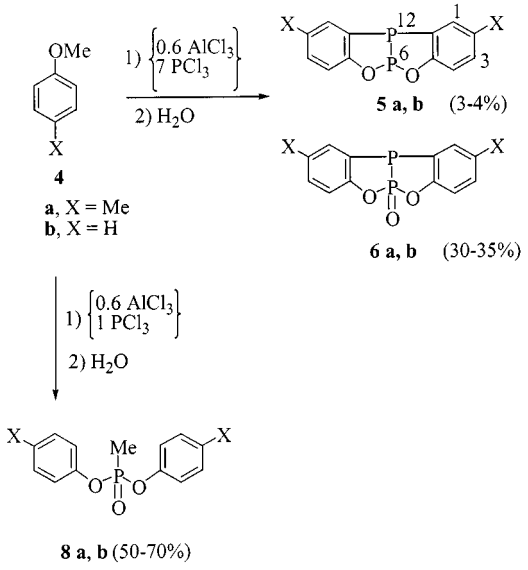


Scheme 3. Pathway of the domino reaction giving the benzothiadiphosphole system

to verify whether the reported[3,4] large amounts of undistillable residues and the conflicting reported results might be due to the formation of heterocyclic compounds related to **2** or of other unexpected products.

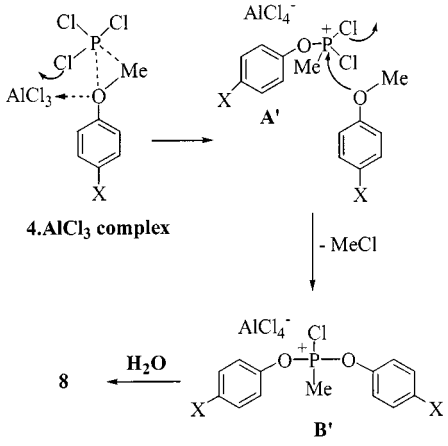
At the beginning of this study we noted by GLC-MS that the reaction of PCl_3 and $AlCl_3$ with *p*-methylanisole (**4a**) is indeed very complex as it gives a reaction mixture containing several products. We found great variations in these final products and in their relative ratios on varying the ratio of the reagents and reaction conditions. However, we noted, under some reaction conditions, the formation of traces of heterocycle **5a** among several other products. The identification of **5a** was facilitated by comparison of its mass spectra fragmentations with the fragmentations of **2a.**

Recently, after several studies on the structure of the other products, we found[7] that, when the reaction is carried out under appropriate reaction conditions, an unexpected "insertion" of a phosphorus moiety into the O−Me bond of anisole **4** occurs, to give compound **8** as the major product in place of the expected Friedel−Crafts phosphonation (Scheme 4). The best selective formation of **8** (50−70% yield) was obtained with an anisole **4**/$AlCl_3$/PCl_3 ratio of 1:0.6:1, at 70−80 °C for 7−10 h under dry nitrogen and without solvent.



Scheme 4. Results obtained from the reaction of anisole and $AlCl_3$/PCl_3 in different ratios of the reagents

A suggested mechanism, depicted in Scheme 5, for this phosphorus insertion reaction was also reported.[7] The insertion of a P moiety is explained by the attack of a molecule of PCl_3 on an anisole−$AlCl_3$ complex and subsequent migration of the methyl group to the same P atom giving the intermediate **A′**. Subsequent nucleophilic attack of free anisole on phosphonium salt **A′** gives **B′** which, after quenching with water, gives phosphonate **8**.

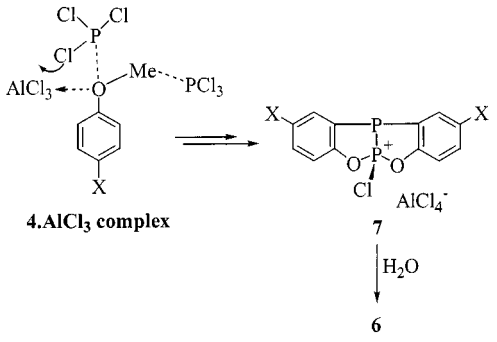


Scheme 5. Pathway of the formation of **8**

It should be noted that in the same reagent ratios and reaction conditions thioanisoles **1** did not give formation of P−Me compounds related to **8** and the single product was always **2**. This fact may be explained as follows: In the case of thioanisole the S atom can be hypervalent such as in intermediate **B** of Scheme 3, while in the case of anisole the O atom cannot give this hypervalent coordination. In the first step it prefers to expel the Me group which is captured by a phosphorus atom giving stable intermediate **A′** (as de-

picted in Scheme 5) thus explaining the insertion of the P moiety on the O−Me bond.

