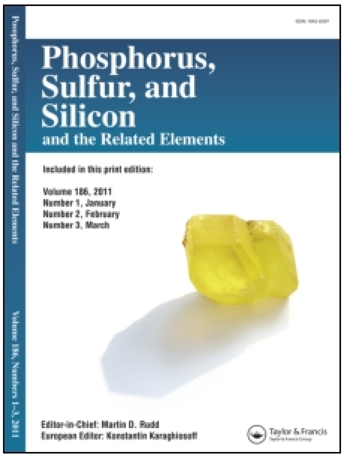

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Syntheses and Characterization of Ten-Membered Cyclic and Large Bite Acyclic Bis(phosphines)

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To cite this Article Balakrishna, Maravanji S. and Panda, Rashmishree(2003) 'Syntheses and Characterization of Ten-Membered Cyclic and Large Bite Acyclic Bis(phosphines)', Phosphorus, Sulfur, and Silicon and the Related Elements, 178: 6, 1391 — 1396

To link to this Article: DOI: 10.1080/10426500307891

URL: http://dx.doi.org/10.1080/10426500307891

Phosphorus, Sulfur, and Silicon, 178:1391–1396, 2003

ISSN: 1042-6507 print
DOI: 10.1080/10426500390200710

SYNTHESES AND CHARACTERIZATION OF TEN-MEMBERED CYCLIC AND LARGE BITE ACYCLIC BIS(PHOSPHINES)

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(Received October 14, 2002; accepted December 6, 2002)

Reaction of bis(dichlorophosphino)aniline with CH_2 bridged bis(phenols) or substituted diamine gives the 10-membered heterocyclic phosphorochloridities in quantitative yield. The bis(phenols) also react with chlorodiphenylphosphine to afford the bulky acyclic bis(phosphinites).

Keywords: Acyclic; heterocycles; phosphorochloridites; tervalent phosphorus centers

The syntheses of the new cyclic phosphorochloridites are interesting owing to their steric and electronic properties. Here, both the steric and electronic attributes can be readily altered at phosphorus(III) centers by carrying out a variety of nucleophilic substitution reactions. In case of compounds containing P—N bonds the steric environment can be fine tuned by changing the substituents on the aromatic groups and the nitrogen atom as well. Beside this, acyclic phosphorus compounds with bulky substituents are used widely as homogeneous catalysts in industrial applications. In this context, bis(phosphinites) with bulky substituents have shown encouraging regioselectivity in organic synthesis.[1–5]

In our previous study[6] we explored the rich transition metal chemistry of heterocyclic phosphorochloridite and its fluoro derivative with sulfur spacer between the two phenolic groups, where the heterocycles retain the P—Cl and P—F bonds after complexation. As a part of our interest[7–11] in designing new P(III) based ligand systems, we report

We are grateful to the Department of Science and Technology (DST), India for financial support. We also thank the RSIC, IIT, Bombay, and Sophisticated Instrumentation Facility (SIF), IISc, Bangalore for NMR spectra.

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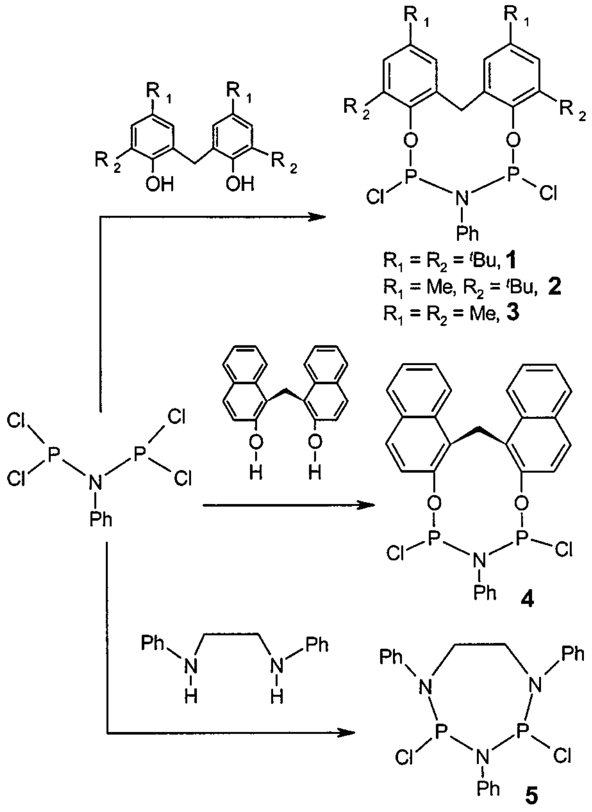
here the easy, high-yield, and one-pot syntheses of some novel heterocycles and bulky acyclic bis(phosphinites) containing two tertiary phosphine centres.

