Synthesis of novel macroheterocycles containing phosphorus and nitrogen

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Synthesesofnovel3-[1-(4-chlorophenyl)ethyl]-1(indol-1-yl-methylphenyl-phosphinoyl/thiophosphinoyl/selenophosphinoyl methyl)-1*H*-indole derivatives were accomplished in two steps. The synthetic route involves the cyclisation of equimolar quantities of 3-[4-chlorophenyl(1*H*-3-indolyl)methyl]-1*H*-indole (**1**) with bis(iodomethyl)phenylphosphine, bis(2-bromoethyl)phenylphosphine and tris-2-chloroethylphosphite (**2a–c**) in the presence of NaH under nitrogen atmosphere in dry THF to get P(III) intermediates (**3a–c**). These were further converted into the corresponding oxides, sulfides and selenides (**4a–i**) by reacting them with hydrogen peroxide, sulfur and selenium respectively.

Keywords: bis(iodomethyl)phenylphosphine, bis(2-bromoethyl)phenylphosphine, tris-2-chloroethylphosphite, macroheterocycle

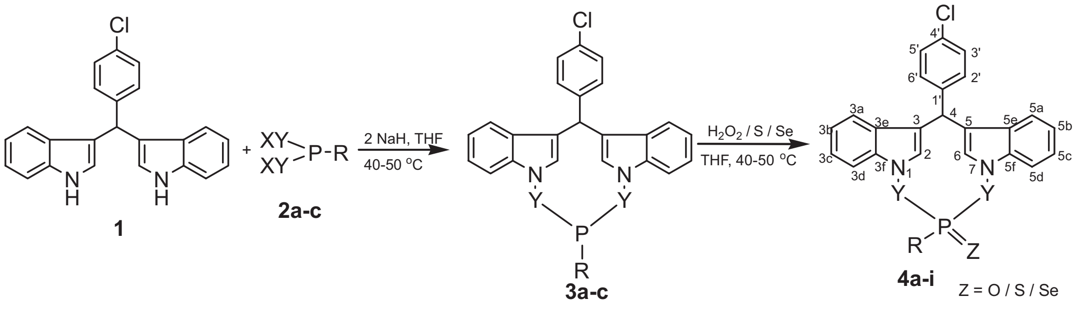
Phosphorus-containing macrocycles are interesting molecules with potential application in supramolecular and synthetic organic chemistry.[1] They have been synthesised as phosphine oxides, phosphines, phosphates, phosphonates and phosphoranes.[2] The importance of these molecules, as phosphorus analogues of crown ethers, is derived from their potential catalytic activity and ion carrying properties. The design of host molecules capable of binding neutral/ionic metals as guests is an important area which is rapidly expanding.[3] Cram,[4] Lehn,[5] Vogtle,[6] Majoral[1] and others and their coworkers have made significant advances in this field of host–guest complexation.[7] The past and present research has led to the construction of phosphorus macrocycles with large preorganised macrocyclic cavities bearing concave functionalities.[8] They are expected to function as good hosts in 'host–guest chemistry'. One-pot syntheses of new macroheterocyclic phosphoranes were reported from our research group[9] with low yields under dilute conditions. Template synthesis of 9-membered triphospha-macrocycles with rigid *o*-phenylene backbone functions was reported by Edwards and Whatton.[10] In view of the several possible applications and novelty in the chemistry of host–guest molecular assemblies, it is thought worthwhile to synthesise and study the properties of several phosphorus macrocycles with nitrogen and phosphorus(III) as donor atoms. These may also be of interest in the pharmaceutical industry.

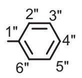
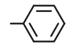
Results and discussion

Syntheses of novel 3-[1-(4-chlorophenyl)ethyl]-1(indol-1-yl-methylphenyl-phosphinoyl/thiophosphinoyl/selenophosphinoyl-methyl)-1*H*-indole derivatives **4a–i** were accomplished in two steps. The synthetic route involves the cyclisation of equimolar quantities of 3-[4-chlorophenyl(1*H*-3-indolyl)methyl]-1*H*-indole (**1**) with bis(iodomethyl)/bis(2-bromoethyl)-phenylphosphine and tris-2-chloroethylphosphite (**2a–c**) in the presence of sodium hydride in dry tetrahydrofuran at 40–50°C in nitrogen atmosphere to get the P(III) intermediates (**3a–c**). These were further converted into the corresponding oxides, sulfides and selenides (**4a–i**) by reacting them at 40–50°C with hydrogen peroxide, sulfur and selenium respectively. Purification of these macrocycles (**4a–i**) was achieved by filtering the reaction mixture to separate the sodium iodide/sodium bromide/sodium chloride. The filtrate was removed in a rotary evaporator to obtain a residue. This was washed with water and crystallised from ethanol. Physical data along with IR absorptions, elemental analysis and ^{31}P NMR data of **4a–i** are given in Table 1.