After repeated attempts varying the reagent ratios and reaction conditions, we have been able to obtain the benzooxadiphosphole system as prevalent product (30−40% yield), as reported in Scheme 4 using a ratio of **4a**/$AlCl_3$/PCl_3 of 1:0.6:7 and refluxing for about 20−25 h without solvent. In contrast with the reaction with thioanisoles **1**, the reaction with anisole **4a** gives a large amount of its monoxide **6a** and only traces of the benzooxadiphosphole **5a**. An amount of 10−20% of **8a** was also obtained. Presumably, the formation of the benzooxadiphosphole derivatives **5a** and **6a** is favoured, with respect to the formation of **8**, by the large excess of PCl_3. Thus, the concomitant methylation of the same phosphorus atom which attacks the oxygen atom of anisole giving the intermediate **A′** (as reported in Scheme 5) is unfavourable in the first step.This is because the anisole−$AlCl_3$ complex now presumably undergoes attack by two or more molecules of PCl_3, as depicted in Scheme 6. The subsequent steps of the pathway for the formation of **6** are, tentatively, very similar to the domino reaction reported[5c] for the formation of **2** (Scheme 3).



Scheme 6. Intermediate **7** to obtain **6**

It should be noted that compounds **5a** and **6a** are very oxygen- and water-sensitive and that their prolonged workup gives oxidation and decomposition products. In addition, chromatographic purification cannot be performed. The proposed structure for **5a** is mainly supported by its NMR-spectroscopic data. The ^{31}P NMR spectrum shows the presence of two magnetically non-equivalent phosphorus atoms and the presence of a large coupling between them (J_{PP} = 175 Hz) indicates the presence of a P−P bond. The strongly deshielded doublet at δ = 188.0 can be unambiguously assigned to the phosphorus atom between the two oxygen atoms whereas the other signal at δ = −11.8 as a doublet of triplets (J_{PP} = 175 Hz, J_{PH} = 6 Hz) is unambiguously assigned to the other phosphorus atom. In addition, these values are in good agreement with or very close to those reported for related nonfused 1,2,3-benzoxadiphosphole derivatives obtained as decomposition products from the distillation of *o*-phosphanylphenols.[8] The mass spectrum of **5a** exhibit ion peaks at *m*/*z*: 274 [M^+], 227 (base peak, [M^+ − PO]), 211, 197, 153, 121, 77, 47 [PO]. It should be noted that the mass spectrum of the related compound **2a** exhibits ion peaks at *m*/*z*: 306 [M^+], 243 (base peak) [M^+ − PS], 211, 197, 153, 121, 77, 63 [PS]. As a consequence of the assignment of **5a**, the structure of **6a** is easily deduced from its mass and NMR spectra. Its mass peaks are: *m*/*z*: 290 (base peak) [M^+], 243 [M^+ − PO], and 227 [M^+ − PO_2], 196, 152, 121, 77, 47. The ^{31}P NMR spectrum of **6a** contains a set of two doublets; the ones at lower field (δ = 69.9, J_{PP} = 209 Hz) being assignable to the OP(O)O phosphorus atom while the other as doublet of triplets (δ = −112.5, dt, J_{PP} = 209 Hz, J_{PH} = 7 Hz) characterises the phosphane phosphorus atom. The configuration of **5a** and **6a** should be *cis* according to the structure of related benzothiadiphosphole **2** determined by X-ray analysis and as predicted by semi-empirical MM2 calculations. This predicted configuration was ascribed to easier accommodation of the long P−P bond in the *cis* relative to the *trans* isomer and this preference appears to be general, according to other fused-ring systems.[9]

