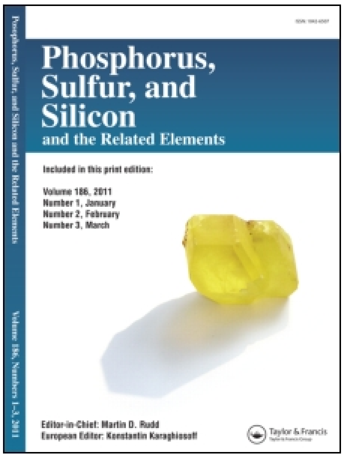

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A Novel Synthesis of $AlCl[(NPh)_2P(O)H]$ and $SiCl_2[(NPh)_2P(O)H]$: Two New Phosph(V)azane Derivatives

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To cite this Article Tarassoli, Abbas and Khodamoradpur, Ziba(2006) 'A Novel Synthesis of $AlCl[(NPh)_2P(O)H]$ and $SiCl_2[(NPh)_2P(O)H]$: Two New Phosph(V)azane Derivatives', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 7, 1675 — 1680

To link to this Article: DOI: 10.1080/10426500500366848

URL: http://dx.doi.org/10.1080/10426500500366848

Phosphorus, Sulfur, and Silicon, 181:1675–1680, 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500500366848

A Novel Synthesis of $AlCl[(NPh)_2P(O)H]$ and $SiCl_2[(NPh)_2P(O)H]$: Two New Phosph(V)azane Derivatives

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Reactions of phosph(V)azane derivatives of bis(anilino)phosphine oxide $(PhNH)_2P(O)H$ *(**1**) with* $AlCl_3$ *and* $SiCl_4$ *produce two new phosph(V)azane complexes,* $AlCl[(NPh)_2P(O)H]$ *(**2**) and* $SiCl_2[(NPh)_2P(O)H]$ *(**3**). In these reactions, an HCl elimination occurs and M—N bonds (M = Si, Al) form directly between a bis(anilino)phosphine oxide ligand with aluminum and silicon halides. The reactions do not require any base to deprotonate the phosphazane ligand. The final products have been fully characterized by means of elemental analysis and IR, MS, and multinuclear NMR (*^1H, ^{13}C, ^{31}P, ^{27}Al, *and* ^{29}Si*) spectroscopy.*

Keywords ^{27}Al NMR; aluminum halides; bis(anilino)phosphine oxide; phosph(V)azane derivatives; silicon halides

Phosphazanes that contain phosph(III)azanes and phosph(V)azanes have attracted by far the most attention because they offer different coordination modes involving the "hard"(N) in phosph(V)azanes and the "soft"(P) centers in phosph(III)azanes for a generation of chelation complexes containing different metals with a main group and transition metals.[1–11]

Our studies, including the investigation of synthesis and the coordination chemistry of some acyclic phosph(V)azanes, led us to study the novel ligand bis(anilino)phosphine oxide, $(PhNH)_2P(O)H$ (**1**).[12] This ligand has been synthesized about 20 years ago, but its coordination chemistry as an amido phosphazane ligand has not been known and had very little attention (Scheme 1). It bears active sites as hard and soft centers

Received April 12, 2005; accepted September 1, 2005.
Support of this work by the Shahid Chamran University, Ahvaz, Iran (project No. 217) is gratefully acknowledged.

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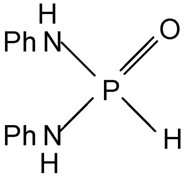
N, O, and P, and is very reactive to form various coordination complexes with main-group and transition metals.[1,5]

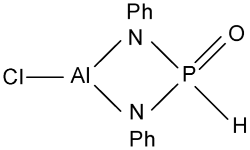


(1)

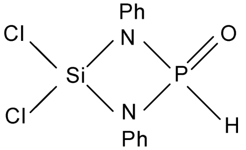
SCHEME 1

We were interested in the investigation of its reaction with active main group metal halides such as $AlCl_3$ and $SiCl_4$. Because of the critical role of aluminum compounds in polyolefin catalysis, there has been a growing interest in the coordination chemistry of this metal. These systems have long been known to function as useful Lewis acid catalysts, with applications as mediators in Friedel-Crafts and Diels-Alder reactions, as alkylation reagents, and as initiators for cationic polymerizations.[1,13] On the other hand, applications of silicon compounds in organic synthesis, such as hydroxy protection, Peterson olefination, and Wittig reactions,[14] also have attracted research interest in the synthesis and characterization of various silicon derivatives.

