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## 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>

## The Dianion Cyclization Strategy for the Synthesis of Dibenzoheterocycles

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**To cite this Article** Singh, M. S. and Singh, Shweta(2008) 'The Dianion Cyclization Strategy for the Synthesis of Dibenzoheterocycles', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 183: 6, 1510 — 1517

**To link to this Article:** DOI: 10.1080/10426500701690863

**URL:** <http://dx.doi.org/10.1080/10426500701690863>

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## The Dianion Cyclization Strategy for the Synthesis of Dibenzoheterocycles

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*A useful sequence of reaction for the synthesis of a variety of dibenzoheterocycles is described in one-pot. This synthesis involves the initial formation of dianion via deprotonation of Schiff base followed by nucleophilic attack on the suitable dielectrophiles. Products (1–9) were characterized by spectroscopic data and elemental analyses. A plausible mechanistic logic and concept utilized in the synthesis have been discussed in detail.*

**Keywords** dianion; dibenzoheterocycles; dielectrophiles; nucleophilic cyclization; Schiff base

### INTRODUCTION

Increasing interest has been paid for several years in the field of synthetic organic chemistry due to its creative power and unlimited scope. Schiff base ligands are considered “Privileged ligands”<sup>1</sup> because they are easily prepared by the condensation of aldehydes/ ketones and amines. The more general term salen type<sup>2</sup> is used in the literature to describe the class of [O,N,N,O] tetradentate bis Schiff base ligands. Stereogenic centers or other elements of chirality (planes, axes) can be introduced in the synthetic design. In fact, these ligands are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a variety of useful catalytic transformations. From a practical point of view, the aspects involved in the preparation of Schiff base metal complexes are spread out in the literature.<sup>3–7</sup> Vanadium and Ruthenium complexes of this ligand have already been reported.<sup>8,9</sup> Schiff bases are valuable synthons for the preparation

Received 8 August 2007; accepted 9 August 2007.

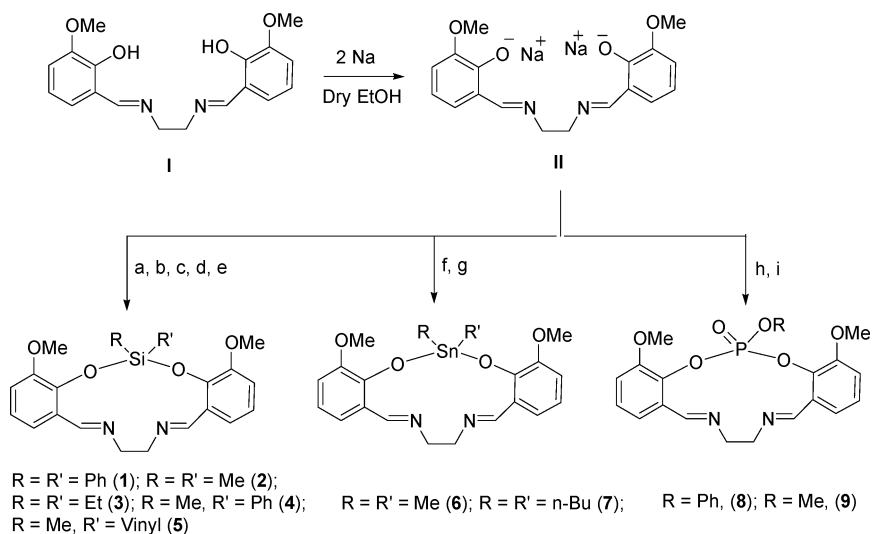
This work was supported by a research grant from the Department of Science and Technology (DST), New Delhi.