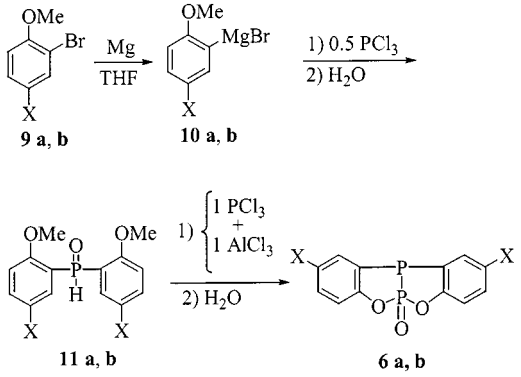
When the reaction was carried out with **4b**, products **5b** and **6b** were obtained in minor amounts, 20−25% yield. The ^{31}P NMR spectrum of **5b** shows a doublet at δ = 186 (J_{PP} = 175 Hz) and a doublet of triplets at δ = −13 (J_{PP} = 175 Hz, J_{PH} = 7 Hz), while **6b** (as white solid, m.p. 166−167 °C) shows a doublet at δ = 69.3 (J_{PP} = 211 Hz) and a doublet of triplets at δ = −114 (J_{PP} = 211 Hz, J_{PH} = 7 Hz). The mass spectrum of **5b** exhibits ion peaks at *m*/*z*: 246, 199 (base peak) [M^+ − PO], 183, 170, 152, 107, 69, 47, while the mass spectrum of **6b** exhibits ion peaks at *m*/*z*: 262 (base peak), 215 [M^+ − PO], 199, 168, 152, 107, 69, 47.

In order to obtain supporting evidence for a possible pathway of this presumed domino reaction, aliquots of the reaction mixture from **4a**, $AlCl_3$ and PCl_3 were analysed by ^{31}P NMR spectroscopy. After 10 h and after removal of PCl_3, the $^{31}P(^1H)$ NMR spectrum showed several signals at δ = 178, 158, 104, 69, and 49 as broad singlets and an intense doublet of doublets at δ = 88.3 (d, J_{PP} = 262 Hz), −105.0 (dt, J_{PP} = 262 Hz, J_{PH} = 7.5 Hz). At the end of the reaction we noted the prevalence of the above doublets over the singlets and after addition of water we noted the disappearance of the above doublets and the appearance of the doublets of **6a**. Very small signals of the doublets of **5a** were also observed. Thus, the couple of doublets, observed before quenching with water, might be assigned to the final intermediate **7** in Scheme 6. From these data we can affirm that the final intermediate **7** corresponds to the final intermediate **G** (Scheme 3) observed for the same reaction with thioanisole **1**, but the results of the treatment with water are very different. In fact the treatment of phosphonium salt **7** with water gives the expected product of hydrolysis **6** while the same treatment of phosphonium salts **G** gives **2** as an unexpected reduction product.

It should be noted that compounds **5** are very unstable, air- and moisture-sensitive compounds, while the related bicyclic compounds **2** are very stable and air-insensitive solids. This difference is due only to the replacement of two oxygen atoms with the sulfur atoms. We think that this simple substitution might favour a quasi-aromatic structure

or a more delocalised structure in the case of compounds **2** in contrast to **5**. This stabilization of **2** might also be responsible for its preferred formation with respect to the oxidized derivative **3** in the final hydrolysis of its precursor phosphonium salt **G** (Scheme 3). In contrast, the oxidised derivative **6** is preferred in the case of **5**. The quasi-aromatic structure of **2** might explain also the large difference between the ^{31}P NMR spectra of **5a** [δ = 188.0 (d, P-6); −11.8 (dt, P-12, $^{3}J_{PH}$ = 6 Hz, $^{1}J_{PP}$ = 175 Hz)] and the ones of **2a** [δ = 88.3 (d, P-6); δ = 65.4 (dt, P-12, $^{3}J_{PH}$ = 7.8 Hz, $^{1}J_{PP}$ = 211.5 Hz)] in which we have two signals for the two P atoms in the same region, indicating a possible delocalization of the two P lone pairs.

In order to obtain other data to support the structures of the benzo-fused compound **6** we carried out a multi-step synthesis of this system. As reported in Scheme 7, in the first step *o*-bromoanisole **9** was transformed to its Grignard derivative **10**. In the second step **10** was transformed to diarylphosphane oxide **11** by PCl_3 in high dilution with THF and then hydrolysis. In the last step, again using the couple $PCl_3/AlCl_3$, demethylation, formation of two O−P bonds, and formation of one P−P bond yield **6** in a one-pot procedure.



