Preparation of Bicyclic Phosphonic and Phosphinic Amides via N→C Migration of Phosphorus

Zhengjie He, Tom A. Modro*

Center for Heteroatom Chemistry, Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa

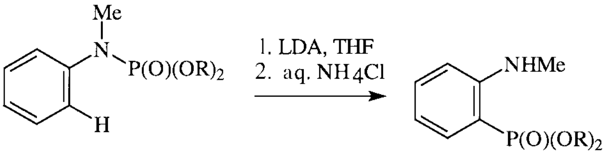
Fax +27(12)3625297; E-mail: tamodro@scientia.up.ac.za

Received 4 October 1999; revised 19 November 1999

Abstract: New phosphonic diamides and phosphinic amides of the 4,7,10-triaza-1λ^5-phosphabicyclo[5.3.0]decane and 4,7,10-triaza-1λ^5-phosphabicyclo[5.5.0]dodecane structures were prepared from bicyclic phosphoric triamides via the lithiation-induced N→C migration of phosphorus, followed by proton or haloalkane quenching.

Key words: metallation induced rearrangement, bicyclic structures, phosphonic diamides, phosphinic amides, N-alkylation

Preparation of (2-hydroxyaryl)phosphonic and phosphinic derivatives from the corresponding aryl phosphate esters via the O→C migration of the phosphoryl function, induced by *ortho*-lithiation was first observed by Melvin[1] and developed by Dhawan and Redmore.[2] The reaction was extended to the metallation of (2-haloaryl)phosphates,[3] and to the aromatic heterocyclic substrates,[4] and has become an accepted method for the formation of the C(aromatic)–P bond. The work of Masson et. al. demonstrated the applicability of the method to thiophosphates which undergo a similar S→C migration of phosphorus.[5] We have reported previously that a similar transformation, but involving the N→C migration of phosphorus, can be performed using the N-phosphorylated secondary aromatic amines as substrates (Scheme 1).[6]



Scheme 1

We report now the application of such lithiation-induced rearrangement to the recently synthesized bicyclic phosphoric triamide system, 2,8-diaryl-2,5,8-triaza-1λ^5-phosphabicyclo[3.3.0]octane 1-oxide **1**.[7] In a recent communication we reported that the 2,8-diphenyl derivative **1a** can undergo a single, or a double rearrangement involving the N→C migration of phosphorus, leading to two types of new bicyclic systems.[8] The reaction was now applied to other substrates of **1**, and was also modified to give the N-alkylated rearrangement products in a one-pot procedure using haloalkanes rather than MeOH in the final quenching step (Scheme 2).

An unsymmetrical, mono-N-alkylated phosphinic diamide **3f** could be obtained by quenching the product of the first migration with haloalkane, and of the second migration with MeOH, respectively (Scheme 3).

The N(4)-alkylated phosphonic amides **2d**−**2i** could also be prepared (in better yields and higher purity) by direct alkylation of their corresponding N(4)-H precursors **2a**−**2c**.

Products **2** and **3** represent interesting objects for further studies. Solvolytic cleavage of the P–N bond in **3** leads to a new, twelve-membered cyclic phosphinic ester system with three amine nitrogen atoms in the ring.[9] The P–N bond cleavage in **2** can lead, depending on the conditions, to new monocyclic, seven-membered phosphonic amidoesters, or to the noncyclic phosphonic diesters with a side chain of the bis-(2-aminoethyl)amine functionality.[10] All those compounds can be considered as polydentate ligand structures, and their chemistry and application are currently under investigation.

NMR spectra were recorded from $CDCl_3$ solutions on a Bruker AC 300 spectrometer and the ^{31}P chemical shifts are given relative to 85% H_3PO_4. Melting points are uncorrected. For column chromatography, Merck Kieselgel 60 (0.063 − 0.200 mm) was used as a stationary phase. Elemental analysis was performed at the Department of Chemistry, University of Cape Town.

