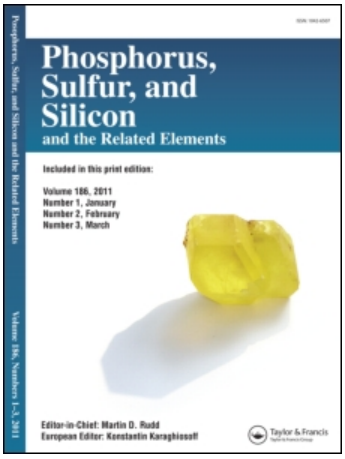

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of Diaminophosphonium Salts $[Ph_2(ArNH)_2P]^+Br^-$ (Ar = *o*-MeC_6H_4, *p*-MeC_6H_4, *p*-$Pr^{<i>i</i>}C_6H_4$, *p*-$EtO_2CC_6H_4$, *p*-$MeOC_6H_4$)

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To cite this Article Gusev, O. V. , Peganova, T. A. , Gonchar, A. V. , Petrovskii, P. V. , Lyssenko, K. A. and Ustynyuk, N. A.(2009) 'Synthesis of Diaminophosphonium Salts $[Ph_2(ArNH)_2P]^+Br^-$ (Ar = *o*-MeC_6H_4, *p*-MeC_6H_4, *p*-$Pr^{<i>i</i>}C_6H_4$, *p*-$EtO_2CC_6H_4$, *p*-$MeOC_6H_4$)', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 2, 322 — 331
To link to this Article: DOI: 10.1080/10426500802116073
URL: http://dx.doi.org/10.1080/10426500802116073

Phosphorus, Sulfur, and Silicon, 184:322–331, 2009

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802116073

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Synthesis of Diaminophosphonium Salts $[Ph_2(ArNH)_2P]^+Br^-$ (Ar = *o-*MeC_6H_4, *p-*MeC_6H_4, *p-*$Pr^iC_6H_4$, *p-*$EtO_2CC_6H_4$, *p-*$MeOC_6H_4$)

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The behavior of different anilines $H_2NC_6H_4R$ (*R* = o-*Me,* p-*Me,* o-, m- *and p–*^{i}*Pr,* p-*OMe,* p-CO_2Et) *and 2,6-*$Me_2C_6H_3NH_2$ *towards trihalophosphoranes was studied. 2,6-*$Me_2C_6H_3NH_2$ *failed to form the diaminophosphonium salt [*$Ph_2P\{NH(2,6\text{-}Me_2C_6H_3)\}_2$*]Br, and the aminophosphine oxide* $Ph_2(2,6\text{-}Me_2C_6H_3NH)PO$ *was the only isolated product. Both* o- *and* p-*toluidine gave the corresponding diaminophosphonium salts; however in the case of o-toluidine, the yield was low and a mixture with the respective aminophosphine oxide was observed. Anilines containing methoxy and ethoxycarbonyl groups in* para-*position form the diaminophosphonium salts in reasonable yields.*

Keywords Anilines; diaminophosphonium salts; ^{1}H, ^{31}P NMR spectra; X-ray structure

INTRODUCTION

Diaminophosphonium salts $[R_2P(NHR')_2]^+X^-$ are convenient starting materials for synthesis of chelate complexes $[M]\{(NR')_2PR_2\}$.[1–3] In recent years, the latter have attracted considerable attention as potential catalysts. Although the first representatives of these compounds were synthesized in 1970s, there is still no systematic study of this class of substances. Two reviews dedicated to phosphazane and phosphazene complexes[4] and to metallated phosphonium ylides[5] have been published, which consider only partly the problems of synthesis of aminoiminophosphoranate complexes and their organophosphorus precursors. A new impetus to the investigation of these compounds