Scheme 7. Alternative multi-step synthesis of **6**

It should be noted that the described formation of **11** is a new and simple synthesis of this type of phosphorus derivatives. In fact, according to the literature[10] these compounds are formed in a dry box under nitrogen by reaction of aryllithium compounds with diethyl phosphite.

Conclusion

We have reported that the "domino reaction" which occurs when thioanisole reacts with the couple $PCl_3/AlCl_3$ giving the fused bicyclic system **2** can occur also with anisoles giving the related fused system **5**, but with a very large amount of its monoxide **6**. However, for anisoles, the best reaction conditions have been more difficult to find because another unexpected reaction (insertion of a P moiety into the O−Me bond) giving diaryl methylphosphonates **8** can also occur. We have, however, been able to control the two different pathways by simple control of the reagent ratios and reaction conditions. These results also give an explanation about the limited success in the phosphonation of anisoles obtained so far with the same reagents. In addition, we have applied the reactivity of the couple $PCl_3/AlCl_3$ to bis(*o*-methoxyaryl)phosphane oxides **11** to form in a one-pot procedure two O−P bonds and one P−P bond to yield **6**. Finally, these findings represent a generalisation of a facile one-pot route to obtain benzo-fused systems containing the P−PX_2 unit (X = S, O, etc.). It should be noted that recently the fused-ring compound **2a** has been used[11] as an efficient phosphorus-donating reagent and **6a** might also be an interesting P=O donating reagent.

Experimental Section

General Remarks: ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a Varian Gemini spectrometer at 300 MHz, 75.46 MHz, and 120.75 MHz, respectively, in $CDCl_3$. Chemical shifts are referenced to internal standard TMS (^{1}H NMR), to solvent (δ = 77.0 for ^{13}C NMR), and to external standard 85% H_3PO_4 (^{31}P NMR); *J* values are given in Hz. − IR spectra were recorded with a Perkin−Elmer spectrophotometer model 1600 FT-IR. IR spectra of compounds **6a** and **6b** showed typical signals: P=O (1254 cm^{-1}), P−O−C (1086 cm^{-1}) and P−Ph (1466 cm^{-1}). − MS data were recorded at an ionisation voltage of 70 eV with a VG 7070 E spectrometer. GC-MS analyses were performed with an HP-5890 gas chromatograph equipped with a methyl silicone capillary column and an HP-5970 mass detector. − Thin-layer chromatography was performed on Merck Kieselgel 60 F_{254}. Melting points were measured with a Büchi apparatus and are uncorrected. − THF was distilled from sodium benzophenone ketyl. All reagents were commercial samples (Aldrich). Air- and moisture-sensitive solutions and reagents were handled in a dried apparatus under dry nitrogen. Chemical and physical data of compounds **8a** and **8b** are in agreement with literature values.[7]

One-Step Synthesis of the [1,2,3]Benzooxadiphospholo[2,3-*b*][1,2,3]-benzooxadiphosphole Systems 5a,b and 6a,b from Anisoles 4a,b and $PCl_3/AlCl_3$. − Typical Procedure: *p*-Methylanisole (**1a**) (5.04 mL, 0.04 mol), $AlCl_3$ (3.20 g, 0.024 mol), and PCl_3 (24.26 mL, 0.28 mol) were placed in a dried apparatus, filled with dry nitrogen. The mixture was stirred at 80 °C. The reaction was monitored by GC-MS analysis. After about 20−25 h, the reaction mixture was treated quickly with a mixture of water and dichloromethane. After extraction with dichloromethane, the organic layer was dried with anhydrous Na_2SO_4 and the solvent was removed giving a greasy mixture containing **5a**, **6a**, and **8a** in the ratio of about 1:7:2. After removing **8a** by bulb-to-bulb distillation at 0.1 Torr at 200 °C, the undistillable residue was crystallised from CH_2Cl_2/Et_2O giving a white solid, containing compounds **5a** and **6a** in a 1:7 ratio. Fast recrystallization of this solid gave pure **6a** (2.13 g, 35%) as a white solid. The procedure shown above was followed using the anisole **4b** as reagent. From this reaction, compound **5b** was obtained in traces and **6b** in 20−25% yield.