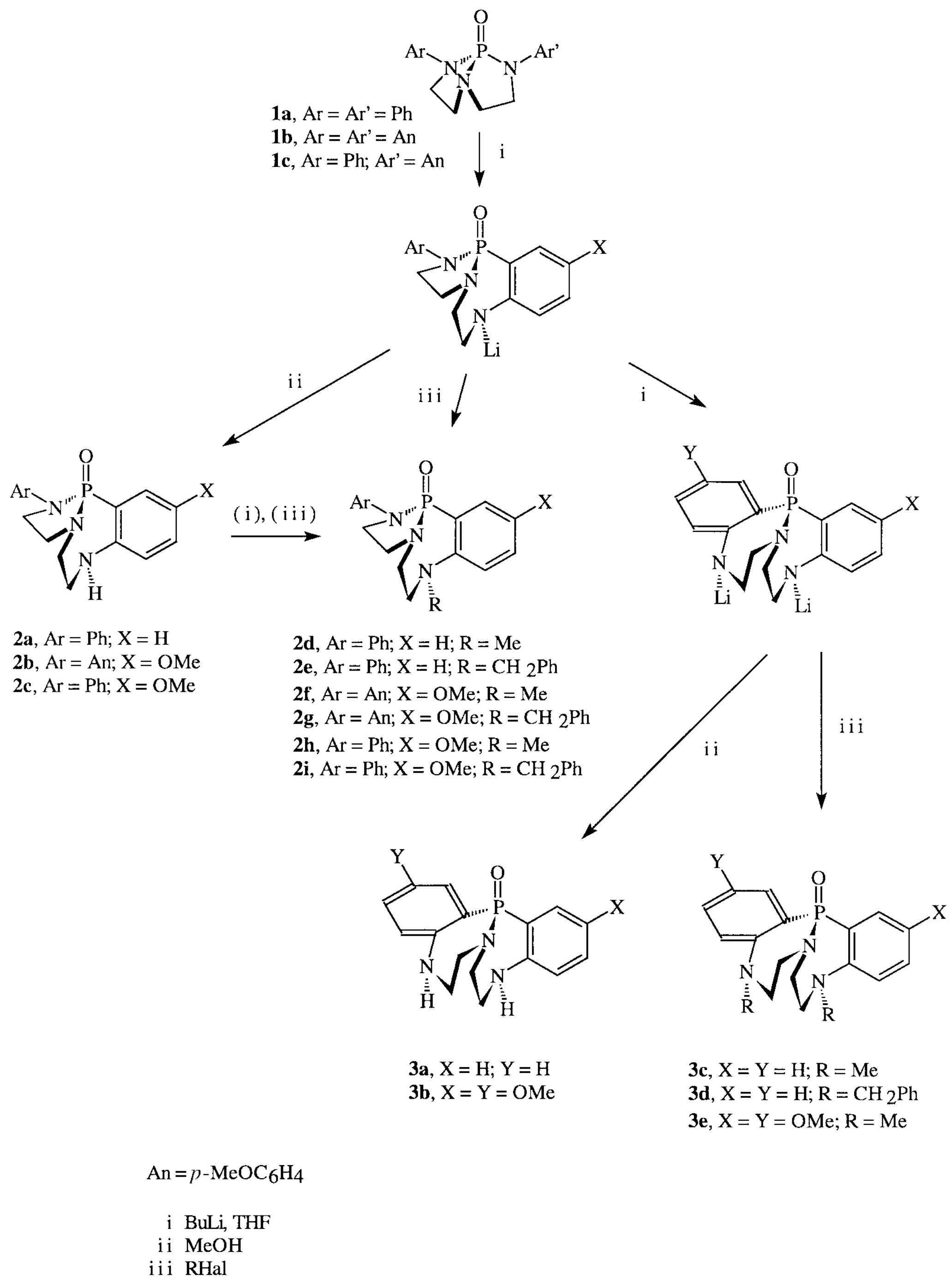
Preparation of substrates **1** was described before.[7]

Bicyclic Phosphonic Diamides (2a, 2b, 2c) and Phosphinic Amides (3a, 3b) (Quenching with MeOH); General Procedure

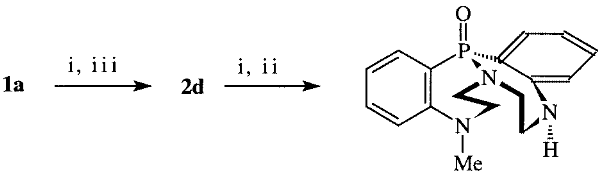
A solution of **1** (2.0 mmol) in anhyd THF (60 − 100 mL) was cooled to –78 °C under an atmosphere of anhyd N_2. The required amount of BuLi (1.6 M solution in hexane) was added by means of a syringe while stirring and cooling. The solution was stirred at –78 °C for 1 h, warmed to r.t. and stirred for the required period. MeOH (1−2 mL) was added, followed by $CHCl_3$ (200 mL), the solution was washed with H_2O (3 x 20 mL), dried (Na_2SO_4) and evaporated under reduced pressure. The crude product was purified by column chromatography using $CHCl_3$/acetone (1:1) as eluent. The individual products are listed in the Table.