All the compounds **4a–i** exhibited characteristic IR absorptions[11-14] for (Table 1) P = O/S/Se, P–C$_{(aliphatic)}$ and P–O–C$_{(aliphatic)}$ groups.

The ^{1}H NMR spectra of **4a–i** (Table 2) showed[15,16] singlets for H-2 and 6 at δ 6.57–6.67. The triplets at δ 6.67–6.96 and δ 7.12–7.18 are attributed to H-2' and 6' and H-3' and 5' respectively. The aromatic protons of the indole moiety H-3a and 5a, H-3b and 5b, H-3c and 5c and H-3d and 5d showed



Compd.	X	Y	R
2a	I	-CH$_2$-	
2b	Br	-CH$_2$CH$_2$-	
2c	Cl	-CH$_2$CH$_2$O-	1" 2" -OCH$_2$CH$_2$Cl

Compd.	Y	Z	R
4a	CH$_2$	O	C$_6$H$_5$
4b	CH$_2$	S	C$_6$H$_5$
4c	CH$_2$	Se	C$_6$H$_5$
4d	CH$_2$CH$_2$	O	C$_6$H$_5$
4e	CH$_2$CH$_2$	S	C$_6$H$_5$

Compd.	Y	Z	R
4f	CH$_2$CH$_2$	Se	C$_6$H$_5$
4g	CH$_2$CH$_2$O	O	-OCH$_2$CH$_2$Cl
4h	CH$_2$CH$_2$O	S	-OCH$_2$CH$_2$Cl
4i	CH$_2$CH$_2$O	Se	-OCH$_2$CH$_2$Cl

Scheme 1

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Table 1 Physical IR and ^{31}P NMR spectroscopic data of **4a–i**

Compd no.	M.p./°C	Yield^a/%	Molecular formula	Elemental analysis calcd. (found)			IR/cm^{-1}		^{31}P NMR^{b,c} data/ppm
				C	H	N	P = O/S/Se	P–C$_{(aliphatic)}$/ P–O–C$_{(aliphatic)}$	
4a	121–123	53	$C_{31}H_{24}N_2OPCl$	73.4 (73.5	4.7 4.7	5.5 5.55)	1274	771	21.23
4b	134–135	62	$C_{31}H_{24}N_2PSCl$	71.2 (71.25	4.6 4.6	5.35) 5.3	774	762	33.18
4c	118–119	58	$C_{31}H_{24}N_2PSeCl$	65.3 (65.4	4.2 4.2	4.9 5.0)	628	768	69.61
4d	104–105	67	$C_{33}H_{28}N_2OPCl$	74.1 (74.1	5.2 5.3	5.2 5.2)	1279	754	27.12
4e	112–114	57	$C_{33}H_{28}N_2PSCl$	72.0 (71.9	5.1 5.1	5.1 5.1)	776	788	54.38
4f	129–130	70	$C_{33}H_{28}N_2PSeCl$	66.3 (66.2	4.7 4.65	4.7 4.65)	621	769	63.19
4g	114–115	68	$C_{29}H_{27}N_2O_4PCl_2$	61.15 (61.2	4.8 4.7	4.9 4.95)	1278	1136	9.32
4h	127–128	65	$C_{29}H_{27}N_2O_3PSCl_2$	59.5 (59.4	4.6 4.65	4.8 4.8)	771	1148	19.12
4i	139–140	59	$C_{29}H_{27}N_2O_3PSeCl_2$	55.1 (55.1	4.3 4.3	4.4 4.4)	623	1139	25.17

^{a}Recrystallised from ethanol.
^{b}Recorded in $CDCl_3$
^{c}Chemical shifts in ppm from 85% phosphoric acid.