2,10-Dimethyl[1,2,3]benzooxadiphosphole[2,3-*b*][1,2,3]benzooxadiphosphole (5a): $^{31}P\{^{1}H\}$ NMR (120.75 MHz, $CDCl_3$): δ = 188.0 (d, J_{PP} = 175 Hz, P-6), −11.8 (dt, J_{PP} = 175 Hz, J_{PH} = 6 Hz, P-12). − MS (70 eV, EI): *m/z* (%) = 274 [M^+] (95), 227 [M^+ − PO] (100), 211 (45), 197 (26), 153 (18), 121 (20), 77 (28), 63 (35).

2,10-Dimethyl-6λ^5-[1,2,3]benzooxadiphosphole[2,3-*b*][1,2,3]benzooxadiphosphol-6-one (6a): M.p. 176−177 °C (from CH_2Cl_2/Et_2O).

− ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.30 (s, 6 H, CH_3), 6.95−7.50 (m, 2 H, 3-H, 9-H), 7.10−7.18 (m, 2 H, 4-H, 8-H), 7.32−7.39 (m, 2 H, 1-H, 11-H). − $^{31}P\{^1H\}$ NMR (120.75 MHz, $CDCl_3$): δ = 69.9 (d, J_{PP} = 209 Hz, P-6), −112.5 (dt, J_{PP} = 209 Hz, J_{PH} = 7.0 Hz, P-12). − MS (70 eV, EI): *m*/*z* (%) = 290 [M^+] (100), 243 [M^+ − PO] (75), 227 (45), 196 (26), 152 (7), 121 (11), 77 (9), 47 (32). − HRMS: calcd. for $C_{14}H_{12}O_3P_2$: 290.0262, found 290.0266; calcd. C 57.95, H 4.17; found C 57.87, H 4.12.

[1,2,3]-Benzooxadiphosphole[2,3-*b*][1,2,3]benzooxadiphosphole (5b): $^{31}P\{^1H\}$ NMR (120.75 MHz, $CDCl_3$): δ = 186.0 (d, J_{PP} = 175 Hz, P-6), −13.0 (dt, J_{PP} = 175 Hz, J_{PH} = 7.0 Hz, P-12). − MS (70 eV, EI): *m*/*z* (%) = 246 [M^+] (95), 199 [M^+ − PO] (100), 183 (15), 170 (18), 152 (20), 107 (16), 69 (28), 47 (25).

[1,2,3]-Benzooxadiphosphole[2,3-*b*][1,2,3]benzooxadiphosphol-6-one (6b): M.p. 165−166 °C (from CH_2Cl_2/Et_2O). − ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.07−7.19 (m, 4 H, 2-H, 3-H, 9-H, 10-H), 7.35−7.42 (m, 2 H, 4-H, 8-H), 7.58 (dd, J_{PH} = J_{HH} = 7.1 Hz, 2 H, 1-H, 11-H). − $^{31}P\{^1H\}$ NMR (120.75 MHz, $CDCl_3$): δ = 69.3 (d, J_{PP} = 211 Hz, P-6), −114.0 (d, J_{PP} = 211 Hz, J_{PH} = 7.1 Hz, P-12). − MS (70 eV, EI): *m*/*z* (%) = 262 [M^+] (100), 215 [M^+ − PO] (72), 199 (38), 168 (48), 152 (13), 107 (15), 69 (26), 47 (24). − HRMS: calcd. for $C_{12}H_8O_3P_2$: 261.9949, found 261.9945; calcd. C 54.98, H 3.08, found C 54.83, H 3.02.

