

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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>

REACTION OF N-(N',N',N'',N''-TETRAMETHYL)GUANIDINE-SUBSTITUTED PHOSPHINES WITH ANTIMONY PENTACHLORIDE AND WITH BORON TRIFLUORIDE

Jochen Münchenberg^a; Reinhard Schmutzler^a

^a Institut für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig, Germany

To cite this Article Münchenberg, Jochen and Schmutzler, Reinhard(1997) 'REACTION OF N-(N',N',N'',N''-TETRAMETHYL)GUANIDINE- SUBSTITUTED PHOSPHINES WITH ANTIMONY PENTACHLORIDE AND WITH BORON TRIFLUORIDE', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 126: 1, 171 — 176

To link to this Article: DOI: 10.1080/10426509708043556

URL: <http://dx.doi.org/10.1080/10426509708043556>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

REACTION OF N-(N',N',N'',N''-TETRAMETHYL)GUANIDINE- SUBSTITUTED PHOSPHINES WITH ANTIMONY PENTACHLORIDE AND WITH BORON TRIFLUORIDE

JOCHEN MÜNCHENBERG and REINHARD SCHMUTZLER*

*Institut für Anorganische und Analytische Chemie der Technischen Universität,
Postfach 3329, D-38023 Braunschweig, Germany*

(Received 13 January, 1997; In final form 28 January, 1997)

The N-(N',N',N'',N''-tetramethyl)guanidinyll substituted phosphines **1** and **2** were allowed to react with the Lewis acids, boron trifluoride and antimony pentachloride. Instead of the expected Lewis acid-base adducts the phosphonium compounds **3** - **5** were obtained. The reaction with boron trifluoride lead to the rupture of the P-N bond, followed by the formation of the $\sigma^3\text{Po}^4\text{P}^+$ -phosphonium compound **3** by reaction with a further molecule of **1**. Antimony pentachloride acted as oxidizing agent, leading to the chlorophosphonium hexachloroantimonates **4** and **5**.

Keywords: N-(N',N',N'',N''-tetramethyl)guanidine; Phosphines, N-(N',N',N'',N''-tetramethyl)guanidinyll-substituted; chlorophosphonium compounds, N-(N',N',N'',N''-tetramethyl)guanidinyll substituted; $\sigma^3\text{Po}^4\text{P}^+$ -phosphonium compounds.

INTRODUCTION

In N-(N',N',N'',N''-tetramethyl)guanidinyll (TMG)-substituted phosphines a hard Lewis basic center (the imino nitrogen atom) is directly bonded to a soft Lewis acid center (the phosphorus atom).

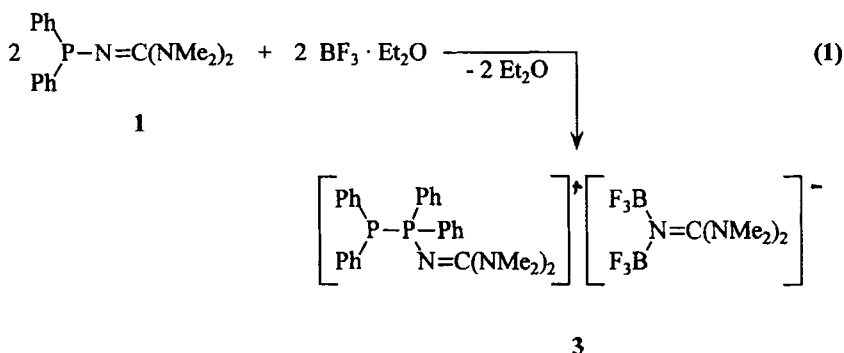
We have shown before, that the imino nitrogen in TMG-substituted phosphoryl compounds is a harder Lewis acid center than the phosphoryl oxygen¹; boron trifluoride reacted with methylphosphonic-bis-N-(N',N',N'',N''-tetramethyl)guanidinide with formation of a 2:1 complex containing two BF_3 moieties bonded to the imino nitrogen atoms. The possibility of boron trifluoride being bonded to

nitrogen instead of phosphorus has been discussed previously for dialkylaminodifluorophosphines².