RESULTS AND DISCUSSION

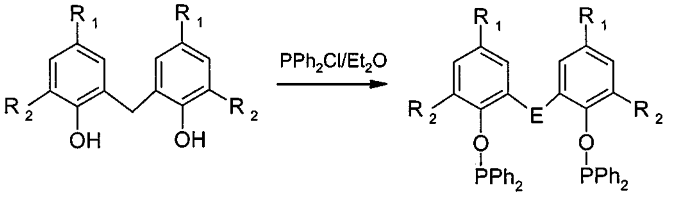
Stoichiometric reactions of 2,2′-methylenebis(2,4-di-alkyllphenol) with $Cl_2PN(Ph)PCl_2$ afford the 10-membered heterocycles, $PhN(PCl)_2\{(-OC_6H_2(R_1R_2))(\mu\text{-}CH_2)((R_1R_2)C_6H_2O-)\}$ (R_1, R_2 = ${}^tBu$, **1**; R_1 = Me, R_2 = ${}^tBu$, **2**; R_1, R_2 = Me, **3**) in good yield (Scheme 1). In a similar way, bis(2-hydroxy-1-naphthyl)methane and N,N′-diphenylethylenediamine react with $Cl_2PN(Ph)PCl_2$ to afford the heterocycles $PhN(PCl)_2\{(-OC_{10}H_6)\ (\mu-CH_2)(C_{10}H_6O-)\}$ (**4**) and $PhN(PCl)_2\ \{-N(Ph)CH_2CH_2(Ph)N-)\}$ (**5**) respectively.



SCHEME 1

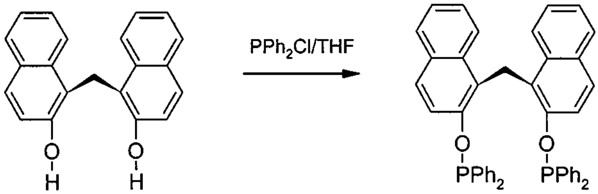
The compounds **1–5** are crystalline white solids, highly air and moisture sensitive both in solid state and in the solution; on exposure to air they rapidly form the corresponding oxides, which is, confirmed by the $^{31}P\{^1H\}$ NMR spectroscopic studies. The structure and molecular composition of all the heterocycles were confirmed by NMR (^1H, ^{31}P $\{^1H\}$) spectroscopic data and by elemental analyses (Table I).

Reaction of 2,2′-thiobis(4,6-di-*tert*-butylphenol) with two equivalents of chlorodiphenylphosphine in the presence of triethylamine affords the expected compound $Ph_2P(-OC_6H_2(R_1R_2)_2)(\mu-S)((R_1R_2)_2C_6H_2O-)$-$PPh_2$ (**6**) in good yield. Compounds of the type $Ph_2P(-OC_6H_2(R_1R_2)_2)$ $(\mu-CH_2)((R_1R_2)_2C_6H_2O-)PPh_2$, ($R_1 = R_2 = {}^tBu$, **7**; $R_1 = Me$, $R_2 = {}^tBu$, **8**; $R_1 = R_2 = Me$, **9**) were obtained in 85–88% yield by reacting the corresponding 2,2′-methylenebis(4,6-di-alkylphenol) with chlorodiphenylphosphine (Eq. 1). The analogous bis(naphthol) derivative, bis{2-(diphenylphosphinoxy)-1-naphthyl} (**10**) was prepared in a similar way (Eq. 2). All these compounds **6–10** have been characterized by NMR (^1H, $^{31}P\{^1H\}$) spectroscopic studies and the molecular composition have been established by microanalyses (Table I). The coordinatively unsaturated phosphorus(III) centers present in these compounds are prone to both oxidation reactions and Lewis base activity. The oxidation and coordination properties of the compound **10** have been explored[12] and the reactivity and transition metal chemistry of other compounds is in progress.



