# 1*H*-1,3-Benzazaphospholes: The Organometallic Route and a New Three-Step Synthesis with Reductive Ring Closure

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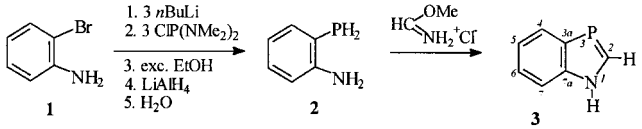
**Abstract:** Primary and *N*-secondary 2-phosphanylanilines were synthesized via metallation of 2-bromoanilines, coupling with $ClP(NMe_2)_2$, alcoholysis and reduction with $LiAlH_4$, and subsequently reacted with formimidoester hydrochloride to give 1,3-benzazaphospholes. For 1*H*-1,3-benzazaphospholes, a shorter alternative three-step synthesis was developed, based on *N*-acylation of 2-bromoaniline, $NiCl_2$-catalyzed arylation of triethyl phosphite and a new reductive cyclization of amidophosphonic acid ester with excess $LiAlH_4$.

**Key words:** *C,N*-dilithium reagent, phosphanylaniline, amidoarylphosphonate, reductive cyclization, 1,3-benzazaphosphole

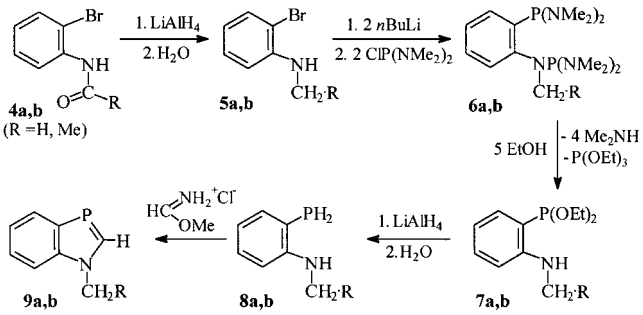
The complex chemistry of phospholes and phosphole anions has found considerable interest in recent years.[1,2] Little is known, however, about metal derivatives or complexes of related 1,3-azaphospholes[3] or annulated azaphospholes.[4–7] The early papers presented an interesting ambident reactivity of the "*N*"-lithiated and the first stable RP=C(Li)-X species, but since then no further work on these compounds has been reported.[8] One of the reasons may be the cumbersome synthetic access of azaphospholes[8] and benzazaphospholes[4,5] by multi-step procedures. We describe here in more detail the organometallic route[5] and a new and shorter way to prepare 1*H*-1,3-benzazaphospholes.

The original synthesis of 1*H*-1,3-benzazaphospholes was based on cyclocondensations of various carbonic acid derivatives with 2-phosphanylanilines. The latter were prepared by photoinitiated Michaelis–Becker reaction of sodium diethyl phosphite with 2-iodoaniline in liquid ammonia and subsequent reduction with $LiAlH_4$.[9] For further studies of benzazaphospholes, we explored a preliminary reported organometallic route[5] with respect to a more general use in the synthesis of 2-phosphanylanilines. 2-Bromoaniline **(1)** was reacted successively with three equivalents of butyllithium, phosphorous acid bis(dimethylamide) chloride and ethyl alcohol in a one-pot reaction. After removal of volatile components (bath temperatutre 100°C/0.01 Torr), the resulting mixture was reduced with excess $LiAlH_4$ to give 2-phosphanylaniline **2** in a total yield of 30% (Scheme 1). Small impurities of secondary phosphanes could not be removed by distillation but did not interfere with the further reaction of **2** with formimidoester hydrochloride affording the non-basic 1*H*-1,3-benzazaphosphole **3**, which can easily be purified.




**Scheme 1**

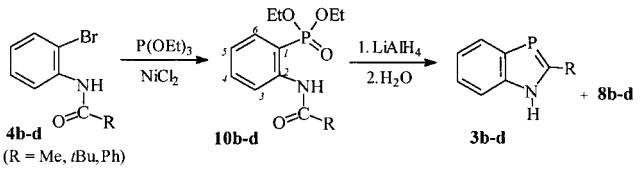
For *N*-substituted derivatives, the following reaction sequence was established. 2-Bromo-*N*-acylanilides **4**, obtained from **1**,were reduced with $LiAlH_4$ to give *N*-alkyl-2-bromoanilines **5**. The latter were dilithiated and reacted with $ClP(NMe_2)_2$ to give **6** which were converted to **7** with ethanol. Then **7** was reduced to **8** with $LiAlH_4$ and the latter underwent cyclocondensation with formimidoester hydrochloride affording the *N*-alkyl-1,3-benzazaphospholes **9** (Scheme 2). Shortcomings of these procedures were low yields in the substitution of the tri- or dilithium compounds if the reactions were carried out on a larger scale.




**Scheme 2**

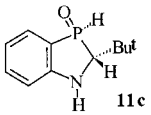
A further disadvantage is the easy replacement of bromine by hydrogen during the reduction of **4** with $LiAlH_4$ which therefore requires careful control of the reaction conditions. To overcome these problems, we investigated a primary P–C coupling by $NiCl_2$-catalyzed arylation of triethyl phosphite with 2-bromoaniline **(1)** and the *N*-acyl derivatives **4**. Metal-catalyzed arylations of phosphites were described by Tavs[10] and reported to be useful for aryl halides activated by electron-withdrawing substituents.[10–12]