Table 2 ^{1}H NMR spectroscopic data^{a,b} of **4a–i**

4a	δ = 5.93 (s, 1H, –CH), 6.60 (s, 2H, ArH), 6.96 (t, 2H, *J* = 5.8 Hz, ArH), 7.12 (t, 2H, *J* = 5.8 Hz, ArH), 7.20–7.34 (m, 8H, ArH), 5.58–5.81 (m, 4H, N-CH_2), 7.51–7.62 (m, 5H, ArH)
4b	δ = 5.87 (s, 1H, –CH), 6.61 (s, 2H, ArH), 6.84 (t, 2H, *J* = 5.6 Hz, ArH), 7.18 (t, 2H, *J* = 5.6 Hz, ArH), 7.26–7.32 (m, 8H, ArH), 5.54–5.77 (m, 4H, N-CH_2), 7.42 – 7.56 (m, 5H, ArH)
4c	δ = 5.90 (s, 1H, –CH), 6.58 (s, 2H, ArH), 6.92 (t, 2H, *J* = 5.7 Hz, ArH), 7.15 (t, 2H, *J* = 5.7 Hz, ArH), 7.22–7.30 (m, 8H, ArH), 5.59–5.80 (m, 4H, N-CH_2), 7.46–7.58 (m, 5H, ArH)
4d	δ = 5.91 (s, 1H, –CH), 6.62 (s, 2H, ArH), 6.87 (t, 2H, *J* = 5.6 Hz, ArH), 7.16 (t, 2H, *J* = 5.8 Hz, ArH), 7.24–7.34 (m, 8H, ArH), 5.05–5.12 (m, 4H, N-CH_2), 2.16–2.22 (m, 4H, –CH_2–PO), 7.39–7.51 (m, 5H, ArH)
4e	δ = 5.86 (s, 1H, –CH), 6.67 (s, 2H, ArH), 6.87 (t, 2H, *J* = 5.6 Hz, ArH), 7.14 (t, 2H, *J* = 5.7 Hz, ArH), 7.21–7.32 (m, 8H, ArH), 5.09–5.14 (m, 4H, N-CH_2), 2.19–2.23 (m, 4H, –CH_2–PO), 7.39–7.51 (m, 5H, ArH)
4f	δ = 5.90 (s, 1H, –CH), 6.57 (s, 2H, ArH), 6.76 (t, 2H, *J* = 5.4 Hz, ArH), 7.12 (t, 2H, *J* = 5.5 Hz, ArH), 7.25–7.33 (m, 8H, ArH), 5.07–5.13 (m, 4H, N-CH_2), 2.18–2.22 (m, 4H, –CH_2–PO), 7.38–7.52 (m, 5H, ArH)
4g	δ = 5.88 (s, 1H, –CH), 6.58 (s, 2H, ArH), 6.79 (t, 2H, *J* = 5.5 Hz, ArH), 7.15 (t, 2H, *J* = 5.7 Hz, ArH), 7.23–7.34 (m, 8H, ArH), 5.11–5.18 (m, 4H, N-CH_2), 4.29–4.63 (m, 4H, N-CH_2-$C\underline{H_2}OP$), 4.23 (t, 2H, –$OC\underline{H_2}CH_2Cl$), 3.53 (t, 2H, –$C\underline{H_2}Cl$)
4h	δ = 5.87 (s, 1H, –CH), 6.64 (s, 2H, ArH), 6.93 (t, 2H, *J* = 5.8 Hz, ArH), 7.16 (t, 2H, *J* = 5.8 Hz, ArH), 7.24–7.31 (m, 8H, ArH), 5.14–5.17 (m, 4H, N-CH_2), 4.29–4.64 (m, 4H, N-$CH_2C\underline{H_2}OP$), 4.21 (t, 2H, –$OC\underline{H_2}CH_2Cl$), 3.54 (t, 2H, –$C\underline{H_2}Cl$)
4i	δ = 5.84 (s, 1H, –CH), 6.61 (s, 2H, ArH), 6.90 (t, 2H, *J* = 5.7 Hz, ArH), 7.15 (t, 2H, *J* = 5.8 Hz, ArH), 7.23–7.31 (m, 8H, ArH), 5.12–5.16 (m, 4H, N-$C\underline{H_2}$), 4.27–4.61 (m, 4H, N-$CH_2C\underline{H_2}OP$), 4.23 (t, 2H, –$OC\underline{H_2}CH_2Cl$), 3.51 (t, 2H, –$C\underline{H_2}Cl$)