(1)

$R_1 = R_2 =$ tert-Butyl, E = S, **6**
$R_1 = R_2 =$ tert-Butyl, E = $-CH_2-$, **7**
$R_1 =$ Me, $R_2 =$ tert-Butyl, E = $-CH_2-$, **8**
$R_1 = R_2 =$ Me, E = $-CH_2-$, **9**



10

(2)

TABLE I Spectroscopic and Analytical Data for the Compounds **1–10**[a]

Entry	Yield (%)	m.p. (°C)	^{1}H δ in ppm	^{31}p[b]δ	Elemental analyses calcd found (%)
1	95 (6.20 g)	172–174	δ 7.14–7.22 (m, 5H, N-phenyl), 7.29 (d, 2H, Ar), 7.22 (d, 2H, Ar), 4.42 (d, 1H, CH_2 $^2J_{HH}$ = 14.46 Hz), 3.73 (d, 1H, CH_2 $^2J_{HH}$ = 14.46 Hz), 1.42 (s, 18H, *tert*-butyl), 1.30 (s, 18H, *tert*-butyl)	138.2 (s)	C, 65.00; H, 7.32; N, 2.16 C, 65.24; H, 7.48; N, 1.98
2	95 (5.30 g)	164–166	δ 7.08–7.20 (m, 5H, N-phenyl), 7.19 (s, 2H, Ar), 7.13 (s, 2H, Ar), 4.35 (d, 1H, Ar—CH_2—Ar $^2J_{HH}$ = 14.65 Hz), 3.79 (d, 1H, CH_2 $^2J_{HH}$ = 14.65 Hz), 2.3 (s, 6H, CH_3), 1.37 (s, 18H, *tert*-butyl)	134.4 (s)	C, 61.92; H, 6.27; N, 2.49 C, 61.88; H, 6.21; N, 2.35
3	93 (4.50 g)	150–152	δ 7.12–7.18 (m, 5H, N-Phenyl), 7.14 (s, 2H, Ar), 6.92 (s, 2H, Ar), 4.15 (d, 1H, Ar—CH_2—Ar $^2J_{HH}$ = 13.20 Hz), 3.75 (d, 1H, CH_2 $^2J_{HH}$ = 13.20 Hz), 2.23 (s, 6H, CH_3), 2.10 (s, 6H, CH_3)	128.8 (s)	C, 57.79; H, 4.85; N, 2.93 C, 57.88; H, 4.79; N, 2.86
4	87 (4.52 g)	186–188	δ 8.26 (d, 2H, Ar), 7.86 (d, 2H, ArH), 7.78 (d, 2H, Ar), 7.56 (t, 2H, Ar), 7.48 (t, 2H, Ar), 7.25–7.29 (m, 5H, N-Phenyl), 5.16 (d, 1H, Ar—CH_2—Ar $^2J_{HH}$ = 16.48 Hz), 4.84 (d, 1H, Ar—CH_2—Ar $^2J_{HH}$ = 16.48 Hz)	152.6 (s)	C, 62.32; H, 3.29; N, 2.69 C, 62.01; H, 3.32; N, 2.57
5	89 (3.86 g)	128–130	δ 6.82–7.43 (m, 15H, phenyl), 3.32 (m, 4H, CH_2CH_2)	138.4 (s)	C, 55.32; H, 4.41; N, 9.67 C, 55.48; H, 4.32; N, 9.50
6	86 (6.97 g)	145–147	δ 7.50–7.71 (m, 24H, Phenyl), 1.13 (s, 18H, *tert*-butyl), 1.21 (s, 18H, *tert*-butyl)	115.8 (s)	C, 77.00; H, 7.46 C, 77.32; H, 7.19
7	88 (7.00 g)	174–176	δ 7.45–7.64 (m, 24H, Phenyl), 4.03 (s, 2H, CH_2), 1.38 (s, 18H, *tert*-butyl), 1.30	116.1 (s)	C, 80.27; H, 7.88 C, 80 60; H, 7.35
8	85 (6.00 g)	168–170	δ 7.48–7.67 (m, 24H, Ar), 3.83 (s, 2H, CH_2), 2.22 (s, 6H, CH_3), 1.41 (s, 18H, *tert*-butyl)	114.4 (s)	C, 79.63; H, 7.11 C, 80.03; H, 7.49
9	81 (5.10 g)	178–180	δ 7.51–7.69 (m, 24H, Ar), 3.80 (s, 2H, CH_2), 2.19 (s, 6H, *p*-CH_3), 2.13 (s, 6H, *o*-CH_3)	112.7 (s)	C, 78.82; H, 6.13 C, 79.16; H, 592
10	94 (6.30 g)	182–184	δ 8.27 (d, 2H, Ar), 7.65–7.71 (m, 4H, Ar), 7.61 (d, 2H, Ar), 7.47–7.51 (m, 2H, Ar), 7.34–7.41 (m, 20H, $OPPh_2$), 7.19 (t, 2H, Ar), 4.89 (s, 2H, Ar—CH_2—Ar)	112.2 (s)	C, 80.82; H, 5.92 C, 80.71; H, 5.03

