Armentrout, V. I. Baranov, D. K. Böhme, *Int. J. Mass Spectrom. Ion Proc.* **1997**, *161*, 175–191.

[29] D. E. Clemmer, Y.-M. Chen, F. A. Khan, P. B. Armentrout, *J. Phys. Chem.* **1994**, *98*, 6522–6529.

[30] Y.-M. Chen, D. E. Clemmer, P. B. Armentrout, *J. Am. Chem. Soc.* **1994**, *116*, 7815–7826.

[31] A. Fiedler, D. Schröder, S. Shaik, H. Schwarz, *J. Am. Chem. Soc.* **1994**, *116*, 10734–10741.

[32] S. Shaik, D. Danovich, A. Fiedler, D. Schröder, H. Schwarz, *Helv. Chim. Acta* **1995**, *78*, 1393–1407.

[33] D. Danovich, S. Shaik, *J. Am. Chem. Soc.* **1997**, *119*, 1773–1786.

[34] K. Yoshizawa, Y. Shiota, T. Yamabe, *J. Am. Chem. Soc.* **1998**, *120*, 564–572.

[35] S. Shaik, M. Filatov, D. Schröder, H. Schwarz, *Chem. Eur. J.* **1998**, *4*, 193–199.

[36] M. Newcomb, M.-H. Le Tadic, D. A. Putt, P. F. Hollenberg, *J. Am. Chem. Soc.* **1995**, *117*, 3312–3313; M. Newcomb, M.-H. Le Tadic-Biadatti, D. L. Chestrey, E. S. Roberts, P. F. Hollenberg, *J. Am. Chem. Soc.* **1995**, *117*, 12085–12091; S.-Y. Choi, P. E. Eaton, P. F. Hollenberg, K. E. Liu, S. J. Lippard, M. Newcomb, D. A. Putt, S. P. Upadhyaya, Y. Xiong, *J. Am. Chem. Soc.* **1996**, *118*, 6547–6555; P. H. Toy, M. Newcomb, P. F. Hollenberg, *J. Am. Chem. Soc.* **1998**, *120*, 7719–7729.

[37] The comparison of the MO diagram for FeO^+ with the elecronic configuration of the triplet ground state of O_2 reveals that both molecules exhibit a similar bonding situation (see ref. [31]). Ground-state triplet oxygen reacts with closed-shell molecules through radical mechanisms, whereas the first excited state $^1\Delta_g$ readily undergoes concerted reactions such as cycloadditions.

Parent Substances of Inorganic Chemistry: Homoleptic Pnictogenyl Compounds of Group 14, $E(ZR_2)_4$

Norbert W. Mitzel*

A new parent substance of inorganic nonmetal chemistry has been prepared and structurally characterized: the simplest compound containing a SiP_4 unit, tetraphosphanylsilane, $Si(PH_2)_4$.[1] Driess and Monsé achieved the synthesis of this compound by treating lithium tetraphosphanylalanate, $Li[Al(PH_2)_4]$, with $SiCl_4$; Boese and Bläser have grown a single crystal at low temperatures and determined its structure (Figure 1). Thus, $Si(PH_2)_4$ is the first example of the successful synthesis of an $E(ZH_2)_4$ compound (E = C, Si, Ge, Sn, Pb; Z = N, P, As, Sb, Bi), that is an EZ_4 fragment without organic substituents. $Ge(PH_2)_4$ was also prepared, but was so far only detected by means of GC/MS analysis. The simplest representative of an Si–P compound, H_3SiPH_2, had already been prepared in 1955 by G. Fritz,[2] while $HSi(PH_2)_3$ was described in 1968.[3]

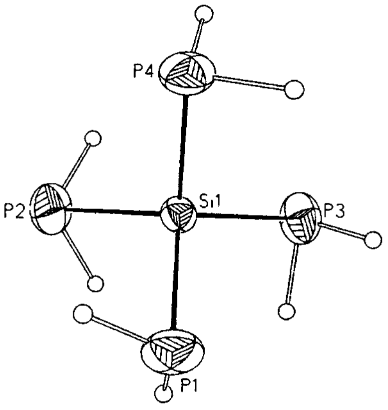


Figure 1. Molecular structure of $Si(PH_2)_4$.

The synthesis of compounds without organic substituents is of importance because their existence allows conclusions to be drawn regarding the inherent stability of the core structure and allows an assessment of the influence of the stabilization by more or less space-filling organic substituents, which is important for the synthesis of derivatives. Moreover, since in most cases direct comparisons with the results of high-level quantum chemical calculations is only possible for the simplest unsubstituted systems, such studies serve to confirm theoretical methods and allow for their further development.

Recently the research on $E(ZR_2)_4$ compounds was intensified. On the one hand, attempts were made to apply such compounds as precursors for new IV/V materials, on the other to provide representative objects for structural studies. The presence of four donor centers in these molecules makes them attractive as ligands for complex chemistry and for the design of supramolecular aggregates.