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of macroheterocyclic molecules.<sup>10,11</sup> The vigorous development in the chemistry of macroheterocyclic compounds has been observed in recent years.<sup>12,13</sup> The peculiar behavior of silicon, tin and its complexes<sup>14,15</sup> are of immense importance in chemical and biological processes, and are thought provoking in the reaction of coordination chemistry.<sup>16</sup> Phosphorus heterocycles are found in the usual broad variety of ring size and ring multiplicity familiar to the entire field of heterocyclic chemistry. Phosphorus heterocycles containing another heteroatom in the ring was not included till 1976.<sup>17</sup> Since phosphorus is a well-established atom for stabilization of low oxidation state transition metal complexes,<sup>18</sup> crown ethers incorporating phosphorus atoms in different valences have become an important area of chemistry.<sup>19</sup> Thus, in view of the synthetic and catalytic importance of the ligand and in continuation of our work<sup>20–26</sup> on the chemistry of heterocycles, we herein report the synthesis and characterization of some new organosilicon, organotin, and organophosphorus macroheterocycles via dianion-mediated cyclizations.

## RESULTS AND DISCUSSION

Considering the importance of benzoheterocycles in organic synthesis, we explored the possibility for the preparation of previously unknown dibenzoheterocyclic rings. Dibasic Schiff base ligand was prepared by



**SCHEME 1** (a)  $\text{Cl}_2\text{SiPh}_2$ ; (b)  $\text{Cl}_2\text{SiMe}_2$ ; (c)  $\text{Cl}_2\text{SiEt}_2$ ; (d)  $\text{Cl}_2\text{SiMePh}$ ; (e)  $\text{Cl}_2\text{SiMeVinyl}$ ; (f)  $\text{Cl}_2\text{SnMe}_2$ ; (g)  $\text{Cl}_2\text{SnBu}_2$ ; (h)  $\text{Cl}_2\text{POPh}$ ; (i)  $\text{Cl}_2\text{PO}_2\text{Me}$

condensation of ethylene diamine and *o*-vanillin in 1:2 molar ratios. This synthesis involves the initial formation of dianion (**II**) from deprotonation of Schiff base (**I**) followed by nucleophilic attack on the suitable dielectrophiles leading to the formation of macroheterocycles **1–9** (Scheme 1). In general, sodium chloride formed during the course of the reaction is filtered using vacuum pump. Products **1–9** (Scheme 1) were characterized by spectroscopic data and elemental analyses. All these compounds were fully or partially soluble in common organic and coordinating solvents like  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$ , DMF, DMSO, etc.

The broad band present at  $3450\text{ cm}^{-1}$  in the infrared spectrum of the Schiff base *N,N'*-bis (*o*-vanillinidene)ethylenediamine is due to  $\nu$  (OH),<sup>27</sup> which is found to be absent in all its compounds **1–9**, suggesting deprotonation of the proton from both  $-\text{OH}$  groups. Comparison of IR spectrum of the Schiff base with those of the heterocycles shows that the band in the region  $1631\text{--}1633\text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$  is observed almost at the same position in all compounds, indicating that the  $\text{C}=\text{N}$  groups are part of the ring. The disappearance of absorption band and signals corresponding to  $-\text{OH}$  groups in both IR and  $^1\text{H}$  NMR spectra of the compounds suggested formation of the metal–oxygen bond. This fact is further supported by the appearance of new bands in region  $870\text{--}892\text{ cm}^{-1}$  and  $488\text{--}478\text{ cm}^{-1}$ , which may be assigned to  $\text{Si-O}$ <sup>28</sup> and  $\text{Sn-O}$ <sup>29</sup> bands, respectively. The stretching frequency for  $\text{P}=\text{O}$  group in compound **8 & 9** appears at  $1275$  and  $1251\text{ cm}^{-1}$ , respectively.