^{a}Recorded in DMSO.
^{b}Chemical shifts in ppm and *J* (Hz) in parenthesis.

complex multiplets in the region δ 7.20–7.34. The bridging methyne proton (H-4) showed a singlet at δ 5.84–5.91. The protons of the aromatic moiety linked at phosphorus in **4a–f** resonated as multiplets in the region δ 7.38–7.62. The protons of N–CH_2(C-8) gave a multiplet due to coupling with phosphorus in the region δ 5.54–5.81 in compounds, **4a–c**. A multiplet in the region δ 5.04–5.14 (4H) is assigned to –NCH_2 protons in compounds **4d–f**, whereas –CH_2–P(O)/S/Se protons resonated upfield as a multiplet (4H) in the range of δ 2.16–2.23 in **4d–f**. In compounds, **4g–i** two multiplets appeared one at δ 5.11–5.18 and the other at δ 4.29–4.64 for –N–CH_2 and –CH_2–O–P(O/Se/Se) respectively. The exocyclic P–O–CH_2–CH_2–Cl moiety gave two triplets for each methylene proton, one at δ 4.21–4.23 (OCH_2) and the other at δ 3.51–3.53 (–CH_2–Cl) as expected.

The ^{13}C NMR spectra (Table 3) were recorded[17,18] for a few of the title compounds (**4c, 4e** and **4g**). The bridged methyne carbon (C-4) resonated upfield as a singlet in the range of 35.0–36.9 ppm due to its aliphatic nature and steric environment. In compound **4c**, the methylene carbon, P–CH_2–N, resonated[18b] as a doublet at δ 44.2(d, $^1Jp\text{-}c$ = 136 Hz). In compound **4e**, the N-CH_2 methylene carbon gave a doublet at δ 35.0 (d, ^2Jpcc = 4.2 Hz) and the P-CH_2 carbon resonated as a doublet at δ 44.5 (d, ^1Jpc = 132 Hz) due to coupling with phosphorus. In **4g,** the N–CH_2– carbon signal appeared as a doublet at δ 35.6 (d, *J* = 4.7 Hz). The carbon of P–O–CH_2– resonated downfield as a doublet at δ 61.3 (d, ^2Jpoc = 5.1 Hz). The exocyclic P–O–CH_2– moiety gave a doublet at δ 63.5 (d, ^2Jpoc = 4.3 Hz) and –CH_2–Cl resonated as a singlet at δ 42.8. ^{31}P NMR spectra of all the compounds **4a–i** showed only one phosphorus signal in the range of 9.32–69.61 ppm depending on the elements present at phosphorus.[19]

Experimental

All reactions were carried out under anhydrous conditions under a nitrogen atmosphere. Melting points were determined with open capillary tubes using a Mel-temp apparatus. Elemental analyses were performed by the Central Drug Research Institute, Lucknow, India. All IR spectra were recorded as KBr pellets on a Perkin-Elmer 1430 instrument, ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on AMX 400 MHz spectrometer, operating at 400 MHz for ^{1}H, 100 MHz for ^{13}C and 161.9 MHz for ^{31}P as solutions in $CDCl_3$ and the chemical shifts were referenced to TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P).

Table 3 ^{13}C NMR chemical shifts^{a,b} of some members of **4c**, **4e** and **4g**

