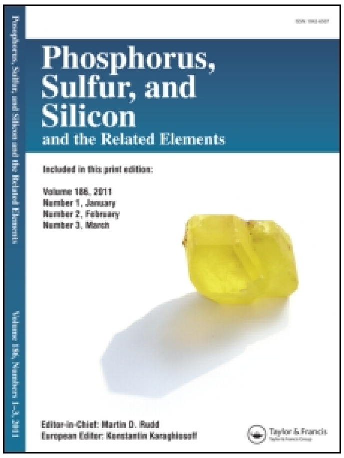

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Properties of Di-*iso*propylamino Derivatives of Diphosphanes and Triphosphanes: The X-Ray Structure of (<i>i</i>$Pr_2N)_2P$-$P(SiMe_3)_2$

Wioleta Domańska-Babul[a]; Katarzyna Baranowska[a]; Jerzy Pikies[a]
[a] Chemical Faculty, Department of Inorganic Chemistry, Gdańsk University of Technology, Gdańsk, Poland

To cite this Article Domańska-Babul, Wioleta , Baranowska, Katarzyna and Pikies, Jerzy(2009) 'Synthesis and Properties of Di-*iso*propylamino Derivatives of Diphosphanes and Triphosphanes: The X-Ray Structure of (<i>i</i>$Pr_2N)_2P$-$P(SiMe_3)_2$', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 4, 936 — 941

To link to this Article: DOI: 10.1080/10426500902718273

URL: http://dx.doi.org/10.1080/10426500902718273

Phosphorus, Sulfur, and Silicon, 184:936–941, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902718273

Synthesis and Properties of Di-*iso*propylamino Derivatives of Diphosphanes and Triphosphanes: The X-Ray Structure of $(^i\mathrm{Pr_2N})_2\mathrm{P{-}P(SiMe_3)_2}$

Wioleta Domańska-Babul, Katarzyna Baranowska, and Jerzy Pikies
Chemical Faculty, Department of Inorganic Chemistry, Gdańsk University of Technology, Gdańsk, Poland

*$(^i\mathrm{Pr_2N})_2\mathrm{PCl}$ (**3**) reacts with $\mathrm{P(SiMe_3)_2Li}$ yielding crystalline $(^i\mathrm{Pr_2N})_2\mathrm{P{-}P(SiMe_3)_2}$ (**1**). Compound **1** crystallizes in the orthorhombic space group Pbca. The lithiation of **1** with BuLi yields $(^i\mathrm{Pr_2N})_2\mathrm{P{-}P(SiMe_3)Li}$ (**2**). Compound **2** reacts with **3** with the formation of $(^i\mathrm{Pr_2N})_2\mathrm{P{-}P(SiMe_3){-}P(N}^i\mathrm{Pr_2})_2$ (**4**) in high yield. Attempts to lithiate **4** with BuLi in THF solution in order to obtain $(^i\mathrm{Pr_2N})_2\mathrm{P{-}PLi{-}P(N}^i\mathrm{Pr_2})_2$ were unsuccessful, probably due to strong electron donation of the $^i\mathrm{Pr_2N}$ groups into the P-P-P skeleton in **4**.*

Keywords Diphosphanes; lithiation; triphosphanes; X-ray structures

INTRODUCTION

In the course of our studies on the phosphanylphosphinidenes $\mathrm{R_2P{-}P}$ as ligands in transitions metal complexes,[1,2] we successfully exploited lithiated diphosphanes $\mathrm{R_2P{-}P(SiMe_3)Li}$ as precursors of $\mathrm{R_2P{-}P}$ ligands. From the reaction of $^t\mathrm{Bu_2P{-}P(SiMe_3)Li}$ with $\mathrm{Cp_2ZrCl_2}$, we obtained the complex $[\mu\text{-}(1,2{:}2\text{-}\eta\text{-}^t\mathrm{Bu_2P{=}P})\{\mathrm{Zr(Cl)Cp_2}\}_2]$ containing both a side-on and a terminally bonded $^t\mathrm{Bu_2P{-}P}$ ligand with two zirconium metal centers. In the presence of $\mathrm{PPhMe_2}$, this reaction yields $[(\eta^1{-}^t\mathrm{Bu_2P{-}P)Zr(PPhMe_2)Cp_2}]$—a complex with terminally bonded $^t\mathrm{Bu_2P{-}P}$.[3] Moreover we have found that $^t\mathrm{Bu_2P{-}PLi{-}P}^t\mathrm{Bu_2}$ reacts with $[\mathrm{(Et_3P)_2MCl_2}]$ (M = Ni, Pd) to form $[(1,2\text{-}\eta{-}^t\mathrm{Bu_2P{=}P{-}P}^t\mathrm{Bu_2})\mathrm{M(PEt_3)Cl}]$

Received 14 December 2007; accepted 30 January 2008.