Received 24 March 2008; accepted 8 April 2008.
The authors are thankful to Exxon Mobil Chemical Company for financial support.
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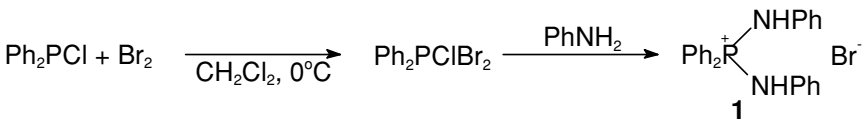
has been given by reports on the activity of aminoiminophosphoranate complexes in a series of catalytic processes.[3,6–9] A further development of this field is essentially restricted by the low accessibility of diaminophosphonium salts $[R_2P(NHR')_2]^+X^-$ as the most general precursors of aminoiminophosphoranate complexes. The main synthetic routes to these salts include aminolysis/chloroaminolysis of dialkylchlorophosphines or tetraalkyldiphosphines,[10,11] interaction of tetraalkyl- or tetraphenyldiphosphines with carbon tetrachloride in the presence of primary amines,[12] quaternization of diaminophosphines by alkyl halides,[1,13] and *in situ* generation of trihalophosphoranes followed by the reaction with primary alkyl amines.[14,15] The latter approach, developed by Cristau and Garcia,[14] seems to be the most efficient and most often used. To expand the set of diaminodiphenylphosphonium salts, we applied the Cristau reaction to some substituted anilines and the results obtained are presented here.

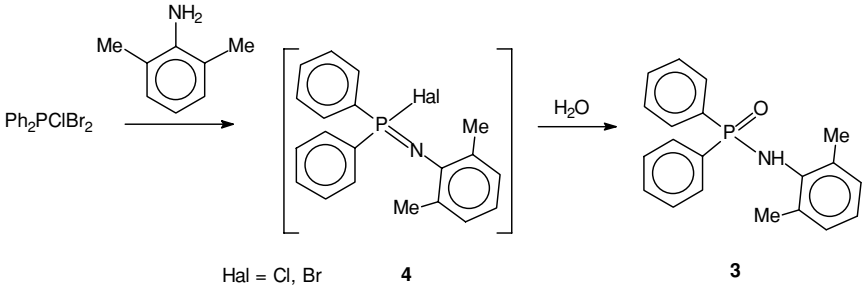
RESULTS AND DISCUSSION

As mentioned above, diphenyl bis(phenylamino) phosphonium bromide $[Ph_2P(NHPh)_2]^+Br^-$ (**1**) was prepared by Cristau and Garcia[14] from aniline according to Scheme 1; substituted anilines were practically not used in these reactions, however.

We studied the reaction shown in Scheme 1 with some substituted anilines and found that the nature and position of the substituent exert considerable influence on the reaction outcome. The reaction of 2,6-dimethylaniline with Ph_2PClBr_2 did not yield the diaminophosphonium salt $[Ph_2(2,6\text{-}Me_2C_6H_3NH)_2P]^+Br^-$ (**2**) even after prolonged refluxing in methylene chloride; instead, the new aminophosphine oxide **3** was isolated and characterized by elemental analysis and spectroscopic data (^{31}P NMR: a singlet at $\delta = 20.8$; ^1H NMR: $\delta = 2.26$ and 6.93 ($2,6\text{-}Me_2C_6H_3$); $\delta = 7.39$, 7.48, and 7.81, Ph, corresponding to two aryl moieties in the ratio of 1:2). Presumably, the bulkiness of two *o*-methyl groups forces the reaction to stop at the step of the monosubstituted



SCHEME 1



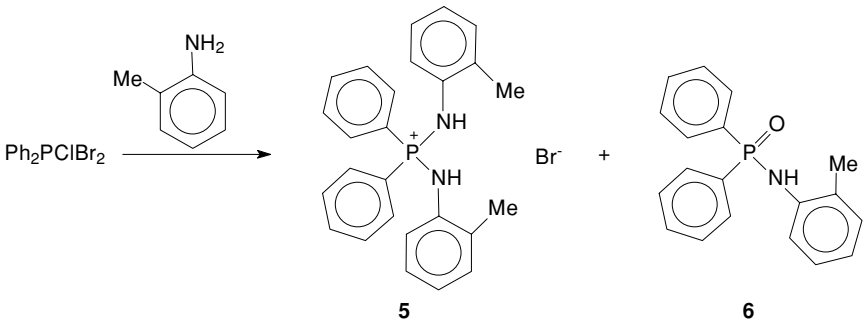
SCHEME 2

product [Ph_2(2,6-$Me_2C_6H_3N$=)PHal] (**4**); its hydrolysis during workup gives **3** as the only isolable product (Scheme 2).