Later, bromobenzene[13] and even 4-bromoanisole[14] were used in this reaction. Our attempts to react 2-bromoaniline **(1)** with triethyl phosphite in the presence of $NiCl_2$ did not lead to P–C bond formation. At high temperature (180–220 °C), we observed the formation of $HP(O)(OEt)_2$, $HP(O)(OEt)(NHC_6H_4Br)$ and smaller amounts of a diamide and other products ($^{31}P$ NMR: δ = 7.6, dp, $^1J_{PH}$ = 692 Hz, $^3J_{PH}$ = 9.1 Hz; δ = 4.6, dt, $^1J_{PH}$ = 646 Hz, $^3J_{PH}$ = 7.9 Hz; δ = 2.7, d, $^1J_{PH}$ = 659 Hz). However, the reaction of the *N*-acylated derivatives **4b–d** with triethyl phosphite in the presence of $NiCl_2$ proceeded smoothly and furnished high yields of *N*-acyl-2-aminobenzenephosphonic acid ester **10b–d**. The reaction of **4b** with triisopropyl phosphite gave similar results, whereas in the case of **4c** thermal decomposition (gas evolution) and formation of the respective phosphonic acid was observed. The 2-bromoformanilide **4a** reacted in a different way and underwent, at 180–200 °C, a vigorous condensation affording an insoluble brown polymer. The reduction of **10b–d** with excess $LiAlH_4$ (2.5 equivalents) in $Et_2O$ at 0–10 °C provided small amounts of the expected *N*-secondary 2-phosphanylanilines **8b–d**. The main products, however, were 1*H*-1,3-benzazaphospholes **3b–d** (Scheme 3) which thus are available now in a three-step procedure. The key step in the formation of the heterocycles is probably a base-catalyzed cyclocondensation of a primarily formed *o*-phosphanylanilide in competition with its reduction to **8b–d**. This is supported by the failure of attempts to prepare *o*-phosphanylacetanilide using a smaller amount of $LiAlH_4$ (1.5 equiv) which, instead, gave mainly a mixture of unreacted **10b** and **8b**. Furthermore, the high excess of the reducing agent should favor the reduction of the amide function relative to the condensation unless it also catalyzes the condensation. It seems reasonable that intermediately formed phosphides undergo instantaneous ring closure to "*N*"-metallated benzazaphospholes. The $\lambda^3$-P=C compounds resist an extensive reduction by the reactive hydride underlining the high stabilization of the p-excess heteroaromatic 1,3-benzazaphospholate system. Only small amounts of 2,3-dihydro-1,3-benzazaphospholes were observed (R = Me and *t*-Bu) which increased if the reduction was carried out at room temperature.




**Scheme 3**

The separation of **3b** and **3d** from the phosphanylanilines **8b** or **8d** and impurities like dihydro-1,3-benzazaphospholes was accomplished by extraction of the latter with dilute cold sulfuric acid. The 1*H*-benzazaphospholes remain in the solvent (diethyl ether) phase. They are not basic since the lone electron pair at nitrogen takes part in the aromatic delocalization. The somewhat more basic 2-*tert*-butyl-1,3-benzazaphosphole **(3c)**, although with highest steric shielding, is partly attacked by 10% sulfuric acid and forms diastereoselectively the water adduct **11c**. The two bond coupling constants $^2J_{PH}$ = 19.8 Hz and $^3J_{HH}$= 3.9 Hz of the hydrogen in position 2 are consistent with an *E*-configuration with 2-H and oxygen at phosphorus on the same side[15]. Compound **11c** was separated from **8c** and smaller amounts of *E/Z*-2-*tert*-butyldihydro-1,3-benzazaphosphole by distillation and subsequent recrystallization or by repeated recrystallization from hexane.




**11c**

Hexane, $Et_2O$, THF and toluene were dried under argon with sodium/benzophenone and freshly distilled from the ketyl solutions before use. All reactions except the *N*-acylations of 2-bromoaniline **(1)** were carried out under an atmosphere of purified argon using standard Schlenk techniques. Melting points were uncorrected. NMR data were recorded on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 ($^1H$), 75.5 ($^{13}C$), and 121.5 MHz ($^{31}P$) with reference to TMS and $H_3PO_4$ (85%), respectively. $CDCl_3$ was used as solvent unless otherwise indicated. Mass spectra (EI, 70eV) were measured on a single focussing sector-field mass spectrometer AMD40 (Intectra).

2-Bromoanilides **4a**,[16] **4b**,[17] **4d**[18] and the aniline derivative **5a**[16] were prepared according to known procedures.

**2-Bromoanilides 4b–d; General Procedure[16–18]**

To a solution of **1** (29.0 g, 169 mmol) and $Et_3N$ (23.5 mL) in $Et_2O$ (300 mL) was added dropwise an equimolar amount of the respective carboxylic acid chloride at 0–5 °C with stirring. After 2d the mixture was filtered and the precipitate thoroughly washed with $Et_2O$. Evaporation of the solvent in vacuo furnished the crude amides which were sufficiently pure for direct use.

The new compound **4c** was obtained by using pivaloyl chloride; yield: 84%: mp 56–58 °C. NMR data of **4b–d** are given for comparison with respective phosphorus compounds.

**4b**

$^1H$ NMR (CH-COSY): δ = 2.44 (s, 3 H, $CH_3$), 6.97 ("t"d, $^3J$ = 7.8 Hz, $^4J$ = 1.4 Hz, 1 H, H-4), 7.31 ("t"d, $^3J$ = 7.8 Hz, $^4J$ = 1.4 Hz, 1 H, H-5), 7.53 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.4 Hz, 1 H, H-3), 8.34 (br d, $^3J$ = 8.1 Hz, 1 H, H-6), 7.60 (br, 1 H, NH).

$^{13}C$ NMR: δ = 24.8 ($CH_3$), 113.2 ($C_p$-2), 121.9 (C-6), 125.1 (C-4), 128.3 (C-5), 132.1 (C-3), 135.6 ($C_q$-1).

**4c**

$^1H$ NMR: δ = 1.35 (s, 9 H, $CH_3$), 6.95 ("t"d, $^3J$ = 7.5 Hz, $^4J$ = 1.6 Hz, 1 H, H-4), 7.29 ("t"d, $^3J$ = 7.9 Hz, $^4J$ = 1.3 Hz, 1 H, H-5), 7.52 (dd, $^3J$ = 8.1 Hz, $^4J$ = 1.6 Hz, 1 H, H-3), 8.39 (dd, $^3J$ = 8.2 Hz, $^4J$ = 1.6 Hz, 1 H, H-6), 8.00 (br, 1 H, NH).