Compd no.	δ
4c	140.3 (s, 2C, C-2 & 6), 124.1 (s, 2C, C-3 & 5), 35.0 (s, 1C, C-4), 121.4 (s, 2C, C-3a & 5a), 122.1 (s, 2C, C-3b & 5b), 123.6 (s, 2C, C-3c & 5c), 116.8 (s, 2C, C-3d & 5d), 152.6 (s, 2C, C-3e & 5e), 153.0 (s, 2C, C-3f & 5f), 44.2 (d, *J* = 136 Hz, 2C, C-8 & 10, P–$\underline{\text{C}}\text{H}_2$–N), 140.3 (s, 1C, C-1'), 129.1 (d, *J* = 10.1 Hz, 2C, C-2' & 6'), 126.2 (s, 2C, C-3' & 5'), 135.8 (s, 1C, C-4'), 134.8 (s, 1C, C-1''), 127.8 (d, *J* = 9.3 Hz, 2C, C-2'' & 6''), 129.6 (s, 2C, C-3'' & 5''), 133.1 (s, 1C, C-4'')
4e	140.7 (s, 2C, C-2 & 6), 123.8 (s, 2C, C-3 & 5), 36.9 (s, 1C, C-4), 120.2 (s, 2C, C-3a & 5a), 122.4 (s, 2C, C-3b & 5b), 123.9 (s, 2C, C-3c & 5c), 115.8 (s, 2C, C-3d & 5d), 151.4 (s, 2C, C-3e & 5e), 152.9 (s, 2C, C-3f & 5f), 35.0 (d, *J* = 4.2 Hz, 2C, C-8 & 12, P–CH_2–$\underline{\text{C}}\text{H}_2$–N), 44.5 (d, *J* = 132 Hz, 2C, C-9 & 11, P–$\underline{\text{C}}\text{H}_2$), 128.6 (s, 2C, C-2' & 6'), 127.5 (s, 2C, C-3' & 5'), 131.5 (s, 1C, C-4'), 129.5 (s, 1C, C-1''), 128.4 (d, *J* = 9.1 Hz, 2C, C-2'' & 6''), 128.8 (s, 2C, C-3'' & 5''), 129.3 (s, 1C, C-4'').
4g	141.4 (s, 2C, C-2 & 6), 124.6 (s, 2C, C-3 & 5), 35.7 (s, 1C, C-4), 121.8 (s, 2C, C-3a & 5a), 122.6 (s, 2C, C-3b & 5b), 123.6 (s, 2C, C-3c & 5c), 117.4 (s, 2C, C-3d & 5d), 151.6 (s, 2C, C-3e & 5e), 153.2 (s, 2C, C-3f & 5f), 35.6 (d, *J* = 4.7 Hz, 2C, C-8 & 14, N–$\underline{\text{C}}\text{H}_2$), 61.3 (d, *J* = 5.1 Hz, 2C, C-9 & 13, P–O–CH_2), 133.3 (s, 1C, C-1'), 128.4 (s, 2C, C-2' & 6'), 127.1 (s, 2C, C-3' & 5'), 130.7 (s, 1C, C-4'), 63.5 (d, *J* = 4.3 Hz, 1C, C-1''), 42.8 (s, 1C, C-2'')

[a] Recorded in CDCl_3.
[b] Chemical shifts in ppm and *J* (Hz) in parenthesis.

Table 4 Mass spectroscopic data of **4c**, **4e** and **4g**

Compd no.	*m/z* (relative abundance)
4c	571 ($M^{+\bullet}$ + 1, 12), 570 ($M^{+\bullet}$, 10), 537 (15), 521 (2), 491 (16), 457 (21), 445 (14), 427 (13), 404 (7), 391 (2), 381 (6), 357 (13), 355 (34), 337 (6), 314 (16), 312 (23), 284 (6), 271 (10), 253 (23), 223 (8), 222 (14), 221 (100), 211 (18), 192 (19), 174 (38), 156 (21), 137 (4), 129 (22), 116 (7).
4e	552 ($M^{+\bullet}$ + 1, 8), 551 ($M^{+\bullet}$, 5), 542 (6), 512 (13), 510 (21), 413 (3), 411 (9), 371 (3), 369 (7), 349 (2), 314 (8), 312 (24), 294 (2), 293 (12), 284 (7), 244 (2), 243 (9), 242 (100), 216 (3), 195 (2), 194 (8), 192 (26), 183 (2), 174 (6), 156 (6), 129 (19), 116 (11).
4g	570 ($M^{+\bullet}$ + 1, 2), 569 ($M^{+\bullet}$, 4), 529 (4), 496 (6), 483 (4), 465 (2), 448 (10), 447 (5), 406 (3), 404 (11), 395 (9), 391 (3), 379 (5), 363 (17), 347 94), 336 (2), 318 (7), 317 925), 312 (36), 303 (8), 285 (10), 285 (10), 284 (39), 271 (28), 253 95), 239 (8), 238 (53), 236 (58), 235 (4), 213 (14), 194 (31), 192 (100), 174 (28), 156 (3), 135 (7), 116 (15).

Compound **1** was prepared by adopting the reported[15] procedure. Tris 2-chloroethyl phosphite (**2c**) was procured from Sigma-Aldrich Chemical Company, Inc, USA and was used without further purification.