The less bulky *o*-toluidine in this reaction afforded a mixture of the phosphonium salt [Ph_2(2-$MeC_6H_4NH)_2P]^+Br^-$ (**5**) and the aminophosphine oxide Ph_2(2-MeC_6H_4NH)PO (**6**) (Scheme 3).

Analytically pure **5** was obtained by fractional crystallization from isopropyl alcohol; however, the yields did not exceed 20–25 %. The phosphorus resonance in **5** ($\delta = 30.4$) is similar to that reported for **1**;[14] the singlet at $\delta = 2.29$ in the ^{1}H NMR spectrum of **5** corresponds to the methyl groups and indicates free rotation of the 2-MeC_6H_4NH moiety. The signals of the hydrogen atoms of the phenyl rings have chemical shifts and coupling constants typical for compounds of this type.

The molecular geometry of the diaminophosphonium salt **5** was determined by X-ray crystallography (Figures 1 and 2). The phosphorus atom in **5** has a distorted tetrahedral configuration with the N(1)P(1)N(2) angle increased to 119.6(1) degrees. The nitrogen atoms are essentially flattened, the sums of the bond angles are 359.1 degrees



SCHEME 3

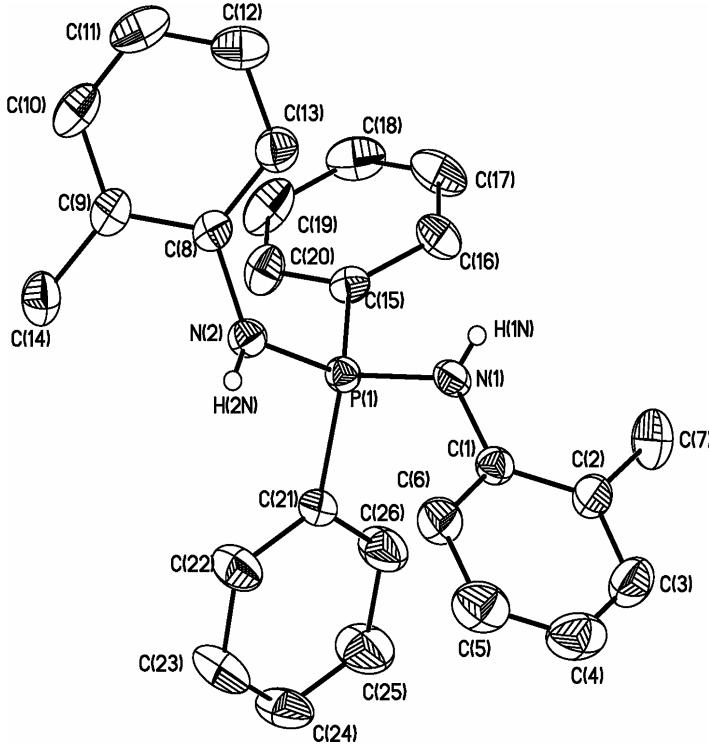


FIGURE 1 ORTEP plot of the diaminophosphonium cation in 5. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths (Å): P(1)-N(1) 1.625(2), P(1)-N(2) 1.633(2), P(1)-C(15) 1.793(2), P(1)-C(21) 1.796(2), N(1)-C(1) 1.434(3), N(2)-C(8) 1.441(3), and bond angles (°): N(1)-P(1)-N(2) 119.64(11), N(1)-P(1)-C(15) 107.37(11), N(2)-P(1)-C(15) 107.03(11), N(1)-P(1)-C(21) 106.30(11), N(2)-P(1)-C(21) 106.92(11), C(15)-P(1)-C(21) 109.32(10), C(1)-N(1)-P(1) 126.96(18), C(8)-N(2)-P(1) 127.76 (17).

and 357.8 degrees for N(1) and N(2), respectively. It should be noted that the bond P(1)–N(2), 1.633(2)Å, is slightly elongated compared to the bond P(1)–N(1), 1.625(1) Å. Such differences in the configuration of the nitrogen atoms can be caused by intermolecular hydrogen bonding. Indeed, the phosphonium cations in the crystal are assembled to infinite chains along the crystallographic *b* axis by rather short N-H. . . Br bonds with similar N. . . Br distances of 3.418(3) Å and 3.356(3) Å for N(1) and N(2), respectively (Figure 2).