Proton magnetic resonance spectral data of these complexes have been recorded in  $\text{CDCl}_3$  using TMS as an internal standard. A singlet at  $\delta$  13.6 ppm due to  $-\text{OH}$  groups of the ligand disappears completely in the compounds **1–9** suggesting deprotonation of both the  $-\text{OH}$  groups leading to dianion (**II**). The protons of methyl and butyl groups appear in their respective fields.  $^{13}\text{C}$  NMR spectra of the compounds have also been recorded in  $\text{CDCl}_3$ . The signal in the region 166 ppm is due to azomethine carbon, which is quite distinguishable from other signals. Signals in the region 118–152 ppm were due to aromatic carbons. Signals at 59.3 and 56.02 ppm show the presence of ( $\text{N}-\text{CH}_2$ ) and ( $-\text{OCH}_3$ ) groups, respectively. The methyl, butyl, and vinyl carbons attached to the metal appear in their respective regions. The  $^{29}\text{Si}$  NMR data support that silicon is tetra-coordinated<sup>30</sup> in all compounds **1–5**. Since R group is bound directly to  $^{29}\text{Si}$  Nucleus; it is not surprising that the value of  $\delta$  depends primarily on the nature of this R group. When R is Phenyl, the complexes give much more negative values of  $\delta$  than when R is alkyl, because the delocalized  $\pi$  system in the phenyl compound allows for  $d\pi\text{--}p\pi$  interaction, which dominate the overall shielding of the  $^{29}\text{Si}$  nucleus.

## EXPERIMENTAL

Chemicals were obtained from Sigma-Aldrich, Merck, Fluka, and Lancaster, and were used as such without further purification. All solvents (AR or extra pure grade) used for spectroscopic and other physical studies were further purified as described in literature.<sup>31</sup> All operations were performed under nitrogen atmosphere using standard glass wares. Infrared spectra were recorded as KBr discs on JASCO FT/IR-5300 spectrophotometers. Melting points were determined using a calibrated thermometer by Remi Digital Melting Point apparatus and were uncorrected. Elemental analyses were performed by Central Drug Research Institute, Lucknow. NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>119</sup>Sn and <sup>29</sup>Si) spectra were recorded on a JEOL AL 300 instrument. All chemical shifts were reported in parts per million relative to TMS as an internal standard in CDCl<sub>3</sub>. Mass spectra were recorded at 70 eV ionizing voltage on a JEOL-D300 MS instrument. Column chromatography was performed on Merck Silica gel. Thin layer chromatography was carried out on Merck silica gel (layer thickness 0.2 mm) and components were located by observation under iodine/ UV chamber.

### Preparation of Ditopic Ligand (I)

An ethanolic solution (30 mL) of *o*-vanillin (7.60 g, 50.0 mmol) was added to the ethanolic solution (20 mL) of ethylenediamine (1.50 g, 25.0 mmol). The reaction mixture was stirred at reflux for 4 h. A yellow colored solid mass separated out on cooling. It was then filtered by suction, washed with ethanol, diethyl ether, and subsequently dried over anhydrous CaCl<sub>2</sub> in a desiccator. The purity of the ligand was checked by TLC.

#### I

Yield, 6.20 g, (76%), m.p. 145°C; IR (KBr, cm<sup>-1</sup>): 3450.96, 1631.93; <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, δ): 13.6 (s, 2H, OH, D<sub>2</sub>O exchangeable), 8.3 (s, 2H, CH=N), 7.00–6.74 (m, 6H, ArH), 3.96 (s, 6H, OCH<sub>3</sub>), 3.89–3.93 (m, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ ppm): 166.79, 151.65, 148.43, 123.32, 118.51, 118.175, 114.32, 59.49, 56.19. MS: m/z (M<sup>+</sup>) 328.15; anal. calcd. for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>: C, 66.21; H, 6.05. Found: C, 65.85; H, 6.14.