Dedicated to Professor Marian Mikołajczyk from the CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

W. D.-B. and J. P. thank the Polish State Committee of Scientific Research (project No. 1 T09A 148 30) for financial support.

Address correspondence to Prof. Dr. Jerzy Pikies, Chemical Faculty, Department of Inorganic Chemistry, Gdańsk University of Technology, G. Narutowicza St. 11/12, Pl-80-952 Gdańsk, Poland. E-mail: pikies@chem.pg.gda.pl

(M = Ni, Pd).[4] We intended to expand our studies on other lithium derivatives of triphosphanes $R_2P\text{–}PLi\text{–}PR_2$ ($R \neq {}^{t}Bu$). However, the attempt to synthesize di-*iso*propylamino derivative ($R = {}^{i}Pr_2N$) failed, and we obtained only $({}^{i}Pr_2N)_2P\text{–}P(SiMe_3)\text{–}P(N^{i}Pr_2)_2$ (**4**). Syntheses and properties of these compounds are reported herein.

RESULTS AND DISCUSSION

Synthesis

$({}^{i}Pr_2N)_2P\text{–}P(SiMe_3)\text{–}P(N^{i}Pr_2)_2$ (**4**) was prepared according to the sequence described by Equations (1) and (2).

$$({}^{i}Pr_2N)_2P - P(SiMe_3)Li\ (\mathbf{2}) + Me_3SiBu \tag{1}$$

$$({}^{i}Pr_2N)_2P - P(SiMe_3)Li\ (\mathbf{2}) + ({}^{i}Pr_2N)_2PCl\ (\mathbf{3}) \rightarrow ({}^{i}Pr_2N)_2P - P(SiMe_3) - P(N^{i}Pr_2)_2\ (\mathbf{4}) + LiCl \tag{2}$$

The syntheses of **1** and **2** were conducted according to Domańska-Babul et al.,[5] the synthesis of **3** similarly to King and Sundaram,[6] and the synthesis of **4** similarly to Bender et al.[7] We obtained a much higher yield of **4** than previously reported, probably because we used the isolated $({}^{i}Pr_2N)_2P\text{–}P(SiMe_3)Li$ (**2**), and the synthesis was conducted at temperatures not higher than 20°C. Moreover, we have found that, even at room temperature, $({}^{i}Pr_2N)_2P\text{–}P(SiMe_3)Li$ undergoes a slow decomposition leading to the formation of phosphetanes and polyphosphorus compounds.[5]

We studied the reactivity of **4** towards BuLi in THF solution in order to obtain the related lithium compound $({}^{i}Pr_2N)_2P\text{–}P(Li)\text{–}P(N^{i}Pr_2)_2$. The expected product was not detected. The ^{31}P-NMR spectrum of the reaction solution revealed only the resonances of **4**. Such an unusual lack of reactivity of this $P\text{–}SiMe_3$ bond can not be caused by the sterical hindrance of the adjacent $P(N^{i}Pr_2)_2$ groups in **4**. In the crowded molecule ${}^{t}Bu_2P\text{–}P(SiMe_3)\text{–}P^{t}Bu_2$, the lithiation of the $P\text{–}SiMe_3$ bond is an easy process.[8] The lithiation product does not form from the reaction of **4** with BuLi, probably because of electronic factors. Tertiary phosphanes containing two NR_2 ligands are very strong σ-donors,[9] and these nitrogen substituents must have strong electron-donor properties towards the P-skeleton. Thus, the electron-donor properties of four $N^{i}Pr_2$ groups increase the anionic character of the $SiMe_3$ group and prevent the nucleophilic substitution at the silicon atom.

X-Ray Crystallographic Studies of 1

Single crystal X-ray diffraction data were recorded on a KUMA KM4 diffractometer with graphite-monochromated MoKα radiation using the Sapphire_2 CCD detector (Oxford Diffraction Ltd.). The apparatus was equipped with an open flow thermostat (Oxford Cryosystems), which enabled experiments at 120 K. Data was collected in four series of 152 frames using ω scan with scan width of 0.75 deg. The structures were solved with direct methods and refined with the SHELX97 program package[10] with the full matrix least-squares refinement based on F^2. Because of low X-ray absorption by the crystals, no absorption corrections were applied. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in geometrically idealized position with isotropic temperature factors 1.2 times the equivalent isotropic temperature factors U_{eq} of their attached atoms (1.5 for CH_3 groups).