Bicyclic Phosphonic Diamides (2d, 2e, 2f,) and Phosphinic Amides (3c, 3d, 3e) (Quenching with Haloalkane); General Procedure

A solution of **1** (2.0 mmol) was lithiated in the same manner as described above. After warming to r.t., the solution was stirred for additional 10 h, and the haloalkane (MeI or $PhCH_2Br$, 5 mmol) was injected into the solution while stirring and cooling with an ice bath. The reaction mixture was stirred overnight at r.t., the excess of BuLi was destroyed by addition of MeOH (1 − 2 mL), and further workup



Scheme 2



3f

Scheme 3

was carried out as described above. The crude products were purified by column chromatography using gradient elution with $CHCl_3$/acetone (4:1 to 2:1). The individual products obtained are listed in the Table.

Bicyclic Phosphonic Diamides (2g, 2h, 2i) (Alkylation of 2b, 2c); General Procedure

A solution of **2** (0.3 mmol) in THF (20 mL) was treated with BuLi (0.6 mmol) in the same manner as described above. After the addition of a haloalkane (0.6 mmol) the solution was stirred at r.t. for 20 h. MeOH (1 mL) was then added, volatile components were

Table Phosphonic Diamides **2** and Phosphinic Amides **3**

Compound[a]	BuLi (equiv) and reaction time at r.t. (h)	Yield (g, %)	Mp (°C) solvent	^{31}P NMR δ	^{1}H NMR (CDCl$_3$) δ, *J* (Hz)	^{13}C NMR (CDCl$_3$) δ, *J* (Hz)
2a	5, 2	0.51, 85	236.4–237.7 THF	23.7	3.05–3.25 (m, 2 H, NCH$_2$), 3.40–3.68 (m, 4 H, 2 NCH$_2$), 3.70–3.82 (m,1 H, NCH), 3.96 (m, 1 H, NCH), 4.32 (br s, 1 H, NH), 6.55–6.64 (m, 2 H$_{arom}$), 7.00 (t, 1 H, J_{HH} = 6.8, *p*-H$_{arom}$), 7.09 (t, 1 H, J_{HH} = 6.7, *p*’-H$_{arom}$), 7.29 (m, 3H$_{arom}$), 7.43 (d, 2 H, J_{HH} = 6.4, 2 *o*-H$_{arom}$)	44.9 (NCH$_2$), 45.5 (d, J_{CP} = 8.9, NCH$_2$), 46.6 (d, J_{CP} = 10.7, NCH$_2$), 49.8 (d, J_{CP} = 6.2, NCH$_2$), 117.8 (d, J_{CP} = 3.6, C$_{arom}$), 118.1 (d, J_{CP} = 11.6, C$_{arom}$), 119.0 (d, J_{CP} = 13.4, C$_{arom}$), 119.7 (d, J_{CP} = 154.3, C$_2$), 121.8 (s, C$_{arom}$), 129.2 (s, C$_{arom}$), 130.4 (d, J_{CP} = 7.1, C$_{arom}$), 131.1 (d, J_{CP} = 2.7, C$_{arom}$), 143.7 (d, J_{CP} = 6.2, C$_{arom}$), 149.9 (d, J_{CP} = 6.2, C$_{arom}$)
2b	5, 5	0.45, 63	201.8–203.0 CHCl$_3$/acetone (1:1)	23.3	3.00–3.27 (m, 2 H, NCH$_2$), 3.34 (s, 3 H, OMe), 3.39–3.82 (m, 6 H, 3 NCH$_2$), 3.75 (s, 3 H, OMe’), 6.58 (dd, 1 H, *J* = 7.0, 8.8, H$_{arom}$), 6.70 (m, 1 H, H$_{arom}$), 6.76 (dd, 1 H, *J* = 15.3, 2.9, H$_{arom}$), 6.85 (d, 2 H, *J* = 8.8, 2 H$_{arom}$), 7.34 (d, 2 H, *J* = 8.6, 2 H$_{arom}$)	45.5 (d, J_{CP} = 8.0, NCH$_2$), 45.8 (s, NCH$_2$), 47.3 (d, J_{CP} = 10.7, NCH$_2$), 49.0 (d, J_{CP} = 6.2, NCH$_2$), 55.1 (s, 3H, OCH$_3$), 55.6 (s, OCH$_3$’), 113.7 (d, J_{CP} = 8.9, C$_{arom}$), 114.7 (s, C$_{arom}$), 119.4 (d, J_{CP} = 2.7, C$_{arom}$), 120.2 (d, J_{CP} = 13.4, C$_{arom}$), 120.4 (d, J_{CP} = 3.6, C$_{arom}$), 120.9 (d, J_{CP} = 153.4, C$_2$), 136.6 (d, J_{CP} = 6.2, C$_{arom}$), 143.8 (d, J_{CP} = 6.2, C$_{arom}$), 152.8 (d, J_{CP} = 16.0, C$_{arom}$), 155.4 (s, C$_{arom}$)