Using the geometry of **5** obtained by X-ray diffraction as the starting point, we have performed DFT calculations (PBE/TZ2p) of the cation $[Ph_2(2,6\text{-}Me_2C_6H_3NH)_2P]^+$using the PRIRODA program package.[16]

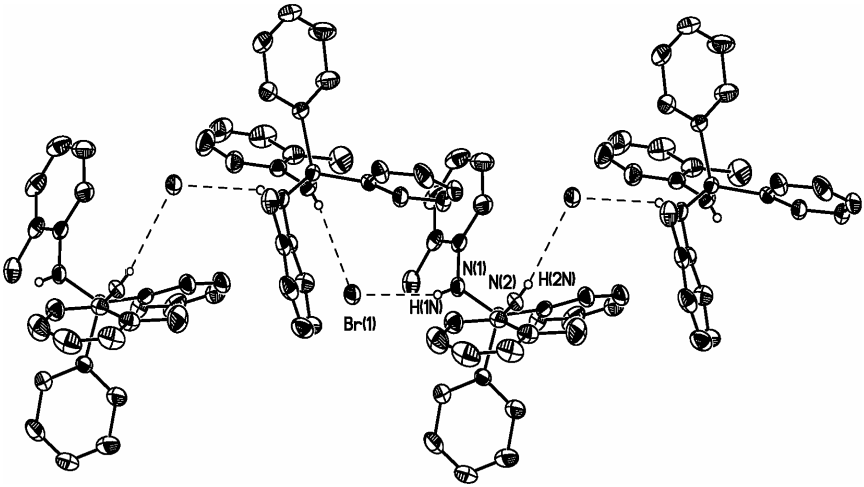


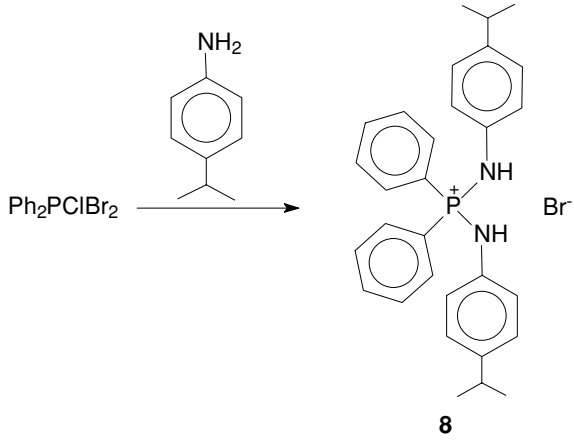
FIGURE 2 The N-H. . . Br bonded chains in the crystal of **5**. The parameters for the hydrogen bonds are N(1). . . Br(1) 3.431(1) Å, H(1N). . . Br(1) 2.51 Å, N(1)-H(1N)-Br(1) 157°; N(2). . . Br(1) 3.358(1) Å, H(2N). . . Br(1) 2.54 Å, N(2)-H(2N)-Br(1) 168°.

The optimization of the cation geometry revealed that although the presence of the methyl groups at C(6) and C(13) (Figure 1) results in some steric repulsion between these methyl groups and the atom N(1), the intramolecular contacts in the cation are in general within the sum of the van-der-Waals radii. Thus according to DFT calculations, the steric overcrowding cannot fully explain the low yields of **5** and the impossibility of formation of **2**.

The reaction of *p*-toluidine leads smoothly to the phosphonium salt $[Ph_2(p\text{-}MeC_6H_4NH)_2P]Br$ (**7**) in 59% yield. The phosphorus resonance was observed at $\delta = 28.0$, close to the corresponding resonances in **1** and **5**. It is noteworthy that the corresponding chloride salt has been recently synthesized from Ph_2PCl_3 and *p*-tolylamine.[3]

The presence of a bulky isopropyl group in the *para*-position of aniline also does not prevent the formation of the phosphonium salt **8**, which was obtained in 70% yield and characterized by elemental analysis and its spectroscopic data (Scheme 4).

The fact that *o*-substituted anilines are much less prone to form the corresponding diaminophosphonium salts allowed us to use the more easily available isomeric mixture of isopropyl aniline (71.5% *p*-, 25.6% *o*-, and 2.9% *m*-) instead of the pure *p*-isomer. Although the content of the *o*-isomer in this mixture is high, the formation of its phosphonium salt is sterically unfavorable, and it is mainly consumed to bind the



8

SCHEME 4

acid produced in the reaction. Trace amounts of the phosphonium salt that should form from *m*-isopropylaniline were probably lost during the workup procedure.