Crystal Data, Measurement Conditions, and Refinement Parameters for $({}^{i}Pr_2N)_2P–P(SiMe_3)_2$ (1)

$C_{18}H_{46}N_2P_2Si_2$, yellow plate, 0.5 × 0.2 × 0.2 mm, orthorhombic, space group Pbca, $a = 15.687(3)$ Å, $b = 17.353(3)$ Å, $c = 19.033(4)$ Å, $\alpha =$ ß $= \gamma = 90.00^\circ$, V = 5181.1(17) Å^3, $\rho_{calc.} = 1.048$ g·cm^{-3}. Data collection: $2\theta_{max} = 51^\circ$, Mo K_α 0.71073 Å, ω -2θ scan mode; T = 120.0(2) K, 32463 measured and 4811 independent reflections, 4504 reflections with $I > 2\sigma(I)$, Lorentzian polarization[10]), absorption corrections: none ($\mu = 0.269$ mm^{-1}). Structure solution and refinement: SHELX 97[11], no. of parameters 231, refinement against $|F^2|$ R = 0.0890, wR = 0.1482 for $I > 2\sigma(I)$, R = 0.0972, wR = 0.1519 for all data, residual electron density: peak 0.344, hole –0.304 eA^{-3}.

Compound **1** crystallized orthorhombic in a space group Pbca. An ORTEP view of **1** is shown in Figure 1.

The molecular structure of **1** in the crystal is similar to that of $({}^{i}Pr_2N)_2P–P(SiMe^{t}_2Bu)_2$.[12] The P1-P2 distance of 224.03(13) pm is in the range of a P-P single bond, and the P-Si distance 225.97(14) pm (mean) is typical for a P–Si single bond. The coordination around the phosphorus atoms P1 and P2 is tetrahedral, with the sum of angles around these phosphorus atoms being 332.00(6) deg and 321.39(12) deg, respectively. The arrangement around N1 and N2 is almost planar; the sum of angles around N1 is 359.5(2)deg and around N2 is 356.7(2) deg. In the apparently similar compound $({}^{i}Pr_2N)_2P–P\,(SiMe_3)Li$, the P-P distance (218.9 pm) and the P-Si distance (220.2 pm) are shorter, and the arrangement around the anionic phosphorus atom is much more planar (sum of angles = 348.29 deg).[5]

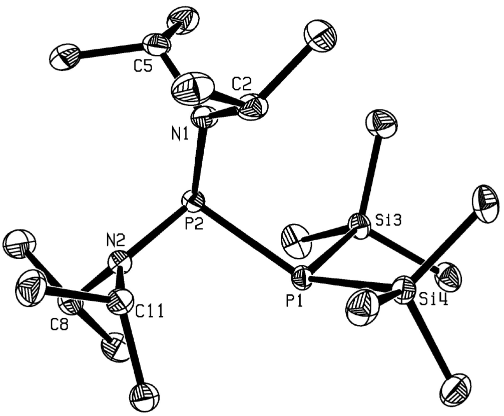

FIGURE 1 An ORTEP view of the molecular structure of **1** in the crystal; hydrogen atoms not shown, ellipsoids are drawn at 30 % probability level. Selected bond lengths [pm] and angles [°]: P1-P2 224.03(13); N1-P2 169.6(3); N2-P2 170.3(3); P1-Si3 225.22(14); P1-Si4 226.78(14); Si3-P1-Si4 105.54(5); P2-P1-Si3 98.94(5); P2-P1-Si4 127.52(6); N1-P2-N2 109.22(15); N1-P2-P1 109.80(11); N2-P2-P1 102.37(11); C2-N1-C5 115.0(3); C2-N1-P2 127.9(2); C5-N1-P2 116.6(2); C11-N2-C8 116.3(3); C11-N2-P2 123.5(2); C8-N2-P2 116.9(2).

We studied the molecular structure of **4** at a low temperature by single crystal X-ray diffraction. The results were however very similar to those reported previously.[7]

Crystallographic data for the structures of compounds **1** and **4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC-670414 (**1**) and CCDC-670415 (**4**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code (1223)336 033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

EXPERIMENTAL

All manipulations were performed in flame-dried Schlenk type glassware on a vacuum line. THF and toluene were dried over Na/benzophenone and distilled under nitrogen. Petroleum ether was dried over Na/benzophenone/diglyme and distilled under nitrogen. ^{31}P NMR spectra were recorded with a Varian 500 spectrometer (external standard 85% H_3PO_4) at ambient temperature.