2c	5, 5	0.39, 59	208.4–209.0 CHCl$_3$/acetone (1:1)	24.0	3.01–3.27 (m, 2 H, NCH$_2$), 3.32 (s, 3 H, OMe), 3.38–3.45 (m, 1 H, NCH), 3.49–3.71 (m, 4 H, 2 NCH$_2$), 3.74–3.83 (m, 1 H, NCH), 6.59 (dd, 1 H, *J* = 8.8, 7.2, H$_{arom}$), 6,70 (dd, 1 H, *J* = 8.8, 2,8, H$_{arom}$), 6.88 (dd, 1 H, *J* = 15.5, 2.8, H$_{arom}$), 6.97 (t, 1 H, J_{HH} = 7.5, *p*-H$_{arom}$), 7.27 (t, 2 H, *J* = 7.5, 2 H$_{arom}$), 7.41 (d, 2 H, *J* = 8.0, H$_{arom}$)	45.2 (d, J_{CP} = 8.9, NCH$_2$), 45.7 (s, NCH$_2$), 46.6 (d, J_{CP} = 10.7, NCH$_2$), 48.8 (d, J_{CP} = 6.2, NCH$_2$), 55.1 (s, OCH$_3$), 113.7 (d, J_{CP} = 8.9, C$_{arom}$), 117.9 (d, J_{CP} = 3.6, C$_{arom}$), 119.6 (d, J_{CP} = 2.7, C$_{arom}$), 120.5 (d, J_{CP} = 13.4, C$_{arom}$), 121.0 (d, J_{CP} = 149.0, C$_2$), 122.0 (s, C$_{arom}$), 129.2 (s, C$_{arom}$), 143.5 (d, J_{CP} = 6.2, C$_{arom}$), 143.7 (d, J_{CP} = 6.2, C$_{arom}$), 153.0 (d, J_{CP} = 15.2, C$_{arom}$)
2d	10, 10	0.25, 39 (separated from 57% of **3c**)[b]	187.6–188.7 THF/hexane (2:1)	28.8	2.91 (s, 3 H, NCH$_3$), 3.11–3.50 (m, 5 H, 5 NCH), 3.60–3.90 (m, 3 H, 3 NCH), 6.90 (m, 3 H, 3 H$_{arom}$), 7.25 (m, 4 H, 4 H$_{arom}$), 7.35 (m, 1 H, H$_{arom}$), 7.80 (ddd, 1 H, J_{HP} = 14.2, J_{HH} = 7.5, 1.5, H$_{arom}$ ortho to P)	41.3 (s, NCH$_3$), 44.0 (d, J_{CP} = 8.0, NCH$_2$), 46.1 (d, J_{CP} = 6.2, NCH$_2$), 47.8 (d, J_{CP} = 11.6, NCH$_2$), 53.8 (s, NCH$_2$), 116.9 (d, J_{CP} = 3.6, C$_{arom}$), 117.7 (d, J_{CP} = 9.8, C$_{arom}$), 121.2 (s, C$_{arom}$), 121.3 (d, J_{CP} = 13.4, C$_{arom}$), 123.3 (d, J_{CP} = 149.0, C$_2$), 129.0 (s, C$_{arom}$), 132.7 (d, J_{CP} = 2.7, C$_{arom}$), 134.4 (d, J_{CP} = 7.1, C$_{arom}$), 143.1 (d, J_{CP} = 7.1, C$_{arom}$), 151.8 (d, J_{CP} 7.1, C$_{arom}$)
2e	10, 10	0.22, 29 (separated from 39% of **3d**)[c]	199.2–201.6 THF/hexane (2:1)	27.2	2.98–3.15 (m, 2 H, 2 NCH), 3.42 (m, 3 H, 3 NCH), 3.50–3.81 (m, 3 H, 3 NCH), 4.38 (d, 1 H, J_{HH} = 15.0, NC*H*Ph), 4.53 (d, 1 H, J_{HH} = 15.0, NC*H*Ph), 6.83–6.99 (m, 3 H, 3 H$_{arom}$), 7.16–7.33 (m, 10 H, 10 H$_{arom}$), 7.72 (ddd, 1 H, J_{HP} = 14.5, J_{HH} = 7.8, 1.8, H$_{arom}$ ortho to P)	44.1 (d, J_{CP} = 8.0, NCH$_2$), 46.0 (d, J_{CP} = 6.2, NCH$_2$), 46.7 (d, J_{CP} = 10.7, NCH$_2$), 51.3 (s, NCH$_2$), 57.2 (s, *C*H$_2$Ph), 117.2 (d, J_{CP} = 4.5, C$_{arom}$), 118.8 (d, J_{CP} = 10.7, C$_{arom}$), 121.4 (d, J_{CP} = 13.4, C$_{arom}$), 121.5 (s, C$_{arom}$), 124.0 (d, J_{CP} = 150.8, C$_2$), 127.2 (s, C$_{arom}$), 127.9 (s, C$_{arom}$), 128.5 (s, C$_{arom}$), 129.2 (s, C$_{arom}$), 132.4 (d, J_{CP} = 2.7, C$_{arom}$), 133.6 (d, J_{CP} = 7.1, C$_{arom}$), 137.8 (s, C$_{arom}$), 143.2 (d, J_{CP} = 6.2, C$_{arom}$), 151.4 (d, J_{CP} = 6.2, C$_{arom}$)