The anilines *p*-$MeOC_6H_4NH_2$ and *p*-$EtO_2CC_6H_4NH_2$ were reacted in the presence of triethylamine as HCl quencher. The corresponding bis(arylamino) diphenylphosphonium salts **9** and **10** were prepared in 35–40% yields and characterized by their spectroscopic data. The ^{31}P NMR spectra of **9** and **10** showed a singlet at 27.4 and 27.7, respectively. The diaminophosphonium bromides obtained are white crystalline air stable substances.

In summary we demonstrated that the Cristau reaction is very applicable to *p*-substituted anilines and gives the corresponding diaminophosphonium salts in reasonable yields, whereas *o*-substituted anilines do not easily afford the respective diaminophosphonium salts due to steric reasons.

EXPERIMENTAL

All reactions were carried out in dry argon atmosphere in freshly dried and distilled CH_2Cl_2; isolation and purification were performed in air. ^1H and ^{31}P NMR spectra were obtained with a Bruker AMX-400 spectrometer, and chemical shifts are given in δ scale relative to TMS and 85% H_3PO_4, respectively.

Single crystal X-ray diffraction analysis of **5**: ($C_{26}H_{26}N_2PBr$, M = 477.37), monoclinic, space group $P2_1/n$, measurement at 120(2) K: a = 11.731(1), b = 12.4295(10), c = 17.299(3) Å, β = 98.568(1)°,

V = 2494.2(5) Å^3, Z = 4 (Z′=1), d_{calc} = 1.271 g·cm^{-3}, μ(MoKα) = 17.26 ñm^{-1}, F(000) = 984. Intensities of 16,781 reflections were measured with a Bruker AXS Smart 1000 CCD (ω-scan, $\theta < 55.8^\circ$), and 5927 independent reflections [R_{int} = 0.0416] were used in further refinement. The refinement converged to wR2 = 0.0786 and GOOF = 0.945 for all independent reflections (R1 = 0.0393 was calculated against F for 3808 observed reflections with $I > 2\sigma(I)$). The hydrogen atoms of the NH groups were located from the Fourier density synthesis, while the positions of the other hydrogen atoms were calculated geometrically. All calculations were performed using SHELXTL PLUS 5.0. The crystallographic data for **5** have been deposited with the Cambridge Crystallographic Data Center, CCDC 623570. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Synthesis of Ph_2(2,6-$Me_2C_6H_3NH$)PO (3)

A solution of Br_2 (4.0 g, 1.26 mL, 25 mmol) in CH_2Cl_2(10 mL) was added dropwise to a solution of chlorodiphenylphosphine (5.5 g, 4.5 mL, 25 mmol) in CH_2Cl_2(25 mL) during 30 min. Then a solution of 2,6-dimethylaniline (12.1 g, 12.5 mL, 100 mmol) in CH_2Cl_2(100 mL) was added dropwise at 0°C during 1 h. The mixture was refluxed for 144 h with vigorous stirring. The solvent was evaporated in vacuum and the residue was recrystallized from ethanol (30 mL) to give white crystals of **3**. Yield: 3.77 g (47 %). M.p. 219°C. Calcd for $C_{20}H_{20}NPO$: C, 74.75; H, 6.27; N, 4.36 %. Found: C, 74.57; H, 6.31; N, 4.44 %. ^{1}H NMR ($CDCl_3$): δ = 2.26 (s, 6H, Me); 4.66 (m, 1H, NH); 6.93 (m, 3H, *m*-H, *p*-H, $C_6H_3Me_2$); 7.39 (m, 4H, *m*–H, Ph); 7.48 (t, J = 3.6 Hz, 2H, *p*-H, Ph); 7.81 (dd, J = 3.8 Hz, J_{PH} = 3.0 Hz, 4H, *o*-H, Ph). ^{31}P NMR ($CDCl_3$): δ = 20.8.