In coordination reactions of phosph(III)azanes and phosph(V)azanes, an anionic form of a ligand can be produced either by using organolithium reagents such as n-butyllithium (Bu^nLi) as a deprotonating base, in which anions bind to Li^+ via nitrogen (chalcogen) atoms, or by using a base, such as triethylamine, to abstract hydrogen from a N—H bond.[1,2] In our reactions, no base was required to abstract hydrogen from a phosph(V)azane ligand, and the reactions were performed directly to produce new phosph(V)azane complexes, $AlCl[(NPh)_2P(O)H]$ (**2**) and $SiCl_2[(NPh)_2P(O)H]$ (**3**).



(2)



(3)

SCHEME 2

RESULTS AND DISCUSSION

In the present research, at first we reexamined bis(anilino)phosphine oxide $(PhNH)_2P(O)H$ (**1**) prepared according to an improved procedure with a better yield (84%) than was previously reported (60%),[12] which is shown in Eq. (1).[15]

$$PCl_3 + PhNH_2 + H_2O \xrightarrow{80^\circ C} (PhNH)_2P(O)H \qquad (1)$$

The addition of $AlCl_3$ to $(PhNH)_2P(O)H$ (**1**) in the ratio of 1:1 in dry THF at 25°C resulted in the formation of the complex $AlCl[(NPh)_2P(O)H]$ (**2**) as a white powder in a 74% yield (Eq. (**2**)).

$$AlCl_3 + (PhNH)_2P(O)H \longrightarrow 2HCl + AlCl[(NPh)_2\,P(O)H] \qquad (2)$$

Under similar conditions, **1** reacted with $SiCl_4$ at 0°C to give $SiCl_2[(NPh)_2P(O)H]$ (**3**) in a good yield of 82% (Eq. (**3**)).

$$SiCl_4 + (PhNH)_2P(O)H \longrightarrow 2HCl + SiCl_2[(NPh)_2\,P(O)H] \qquad (3)$$

Both reactions proceeded with the loss of 2 equiv. of HCl, and M—N bonds (M = Al and Si) were formed. They did not require a base for the activation of the N—H bonds. The products were air sensitive, and all of the manipulations were carried out in an inert atmosphere. Multinuclear (^{31}P, ^{1}H, ^{13}C, ^{27}Al, and ^{29}Si) NMR spectra indicated that **2** and **3** contained the ligand **1** bonded to Al and Si through nitrogen atoms. ^{31}P NMR spectra exhibited one doublet directly coupled to bonded-hydrogen. Also, $^{31}P\{^{1}H\}$ NMR spectra showed only one singlet, which confirmed the existence of one type of phosphorus and one type of product. ^{1}H NMR spectra of **2** and **3** showed phenyl and P–H resonances with the appropriate relative intensities at δ 7.27–7.44 as a multiplet and δ 6.33 as a doublet in **2** and at δ 7.26–7.44 as multiplet and δ 6.71 as a doublet in **3**. Also $^{13}C\{^{1}H\}$ NMR spectra exhibited four signals in the aromatic region that were consistent with a C_s symmetry of the molecules. In the ^{27}Al NMR spectrum of **2**, one signal was detected that proved the existence of just one type of aluminum center. The ^{29}Si NMR spectrum of **3** contained only one sharp singlet at 10.52 ppm indicating the formation of a single product, with the silicon-29 resonance appearing at a low field that supported the coordination number of four around the silicon atom in **3**.[16,17]

