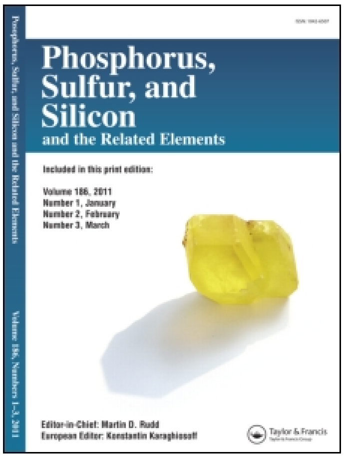


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Characterization of New Silicon and Titanium Derivatives of Bis(anilino)phosphine Oxide

Abbas Tarassoli[a]; Lida Ezzedinloo[a]
[a] Department of Chemistry, College of Science, Shahid Chamran University, Ahvaz, Iran

To cite this Article Tarassoli, Abbas and Ezzedinloo, Lida(2008) 'Synthesis and Characterization of New Silicon and Titanium Derivatives of Bis(anilino)phosphine Oxide', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 12, 3013 — 3017

To link to this Article: DOI: 10.1080/10426500802053144

URL: http://dx.doi.org/10.1080/10426500802053144

Phosphorus, Sulfur, and Silicon, 183:3013–3017, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802053144

Synthesis and Characterization of New Silicon and Titanium Derivatives of Bis(anilino)phosphine Oxide

Abbas Tarassoli and Lida Ezzedinloo
Department of Chemistry, College of Science, Shahid Chamran University, Ahvaz, Iran

The reactions of bis(anilino)phosphine oxide $(C_6H_5\ NH)_2\ P(O)\ H$ *with* $(C_5H_5)_2TiCl_2$ *or* Me_2SiCl_2 *in a 1:1 molar ratio in THF results in the isolation of new phosph(V)azane complexes* $(C_5H_5)_2Ti[(N\ C_6H_5)_2P(O)H]$ *(1) or* $Cl\ _2Si[(N\ C_6H_5)_2P(O)H]$ *(2), respectively. In these reactions, HCl or* CH_4 *elimination occurs and N-Ti or N-Si bonds form directly between a bis(anilino)phosphine oxide ligand and organotitanium or organosilicon compounds. The products(1) and (2) have been fully characterized by elemental analysis as well as* ^1H, ^{31}P, ^{29}Si *NMR, and IR spectroscopy.*

Keywords Bis(anilino)phosphine oxide; multidentate ligand; phosphazene; silicon; titanium

INTRODUCTION

Phosphorus and nitrogen form compounds of greater structural diversity than any other two elements in the periodic table. Of these compounds, the phosphazanes are known as an established system of P-N bonds.[1] Although the synthetic, mechanistic studies and applications of phosphazanes have attracted much attention, still a little chemistry has been done in the field of coordination abilities.[2–6] In the course of our studies on phosphazanes derivatives of main group elements, we found that only a few transition metal compounds are existed.[7,8] Phosphazanes containing a P-NH group exhibit immense structural diversity and are the most suitable system for these purposes.[2,3] The reaction of these phosphazanes with main group element and transition metal compound leads to the formation of new inorganic rings and complexes.[2,9,10] In this respect, bis(anilino)phosphine

Received 14 January 2008; accepted 13 March 2008.

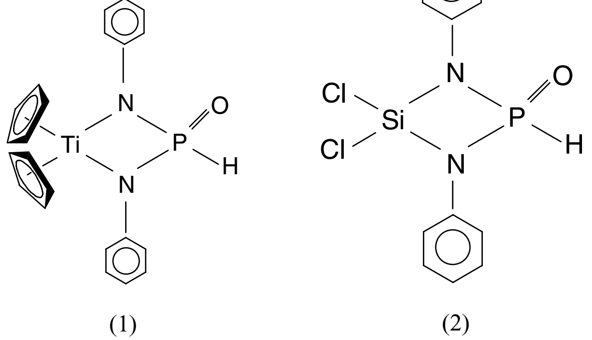
Support of this work by the Shahid Chamran University (Grant No.235-1386) is gratefully acknowledged.

Address correspondence to Abbas Tarassoli, Department of Chemistry, College of Science, Shahid Chamran University, Ahvaz, Iran. E-mail: tarassoli@sua.ac.ir

oxide which has both "hard" and "soft" coordination sites is an excellent precursor for synthetic purposes.[11] We had previously reported the preparation of bis(anilino)phosphine oxide and described the synthesis of $ClAl[(NC_6H_5)_2P(O)H]$ and $Cl_2Si[(NC_6H_5)_2P(O)H]$ (2) from bis(anilino)phosphine oxide and $AlCl_3$ and $SiCl_4$, respectively.[7,9] To further explore the chemistry of this bis(anilino)phosphine oxide and its complexation and expand our investigations to titanium, now we report the synthesis of $(C_5H_5)_2Ti[(NC_6H_5)_2P(O)H]$ (1), which is a novel analogues to $ClAl[(NC_6H_5)_2P(O)H]$ and $Cl_2Si[(NC_6H_5)_2P(O)H]$. We also report here the synthesis of $Cl_2Si[(N\ C_6H_5)_2P(O)H]$ (2) from the reaction of Me_2SiCl_2 with bis(anilino)phosphine oxide (Scheme 1).