**4d**

$^1H$ NMR: δ = 7.01 (ddd, $^3J$ = 8.1, 7.4 Hz, $^4J$ = 1.6 Hz, 1 H, H-4), 7.35 (m, $^3J$ = 8.4, 7.4 Hz, $^4J$ = 1.4 Hz, $J$ = 0.3 Hz, 1 H, H-5), 7.48–7.60 (m, 4 H, H-3 and $C_6H_5$), 7.94 (dm, $^3J$ = ca. 8 Hz, $^4J$ = ca. 1.3 Hz, 2 H, H-*o*), 8.47 (br, 1 H, NH), 8.55 (dd, $^3J$ = 8.3 Hz, $^4J$ = 1.6 Hz, 1 H, H-6).

**2-Phosphanylaniline (2)**

A 1.55 M hexane solution of BuLi (70 mL of a total of 100 mL, 155 mmol) were added dropwise at –40 °C to a solution of **1** (8.2 g, 48 mmol) in $Et_2O$ (50 mL). Then the residual amount of BuLi (30 mL) was added rapidly and the mixture stirred for 3 h at r.t. Af-

ter cooling to –40 °C, $ClP(NMe_2)_2$ (24.0 g, 155 mmol) was added dropwise. The suspension was stirred overnight, filtered and the precipitate thoroughly washed with $Et_2O$. Removal of the solvent from the filtrate gave an oil which exhibited in $^{31}P$ NMR three main signals in the $CPN_2$ (δ = 94.9, 99.7, 102.7) and $PN_3$ regions (δ = 122.6, 122.9, 123.0) and a smaller amount of a P–P compound [δ = 73.2, 21.9 (br), $J_{PP}$ = 253 Hz]. Excess absolute EtOH (17 mL) was added and the mixture heated for 3 h at 60 °C. Then, all volatile compounds were removed in vacuo (0.01Torr). $Et_2O$ (100 mL) was added and the resulting suspension was poured in small portions to $LiAlH_4$ tablets (3.0 g, 79 mmol) stirred in $Et_2O$ (100 mL). Stirring was continued for 2 d at r.t. to complete the reduction. Then, in order to hydrolyze phosphides, amides and excess hydride, degassed $H_2O$ was added dropwise at 5–10 °C until evolution of $H_2$ ceased. The precipitate was removed by filtration, the filtrate was dried ($Na_2SO_4$) and the solvent evaporated. Distillation of the residue at 110–118 °C/1 Torr gave 1.8 g (ca. 30%) of **2** contaminated with a small amount of two other anilines. Typical NMR signals: $^1H$ NMR: δ = 3.38 (d, $^1J_{PH}$ = 199 Hz, $PH_2$); $^{31}P$ NMR: δ = –152.7 (cf. Ref.[4]).

**1*H*-1,3-Benzazaphosphole (3a)**

To a solution of **2** (1.8 g, 14.4 mmol) in absolute MeOH (5 mL) was added a solution of formimidomethylester hydrochloride (1.7 g, 17.8 mmol) in MeOH. The mixture was allowed to stand overnight, $NH_4Cl$ formed and was separated and the solvent removed. The crude 1*H*-1,3-benzazaphosphole was recrystallized from hexane affording 1.2 g (62%) of nearly colorless solid; mp 101–103 °C (Lit.[4] mp 102–103 °C).

$^1H$ NMR ($C_6D_6$): δ = 7.02 ("t"m, $^3J$ = ca. 7–8 Hz, 1 H, H-5), 7.09 (dm, 1 H, H-7), 7.18 ("t"m, 1 H, H-6), 7.97 (dd, $J_{HH}$ = 4.7 Hz, $^2J_{PH}$ = 38.2, $^4J$ = 1 Hz, 1 H, H-2), 8.20 (ddd, $^3J$ = 7.8 Hz, $^3J_{PH}$ = 3.6, $^4J$ = 1 Hz, 1 H, H-4), (NH appeared at >10).

$^{31}P$ NMR ($C_6D_6$): δ = 82.6.

**2-Bromo-*N*-ethylaniline (5b)**

To a suspension of $LiAlH_4$ tablets (13 g, 342 mmol) in $Et_2O$ (200 mL) was added dropwise a solution of **4b** (68.0 g, 317.7 mmol) in $Et_2O$ (100 mL) at 0–10 °C. The mixture was stirred at r. t. and the progress of the reduction controlled by NMR spectroscopy. (Usually, about 3 d are necessary to achieve good yields. Reflux or prolonged reaction time caused partial replacement of Br by H) Then the mixture was hydrolyzed by dropwise addition of $H_2O$ until the $H_2$ evolution ceased. The precipitate was separated and thoroughly washed with $Et_2O$ and the organic solution dried ($Na_2SO_4$). $Et_2O$ was stripped off to give **5b** (46.2 g, 73%); bp 50–56 °C/0.01 Torr.

$^1H$ NMR: δ = 1.30 (t, $^3J$ = 7.1 Hz, 3 H, $CH_3$), 3.18, 3.19 (q, $^3J$ = 7.1 Hz, 2 H, $NCH_2$), 4.19 (br, 1 H, NH), 6.54 ("t"d, $^3J$ = 7.5, 7.7 Hz, $^4J$ = 1.4 Hz, 1 H, H-4), 6.61 (dd, $^3J$ = 8.1 Hz, $^4J$ = 1.4 Hz, 1 H, H-6), 7.16 ("t"d, $^3J$ = 7.6, 8.1 Hz, $^4J$ = ca. 1 Hz, 1 H, H-5), 7.40 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.4 Hz, 1 H, H-3).

**2-$(Me_2N)_2PC_6H_4N(Me)P(NMe_2)_2$ (6a)**

$PCl_3$ (11.6 mL, 133.3 mmol) was added dropwise with stirring to $P(NMe_2)_3$ (48.5 mL, 266.7 mmol) at 60 °C, kept 1 h at this temperature and then stirred for 4 h at r.t. affording $ClP(NMe_2)_2$. Meanwhile, **5a** (37.2 g, 200 mmol) was dissolved in $Et_2O$ (300 mL) and dilithiated at –50 °C by the addition (the first half dropwise) of a solution of BuLi in hexane (370 mL, 1.08 M, 400 mmol). The mixture was stirred for 2 h at r. t. After cooling to –65 °C, $ClP(NMe_2)_2$ was added dropwise. The resulting suspension was stirred overnight, the precipitation separated by filtration and the solvent removed in vacuum. The residue was distilled to give 49.9 g (72%) of **6a** as a viscous oil; bp 122–127 °C/0.01 Torr. (The first fraction, 9 g of an oil of bp 90–122 °C/0.01 Torr, consisted also mainly of **6a**.)