There was no indication of the presence of a NH bond in **2** and **3** from either ^{1}H NMR or IR spectra. On the other hand, IR spectra exhibited characteristic bands of Si—Cl, Si—N, and Al—N strechings at 476, 955, and 600 cm^{-1}, respectively.[13,18] Also P=O stretchings were without variation, and we obtained no evidence for the involvement of this bond during the course of reaction under the conditions of our experiments. In addition, the quantitative determination of chloride in the products showed the existence of one equivalent chlorine in **2** and two equivalent in **3**.

In the mass spectrum of **2**, a peak at m/z 257 was observed, which was attributed to the loss of a chlorine group from the complex $AlCl[(NPh)_2P(O)H]$ (**2**) as a quasi-molecular ion. The m/z values of 240 ($AlClN_2Ph_2$), 205 ($AlClN_2Ph_2$), 209 (AlN_2Ph_2), 132 (AlN_2Ph), 58 (PN_2), 55 (AlN_2), 47 (PO), 45 (PN), and 41 (AlN) could easily be assigned to major peaks in the envelope in question.

Thus, the reaction of one equivalent of **1** with $AlCl_3$ and $SiCl_4$ proceeded with the elimination of HCl to generate the novel compounds **2** and **3**, respectively. Spectroscopic data indicated that **1** coordinated on N to Al or to Si directly without the presence of any base. We are currently exploring this procedure for a generation of similar complexes using organo-aluminum or organo-silicon halide derivatives.

EXPERIMENTAL

All experiments were performed under nitrogen using standard Schlenk techniques. The solvents were purified and dried as indicated: Tetrahydrofurane was treated with KOH and freshly distilled twice from sodium before use. Aniline was distilled from CaH_2 and stored over molecular sieves. NEt_3 was distilled over $MgSO_4$. Toluene was distilled over sodium. Chloroform was distilled from P_4O_{10}. Phosphorus trichloride, anhydrous aluminum trichloride, silicon tetrachloride, and absolute ethanol were used as purchased from Merck Co. (Germany).

NMR spectra were recorded on a Bruker Avance DPX 500 MHz at an ambient temperature. Chemical shifts were referenced to external TMS for ^1H NMR (500.13 MHz), ^{13}C NMR (125.77 MHz) and ^{29}Si NMR (99.35 MHz), H_3PO_4 85% for ^{31}P NMR (202.45 MHz), and $Al(NO_3)_3$, $9H_2O$ (1 M) in D_2O for ^{27}Al NMR (130.32 MHz) spectra. IR spectra were measured on a Bomem FTIR spectrophotometer. FAB(+) mass spectra were recorded using a JEOL SX-102A instrument. Elemental analysis (C, H, and N) was performed by the microanalytical service of the National Iranian Oil Company (NIOC) Research Institute of Petroleum Industry, Tehran, Iran.

The Preparation of $(PhNH)_2$ P(O)H (1)

PCl_3 (5 mL, 0.057 mol) in 10 mL of toluene was added slowly under N_2 to a sitirred solution of $PhNH_2$ (26.02 mL, 0.285 mol) in 60 mL of dry toluene at 0°C. The reaction mixture was warmed slowly to 25°C. After 2 h, water (0.057 mol) in a H_2O-$CHCl_3$ solution was added slowly to the mixture. Then the mixture was stirred at 80°C for another 2 h. $PhNH_3^+Cl^-$ was filtered from the hot reaction mixture. The solvent was removed, and the white product was washed with cold toluene and then recrystallized from ethanol (yield 84%), m.p. 160°C.

IR (KBr): 3191 (s, NH), 3032–3092 (Ph), 2369 (m, sh, P—H), 1175 (P=O), 749–690 (Ph) cm^{-1}.