RESULTS AND DISCUSSION

Because the structure of derivatives of metals and non-metals is closely related to the structure of their ligands, we begin the discussion section with a short description of the synthesis and properties of the ligand, bis(anilino)phosphine oxide $(C_6H_5NH)_2P(O)H$. This ligand can be prepared by the controlled hydrolysis of $(C_6H_5NH)_3P$ and $[(C_6H_5NH)_2P]_2N\ C_6H_5$ which is published earlier,[11,12] or by the procedure we recently reported.[9] Bis(anilino)phosphine oxide with two P-NH bonds, P-, N-, and O- donor sites makes a compound of this kind a versatile ligand in the reactions towards both transition metals and main group elements. The addition of $(C_5H_5)_2TiCl_2$ or Me_2SiCl_2 in 1:1 molar ratio in THF to bis(anilino)phosphine oxide resulted in the formation of $(C_5H_5)_2Ti[(NC_6H_5)_2P(O)H]$ (1) and $Cl_2Si[(N\ C_6H_5)_2P(O)H]$(2). Both reactions proceeded with the elimination of two equivalent of HCl or CH_4



(1) (2)

SCHEME 1

respectively, and M-N (M=Ti or Si) bonds were formed. The evolution of the gases was noticed and the solid products were obtained. The products (1) and (2) have been extensively characterized by multinuclear (^{1}H, ^{31}P, and ^{29}Si) NMR and IR spectroscopy, as well as elemental analysis.

The ^{31}PNMR spectrum for (1) clearly exhibited one doublet at δ 1.9 ($^1J_{PH}$=641 Hz) indicating that the phosphorus atom is directly coupled to the bonded hydrogen. Whereas, this signal is observed as a doublet at δ 1.6($^1J_{PH}$=632 Hz) for (2). Also, ^{31}P{^{1}H}NMR spectra showed only one singlet which confirmed the existence of one type of phosphorus atom and therefore one type of product. The ^{1}HNMR spectra of (1) and (2) showed P-H and phenyl signals with the appropriate relative intensities at δ 6.72 as a doublet; at δ 7.25–6.91 as a multiplet in (1); δ 6.70 as a doublet; and at δ 6.53–7.04 as a multiplet in (2). The cyclopentadienyl-ring resonances were also observed at δ 6.69 in (1). The ^{29}SiNMR spectrum of (2) contained only one singlet at 10.3 ppm, indicating the existence of only one single product, with the silicon-29 resonances appearing at a low field, which is consistent with a four coordinate silicon atom.[13,14]

The ^{1}HNMR and IR spectra of (1) and (2) clearly showed the absence of the characteristic N-H signals of the ligand, and there were no indication of the presence of CH_3- groups of Me_2SiCl_2. On the other hand, IR spectra exhibited characteristic bands of Si-N, Ti-N and Si-Cl stretching vibrations at 1026, 1631, and 488–464 cm^{-1}, respectively. The P=O stretching vibrations were observed at 1191 and 1197 cm^{-1} for (1) and (2), respectively, which are typical in these compounds[15]. Therefore, there was no evidence for the involvement of P=O bond during the course of reaction under the conditions of our experiments. Further characterization was also made by the elemental analysis as described in the experimental section.

EXPERIMENTAL

Apparatus and Material

All experiments requiring inert atmosphere were carried out in N_{2-} flushed glove bags or standard Schlenk apparatus. The solvents were purified and dried as indicated: Tetrahydrofurane was treated with KOH and freshly distilled twice from sodium before use. Dichloromethane was distilled over phosphorus pentoxide. Aniline was distilled from $CaH_2$and stored over molecular sieves. Toluene was distilled over sodium and diethyl ether was treated with calcium chloride and distilled over sodium. Me_2SiCl_2 and $(C_5H_5)_2TiCl_2$ were used as purchased from Merck Co, Germany. Bis(anilino)phosphine oxide was prepared as we reported earlier.[9,11]

NMR Spectra were recorded on a Bruker Avance 500 MHz or Bruker 400MHz or 250 MHz at ambient temperature. The chemical shifts were referenced to external TMS for ^1H NMR (500.13 MHz or 400.13 MHz or 250.13 MHz), ^{29}Si NMR (99.35 MHz) and H_3PO_4 85% for ^{31}P NMR (202.45 MHz or 161.967 MHz). IR Spectra were measured on a Bomen FT-IR Spectrophotometer. Elemental analyses were performed by the microanalytical service of National Iranian Oil Company (N.I.O.C) Research Institute of Petroleum Industry, Tehran, Iran.