$^{31}P$ NMR (40.5 MHz, no solvent): δ = 97.6 (br, $CPN_2$), 117.5 (br, $NPN_2$).

| | | | | | |
|---|---|---|---|---|---|
| $C_{15}H_{31}N_5P_2$ | calcd | N | 20.39 | P | 18.04 |
| (343.4) | found | | 20.30 | | 18.15 |

**2-$(Me_2N)_2PC_6H_4N(Et)P(NMe_2)_2$ (6b)**

A solution of **5b** (11.6 g, 57.85 mmol) in $Et_2O$ (100 mL) was dilithiated (80 mL BuLi, 1.45 M, 116 mmol) and reacted at –40 °C with $ClP(NMe_2)_2$ (17.9 g, 116 mmol) as described above; yield: 11.0 g (55%); bp 110–115 °C/0.001 Torr.

$^1H$ NMR ($C_6D_6$): δ = 0.99, 1.04 (2 t, $CH_3$, B/A), 2.40 (d, $^3J_{PH}$ = 9.3 Hz, $PNMe_2$, B), 2.48 (d, $^3J_{PH}$ = 8.9 Hz, $PNMe_2$, B), 2.52 (d, $^3J_{PH}$ = 9 Hz, 12 H, $PNMe_2$, A), 2.59 (d, $^3J_{PH}$ = 8.4 Hz, 12 H, $PNMe_2$, A), 3.39 (m, $NCH_2$, B), 3.53 (m, $NCH_2$, A), 7.10–7.25 (m, 3 H, H-4 to 6), 7.82 (m, 1 H, H-3); intensity A:B = ca. 2:1.

$^{31}P$ NMR ($C_6D_6$): δ = 98.4 ($CPN_2$), 117.7 ($NPN_2$), $^4J_{PP}$ = 19.4 Hz.

***N*-Methylaminobenzenephosphonous Acid Diethyl Ester (7a)**

Compound **6a** (49.0 g, 142.7 mmol) was added rapidly to absolute EtOH (45 mL, 1.24 mol) resulting in a moderate reaction and evolution of $Me_2NH$. The temperature was slowly raised to 70 °C and kept there for 3 h. Then the solution was heated for 15 min to 110–140 °C and distilled in vacuum to give 24.7 g (76%) colorless liquid **7a**; bp 90–92 °C/0.01 Torr.

$^{31}P$ NMR ($CDCl_3$): δ = 166.1.

| | | | | | |
|---|---|---|---|---|---|
| $C_{11}H_{18}NO_2P$ | calcd | N | 6.16 | P | 13.63 |
| (227.2) | found | | 5.97 | | 13.45 |

***N*-Methyl-2-phosphanylaniline (8a)**

A solution of **7a** (24.0 g, 105.6 mmol) was added dropwise at 0–5 °C to a suspension of $LiAlH_4$ (5.5 g, 1.447 mol) in $Et_2O$ (100 mL), stirred overnight at r.t. and refluxed for 2 h. The mixture was hydrolyzed with $H_2O$ at 5–10 °C until the $H_2$ evolution was slow, the suspension filtered and the filtrate dried ($Na_2SO_4$). Distillation furnished 8.6 g (57%) of **8a**; 66–71 °C/0.1 Torr.

$^1H$ NMR (100 MHz, $CDCl_3$): δ = 2.83 (br, 3 H, $CH_3$), 3.48 (d, $^1J_{PH}$ = 200 Hz, 2 H, $PH_2$), 3.92 (br, 1 H, NH), 6.50–6.75 (m, 2 H, H-6,4), 7.15–7.55 (n, 2 H, H-5,3).

$^{31}P$ NMR ($C_6D_6$): δ = –150.0.

IR (film): ν = 2280 (s, $PH_2$), 3400 $cm^{-1}$ (br, NH).

| | | | |
|---|---|---|---|
| $C_7H_{10}NP$ | calcd | P | 22.26 |
| (139.1) | found | | 21.90 |

***N*-Ethyl-2-phosphanylaniline (8b)**

EtOH (16 mL) was added to **6b** (16.04 g, 50 mmol) at 40–50 °C whereupon evolution of $Me_2NH$ was observed. The mixture was heated for 3 h at 60–70 °C, and the volatiles were removed in vacuum (120 °C/0.01 Torr). The residue (**7b**) was dissolved in $Et_2O$ (30 mL) and added dropwise to $LiAlH_4$ (3 g, 78.9 mmol) in $Et_2O$ (200 mL) at 0–10 °C. Workup as above yielded 4.0 g (52%) of colorless **8b;** bp 42–45 °C/0.001 Torr.

$^1H$ NMR ($C_6D_6$): δ = 0.88 (t, $^3J$ = 7.2 Hz, 3 H, $CH_3$), 2.77 (m, $^3J$ = 7.2 Hz, 2 H, $NCH_2$), 3.39 (d, $^1J_{PH}$ = 198 Hz, 2 H, $PH_2$) 3.70 (br, NH), 6.44 (d, $^3J$ = 8.1 Hz, 1 H, H-6), 6.63 ("t", $^3J$ = ca. 7–8 Hz, 1 H, H-4), 7.21 (m, $^3J$ = ca. 8 Hz, 1 H, H-5), 7.52 (ddd, 1 H, H-3).

$^{31}P$ NMR ($C_6D_6$): δ = –154.8.

**1-Ethyl-1,3-benzazaphosphole (9b)**
A solution of formimidomethylester hydrochloride (3.5 g, 36.6 mmol) in anhyd MeOH (15 mL) was added to a solution of **8b** (3.5 g, 23 mmol) in anhyd MeOH (10 mL). The mixture was allowed to react for 2 d at r.t., the $NH_4Cl$ was separated and the filtrate distilled to give 3.2 g (86%) of 1-ethyl-1,3-benzazaphosphole; bp 60–65 °C/0.001 Torr; mp 34–35 °C (after distillation).