With protonic acids TMG-substituted phosphines reacted, depending on the further substituents at phosphorus, either at the imino nitrogen or at the phosphorus atom³. In the TMG-substituted phosphines the basicity of the phosphorus atom is increased by the mesomeric effect of the substituents. The positive partial charge at phosphorus, arising as a result of its quaternization, is delocalised over the TMG-substituents. Thus, we were interested in extending our studies of the properties of TMG-substituted phosphines to their reactions with Lewis acids, especially with boron trifluoride and antimony pentachloride. Our aim was to determine whether the imino nitrogen atoms in the TMG substituent or the phosphorus(III) atom of the title compounds are more reactive towards Lewis acids.

RESULTS AND DISCUSSION

Diphenyl-*N*-(*N'*,*N'*,*N''*,*N''*-tetramethylguanidinyl) phosphine **1** reacted with boron trifluoride diethyl etherate at -50°C [Eq. (1)]. In the reaction mixture only traces of the 1:1 adduct of boron trifluoride with **1** could be observed by ^{31}P -NMR spectroscopy. The solid product isolated consisted mainly of the phosphonium salt **3**. A similar product was obtained by Cowley et. al. in the reaction of $t\text{-BuP}(\text{F})\text{NMe}_2$ with PF_5 ⁴.



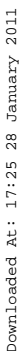
The ^{31}P -NMR spectrum of **3** displayed the AB-pattern expected for such a system, involving a phosphorus-phosphorus bond [$\delta(\sigma^4\text{P}^+) = 20.48$ ppm, $\delta(\sigma^3\text{P}) = -11.90$ ppm, $^1\text{J}(\text{PP}) = 266.96$ Hz]. The $^1\text{J}(\text{PP})$ -coupling constants observed before for such compounds lay, normally, in the range of 160-300 Hz, although in some cases values up to 506 Hz were observed⁴. The value of $^1\text{J}(\text{PP})$ (266.96 Hz) observed for **3** is significantly smaller than that observed for the cation $[\text{Ph}_2\text{PP}(\text{NMe}_2)\text{Ph}_2]^+$ (325 Hz)⁵, a species closely related to the cation of **3**.

Downloaded At: 17:25 28 January 2011

Downloaded At: 17:25 28 January 2011

Downloaded At: 17:25 28 January 2011

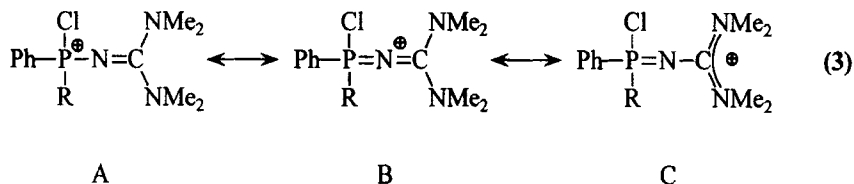
Downloaded At: 17:25 28 January 2011



Downloaded At: 17:25 28 January 2011

Downloaded At: 17:25 28 January 2011

substituents. The electron distribution in **4** and **5** is better represented by structures B and C in Eq. (3) than by structure A.



In the case of **5** the positive charge is delocalised over two TMG-groups. Thus, the phosphorus atom is shielded more strongly, compared to **4**.

The $\delta(^1\text{H})$ values of the protons of the TMG-substituents were nearly the same for **4** (2.96 ppm) and **5** (2.97 ppm). Both $\delta(^1\text{H})$ values are at lower field than in the corresponding phosphines (**1**: $\delta = 2.78$ ppm; **2**: $\delta = 2.72$ ppm)⁸. This down-field shift is observed for nearly all TMG-substituted phosphorus compounds upon increase of the coordination number of phosphorus from three to four^{1,8,9}.