Many compounds of the type $E(ZR_2)_4$ are unknown. Despite numerous attempts, no synthetic pathway to a neutral compound $C(PR_2)_4$ has been found. The same applies for analogous compounds of arsenic, antimony, and bismuth. Some silicon phosphanides have been prepared, for example, tetrakis(*tert*-butyl)-1,2,4,5-tetraphosphasilaspiro[2.2]pentane.[4] Compounds with $SiAs_4$, $SiSb_4$, and $SiBi_4$ units, however, have not been documented so far. $Sn(SbPh_2)_4$ is known as an example from tin chemistry.[5]

The only class of compounds with numerous members in this context are the element amides, while compounds containing CN_4 units are rare, but of actual interest. Plenty

---

[*] Dr. N. W. Mitzel
Anorganisch-chemisches Institut der
Technischen Universität München
Lichtenbergstrasse 4, D-85747 Garching (Germany)
Fax: (+49)89-289-13125
E-mail: n.mitzel@lrz.tum.de

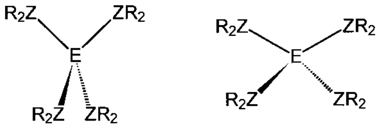
$F^- + {}^1(HNO) \rightleftharpoons [FHNO]^- \rightleftharpoons HF + {}^3(NO^-)$ (a)

of data have been reported for tetraaminosilanes,[6] -germanes, and -stannanes.[7]

However, even with these classes of compounds the simplest representatives $E(NH_2)_4$ are as yet unknown, which is paralleled by the chemistry of the hydroxides $E(OH)_4$: only $Si(OH)_4$ is existent in dilute aqueous solutions.

Structural Chemistry of the Compounds $E(ZR_2)_4$

The structures of compounds of the type $E(ZR_2)_4$ are not yet satisfactorily understood. All the homoleptic element amides show distinct deviations from an ideal tetrahedral geometry at the central atom. In this context two of the N-E-N angles are markedly compressed, while four of them are widened (Scheme 1 A), or the inverse case is observed with two larger and four smaller angles (Scheme 1 B). Examples of this include $C(NMe_2)_4$[8] and $Si(NHMe)_4$.[9] A parallel situation is observed for the homoleptic element alkoxides such as $Si(OCHMe_2)_4$.[10] These findings cannot be attributed to packing effects in crystal lattices, as the deviations are also predicted for $C(NMe_2)_4$ and $Si(NH_2)_4$ by density functional theory (DFT) calculations[11] and have been found in experimentally determined gas-phase structures of $C(OMe)_4$[12] and $Si(OMe)_4$.[13]



(A) (B)

Scheme 1.

Very recently Gillespie et al. have attempted again to explain these anomalies[14] and thus to extend the VSEPR model.[15] In this context they quote the distortions of the electron densities at the ligand atoms (Z in this case). If closely packed about the central atoms E, halogen ligands with rotational symmetry lead to ideally tetrahedral molecules EX_4. In contrast, the electron density at nitrogen or oxygen in OR and NR_2 ligands is not rotationally symmetrical, thus leading to a ligand radius that is dependent on orientaion. Consequently, the nonbonding distances $O\cdots O$ and $N\cdots N$ are dependent on the orientation of the ligands R. Closest packing of these unsymmetrical ligands thus leads to different angles O-E-O and N-E-N about the central atoms.

The structural elucidation of $Si(PH_2)_4$ is important in this context because the results show distinctly smaller deviations from tetrahedral symmetry than the comparable silicon amides. In fact $Si(PH_2)_4$ has an almost ideal tetrahedral geometry at silicon. It might be speculated whether the small hydrogen atoms are completely immersed in the electron cloud of the relatively large phosphorus atom; that is the phosphorus atom in the PH_2 ligand is effectively still rotationally symmetrical or its ligand radius is not orientation-dependent. A closest packing of such ligands about a silicon center leads then to an almost tetrahedral structure. The very low rotational barrier about the Si–P bond can be rationalized in exactly the same way. Is it possible that it turns out that the elements of the first period are an exception to the rule of otherwise almost symmetrical ligand radii?