Table (continued)

Compound[a]	BuLi (equiv) and reaction time at r.t. (h)	Yield (g, %)	Mp (°C) solvent	^{31}P NMR δ	^{1}H NMR (CDCl$_3$) δ, *J* (Hz)	^{13}C NMR (CDCl$_3$) δ, *J* (Hz)
2f	5, 10	0.33, 44 (separated from 13% of **3e**)	183.3–185.0 THF	28.8	2.85 (s, 3 H, NCH$_3$), 2.95–3.38 (m, 4 H, 4 NCH), 3.55–3.75 (m, 4 H, 4 NCH), 3.63 (s, 3 H, OCH$_3$), 3.71 (s, 3 H, OCH$_3$’), 6.76 (dt, 2 H, J_{HH} = 9.0, 2.1, 2 H$_{arom}$), 6.92 (m, 2 H, 2 H$_{arom}$), 7.15 (dt, 2 H, J_{HH} = 9.0, 2.1, 2 H$_{arom}$), 7.32 (dd, 1 H, J_{HP} = 14.7, J_{HH} = 3.1, 1 H$_{arom}$)	41.7 (s, NCH$_3$), 43.7 (d, J_{CP} = 8.9, NCH$_2$), 45.5 (d, J_{CP} = 5.3, NCH$_2$), 48.7 (d, J_{CP} = 12.5, NCH$_2$), 53.7 (s, NCH$_2$), 55.5 (s, OCH$_3$), 55.6 (s, OCH$_3$), 114.5 (s, C$_{arom}$), 118.6 (d, J_{CP} = 8.0, C$_{arom}$), 118.9 (d, J_{CP} = 3.6, C$_{arom}$), 119.7 (d, J_{CP} = 12.5, C$_{arom}$), 119.9 (d, J_{CP} = 2.7, C$_{arom}$), 125.1 (d, J_{CP} = 148.1, C$_2$), 136.2 (d, J_{CP} = 7.1, C$_{arom}$), 145.3 (d, J_{CP} = 6.2, C$_{arom}$), 154.6 (d, J_{CP} = 16.0, C$_{arom}$), 154.7 (s, C$_{arom}$)
2g	d	0.10, 75	153.4–155.9 (decomp.)	27.4	2.95–3.17 (m, 3 H, 3 NCH), 3.34 (m,2 H, 2 NCH), 3.52 (m, 1 H, NCH), 3.63–3.83 (m, 2 H, 2 NCH), 3.58 (s, 3 H, OCH$_3$), 3.74 (s, 3 H, OCH$_3$’), 4.26 (d, 1 H, J_{HH} = 14.7, NC*H*Ph), 4.45 (d, 1 H, J_{HH}= 14.7, NC*H*Ph), 6.80–6.93 (m, 4 H, 4 H$_{arom}$), 7.10–7.27 (m, 7 H, 7 H$_{arom}$), 7.29 (dd, 1 H, J_{HP} = 15.0, J_{HH} = 2.8, H$_{arom}$ ortho to P)	43.6 (d, J_{CP} = 8.0, NCH$_2$), 45.1 (d, J_{CP} = 6.2, NCH$_2$), 47.2 (d, J_{CP} = 11.6, NCH$_2$), 54.1 (s, NCH$_2$), 55.5 (s, OCH$_3$), 55.6 (s, OCH$_3$), 57.7 (s, N*C*H$_2$Ph), 114.6 (s, C$_{arom}$), 117.8 (d, J_{CP} = 8.9, C$_{arom}$), 119.2 (d, J_{CP} = 3.6, C$_{arom}$) 119.7 (d, J_{CP} = 2.7, C$_{arom}$), 120.9 (d, J_{CP} = 12.5, C$_{arom}$), 125.9 (d, J_{CP} = 149.8, C$_2$), 126.9 (s, C$_{arom}$), 128.1 (s, C$_{arom}$), 128.3 (s, C$_{arom}$), 136.3 (d, J_{CP} = 6.2, C$_{arom}$), 138.0 (s, C$_{arom}$), 144.6 (d, J_{CP} = 5.4, C$_{arom}$), 154.6 (d, J_{CP} = 16.0, C$_{arom}$), 154.9 (s, C$_{arom}$)