$^1$H NMR ($C_6D_6$): δ = 0.78 (t, $^3J$ = 7.2 Hz, 3 H, $CH_3$), 3.40 (q, $^3J$ = 7.2 Hz, 2 H, $NCH_2$), 7.07 (m, $^3J$ = ca. 7, 8 Hz, $^4J_{PH}$ ca. 2 Hz, $^4J$ = 1 Hz, 1 H, 5-H), 7.12 (br d, $^3J$ = ca. 8 Hz, 1 H, 7-H), 7.21 (dd"t", $^3J$ = 6.8, 8.5 Hz, $^4J = {}^5J_{PH}$ = 1.1 Hz, 1 H, 6-H), 8.02 (d, $^2J_{PH}$ = 38.1, 1 H, 2-H), 8.14 (ddm, $^3J$ = 7.5 Hz, $^3J_{PH}$ = 3.9 Hz, $J \leq 1$ Hz, 1 H, 4-H).

$^{13}$C NMR ($C_6D_6$): δ = 14.5 (s, $CH_3$), 44.6 (d, $^3J$ = 2.3 Hz, $NCH_2$), 112.6 (s, C-7), 120.2 (d, $^3J$ = 11.7 Hz, C-5), 124.6 (d, $^4J$ = 2.8 Hz, C-6), 130.0 (d, $^4J$ = 21.4 Hz, C-4), 142.2 (d, $^2J$ = 5.8 Hz, C-7a), 143.4 (d, $^1J$ = 41.1 Hz, C-3a), 160.3 (d, $^1J$ = 53.3 Hz, C-2).

$^{31}$P NMR ($C_6D_6$): δ = 75.4.

**2-Acetamidobenzenephosphonic Acid Diethyl Ester (10b)**
A mixture of **4b** (30.0 g, 140 mmol) and anhyd $NiCl_2$ (0.1 g) was heated up to 170 °C in a distillation apparatus. Triethyl phosphite (28.2 mL, 148 mmol) was added dropwise maintaining the temperature at 170–180 °C. After the addition, the mixture was heated for 10 min up to 190 °C during which time 9.4 g of EtBr was collected. Distillation of the residue at 110–120 °C/0.01 Torr afforded 30.6 g (81%) of **10b** as viscous oil.

$^1$H NMR (CH-COSY): δ = 1.33 (t, $^3J$ = 7.1 Hz, 6 H, 2 $OCH_2CH_3$), 2.21 (s, 3 H, $CH_3$), 4.08 (m, 4 H, 2 $OCH_2CH_3$), 7.13 ("t"dd, $^3J$ = 7.5, 7.7 Hz, $^4J_{PH}$ = 3.1 Hz, $^4J$ = 1 Hz, 1 H, H-5), 7.53 (m, $^3J$ = 7.5, 8.5 Hz, $^4J$ = 1 Hz, 1 H, H-4), 7.57 (ddd, $^3J$ = 7.7 Hz, $^3J_{PH}$ = 14.5 Hz, $^4J$ = 1.5 Hz, 1 H, H-6), 8.61 ("t" br, $^3J$ = 8.5 Hz, $^4J_{PH}$ = ca 8 Hz, 1 H, H-3), 10.65 (br, 1 H, NH).

$^{13}$C NMR: δ = 15.9 (d, $^3J$ = 6.2 Hz, $CH_3$), 24.9 (s, $CH_3$), 62.3 (d, $^2J$ = 4.9 Hz, $CH_2$), 113.1 (d, $^1J$ = 179.3 Hz, $C_q$-1), 120.4 (d, $^3J$ = 11.7 Hz, C-3), 122.6 (d, $^3J$ = 13.3 Hz, C-5), 132.1 (d, $^2J$ = 5.8 Hz, C-6), 133.7 (d, $^4J$ = 2.1 Hz, C-4), 142.5 (d, $^2J$ = 7.9 Hz, $C_q$-2), 168.5 (s, CO).

$^{31}$P NMR: δ = 19.8 .

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $C_{12}H_{18}NO_4P$ | calcd | C | 53.14 | H | 6.69 | N | 5.16 |
| (271.3) | found | | 52.6 | | 6.60 | | 5.40 |

**2-Trimethylacetamidobenzenephosphonic Acid Diethyl Ester (10c)**
Triethyl phosphite (12.7 mL, 79.4 mmol) was added dropwise to a mixture of **4c** (17.8 g, 69.5 mmol) and anhyd $NiCl_2$ (0.1 g) while heating to 180–190 °C in a distillation apparatus. After complete addition, heating (up to 200 °C) was continued for 20 min to give 5.5 g of condensed EtBr. The remaining mixture was distilled in vacuum to yield 19.8 g (91%) of **10c** as a viscous oil; bp 112–115 °C/0.01 Torr.

$^1$H NMR: δ = 1.33 (br t, $^3J$ = 7.1 Hz, 6 H, 2 $OCH_2CH_3$), 1.34 [s, 9 H, $C(CH_3)_3$], 4.12 (m, 4 H, 2 $OCH_2CH_3$), 7.11 (dd "t", $^3J$ = 7.6 Hz, $^4J_{PH}$ = 3.1 Hz, $^4J$ = 1.0 Hz, 1 H, H-5), 7.52 ("t"d, $^3J$ = 7.4, $^4J$ = 1.2 Hz, 1 H, H-4), 7.60 (ddd, $^3J$ = 7.7 Hz, $^3J_{PH}$ = 14.5 Hz, $^4J$ = 1.6 Hz, 1 H, H-6), 8.63 ("t" br, $^3J$ = 7.4 Hz, $^4J_{PH}$ = 7.4, 1 H, H-3), 10.55 (br, 1 H, NH).