^1H NMR (25°C, $(CD_3)_2$ SO, ppm): 7.50–6.50 (m, 10 H, Ph), 8.09 (d, $^2J_{PNH} = 8.92$ Hz, 2H, NH), and 7.28 (d , $^1J_{PH} = 596$ Hz, 1H, P—H).

^{31}P NMR (25°C, $(CD_3)_2$ SO, ppm): −4.07 (doublet of triplet, $^1J_{PH} = 612$ Hz, $^2J_{PNH} = 9.19$ Hz).

$^{13}C\{^1H\}$ NMR (25°C, $(CD_3)_2$ SO, ppm): 115.9 (C_p), 118.3 (C_m), 129.4 (C_o), 146.0 (C_i).

Anal. calcd. for $C_{12}H_{13}N_2PO$: C, 62.07; H, 5.64; N, 12.06%. Found: C, 62.09; H, 5.58; N, 12.02%.

The Synthesis of $AlCl[(NPh)_2P(O)H]$ (2)

$AlCl_3$(0.057 g, 0.431 mmol) was added to $(PhNH)_2$ P(O)H (**1**) (0.1 g, 0.431 mmol) in 50 mL of dry THF under N_2 at 25°C. Immediately, a white insoluble solid precipitated, and the evolution of gas was noted. After 2 h, the mixture was filtered. The white solid was washed with THF and dried under a vacuum for 24 h to yield essentially pure **2** (yield 74%), m.p. 175°C dec.

IR (KBr): 3097–3048 (Ph), 2397 (m, sh, P—H), 1170 (br, P=O), 849–805 (s, Ph), 600 (Al—N) cm^{-1}.

^1H NMR (25°C, D_2O, ppm): 7.27–7.44 (m, 10H, Ph), 6.33 (d, $^1J_{PH} = 707$ Hz, 1H, PH).

$^{31}P\{^1H\}$ NMR (25°C, D_2O, ppm): −7.29. ^{31}P NMR: −7.29 (d, $^1J_{PH} = 702$ Hz).

$^{13}C\{^1H\}$ NMR (25°C, D_2O, ppm): 122.88 (NPh), 129.20 (NPh), 129.96 (NPh), 130.12 (d, $^2J_{CNP} = 7.67$ Hz, NPh).

^{27}Al NMR (25°C, D_2O, ppm): 0.143 (s).

Anal. calcd. for $C_{12}H_{11}N_2OPClAl$: C, 49.23; H, 3.76; N, 9.57%. Found: C, 49.1; H, 3.5; N, 9.3%.

The Synthesis of $SiCl_2[(NPh)_2P(O)H]$ (3)

$SiCl_4$ (0.05 mL, 0.431 mmol) in 10 mL of dry toluene was added dropwise to $(PhNH)_2$ P(O)H (**1**) (0.1 g, 0.431 mmol) in 50 mL of dry THF under N_2 at 0°C. Immediately, a white insoluble solid precipitated, and the evolution of gas was noted. After 2 h, the mixture was filtered. The white solid was washed with THF and dried under a vacuum for 24 h to yield essentially pure **3** (yield 82%), m.p. 170°C dec.

IR (KBr): 3095–3025 (Ph), 2388 (m, sh, P—H), 1188 (br, P=O), 955 (Si—N), 849–805 (s, Ph), 476 (Si—Cl) cm^{-1}.

^{1}H NMR (25°C, D_2O, ppm): 7.26–7.44 (m, 10H, Ph), 6.71 (d, $^1J_{PH}$ = 637 Hz, 1H, PH).

$^{31}P\{^1H\}$ NMR (25°C, D_2O, ppm): 3.18. ^{31}P NMR: 3.11 (d, $^1J_{PH}$ = 636 Hz).

$^{13}C\{^1H\}$ NMR (25°C, D_2O, ppm): 124.95 (NPh), 126.00 (NPh), 129.97 (NPh), 131.18 (d, $^2J_{CNP}$ = 5.03 Hz, NPh).

^{29}Si NMR (25°C, D_2O, ppm): 10.52 (s).

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