2h	d	0.080, 78	161.4–162.9 THF/hexane (1:1)	29.6	2.80 (s, 3 H, NCH$_3$), 3.20–3.40 (m, 4 H, 4 NCH), 3.59–3.79 (m, 3 H, 3 NCH), 3.65 (s, 3 H, OCH$_3$), 3.88 (m, 1 H, NCH), 6.80–6.93 (m, 3 H, 3 H$_{arom}$), 7.20 (m, 4 H, 4 H$_{arom}$), 7.46 (m, 1 H, H$_{arom}$)	41.8 (s, NCH$_3$), 43.4 (d, J_{CP} = 8.9, NCH$_2$), 45.4 (d, J_{CP} = 5.4, NCH$_2$), 48.1 (d, J_{CP} = 12.5, NCH$_2$), 53.7 (s, NCH$_2$), 55.6 (s, OCH$_3$), 116.6 (d, J_{CP} = 4.5, C$_{arom}$), 119.0 (d, J_{CP} = 8.9, C$_{arom}$), 120.0 (d, J_{CP} = 10.7, C$_{arom}$), 120.1 (d, J_{CP} = 1.8, C$_{arom}$), 121.1 (s, C$_{arom}$), 125.3 (d, J_{CP} = 149.2, C$_2$), 129.0 (s, C$_{arom}$), 142.8 (d, J_{CP} = 6.2, C$_{arom}$), 145.2 (d, J_{CP} = 5.3, C$_{arom}$), 154.9 (d, J_{CP} = 15.2, C$_{arom}$)
2i	d	0.104, 83	174.2–175.3 THF/hexane (1:1)	27.9	2.92–3.16 (m, 3 H, 3 NCH), 3.34 (m, 2 H, 2 NCH), 3.50–3.85 (m, 3 H, 3 NCH), 3.58 (s, 3 H, OCH$_3$), 4.22 (d, 1H, J_{HH} = 14.5, NC*H*Ph), 4.40 (d, 1 H, J_{HH} = 14.5, NC*H*Ph), 6.81–6.94 (m, 3 H, 3 H$_{arom}$), 7.04–7.26 (m, 9 H, 9 H$_{arom}$), 7.39 (dd, 1 H, J_{HP} = 15.2, J_{HH} = 2.8, H$_{arom}$ ortho to P)	43.4 (d, J_{CP} = 8.0, NCH$_2$), 45.2 (d, J_{CP} = 5.3, NCH$_2$), 46.8 (d, J_{CP} = 11.6, NCH$_2$), 51.5 (s, NCH$_2$), 55.5 (s, OCH$_3$), 57.9 (s, N*C*H$_2$Ph), 117.0 (d, J_{CP} = 4.5, C$_{arom}$), 118.3 (d, J_{CP} = 8.9, C$_{arom}$), 120.0 (d, J_{CP} = 1.8, C$_{arom}$), 121.2 (d, J_{CP} = 10.7, C$_{arom}$), 121.3 (s, C$_{arom}$), 125.9 (d, J_{CP} = 149.0, C$_2$), 127.1 (s, C$_{arom}$), 128.2 (s, C$_{arom}$), 128.3 (s, C$_{arom}$), 129.2 (s, C$_{arom}$), 137.9 (s, C$_{arom}$), 142.9 (d, J_{CP} = 6.2, C$_{arom}$), 144.7 (d, J_{CP} = 6.2, C$_{arom}$), 154.9 (d, J_{CP} = 16.0, C$_{arom}$)
3a	20, 10	0.30, 50	253.6–254.3 CHCl$_3$ (decomp)	33.1	3.12 (m, 2 H, 2 NCH), 3.41 (m, 2 H, 2 NCH), 3.63 (m, 4 H 4 NCH), 4,06 (br s, 2 H, 2 NH), 6.67 (dd, 2 H, J_{HH} = 7.8, 5.4, 2 H$_{arom}$ meta to P), 6.83 (dd, 2 H, J_{HH} = 7.5, 1.3, 2 H$_{arom}$ meta’ to P), 7.73 (m, 2 H, 2 H$_{arom}$ para to P), 7.41 (ddd, 2 H, J_{HP} = 14.3, J_{HH} = 7.8, 1.6, 2 H$_{arom}$ ortho to P)	47.7 (s, NCH$_2$), 53.1 (d, J_{CP} = 2.7, NCH$_2$), 119.2 (d, J_{CP} = 8.9, C$_{arom}$), 120.1 (d, J_{CP} = 12.5, C$_{arom}$), 120.8 (d, J_{CP} = 121.3, C$_2$, C$_{12}$), 132.2 (d, J_{CP} = 1.8, C$_{arom}$), 133.9 (d, J_{CP} = 8.9, C$_{arom}$), 153.3 (d, J_{CP} = 4.5, C$_{arom}$)