Synthesis of Complexes

Sythesis of $(C_5H_5)_2Ti[(NC_6H_5)_2P(O)H]$ (1)

$(C_5H_5)_2TiCl_2$ (0.125gr, 0.5 mmol) was dissolved in 40 mL of dry THF, and added drop wise to the solution of $(C_6H_5NH)_2P(O)H$ (0.116 g, 0.5 mmol) in 80 mL of dryTHF under N_2 gas at 25°C. Then the mixture was stirred for 48 h. At the end of this period, the temperature was raised to 30°C and stirred for another 2 h. Upon cooling, the solvent was removed and the orange precipitate was washed twice with cold THF and dried under vacuum for 24 h to yield essentially pure $(C_5H_5)_2Ti[(NC_6H_5)_2P(O)H]$(1). yield 78%, m.p. 145°C dec. Anal. calcd. for $C_{22}H_{21}N_2POTi$ (M_w= 408.44) C:64.76; H: 5.18; N:6.85. found. C: 64.82; H: 4.97;N:6.81%. IR(KBr): 923(P-N), 2389(P-H),1494 (C=C), 1191(P=O), 3418(Cp), 1631 (Ti-N) cm^{-1}. ^{1}HNMR (25°C, $(CD_3)_2SO$, ppm) 7.25–6.91(m, 10H,Ph), 6.69 (10H,Cp), 6.72 (d, $^1J_{PH}$= 641 Hz, 1H, P-H), ^{31}PNMR (25°C, $(CD_3)_2SO$, ppm): 1.9 (d, $^1J_{PH}$ 641Hz).

Synthesis of $Cl_2Si[(N C_6H_5)_2P(O)H]$ (2)

To a stirring solution of $(C_6H_5NH)_2P(O)H$ (0. 232 g, 1 mmol) in 100 mL of CH_2Cl_2, in an ice bath, a mixture of Me_2SiCl_2(0.12 mL, 1 mmol) in 20 mL of CH_2Cl_2 was added dropwise. After stirring the reaction mixture for 24 h at room temperature, white insoluble solid was formed. The solid was washed with CH_2Cl_2 and dried under vacuum to yield essentially pure $Cl_2Si[(N C_6H_5)_2P(O)H]$ **(2)**, yield 84%, m.p. 170°C dec. Anal calcd. for $C_{12}H_{11}N_2Cl_2POSi$ (M_w= 329.2) C:43.84;H:3.36;N:8.51. Found.C: 44.12; H:3.24, N: 8.43%. IR (KBr): 2407(P-H),1197(P=O),1026 (Si-N), 488–464(Si-Cl) cm^{-1}.^{1}HNMR (25°C, $(CD_3)_2SO$, ppm): 6.53–7.04(m,10H, Ph),6.70(d,$^1J_{PH}$=637 Hz,1H,P-H),^{31}PNMR (25°C, $(CD_3)_2SO$, ppm): 1.6 (d, $^1J_{PH}$= 632 Hz, 1H, P-H). ^{29}SiNMR (25°C, $(CD_3)_2SO$, ppm): 10.3.

REFERENCES

[1] L. Stahl, *Coor. Chem, Rev*., **210,** 203 (2000).

[2] Z. Fei and P. J. Dyson, *Coor. Chem. Rev.*, **249,** 2056 (2005).

[3] G. G. Briand, T. Chives, and M. Krahn, *Coor. Chem. Rev.*, **233–234,** 237 (2002).

[4] M. S. Balakrishna, V. S. Krishnamurthy, J. F. Nixon, J. C. Burcketr and S. Laurent, *Coor. Chem. Rev.*, **129,** 1 (1994).

[5] U. Klingebiel, *The Chemistry of Inorganic Homo-and Heterocycles* (Academic Press, London, 1987), Vol. I, pp. 221–269.

[6] S. E. Thomas, *Organic Synthesis: The Roles of Boron and Silicon* (Oxford University Press, 1991), pp. 47–90.

[7] A. Tarassoli and Z. Khodamoradpur, *Phosphorus, Sulfur, and Silicon and the Related Elements,* **181,** 1675 (2006).

[8] A. Tarassoli, G. Emami, and Z. Khodamoradpur, *Phosphorus, Sulfur, and Silicon and the Related Elements*, **182,** 2497 (2007).

[9] A. Tarassoli and Z. Khodamoradpur, *Phosphorus, Sulfur and Silicon and the Related Elements*, **180,** 527 (2005).

[10] A. Tarassoli, H. J. Chen, M. L. Thompson, V. S. Allured, R. C. Haltiwanger, and A. D. Norman, *Inorg. Chem.*, **25,** 4152 (1986), and references cited therein.

[11] M. L. Thompson, R. C. Haltiwanger, A. Tarassoli, D. E. Coons, and A.D. Norman, *Inorg. Chem.,* **21,** 1287 (1982).

[12] A. Tarassoli, M. L. Thompson, R. C. Haltiwanger, T. G. Hill, and A.D. Norman, *Inorg. Chem.*, **27,** 3382 (1988).

[13] St. N. Tandura, N. V. Alekseev, and M. G. Voronkov, *Top. Curr. Chem.*, **131,** 101 (1986).

[14] I. Kalikhman, B. Gostevskii, O. Girshberg, S. Krivonos, and D. Kost, *Organometallics*, **21,** 2551 (2002).

[15] N. B. Colthrup, L. H. Daly, and S. E. Wiberly, Eds., *Introduction to Infrared and Raman Spectroscopy* (Academic Press, London, 1975), 2nd ed.