EXPERIMENTAL

All operations were carried out in a nitrogen atmosphere, employing standard vacuum and inert gas techniques. The solvents were dried by standard procedures and were freshly distilled before use. The ^1H (200.1 MHz), ^{13}C (50.3 MHz), ^{19}F (188.3 MHz) and ^{31}P (80.1 MHz) NMR spectra were recorded on a Bruker AC-200 spectrometer using CDCl_3 as a solvent, unless indicated otherwise. All shifts are reported relative to TMS (^1H , ^{13}C), CFCl_3 (^{19}F) and H_3PO_4 (^{31}P). The IR-spectrum was recorded in CDCl_3 solution, using KBr cells on a BioRad 165 spectrometer. The abbreviation "i.v." refers to a pressure of 0.1 mm Hg.

The following compounds were prepared according to published methods: diphenyl-*N*-(*N'*,*N'*,*N''*,*N''*-tetramethyl)guanidinyldiphosphine **1** and phenyl-bis-*N*-(*N'*,*N'*,*N''*,*N''*-tetramethyl)guanidinyldiphosphine **2**⁸. Other reagents were commercially available.

*Reaction of diphenyl-*N*-(*N'*,*N'*,*N''*,*N''*-tetramethyl)guanidinyldiphosphine 1 with boron trifluoride diethyl etherate; Synthesis of the $\sigma^3\text{P}\sigma^4\text{P}^+$ -diphosphorus compound 3*

A solution of 0.83 g (5.85 mmol) of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in 20 ml of diethyl ether was added at -50°C to a solution of 1.73 g (5.78 mmol) of **1** in 20 ml of diethyl ether. The mixture was stirred during 2 h at -50°C . The precipitate was filtered off and dried i.v. It was then dissolved in 5 ml of dichloromethane and precipitated by

addition of 10 ml of diethyl ether. The product thus purified was collected by filtration and dried i.v. Yield: 1.06 g (49.9%). Colourless solid, dec. > 50°C.

$^1\text{H-NMR}$: δ = 2.62 (s, 12 H, $\text{PNC}(\text{N}(\text{CH}_3)_2)_2$); δ = 2.93 (s, br, 12 H, $\text{BNC}(\text{N}(\text{CH}_3)_2)_2$); δ = 7.69–7.16 (m, 20 H, $\text{P}(\text{C}_6\text{H}_5)_2$ and $\text{P}^+(\text{C}_6\text{H}_5)_2$), $^{19}\text{F-NMR}$: δ = –153.16 (s, $^{11}\text{BF}_3$); δ = –153.11 (s, $^{10}\text{BF}_3$). $^{31}\text{P-NMR}$: δ = 20.48 (d, $^1\text{J}(\text{PP})$ = 266.73, $\sigma^4\text{P}^+$); δ = –11.90 (d, $^1\text{J}(\text{PP})$ = 267.19, $\sigma^3\text{P}$). $\text{C}_{34}\text{H}_{44}\text{B}_2\text{F}_6\text{N}_6\text{P}_2$ (734.32): calcd.: C 55.61, H 6.04, N 11.44; found: C 53.81, H 6.07, N 10.40.

*Reaction of diphenyl- N -(N' , N' , N'' , N'' -tetramethyl)guanidinyldiphosphine **1** with antimony pentachloride; Synthesis of diphenyl- N -(N' , N' , N'' , N'' -tetramethyl)guanidinyldichlorophosphonium hexachloroantimonate **4***

A solution of 1.25 g (4.2 mmol) of antimony pentachloride in 10 ml of dichloromethane was added at –80°C to a solution of 0.83 g (2.8 mmol) of **1** in 10 ml of diethyl ether. After warming to room temperature the mixture was stirred during 16 h. The solution was separated from an oily precipitate. This was redissolved several times in 5 ml portions of dichloromethane and precipitated by addition of 10 ml of diethyl ether. Yield: 0.78 g (55.5 %). Yellow solid, Mp.: 101°C. $^1\text{H-NMR}$: δ = 2.96 (s, 12 H, $\text{N}(\text{CH}_3)_2$); δ = 7.85–7.64 (m, 10 H, $\text{P}(\text{C}_6\text{H}_5)_2$). $^{31}\text{P-NMR}$: δ = 25.22 (s). $\text{C}_{17}\text{H}_{22}\text{Cl}_7\text{N}_3\text{PSb}$ (669.28): calcd.: C 30.51, H 3.31, N 6.28; found: C 29.89, H 3.31, N 5.92.