Synthesis of phosphorus and nitrogen macroheterocyclic compound (**4a**): A solution of bis (iodomethyl)phenylphosphine (**2a**) (0.39 g, 0.001 mole) in dry THF (15 ml) was added slowly to a solution of 3-[4-chlorophenyl(1*H*-3-indolyl)methyl]-1*H*-indole **1** (0.356 g, 0.001 mole) and sodium hydride (0.048 g, 0.002 mole) in dry THF (30 ml) at 0°C. After completion of the addition, the temperature of the reaction mixture was raised to 40–50°C and the mixture was stirred for one hour to form the trivalent P(III) intermediate, **3a**. The progress of the reaction was judged by the TLC analyses of the reaction mixture using *n*-hexane and ethyl acetate (4:1) on silica gel. The precipitated sodium iodide was separated by filtration under nitrogen atmosphere. Hydrogen peroxide (30% H_2O_2, 0.04 ml, 0.001 mole) was added to it dropwise at 0–5°C. The reaction mixture was brought to 40–50°C and kept with stirring for 2 h for the completion of oxidation as indicated by TLC analyses. The solvent was evaporated in a rotary evaporator. The resulting crude product was crystallised from ethanol to yield 0.26 g (53%) of **4a,** m.p. 121–123°C.

Synthesis of phosphorus and nitrogen macroheterocyclic compounds (**4e**) *and* (**4f**): A solution of bis (2-bromoethyl)phenylphosphine (**2b**, 0.32 g, 0.001 mole) in dry THF (20 ml) was added slowly to a solution of 3-[4-chlorophenyl(1*H*-3-indolyl) methyl]-1*H*-indole **1** (0.356 g, 0.001 mole) and sodium hydride (0.048 g, 0.002 mole) in dry THF (30 ml) at 0°C. After completion of the addition, the temperature of the reaction mixture was raised to 50–55°C and the mixture was stirred for 3 hours to form the trivalent P(III) intermediate, **3b**. The progress of the reaction was judged by the TLC analyses of the reaction mixture using *n*-hexane and ethylacetate (7:3) on silica gel. The precipitated sodium bromide was separated by filtration under a nitrogen atmosphere. To the filtrate sulfur/selenium (0.001 mole) in THF (20 ml) was added dropwise at 5–10°C. The reaction mixture was brought to reflux and kept with stirring for 2 h for the completion of reaction as indicated by TLC analysis. The solvent was evaporated in a rotary evaporator. The resulting crude product (**4e**/**4f**) obtained was crystallised from ethanol.

Synthesis of the other compounds **4b–d** and **4g–i** was achieved by adapting the above procedure.

Preparation of bis (iodomethyl)phenylphosphine (**2a**): In a dry 100 ml three necked flat-bottomed flask, fitted with dropping funnel, a reflux condenser fitted with a calcium chloride tube, an inlet for dry nitrogen and a thermometer were placed magnesium turnings (0.48 g, 0.02 mole) and dry THF (10 ml). The reaction mixture was kept stirring and diiodomethane (5.35 g, 0.02 mole) in dry THF (10 ml) was added at 10–15°C over 10 min. To this mixture, dichlorophenylphosphine (1.79 g, 0.01 mole) in dry THF (10 ml) was added dropwise from a dropping funnel. When the reaction started the temperature increased to 40–45°C. Stirring of the mixture was continued until the magnesium metal was completely dissolved to form bis(iodomethyl)phenylphosphine.

Preparation of bis (2-bromoethyl) phenylphosphine (**2b**): In a dry 100 ml three necked flat-bottomed flask, fitted with dropping funnel, a reflux condenser fitted with a calcium chloride tube, an inlet for dry nitrogen and a thermometer were placed magnesium turnings (0.48 g, 0.02 mole) and 10 ml of dry THF. The reaction mixture was kept stirring and 1,2-dibromoethane (3.76 g, 0.02 mole) in dry THF (20 ml) was added at 5–10°C over 10 min. To this mixture dichlorophenylphosphine (1.79 g, 0.01 mole) in dry THF (10 ml) was added dropwise from a dropping funnel. When the reaction started the temperature was increased to 50–55°C. Stirring of the mixture was continued until the magnesium metal was completely dissolved to form bis(2-bromoethyl)phenylphosphine (**2b**).

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