### Preparation of Tricyclic Dibenzoheterocycles [1]

0.046 g (2.0 mmol) of sodium pieces and 20 mL of ethanol were taken in a two-way round bottom flask, fitted with a cooled water condenser. It was refluxed in an inert atmosphere for about half an hour until a clear solution of sodium ethoxide was obtained. After

TABLE I Synthetic and Analytical Data of Compounds 1-9

Compd no.	Mol. formula (Mmol. wt.)	Reactants (in molar ratio 1:2:1)			M. P. (°C)	Yield (%)	Analysis: % found (calcd.)	
		L	Na	R <sub>2</sub> MX <sub>2</sub>			C	H
1	C <sub>30</sub> H <sub>28</sub> N <sub>2</sub> O <sub>4</sub> Si (508.61)	0.328 g	0.046 g	0.253 g (0.210 mL)	154	63	70.95 (70.85)	5.12 (5.55)
2	C <sub>20</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub> Si (384.47)	0.328 g	0.046 g	0.129 g (0.120 mL)	123	71	62.90 (62.48)	5.98 (6.29)
3	C <sub>23</sub> H <sub>28</sub> N <sub>2</sub> O <sub>4</sub> Si (412.52)	0.328 g	0.046 g	0.157 g (0.148 mL)	142	60	63.59 (64.05)	6.31(6.84)
4	C <sub>25</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4</sub> Si (446.54)	0.328 g	0.046 g	0.191 g (0.162 mL)	119	72	67.55 (67.24)	5.90 (5.86)
5	C <sub>21</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub> Si (396.48)	0.328 g	0.046 g	0.141 g (0.128 mL)	137	68	62.11 (63.62)	5.94 (6.10)
6	C <sub>20</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub> Sn (475.095)	0.328 g	0.046 g	0.219 g	178	58	51.94 (50.56)	5.01 (5.09)
7	C <sub>26</sub> H <sub>36</sub> N <sub>2</sub> O <sub>4</sub> Sn (559.257)	0.328 g	0.046 g	0.304 g	142	69	58.52 (55.84)	6.11 (6.49)
8	C <sub>24</sub> H <sub>23</sub> N <sub>2</sub> O <sub>6</sub> P (466.374)	0.328 g	0.046 g	0.210 g (0.149 mL)	101	63	60.97 (61.81)	4.89 (4.97)
9	C <sub>19</sub> H <sub>21</sub> N <sub>2</sub> O <sub>6</sub> P (404.303)	0.328 g	0.046 g	0.148 g (0.100 mL)	118	65	54.07 (56.44)	5.14 (5.235)