$^{13}$C NMR: δ = 16.2 (d, $^3J$ = 6.6 Hz, $CH_3$), 27.5 [s, $C(CH_3)_3$], 40.2 (s, $CMe_3$), 62.6 (d, $^2J$ = 5.2 Hz, $CH_2$), 114.0 (d, $^1J$ = 180.2 Hz, C-1), 121.1 (d, $^3J$ = 11.5 Hz, C-3), 122.8 (d, $^3J$ = 13.8 Hz, C-5), 132.5 (d, $^2J$ = 6.0 Hz, C-6), 133.9 (d, $^4J$ = 2.3 Hz, C-4), 143.0 (d, $^2J$ = 7.2 Hz, C-2), 177.8 (s, CO).

$^{31}$P NMR: δ = 19.9 .

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $C_{15}H_{24}NO_4P$ | calcd | C | 57.50 | H | 7.72 | N | 4.47 |
| (313.3) | found | | 57.95 | | 7.55 | | 4.11 |

**2-Benzamidobenzenephosphonic Acid Diethyl Ester (10d)**
A mixture of **4d** (27.5 g, 99.6 mmol) and anhyd $NiCl_2$ (0.1 g) was heated up to 165 °C in a distillation apparatus while triethylphosphite (18.2 mL, 114 mmol) was added dropwise. Then the temperature was raised to 180 °C for 20 min. The residue was distilled in a short-path distillation device affording 27.4 g (83%) of a syrupy liquid; bp 178–182 °C/0.001 Torr.

$^1$H NMR: δ = 1.31 (t, $^3J$ = 7.1 Hz, 6 H, 2 $CH_2CH_3$), 4.12 (m, 4 H, 2 $OCH_2CH_3$), 7.15 (dd "t", $^3J$ = 7.5 Hz, $^4J_{PH}$ = 3.1 Hz, $^4J$ = 1 Hz, 1 H, H-5), ca. 7.50 (m, 3 H, H-4, $C_6H_5$), 7.62 (ddd, $^3J$ = 7.8 Hz, $^3J_{PH}$ = ca. 15 Hz, $^4J$ = 1.6 Hz, 1 H, H-6), 7.58 (m, 1 H, $C_6H_5$), 8.15 (m, 2 H, $C_6H_5$), 8.61 ("t" br, $^3J$ = 7.6 Hz, $^4J_{PH}$ = ca. 7.6 Hz, 1 H, H-3), 11.58 (br, 1 H, NH).

$^{13}$C NMR: δ = 15.7 (d, $^3J$ = 6.5 Hz, $CH_3$), 62.2 (d, $^2J$ = 5.0 Hz, $CH_2$), 113.4 (d, $^1J$ = 179.6 Hz, C-1), 120.4 (d, $^3J$ = 11.0 Hz, C-3), 122.6 (d, $^3J$ = 13.3 Hz, C-5), 127.0 (s, 2C-*m*), 128.2 (s, 2C-*o*), 131.4 (s, C-*p*), 132.0 (d, $^2J$ = 5.7 Hz, C-6), 133.6 (d, $^4J$ = 1.8 Hz, C-4), 134.0 (s, C-*i*), 142.6 (d, $^2J$ = 7.7 Hz, C-2), 164.9 (s, CO).

$^{31}$P NMR: δ = 20.0 .

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $C_{17}H_{20}NO_4P$ | calcd | C | 61.26 | H | 6.05 | N | 4.20 |
| (333.3) | found | | 61.11 | | 6.20 | | 4.33 |

**2-Acetamidobenzenephosphonic Acid Diisopropyl Ester**
A mixture of **4b** (31.7 g, 149 mmol) and anhyd $NiCl_2$ (0.1 g) was reacted with triisopropyl phosphite (37.0 mL, 150 mmol) as described for **10b** during which process 13.5 g of isopropyl bromide was distilled out. Distillation of the residue afforded 36.4 g (82%) of 2-acetamidobenzenephosphonic acid diisopropyl ester as a viscous oil; bp 108–118 °C/0.01 Torr.

$^1$H NMR: δ = 1.26 [d, $^3J$ = 6.2 Hz, 6 H, $CH(CH_3)_2$], 1.39 [d, $^3J$ = 6.2 Hz, 6 H, $CH(CH_3)_2$], 2.21 (s, 3 H, $CH_3$), 4.67 (m, 2 H, CH), 7.11 (dd"t", $^3J$ = 7.5 Hz, $^4J_{PH}$ = 3 Hz, $^4J$ = 0.9 Hz, 1 H, H-5), 7.50 ("t", $^3J$ = 7.8 Hz, $^4J$ = 1 Hz, 1 H, H-4), 7.58 (ddd, $^3J$ = 7.7 Hz, $^3J_{PH}$ = 14.5 Hz, $^4J$ = 1.5 Hz, 1 H, H-6), 8.59 ("t" br, $^3J$ = 7.5 Hz, $^4J_{PH}$ = 7.5, 1 H, H-3), 10.74 (br, 1 H, NH).

$^{13}$C NMR: δ = 23.3 [d, $^3J$ = 4.9 Hz, $CH(CH_3)_2$], 23.6 [d, $^3J$ = 3.9 Hz, $CH(CH_3)_2$)], 24.8 (s, $CH_3$), 71.2 (d, $^2J$ = 5.4 Hz, OCH), 114.6 (d, $^1J$ = 179.6 Hz, C-1), 120.9 (d, $^3J$ = 11.6 Hz, C-3), 122.4 (d, $^3J$ = 13.5 Hz, C-5), 132.2 (d, $^2J$ = 5.6 Hz, C-6), 133.3 (d, $^4J$ = 1.6 Hz, C-4), 142.1 (d, $^2J$ = 7.9 Hz, C-2), 168.3 (s, CO).