Synthesis of [Ph_2(*o*-$MeC_6H_4NH)_2$P]Br (5)

A solution of Br_2 (8.0 g, 2.53 mL, 50 mmol) in CH_2Cl_2(30 mL) was added dropwise to a solution of chlorodiphenylphosphine (11.0 g, 9.0 mL, 50 mmol) in CH_2Cl_2(50 mL) during 40 min. Then a solution of *o*-toluidine (21.4 g, 21.4 mL, 200 mmol) in CH_2Cl_2(30 mL) was added dropwise at 0°C during 2 h. The mixture was warmed up to 20°C and stirred for 72 h. The solvent was evaporated in vacuum. ^{31}P NMR spectra of the residue in CD_3OD showed two main signals at 30.4 (the bromide **5**) and 22.4 (the oxide **6**) with an integral ratio of 1:2. The residue was washed with benzene (3 × 30 mL) to remove the largest part of the oxide **6** and

recrystallized twice from Pr^iOH (25 mL) to afford 5.49 g of **5** (23 %). M.p. 243 °C. Calcd for $C_{26}H_{26}BrN_2P$: C, 65.41; H, 5.49; N, 5.87 %. Found C, 65.79; H, 5.78; N, 5.85 %. ^1H NMR ($CDCl_3$): $\delta = 2.29$ (s, 6H, Me); 6.9–7.1 (m, 8H, C_6H_4Me); 7.49 (m, 4H, *m*-H, Ph); 7.67 (m, 2H, *p*-H, Ph); 7.76 (dd, $J = 3.6$ Hz, $J_{PH} = 3.0$ Hz, 4H, *o*-H, Ph); 8.59 (m, 2H, NH). ^{31}P NMR (CD_3OD): $\delta = 30.4$; ($CDCl_3$): $\delta = 35.2$.

Synthesis of [Ph$_2$(p-MeC$_6$H$_4$NH)$_2$P]Br (7)

A solution of Br_2 (8.0 g, 2.53 mL, 50 mmol) in CH_2Cl_2(30 mL) was added to a solution of chlorodiphenylphosphine (11.0 g, 9.0 mL, 50 mmol) in CH_2Cl_2(50 mL) during 40 min. Then a solution of *p*-toluidine (21.4 g, 21.4 mL, 200 mmol) in CH_2Cl_2(30 mL) was added dropwise at 0°C during 2 h. The mixture was warmed up to 20 °C and stirred effectively for 24 h. The solvent was evaporated in vacuum, and the residue was washed with benzene (3 × 30 mL), water (3 × 20 mL) and recrystallized from ethanol (30 mL). Yield: 14.08 g (59%). M.p. 210 °C. Calcd for $C_{26}H_{26}BrN_2P$: C, 65.41; H, 5.49; N, 5.87%. Found C, 65.72; H, 5.48; N, 5.80 %. ^1H NMR ($CDCl_3$): $\delta = 2.09$ (s, 6H, Me); 6.75 (d, $J =$ 10.4 Hz, 4H, C_6H_4Me); 7.29 (d, $J = 10.4$ Hz, 4H, C_6H_4Me,); 7.39 (m, 4H, *m*-H, Ph); 7.52 (m, 2H, *p*-H, Ph); 8.09 (dd, $J = 7.4$ Hz, $J_{PH} = 13.5$ Hz, 4H, *o*-H, Ph); 9.26 (d, $J = 18.0$ Hz, 2H, NH). ^{31}P NMR ($CDCl_3$): $\delta = 28.0$.

Synthesis of [Ph$_2$P(*p*-Pr^{i}C$_6$H$_4$NH)$_2$]Br (8)

Method A

A solution of Br_2 (8.0 g, 2.53 mL, 50 mmol) in CH_2Cl_2(30 mL) was added to a solution of chlorodiphenylphosphine (11.0 g, 9.0 mL, 50 mmol) in CH_2Cl_2(50 mL) during 40 min. Then a solution of *p*-isopropylaniline (27.0 g, 27 mL, 200 mmol) in CH_2Cl_2(30 mL) was added dropwise at 0°C for 2 h. The mixture was allowed to warm to room temperature and was stirred for 24 h. The solvent was evaporated in vacuum and the residue was washed with benzene (3 × 50 mL), water (3 × 30 mL) and recrystallized from ethanol (20 mL) to yield 18.73 g of **8** (70%). M.p. 230 °C. Calcd for $C_{30}H_{34}BrN_2P$: C, 67.54; H, 6.42; N, 5.25 %. Found C, 67.68; H, 6.42; N, 5.31 %. ^1H NMR (CD_3OD): $\delta = 1.38$ (d, $J = 7.0$ Hz, 12H, $CHMe_2$); 3.04 (septet, $J = 7.0$ Hz, 2H, $CHMe_2$); 7.34 (m, 8H, $C_6H_4Pr^i$); 7.86 (m, 4H, *m*-H, Ph); 7.97 (m, 2H, *p*-H, Ph); 8.17 (m, 4H, *o*-H, Ph). ^{31}P NMR (CD_3OD): $\delta = 26.6$.