*Reaction of phenyl-bis- N -(N' , N' , N'' , N'' -tetramethyl)guanidinyldiphosphine **2** with antimony pentachloride; Synthesis of phenyl-bis- N -(N' , N' , N'' , N'' -tetramethyl)guanidinyldichlorophosphonium hexachloroantimonate **5***

A solution of 1.18 g (3.5 mmol) of **2** in 20 ml of diethyl ether was added over a period of 15 min at –80°C to a solution of 2.3 g (7.7 mmol) of antimony pentachloride in 20 ml of dichloromethane. The solution was warmed up to room temperature during 2 h with stirring. The solvent was removed i.v., and the remaining solid was dissolved several times in 5 ml portions of dichloromethane, and precipitated by addition of 10 ml of diethyl ether. Yield: 1.5 g (60.7 %). Yellow solid, Mp.: 108°C. $^1\text{H-NMR}$: δ = 2.97 (s, 24 H, $\text{N}=\text{C}(\text{N}(\text{CH}_3)_2)_2$); δ = 7.87–7.52 (m, 5 H, $\text{P}(\text{C}_6\text{H}_5)_2$). $^{13}\text{C-NMR}$: δ = 40.95 (s, $\text{N}=\text{C}(\text{N}(\text{CH}_3)_2)_2$); δ = 161.46 (s, $\text{N}=\text{C}<$); aromatic C: δ = 128.89, 129.22, 129.60, 129.83 (not assigned); δ = 132.77 (d, $^1\text{J}(\text{PC})$ = 3.39, ipso-C). $^{31}\text{P-NMR}$: δ = –1.93 (s). IR (CDCl_3): ν = 1650 (s), 1570 (vs, br), 1530 (sh), 1480 (s) (CN). $\text{C}_{16}\text{H}_{29}\text{Cl}_7\text{N}_6\text{PSb}$ (706.34): calcd.: C 27.21, H 4.14, N 11.90; found: C 26.07, H 3.95, N 10.43.

References

- [1] J. Münchenberg J.R. Goerlich, A.K. Fischer, P.G. Jones, R. Schmutzler, *Z. Anorg. Allg. Chem.*, **622**, 348 (1996).
- [2] S. Fleming, R.W. Parry, *Inorg. Chem.*, **11**, 1 (1972)
- [3] a) V. Plack, J. Münchenberg, R. Schmutzler, *Eur. J. Inorg. Chem.*, 1998, 000; b) T. Siedentop, I. Neda, J. Münchenberg, R. Schmutzler, to be published.
- [4] A.H. Cowley, M. Lattman, J.C. Wilburn, *Inorg. Chem.*, **20**, 2916 (1981)
- [5] O. Dahl, *Tetrahedron Lett.*, **23**, 1493 (1982)
- [6] S.C. Chaudhry, D. Kummer, *J. Organomet. Chem.*, **339**, 241 (1988).
- [7] J.C. Tebby in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, Eds.: J.G. Verkade, L.D. Quin; VCH Verlagsgesellschaft, Weinheim, Deerfield Beach (Florida), 1987, p 1 ff.
- [8] J. Münchenberg, O. Böge, A.K. Fischer, P.G. Jones, R. Schmutzler, *Phosphorus, Sulfur and Silicon*, **86**, 103 (1994)
- [9] J. Münchenberg, H. Thönnessen, P.G. Jones, R. Schmutzler, *Z. Naturforsch.*, **51b**, 1150 (1996).