$^{31}$P NMR: δ = 17.7.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $C_{14}H_{22}NO_4P$ | calcd | C | 56.18 | H | 7.41 | N | 4.68 |
| (299.3) | found | | 55.44 | | 7.20 | | 4.70 |

**2-Methyl-1*H*-1,3-benzazaphosphole (3b) and 2-Phosphanyl-*N*-ethylaniline (8b)**
To stirred suspension of $LiAlH_4$ tablets (10 g, 263 mmol) in $Et_2O$ (300 mL) was added dropwise **10b** (28.8 g, 106.1 mmol) at 0–5 °C. Stirring was continued at r.t. for 1 d. Then the mixture was hydrolyzed at 0–5 °C by dropwise addition of degassed $H_2O$ until the $H_2$ evolution ceased. Anhyd $Na_2SO_4$ was added, the mixture filtered and the solid thoroughly washed with $Et_2O$. The $Et_2O$ phase was extracted with cold degassed 10% aq $H_2SO_4$ (100 mL) to remove **8b**. Then the $Et_2O$ layer was washed with $H_2O$ until neutral and dried ($Na_2SO_4$). Hexane (10 mL) was added and most of the $Et_2O$ was evaporated in vacuum to give 6.7 g (43%) of **3b**, which may be recrystallized from hexane; colorless crystals; mp 115–116 °C (Lit.[4] mp 116–117 °C).

$^1$H NMR: δ = 2.66 (d, $^3J_{PH}$ = 12.0 Hz, 3 H, $CH_3$), 7.12 ("t"dd, $^3J$ = ca. 7, 7.6 Hz, $^4J_{PH}$= 2.1 Hz, $^4J$ = 1 Hz, 1 H, H-5), 7.28 ("tt", $^3J$ = ca. 7, 8.2 Hz, $^5J_{PH}$= 1 Hz, $^4J$ = 1 Hz, 1 H, H-6), 7.50 (d"q", $^3J$ = 8.2 Hz, $^4J_{PH}$= 1.8 Hz, $^4J$ = 1 Hz, 1 H, H-7), 7.96 (ddd, $^3J$ = 7.6 Hz, $^3J_{PH}$ = 3.6, $^4J$ = 1 Hz, 1 H, H-4), 9.06 (br, 1 H, NH).

$^{13}$C NMR: δ = 17.5 (d, $^2J$ = 22.6 Hz, $CH_3$), 113.0 (s, C-7), 120.2 (d, $^3J$ = 11.4 Hz, C-5), 124.1 (d, $^4J$ = 2.2 Hz, C-6), 128.2 (d, $^2J$ = 20.0 Hz, C-4), 141.0 (d, $^1J$ = 42.3 Hz, C-3a), 142.3 (d, $^2J$ = 5.7 Hz, C-7a), 173.7 (d, $^1J$ = 51.0 Hz, C-2).

$^{31}$P NMR ($CDCl_3$): δ = 73.0 (δ = 69.8 in MeOH[4]).

$^{31}$P NMR ($C_6D_6$): δ = 75.5.

$^{31}$P NMR (THF-$d_8$): δ = 71.1.

MS (EI, 70 eV): *m/z* (%) = 149.4 (100, $M^+$), 148.3 (92), 117.2 (16), 107.2 (22), 77 (20), 57 (26), 39 (30).

The acid extract of **8b** was rendered alkaline with excess 10% aq NaOH solution, **8b** was extracted with $Et_2O$ (2 × 50 mL) and the ethereal solution dried ($Na_2SO_4$). Evaporation of the solvent afforded 3.0 g (19%) of crude **8b;** bp 45–50 °C/0.01 Torr.

$^{31}$P NMR: δ = –153.3.

**2-*tert*-Butyl-1*H*-1,3-benzazaphosphole (3c) and 2-Phosphanyl-*N*-neopentylaniline (8c)**

A solution of **10c** (21.3 g, 68 mmol) in $Et_2O$ (20 mL) was added dropwise at 0–5 °C to a suspension of $LiAlH_4$ tablets (6 g, 158 mmol) stirred in $Et_2O$ (250 mL). Stirring was continued overnight at r.t. Then the mixture was refluxed for 6 h, cooled to 0–5 °C and hydrolyzed with degassed $H_2O$ until the $H_2$ evolution ceased. Anhyd $Na_2SO_4$ was added, the mixture filtered and the solid residue thoroughly washed with $Et_2O$. Removal of $Et_2O$ gave 10.2 g of a syrupy mixture of **3c** and **8c** (ca. 3:1) contaminated with a small amount of phosphanes with $^{31}$P NMR: δ = –84.3, –75.6, 31.3. Pure **3c** (6.0 g, 46%); mp 113–115 °C, was obtained by repeated recrystallization from hexane.

$^1$H NMR: δ = 1.49 [d, $^4J_{PH}$ = 1.2 Hz, 9 H, $C(CH_3)_3$], 7.10 ("t"dd, $^3J$ ca. 7, 7.6 Hz, $^4J_{PH}$= 2.1 Hz, $^4J$ = 1 Hz, 1 H, H-5), 7.27 ("tt", $^3J$ = ca. 7, 8.2 Hz, $^5J_{PH}$= 1 Hz, $^4J$ = 1 Hz, 1 H, H-6), 7.55 (d"q", $^3J$ = 8.2 Hz, $^4J_{PH}$= 1.8 Hz, $^4J$ = 1 Hz, 1 H, H-7), 7.98 (ddd, $^3J$ = 7.6 Hz, $^3J_{PH}$ = 3.6, $^4J$ = 1 Hz, 1 H, H-4), 9.68 (br, 1 H, NH).

$^{13}$C NMR: δ = 31.4 [d, $^3J$ = 9.3 Hz, $C(CH_3)_3$], 35.8 (d, $^2J$ =13.0 Hz, $CMe_3$), 113.2 (s, C-7), 120.1 (d, $^3J$ = 10.8 Hz, C-5), 124.3 (d, $^4J$ = 2.2 Hz, C-6), 128.6 (d, $^2J$ = 21.1 Hz, C-4), 140.2 (d, $^1J$ = 41.1 Hz, C-3a), 142.4 (br, C-7a), 190.2 (d, $^1J$ = 57.4 Hz, C-2).

$^{31}$P NMR: δ = 65.1.

MS (EI, 70 eV): *m/z* (%) = 191.4 (59, $M^+$), 176.3 (100, $M^+$ – Me), 148.3 (20), 144 (22), 136 (21), 135 (22), 107.2 (20).