Method B

Analogously 18.19 g (68%) of [Ph$_2$(*p*-Pr^{i}C$_6$H$_4$NH)$_2$P]Br (**8**) was obtained using the isomeric mixture of *o*-, *m*–, and *p*-isopropylaniline

(27.0 g, 27 mL, 200 mmol) instead of the same amount of pure *p*-isopropylaniline.

Synthesis of $[Ph_2(p\text{-}MeOC_6H_4NH)_2P]Br$ (9)

A solution of Br_2 (4.0 g, 1.3 mL, 25 mmol) in CH_2Cl_2(10 mL) was added to a solution of chlorodiphenylphosphine (5.5 g, 4.5 mL, 25 mmol) in dry CH_2Cl_2(25 mL) during 40 min. Then a solution of *p*-anizidine (6.15 g, 50 mmol) and NEt_3 (5.1 g, 7 mL, 50 mmol) in CH_2Cl_2(20 mL) was added dropwise at 0°C during 1 h. The mixture was warmed up to 20°C and stirred for 24 h. The solvent was evaporated in vacuum, and the residue was washed with benzene (3 × 20 mL), acetone (2 × 10 mL) and recrystallized from ethanol (30 mL). Yield: 3.39 g (39 %). M.p. 187 °C. Calcd for $C_{26}H_{26}BrN_2O_2P$: C, 61.31; H, 5.14; N, 5.50 %. Found C, 61.17; H, 5.17; N, 5.44 %. ^{1}H NMR (CD_3OD): $\delta = 3.92$ (s, 6H, Me); 4.82 (broad s, 2H, NH); 7.05 (d, $J = 8.8$ Hz, 4H, C_6H_4OMe); 7.34 (d, $J = 8.8$ Hz, 4H, C_6H_4OMe); 7.8–7.9 (m, 4H, *m*-H, Ph); 7.98 (t, $J = 7.5$ Hz, 2H, *p*-H, Ph), 8.15 (dd, $J = 8.1$ Hz, $J_{PH} = 13.6$ Hz, 4H, *o*-H, Ph).^{31}P NMR (CD_3OD): $\delta = 27.4$.

Synthesis of $[Ph_2(p\text{-}EtO_2CC_6H_4NH)_2P]Br$ (10)

The synthesis was carried out in analogy to that of **9** using *p*-$NH_2C_6H_4CO_2Et$ (8.25 g, 50 mmol) instead of *p*-anizidine. The reaction mixture was stirred for 20 h. The solvent was evaporated in vacuum, the residue was washed with benzene (3 × 10 mL), water (2 × 10 mL) and recrystallized from ethanol (50 mL). Yield: 5.13 g (35 %). Calcd for $C_{30}H_{30}BrN_2O_4P$: C, 60.72; H, 5.10; N, 4.72 %. Found C, 60.78; H, 5.04; N, 4.77 %. ^{1}H NMR (CD_3OD): $\delta = 1.52$ (t, $J = 7.2$ Hz, 6H, $CH_2\mathit{Me}$); 4.50 (q, $J = 7.2$ Hz, 4H, CH_2Me); 7.50 (d, $J = 8.7$ Hz, 4H, $C_6H_4CO_2Et$); 7.88 (m, 4H, *m*-H, Ph); 8.04 (m, 2H, *p*-H, Ph); 8.11 (d, $J = 8.7$ Hz, 4H, $C_6H_4CO_2Et$), 8.25 (dd, $J = 7.5$, $J_{PH} = 13.8$ Hz, 4H, *o*-H, Ph). ^{31}P NMR (CD_3OD): $\delta = 27.7$.

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