Synthesis of $(^iPr_2N)_2P–P(SiMe_3)_2$ (1)

$P(SiMe_3)_2Li$ (17.83 g, 0.049 mol) was dissolved in THF (120 mL) and then slowly dropped to a cooled (–35°C) solution of $(^iPr_2N)_2PCl$ (13.04 g, 0.049 mol) in THF (100 mL). The reaction mixture was stirred for 3 h at –35°C, then allowed to warm to room temperature and stirred for another 12 h. The obtained solution was evaporated to dryness under vacuum (1 mTorr). The resulting yellow residue was dissolved in petroleum ether, filtrated, and then concentrated. After one day at ambient temperature, pale-yellow crystals of $(^iPr_2N)_2P–P(SiMe_3)_2$ were deposited. Yield: 14.4 g, 72%. $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 80.9$ ($P(N^iPr_2)_2$), –156.1 ($P(SiMe_3)_2$), $^1J_{PP} = 470.3$Hz.[5]

Synthesis of $(^iPr_2N)_2PCl$ (3)

A solution of PCl_3 (80.2 g, 0.58 mol) in petroleum ether (100 mL) was slowly added to a cooled (10°C) solution of $^iPr_2NH$ (232 g, 2.3 mol) in petroleum ether (1000 mL). The reaction mixture was heated to reflux and stirred for 20 h. The reaction mixture was filtrated, and the solvent was evaporated under reduced pressure. The resulting yellow oil residue was dissolved in hexane (300 mL), and after one day at ambient temperature, colorless crystals of $(^iPr_2N)_2PCl$ were obtained. Yield: 89.2 g, 58%. $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 135.0$.[6]

Synthesis of $(^iPr_2N)_2P–P(SiMe_3)–P(N^iPr_2)_2$ (4)

A solution of $(^iPr_2N)_2P–P(SiMe_3)Li\cdot 2.6THF$ (1.38 g, 2.6 mmol) in toluene (20 mL) was added dropwise to a cooled (–40°C) solution of $(^iPr_2N)_2PCl$ (0.41 g, 1.5 mmol) in toluene (20 mL). The obtained mixture was stirred for 3 h at –40°C, then warmed up to room temperature, and the solvent was evaporated under vacuum (1 mTorr). The residue was dissolved in pentane (50 mL), filtrated, and concentrated. After one day at –30°C, pale yellow crystals of $(^iPr_2N)_2P–P(SiMe_3)–P(N^iPr_2)_2$ were deposited. Yield: 0.6 g; 70%. $^{31}P^1H$ NMR (C_6D_6): $\delta =$ 94.9 ($P(N^iPr_2)_2$), –75.9 ($P(SiMe_3)$), $^1J_{PP} = 415.4$ Hz.[7]

REFERENCES

[1] H. Krautscheid, E. Matern, I. Kovacs, G. Fritz, and J. Pikies, *Z. Anorg. Allg. Chem.*,**623,** 1917 (1997).

[2] J. Olkowska-Oetzel and J. Pikies, *Appl. Organometal. Chem.*,**17,** 28 (2003).

[3] J. Pikies, E. Baum, E. Matern, J. Chojnacki, R. Grubba, and A. Robaszkiewicz, *Chem. Commun.*, 2478 (2004).

[4] E. Baum, E. Matern, A. Robaszkiewicz, and J. Pikies, *Z. Anorg. Allg. Chem.*, **632,** 1073 (2006).

[5] W. Domańska-Babul, K. Baranowska, R. Grubba, E. Matern, and J. Pikies, *Polyhedron*, **26,** 2491 (2007).

[6] R. B. King and P. M. Sundaram, *J. Org. Chem.,* **49,** 1784 (1984).

[7] R. G. Bender, M. Nieger, and E. Niecke, *Z. Naturforsch.*, **48b,** 1742 (1993).

[8] I. Kovacs, H. Krautscheid, E. Matern, E. Sattler, G. Fritz, W. Hönle, H. Borrmann, and H. G. von Schnering, *Z. Anorg. Allg. Chem.*, **622,** 1564 (1996).

[9] M. L. Clarke, D. J. Cole-Hamilton, A. M. Z. Slavin, and J. D. Woollins, *Chem. Commun.,* 2065 (2000).

[10] Z. Gałdecki, A. Kowalski, and I. Uszyński, DATAPROC, Oxford Diffraction, WrocŁaw, Poland (1996).

[11] G. M. Sheldrick, SHELXS97 and SHELXL97, University of Góttingen, Germany (1997).

[12] H. R. G. Bender, E. Niecke, M. Nieger, and H. Westermann, *Z. Anorg. Allg. Chem.*, **620,** 1194 (1994).