[a] All spectra in $CDCl_3$.

[b] δ in ppm *vs* 85% H_3PO_4, d = doublet, m = multiplet, s = singlet, t = triplet.

EXPERIMENTAL

All synthetic manipulations were carried out under a pure dinitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use. Ethers and dichloromethane were distilled over Na-benzophenone and calcium hydride respectively. 2,2′-Thiobis{4,6-di-*tert*-butylphenol},[13] 2,2′-methylenebis{4,6-di-alkyl(R_1,R_2)phenol},[14] bis(2-hydroxyl-1-naphthyl)methane[15] and bis(dichlorophosphino)-aniline[16] were prepared according to the cited procedures. The ^{1}H and $^{31}P\{^1H\}$ NMR (δ in ppm) spectra were obtained on a VXR 300S spectrometer operating at appropriate frequencies using tetramethylsilane and 85% H_3PO_4 as internal and external references respectively. Positive shifts lie downfield in all cases. Microanlyses were performed on a Carlo Erba model 1106 elemental analyser.

Syntheses of Compounds 1–5

Representative Procedure

A mixture of 2,2′-methylenebis{4,6-di-alkyl(R_1,R_2)phenol}/bis-(2-hydroxy-1-naphthyl)methane/N,N′-diphenyl ethylenediamine (10.0 mmol) and triethylamine (2.10 g, 20.1 mmol) in THF (50 ml) was added dropwise to a suspension of bis(dichlorophosphino)aniline (3.0 g, 10.0 mmol) and in THF (30 ml) under nitrogen with vigorous stirring at −5°C. The reaction mixture was stirred overnight at 25°C. Triethylamine hydrochloride was filtered off and solvent was removed under reduced pressure to give crude product as pale white solid, which was recrystallized from a mixture of CH_2Cl_2-hexane (3:1).

Syntheses of Compounds 6–10

Representative Procedure

A solution of PPh_2Cl (2 mmol) in diethylether or THF (30 ml) was added dropwise to a mixture of 2,2′-thiobis(4,6-di-*tert*-butylphenol)/2,2′-methylenebis(4,6-dialkylphenol)/bis(2-hydroxyl-1-naphthyl)methane (1 mmol) and triethylamine (2.1 mmol) also in THF (50 ml) at 0°C with vigorous stirring. The reaction mixture was warmed to room temperature and stirring was continued overnight. The triethylamine hydrochloride was removed by filtration. The solvent was removed under vacuum to give a white solid of crude product, which was recrystallized from a mixture of dichloromethane/petroleum ether (2:1). The physical and analytical data is given Table I.

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