Precursors for IV/V Materials

There are numerous interesting materials comprising elements of Groups 14 and 15. Some have already found broad technical application, others are under development or have not been synthesized to date, but are very promising candidates. Of the nitride materials silicon nitride is the most important and among the precursors tested for the chemical vapor deposition of silicon nitride are compounds of the type $Si(NR_2)_4$.[16]

Reports about the nitrides of the heavier elements of Group 14 are comparatively rare (Ge/N;[17] Sn/N[18]), but there are still huge efforts to prepare carbon nitride C_3N_4,[19] for which a hardness greater than that of diamond was predicted. However, so far no unequivocal report about a phase C_3N_4 has appeared. It is only in surface science that there are some reports about the existence of C_3N_4 phases as thin layers.[20] Attempts to develop precursors for this material have also included the synthesis of $C(NR_2)_4$ compounds.[8]

Silicon/phosphorus phases are promising materials for applications in micro- and optoelectronic devices such as heterojunction bipolar transistors, photovoltaic cells, sensors, and light-emitting diodes.[21] Materials under consideration have compositions from single-crystalline p-doted silicon up to phosphorus-rich amorphous phases, the properties of which can be tuned by varying the Si/P ratio. Compounds like $Si(PH_2)_4$ are naturally interesting precursors for the preparation of such phases and the search for new Si/P materials is still uncovering new phases such as $Si_{12}P_5$.[22]

The most recent reports about the successful preparation of $Si(PH_2)_4$ show how important it is to reinvestigate the development of synthetic pathways to the missing members of parent substances of inorganic molecular chemistry. The absence of stabilizing organic substituents in particular make such compounds desirable for studying their fundamental properties but also for hightech applications.

German version: *Angew. Chem.* **1999**, *111*, 91–92

Keywords: germanium • materials science • phosphanes • silanes • silicon

---

[1] M. Driess, C. Mosé, R. Boese, D. Bläser, *Angew. Chem.* **1998**, *110*, 2389–2391; *Angew. Chem. Int. Ed.* **1998**, *37*, 2257–2259.
[2] G. Fritz, *Z. Anorg. Allg. Chem.* **1955**, *280*, 332–345.
[3] A. D. Norman, *J. Am. Chem. Soc.*, **1968**, *90*, 6556–6557.
[4] K.-F. Tebbe, T. Heinlein, M. Feher, *Z. Kristallogr.* **1985**, *172*, 89–90.
[5] H. Schumann, T. Oestermann, M. Schmidt, *J. Organomet. Chem.* **1967**, *8*, 105–110.
[6] G. Huber, A. Jockisch, H. Schmidbaur, *Eur. J. Inorg. Chem.* **1998**, 107–112.
[7] M. F. Lappert, P. P. Power, A. R. Sanger, R. C. Srivastava *Metal and Metalloid Amides*, Ellis Horwood, Chichester, **1980**.
[8] A. Jockisch, H. Schmidbaur, *Chem. Ber.* **1997**, *130*, 1739–1744.
[9] H. Andersch, M. Jansen, *Acta Crystallogr. Sect. C* **1990**, *46*, 1985–1986.
[10] N. W. Mitzel, A. J. Blake, D. W. H. Rankin, *J. Am. Chem. Soc.* **1997**, *119*, 4143–4148.

[11] K. Albert, N. Rösch, *Chem. Ber.* **1997**, *130*, 1745–1749.

[12] F. C. Mijlhoff, H. J. Geise, E. J. M. van Schaick, *J. Mol. Struct*. **1974**, *20*, 393–401.

[13] L. H. Boonstra, F. C. Mijlhoff, G. Renes, A. Spelbos, I. Hargittai, *J. Mol. Struct.* **1975**, *28*, 129–139.

[14] a) R. J. Gillespie, I. Bytheway, E. A. Robinson, *Inorg. Chem.* **1998**, *37*, 2811–2825.

[15] R. J. Gillespie, E. A. Johnson, *Angew. Chem*. **1996**, *108*, 539–560; *Angew. Chem. Int. Ed. Engl*. **1996**, *35*, 495–514.

[16] R. D. Gordon, D. M. Hofmann, K. Riaz, *Chem. Mater.* **1990**, *2*, 480–489.

[17] G. A. Johnson, V. J. Kapoor, *J. Appl. Phys.* **1991**, *69*, 3616–3622.

[18] D. M. Hoffman, P. Rangarajan, S. D. Athavale, D. J. Economou, J. R. Liu, Z. S. Zheng, *J. Vac. Sci. Technol. A* **1995**, *13*, 820–825.

[19] W. Schnick, *Angew. Chem*. **1993**, *105*, 1649–1650; *Angew. Chem. Int. Ed. Engl*. **1993**, *32*, 1580–1581.

[20] S. Vepřek, J. Weidmann, F. Glatz, *J. Vac. Sci. Technol. A* **1995**, *13*, 2914–2919.

[21] X.-H. Li, J. R. A. Carlsson, S. F. Gong, H. T. G. Hentzell, *J. Appl. Phys.* **1994**, *76*, 5179–5184.

[22] J. R. A. Carlsson, L. D. Madsen, M. P. Johansson, L. Hultman, X.-H. Li, H. T. G. Hentzell, L. R. Wallenberg, *J. Vac. Sci. Technol. A* **1997**, *15*, 394–401.

1433-7851/99/3801-0088 $ 17.50+.50/0