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $C_{11}H_{14}NP$ | calcd | C | 69.10 | H | 7.38 | N | 7.33 |
| (191.2) | found | | 68.65 | | 7.24 | | 7.15 |

An attempt to separate **8c** from **3c** by extraction of the ethereal solution with excess 10% aq $H_2SO_4$, washing of the $Et_2O$ layer with $H_2O$ and drying with $Na_2SO_4$, gave a mixture of **3c** and **11c** (ratio ca 1:1) which crystallized from hexane in the same ratio. To isolate **8c**, the aqueous phase was rendered alkaline with a 10% NaOH solution, the aqueous phase was extracted with $Et_2O$, the $Et_2O$ phase dried and distilled; bp 50–60 °C/0.01 Torr.

**11c**

$^1$H NMR: δ = 1.10 [d, $^4J_{PH}$ = 0.9 Hz, 9 H, $C(CH_3)_3$], 3.55 (dd, $^2J_{PH}$= 19.8 Hz, $^3J_{HH}$= 3.9 Hz, 1 H, H-2), ca. 5.1 (v br s, 1 H, NH), 6.76 (dd, $^3J$ = 8.3 Hz, $^4J_{PH}$= 4.4 Hz, 1 H, H-7), 6.84 ("t"d, $^3J$ ca. 7.3, 8 Hz, $^4J_{PH}$ = ca. 3.4 Hz, 1 H, H-5), 7.37 ("tt", $^3J$ = ca. 7.3, 8.3 Hz, $^5J_{PH}$ = ca. $^4J$ = 1–1.4 Hz, 1 H, H-6), 7.68 (dd, br $^3J$ ca. 8 Hz, $^3J_{PH}$ = ca. 8–9 Hz, 1 H, H-4), 8.26 (dd, $^1J_{PH}$ = 491.4 Hz, $^3J_{HH}$= 3.9 Hz, 1 H, PH).

$^{31}$P NMR: δ = 30.8 (dm, $^1J_{PH}$ = ca. 500 Hz).

$^{13}$C NMR: δ = 26.5 (d, $^3J$ = 5.9 Hz, $C(CH_3)_3$], 33.4 (s, $CMe_3$), 68.0 (d, $^1J$ = 72.4 Hz, C-2), 112.6 (d, $^3J$ = 7.8 Hz, C-7), 113.3 (d, $^1J$ = 99.3 Hz, C-3a), 119.3 (d, $^3J$ = 10.9 Hz, C-5), 130.4 (d, $^2J$ = 7.0 Hz, C-4), 135.0 (d, $^4J$ = 1.8 Hz, C-6), 154.9 (d, $^2J$ = 21.9 Hz, C-7a).

**8c**

$^1$H NMR: δ = 1.04 [s, 9 H, $C(CH_3)_3$], 2.05 (br s, 1 H, NH), 2.96 (s, 2 H, $NCH_2$), 3.56 (d, $^1J_{PH}$ = 199.4 Hz, 2 H, $PH_2$), 6.55–6.65 (m, 2 H, H-6, H-4), 7.25 (m, 1 H, H-5), 7.45 (m, 1 H, H-3).

$^{31}$P NMR: δ = –154.9.

**2-Phenyl-1*H*-1,3-benzazaphosphole (3d)**

To a stirred suspension of $LiAlH_4$ tablets (8 g, 210 mmol) in $Et_2O$ (250 mL) was added **10d** (24.6 g, 73.9 mmol) in small portions at 0–5 °C. Stirring was continued at r.t. for 1 d. Then the yellow mixture was hydrolyzed cautiously at 0–5 °C by degassed $H_2O$ until the $H_2$ evolution was slow. Anhyd $Na_2SO_4$ was added, the mixture was filtered and thoroughly washed with $Et_2O$. The $Et_2O$ phase, containing **3d** and a contamination of **8d** ($^{31}$P NMR: δ = –157) and two secondary phosphanes ($^{31}$P NMR: δ = –46.9, –57.2), was treated with cold degassed 10% aq $H_2SO_4$ (100 mL), washed with a little cold water and dried ($Na_2SO_4$). Hexane (10 mL) was added and most of the $Et_2O$ was evaporated in vacuum to give 11.6 g (74%) of a yellow solid slightly contaminated with **8d**. Spectroscopic pure **3d** was obtained by repeated crystallization from a small amount of toluene; mp 162–165 °C (Lit.[4] mp 127–129 °C).

$^1$H NMR: δ = 7.04 ("t"m, $^3J$ = ca. 7, 7.8 Hz, $^4J_{PH}$ = 2.1 Hz, $^4J$ = 0.9 Hz, 1 H, H-5), 7.25 ("tt", $^3J$ ca. 7.5 Hz, $^5J_{PH}$= 1 Hz, $^4J$ = 1 Hz, 1 H, H-6), 7.25–7.42 (m, 3 H, $C_6H_5$), 7.61 (d"q", $^3J$ = 8.3 Hz, $^4J_{PH}$= 1.6 Hz, $^4J$ = 0.8 Hz, 1 H, H-7), 7.95 (ddd, $^3J$ = 7.8 Hz, $^3J_{PH}$ = 3.6, $^4J$ = 1 Hz, 1 H, H-4), 11.70 (br, 1 H, NH).

$^{13}$C NMR: δ = 113.6 (s, C-7), 120.5 (d, $^3J$ = 11.8 Hz, C-5), 125.2 (d, $^4J$ = ca. 2 Hz, C-6), 125.3 (d, $^3J$ = 12.4 Hz, 2C-*o*), 128.8 (d, $^2J$ = 21.0 Hz, C-4), 128.85 (d, $^5J$ = 2.9 Hz, C-*p*), 129.1 (s, 2C-*m*), 134.9 (d, $^2J$ = 15.8 Hz, C-*i*), 141.4 (d, $^1J$ = 41.1 Hz, C-3a), 142.9 (d, $^2J$ = 6.7 Hz, C-7a), 174.4 (d, $^1J$ = 50.6 Hz, C-2).

$^{31}$P NMR ($CDCl_3$): δ = 75.7 (72.1).

$^{31}$P NMR (THF-$d_8$): δ = 75.1.

MS (EI, 70 eV): *m/z* (%) = 211.2 (100, $M^+$), 183.2 (19), 107.2 (32), 91 (44).

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