Compd no.	IR (KBr, cm <sup>-1</sup> )	NMR (δ, ppm)		
		<sup>1</sup> H	<sup>13</sup> C	<sup>29</sup> Si/ <sup>119</sup> Sn/ <sup>31</sup> P
1	1633 (C=N), 800 (Si-O), 526 (Si-N)	8.33 (s, 2H, CH=N), 7.46-6.78 (m, 16H, ArH), 3.96 (s, 6H, OCH <sub>3</sub> ), 3.91 (t, 4H, NCH <sub>2</sub> )	166.62, 151.40, 148.24, 133.54, 128.05, 123.43, 118.56, 117.92, 114.36, 59.49, 56.19	-74.11
2	1635 (C=N), 962 (Si-O), 418 (Si-N)	8.33 (s, 2H, CH=N), 6.91-6.76 (m, 6H, ArH), 3.96 (s, 6H, OCH <sub>3</sub> ), 3.88 (t, 4H, NCH <sub>2</sub> ), 1.30 (s, 6H, Si-Me)	166.61, 151.44, 148.26, 123.13, 118.38, 117.99, 114.10, 59.38, 56.02, 29.63	-53.57
3	1632 (C=N), 802 (Si-O), 410 (Si-N)	9.9 (s, 2H, CH=N), 7.19-6.79 (m, 6H, ArH), 3.91 (s, 6H, OCH <sub>3</sub> ), 3.88 (t, 4H, NCH <sub>2</sub> ), 0.94 (t, 6H, SiCH <sub>3</sub> ), 0.58 (q, 4H, SiCH <sub>2</sub> )	166.35, 151.20, 147.3, 133.93, 128.32, 118.23, 59.11, 56.73, 14.31, 16.82	-56.85
4	1631 (C=N), 875 (Si-O), 484 (Si-N)	8.34 (s, 2H, CH=N), 6.80-7.12 (m, 11H, ArH), 3.96 (s, 6H, OCH <sub>3</sub> ), 3.90 (t, 4H, NCH <sub>2</sub> ), 0.40 (s, 3H, Si-Me)	166.94, 151.171, 148.54, 133.36, 128.05, 123.43, 118.32, 114.36, 59.72, 56.34, 27.6	-68.02
5	1633 (C=N), 815 (Si-O), 442 (Si-N)	8.33 (s, 2H, CH=N), 6.90-7.72 (m, 6H, ArH), 3.96 (s, 6H, OCH <sub>3</sub> ), 3.89 (t, 4H, NCH <sub>2</sub> ), 0.32 (s, 3H, Si-CH <sub>3</sub> ), 6.02-5.85 (m, 3H, CH=CH <sub>2</sub> )	166.43, 151.39, 148.06, 133.57, 122.95, 118.15, 117.77, 113.94, 59.03, 55.79, 18.06, 0.78, -0.99, -1.55, -2.80	-67.75
6	1632 (C=N), 638 (Si-O), 572 (Sn-N)	8.33 (s, 2H, CH=N), 6.90-6.72 (m, 6H, ArH), 3.96 (s, 6H, OCH <sub>3</sub> ), 3.88 (t, 4H, NCH <sub>2</sub> ), 1.25 & 0.82 (s, 6H, Sn-Me)	166.22, 151.73, 148.52, 132.51, 128.12, 124.03, 118.32, 114.36, 56.36, 9.76, 6.32	-408.5
7	1633 (C=N), 634 (Si-O), 594 (Sn-N)	8.33 (s, 2H, CH=N), 6.92-6.75 (m, 6H, ArH), 3.96 (s, 6H, OCH <sub>3</sub> ), 3.82 (t, 4H, NCH <sub>2</sub> ), 2-0.69 (m, 18H, Sn-Bu)	166.72, 125.01, 148.56, 138.12, 118.32, 59.72, 56.34, 9.67, 28.04	-415.1
8	1633 (C=N), 1275 (P=O), 1219(P-O-aryl)	8.33 (s, 2H, CH=N), 7.25-6.73 (m, 11H, ArH), 3.96 (s, 6H, OCH <sub>3</sub> ), 3.90 (t, 4H, NCH <sub>2</sub> )	166.60, 152.34, 151.62, 148.32, 133.54, 127.52, 128.4, 123.54, 118.5, 114.32, 59.73, 56.19	-4.91
9	1631 (C=N), 1251 (P=O), 1040(P-O-alkyl)	8.33 (s, 2H, CH=N), 6.90-6.74 (m, 6H, ArH), 3.96 (s, 6H, OCH <sub>3</sub> ), 3.88 (t, 4H, NCH <sub>2</sub> ), 1.2 (s, 3H, Me)	166.2, 151.4, 147.2, 123.42, 118.65, 117.8, 114.5, 59.49, 56.14	-6.39

cooling, 20 mL of toluene containing 0.33 g (1.0 mmol) of N, N'-bis(*o*-vanillinidene)ethylenediamine was added slowly at room temperature. The mixture was stirred under reflux for 4 h. The solution became light brown, which was allowed to attain room temperature and then 0.25 g (1.0 mmol) of dichlorodiphenylsilane was added slowly. The solution became yellow and the reaction mixture was further refluxed for 2 h to ensure the completion of the reaction. The precipitated sodium chloride was removed by filtration. A novel product was obtained following removal of solvent under reduced pressure, which was further washed with water and brine, and then dried over anhydrous MgSO<sub>4</sub>. The solvent was evaporated in vacuo and the residue was column chromatographed on silica gel (hexane/ethyl acetate 5:1) to purify the product **1**. All other dibenzoheterocycles **2–9** were also synthesized analogously as described above in the desired molar ratios. The analytical and spectral data for the compounds **1** to **9** are listed in Tables I and II, respectively.

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