Table (continued)

Compound[a]	BuLi (equiv) and reaction time at r.t. (h)	Yield (g, %)	Mp (°C) solvent	^{31}P NMR δ	^{1}H NMR ($CDCl_3$) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$) δ, *J* (Hz)
3b	5, 5	0.11 15 (separated from 63% of **2b**)	ca 80 (softening)	32.4	3.04 (m, 2 H, 2 NCH), 3.33 (m, 4 H, 4 NCH), 3.57–3.68 (m, 2 H, 2 NCH), 3.66 (s, 6 H, 2 OCH_3), 6.72 (dd, 2 H, J_{HH} = 8.6, 6.0, 2 H_{arom}), 6.82 (dd, 2 H, J_{HH} = 8.6, 2.8, 2 H_{arom}), 7.07 (dd, 2 H, J_{HP} = 14.7, J_{HH} = 2.8, 2 H_{arom} ortho to P)	48.4 (s, NCH_2), 51.4 (d, J_{CP} = 3.6, NCH_2), 55.7 (s, OCH_3), 117.6 (d, J_{CP} = 10.6, C_{arom}), 119.4 (d, J_{CP} = 1.8, C_{arom}), 122.7 (d, J_{CP} = 11.6, C_{arom}), 124.3 (d, J_{CP} = 126.7, C_2, C_{12}), 143.1 (d, J_{CP} = 4.5, C_{arom}), 154.5 (d, J_{CP} = 15.2, C_{arom})
3c	10, 10	0.37, 57	144.4–146.3 (not recrystallized)	32.1	2.70 (s, 6 H, 2 NCH_3), 3.02 (m, 2 H, 2 NCH), 3.19 (m, 2 H, 2 NCH), 3.33 (m, 2 H, 2 NCH), 3.50 (m, 2H, 2 NCH), 6.80 (m, 4 H, 4 H_{arom}), 7.28 (m, 2 H, 2 H_{arom}), 7.38 (ddd, 2 H, J_{HP} = 14.5, J_{HH} = 7.5, 1.6, 2 H_{arom} ortho to P)	39.8 (s, NCH_3), 50,9 (d, J_{CP} = 4.5, NCH_2), 56.3 (s, NCH_2), 116.4 (d, J_{CP} = 8.0 C_{arom}), 120.3 (d, J_{CP} = 13.4, C_{arom}), 125.3 (d, J_{CP} = 130.2, C_2, C_{12}), 131.8 (d, J_{CP} = 1.8, C_{arom}), 132.9 (d, J_{CP} = 9.8, C_{arom}), 151.9 (d, J_{CP} = 4.5, C_{arom})
3d	10,10	0.38, 39	70.0–74.5 (not recrystallized)	32.6	2.70–2.89 (m, 2 H, 2 NCH), 3.21–3.49 (m, 6 H, 6 NCH), 4.16 (d, 1 H, J_{HH} = 14.5, NC*H*Ph), 4.34 (d, 1 H, J_{HH} = 14.5, NC*H*Ph), 6.84 (m, 4 H, 4 H_{arom}), 6.90–6.98 (m, 4 H, 4 H_{arom}), 7.18 (m, 6 H, 6 H_{arom}), 7.36 (m, 2 H, 2 H_{arom}), 7.57 (m, 2 H, 2 H_{arom})	50.4 (d, J_{CP} = 4.5, NCH_2), 53.2 (s, N*C*HPh), 56.7 (s, NCH_2), 117.8 (d, J_{CP} = 8.0, C_{arom}), 120.7 (d, J_{CP} = 12.5, C_{arom}), 124.3 (d, J_{CP} = 130.2, C_2, C_{12}), 127.1 (s, C_{arom}), 128.0 (s, C_{arom}), 128.4 (s, C_{arom}), 132.1 (d, J_{CP} = 0.9, C_{arom}), 133.5 (d, J_{CP} = 9.8, C_{arom}), 137.9 (s, C_{arom}), 151.8 (d, J_{CP} = 4.5, C_{arom})
3e	5, 10	0.10, 13	viscous oil	33.6	2.67 (s, 6 H, 2 NCH_3), 2.90–3.18 (m, 4 H, 4 NCH), 3.36 (m, 2 H, 2 NCH), 3.54–3.70 (m, 2 H, 2 NCH), 3.62 (s, 6 H, 2 OCH_3), 6.79–6.95 (m, 6 H, 6 H_{arom})	40.4 (s, NCH_3), 50.1 (br s, NCH_2), 55.6 (s, NCH_2), 56.4 (s, OCH_3), 117.3 (d, J_{CP} = 10.7, C_{arom}), 118.5 (d, J_{CP} = 1.8, C_{arom}), 118.6 (d, J_{CP} = 9.8, C_{arom}), 127.2 (d, J_{CP} = 128.4, C_2, C_{12}), 145.4 (s, C_{arom}), 154.3 (d, J_{CP} = 15.2, C_{arom})
3f	2.5, 5	0.15, 48	252.2–254.4 $CHCl_3$ (decomp)	31.8	2.48 (s, 3 H, NCH_3), 2.63 (dt, 1 H, J_{HH} = 11.2, 2.9, NCH), 2.90 (m, 1 H, NCH), 3.07 (m, 1 H, NCH), 3.24 (dt, 1 H, J_{HH} = 11.3, 4.1, NCH), 3.42 (m, 2 H, 2 NCH), 3.72 (m, 1 H, NCH), 4.04 (m, 1 H, NCH), 4.57 (br s, 1 H, NH), 6.47 (m, 1 H, H_{arom}), 6.59 (dd, 1 H, J_{HH} = 7.5, 5.6, H_{arom}), 6.70 (ddd, 1 H, J_{HP} = 15.6, J_{HH} = 7.6, 1.2, H_{arom} ortho to P), 6.87 (dd, 1 H, J_{HH} = 7.5, 5.4, H_{arom}), 7.00 (m, 1 H, H_{arom}), 7.13 (m, 1 H, H_{arom}), 7.46 (m, 1 H, H_{arom}), 8.01 (ddd, 1 H, J_{CP} = 13.0, J_{HH} = 7.5, 1.2, H_{arom} ortho to P)	40.1 (s, NCH_3), 46.6 (s, NCH), 50.6 (d, J_{CP} = 4.8, NCH), 54.2 (d, J_{CP} = 2.9, NCH), 56.7 (s, NCH), 116.9 (d, J_{CP} = 9.5, C_{arom}), 118.1 (d, J_{CP} = 13.4, C_{arom}), 118.7 (d, J_{CP} = 7.6, C_{arom}), 120.7 (d, J_{CP} = 128.8, C_2), 122.0 (d, J_{CP} = 12.4, C_{arom}), 125.6 (d, J_{CP} = 128.8, C_{12}), 130.4 (d, J_{CP} = 1.9, C_{arom}), 131.5 (d, J_{CP} = 11.4, C_{arom}), 133.3 (d, J_{CP} = 1.0, C_{arom}), 134.3 (d, J_{CP} = 7.6, C_{arom}), 151.0 (d, J_{CP} = 4.8, C_{arom}), 151.5 (d, J_{CP} = 2.9, C_{arom})