Two-Step Synthesis of Benzooxadiphospholes 6a,b from *o*-Bromoanisoles 9a,b. − Preparation of 11a and 11b. − Typical Procedure: A solution of PCl_3 (0.654 mL, 0.0075 mol) in THF (30 mL) was placed in a dried apparatus filled with dry nitrogen. A solution of 2-(4-methyl)anisylmagnesium bromide [prepared from 2-bromo-4-methylanisole (**9a**) (2.17 mL, 0.015 mol) and magnesium turnings in THF (30 mL)] was added dropwise and under quick stirring, at 0 °C for 4 h. After the addition, the mixture was left under stirring at room temperature, and the reaction was monitored by GC-MS analysis. After 5 h the reaction mixture was hydrolysed with an aqueous acid solution for almost 30 min. After extraction with dichloromethane, the organic layer was dried with anhydrous Na_2SO_4 and the solvent was removed. The residue was crystallised from CH_2Cl_2/Et_2O giving a white solid containing compound **11a** (0.76 g, 70%). The procedure shown above was followed using 2-bromoanisole (**9b**) as reagent. From this reaction compound **11b** was obtained in 70% yield.

Bis(2-methoxy-5-methylphenyl)(oxo)phosphorane (11a): R_F = 0.15 (in Et_2O). − ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.31 (s, 6 H, CH_3), 3.74 (s, 6 H, OCH_3), 6.77−6.85 (m, 2 H, 4-H), 7.27−7.34 (m, 2 H, 3-H), 7.41 (dd, $^3J_{PH}$ =15.3, ^4J = 2.4 Hz, 2 H, 6-H), 8.22 (d, J_{PH} = 520 Hz, 1 H, PH). − $^{31}P\{^1H\}$ NMR (120.75 MHz, $CDCl_3$): δ = 10.0 (dt, J_{PH} = 520 Hz, J_{PH} = 15 Hz). − MS (70 eV, EI): *m*/*z* (%) = 290 [M^+] (100), 259 (52), 241 (39), 135 (95), 105 (54). − HRMS: calcd. for $C_{16}H_{19}O_3P$: 290.1072, found 290.1067, calcd. C 66.20, H 6.60; found C 66.05, H 6.45.

Bis(2-methoxyphenyl)(oxo)phosphorane (11b): M.p. 136 °C (ref.[11a] 135−136 °C), R_F = 0.30 (in Et_2O). − ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.76 (s, 6 H, OCH_3), 6.90 (dd, ^3J =8.5, ^3J = 6.0 Hz, 2 H, 4-H), 7.02−7.12 (m, 2 H, 5-H), 7.46−7.56 (m, 2 H, 3-H), 7.67 (qd, ^3J =7.5 Hz, $^3J_{PH}$ = 15.0, ^4J = 1.8 Hz, 2 H, 6-H), 8.25 (d, J_{PH} = 515 Hz, 1 H, PH). − $^{31}P\{^1H\}$ NMR (120.75 MHz, $CDCl_3$): δ = 8.2 (dt, J_{PH} = 515 Hz, $^3J_{PH}$ = 15 Hz). − MS (70 eV, EI): *m*/*z* (%) = 262 [M^+] (100), 231 [M^+ − 31] (31), 213 (44), 121 (85), 91 (32). − HRMS: calcd. for $C_{14}H_{15}O_3P$: 262.0759, found 262.0709.

Reaction of 11a and 11b with $AlCl_3/PCl_3$. − Typical Procedure: Compound **11a** (0.46 g, 0.0016 mol), PCl_3 (0.96 mL, 0.0075 mol), and $AlCl_3$ (0.22 g) were placed in a dried apparatus filled with dry nitrogen. The mixture was stirred at 80 °C, and the reaction was monitored by GC-MS analysis. After 4 h, the reaction mixture was quickly treated with a mixture of water and dichloromethane. After extraction with dichloromethane, the organic layer was dried with anhydrous Na_2SO_4 and the solvent was removed. The residue was crystallised from CH_2Cl_2/Et_2O giving **6a** (0.232 g, 50%). The procedure shown above was followed using compound **11b** as reagent. From this reaction compound **6b** was obtained in 53% yield.

Reaction of *p*-Methylthioanisole (1a)/$AlCl_3/PCl_3$ (1.0:0.6:1.0): A solution of *p*-methylthioanisole (**1a**) (13.26 mL, 0.1 mol), PCl_3 (8.7 mL), and $AlCl_3$ (0.6 mol) (sublimed prior to use) was refluxed and stirred under dry nitrogen for 10 h. The reaction mixture was treated with a mixture of ice and dichloromethane; the organic layer was washed with a 5% aq. NaOH solution and twice with water. After removal of the solvent, no traces of methylphosphorylation products were detected, only benzothiadiphosphole **2a**.

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