[a] Satisfactory elemental analyses were obtained for each compound.

[b] Prepared also in 87% by direct methylation of **2a**.

[c] Prepared also in 86% by direct benzylation of **2a**.

[d] Prepared by direct alkylation of the corresponding **2** (see General Procedure).

removed under reduced pressure, $CHCl_3$ (40 mL) was added and the solution was washed with H_2O (2 x 5 mL). After drying (Na_2SO_4) and evaporation of the solvent, the products were purified by column chromatography ($CHCl_3$/acetone, 4:1) and/or crystallization. The individual products obtained are listed in the Table.

2,3,11,12-Dibenzo-4-methyl-4,7,10-triaza-1λ^5-phosphabicyclo[5.5.0]dodecane 1-Oxide (3f)

A solution of **2d** (0.313 g, 1.0 mmol) in THF (40 mL) was cooled to –78 °C under the atmosphere of anhyd N_2. BuLi (1.6 mL of 1.6 M solution in hexane, 2.5 mmol) was added with stirring and cooling. The solution was stirred at –78 °C for 1 h, warmed up to r.t. and stirred for additional 5 h. MeOH (1 mL) was added, followed by $CHCl_3$ (50 mL), the solution was washed with H_2O (2 x 10 mL), dried (Na_2SO_4) and evaporated under reduced pressure. The product was purified by column chromatography using $CHCl_3$/acetone (2:1) as eluent. The data for the pure product are given in the Table.

Acknowledgement

We gratefully acknowledge financial support of this work by the University of Pretoria and the National Research Foundation.

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Article Identifier:
1437-210X,E;2000,0,04,0565,0570,ftx,en;P05699SS.pdf