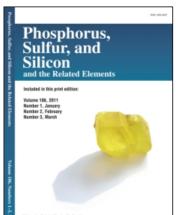
This article was downloaded by:

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

The Suprising Variety of Products from Reactions of P-P Bonds with Dichlorogermylene

Wolf-Walther Du Mont^a; Christian Druckenbrodt^a; Michael Karnop^a; Jens Mahnke^a Institut für Anorg. u. Analyt. Chemie der TUBS, Braunschweig, Germany

To cite this Article Mont, Wolf-Walther Du , Druckenbrodt, Christian , Karnop, Michael and Mahnke, Jens(1999) 'The Suprising Variety of Products from Reactions of P-P Bonds with Dichlorogermylene', Phosphorus, Sulfur, and Silicon and the Related Elements, 147: 1, 77

To link to this Article: DOI: 10.1080/10426509908053519 URL: http://dx.doi.org/10.1080/10426509908053519

Taylor & Fro

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.

The Surprising Variety of Products from Reactions of P-P Bonds with Dichlorogermylene

WOLF – WALTHER DU MONT, CHRISTIAN DRUCKENBRODT, MICHAEL KARNOP and JENS MAHNKE

Institut für Anorg. u. Analyt. Chemie der TUBS, D 38023 Braunschweig, Germany

Insertion of dichlorogermylene (from GeCl₂-dioxane) into the P-P bonds of tetraalkyldiphosphanes (PRR')₂ (2a: R,R'= i-Pr; 2b: R= t-Bu, R'= i-Pr; 2c: R,R'= t-Bu) leads to dichlorobis(dialkylphosphanyl)germanes 3a-c. With 2a, the insertion remains incomplete: 3a exists in an equilibrium with an adduct of diphosphane 2a with GeCl₂. Subsequently 3b and 3c undergo α-eliminations to dialkylchlorophosphanes 5b and 5c and the dimeric phosphanylgermylenes (RR'PGeCl)₂ 4b and 4c [1]. Similar to the above (but in absence of dioxane), reacting the trichlorogermylphosphane i-Pr(t-Bu)PGeCl₃ 7c [2] with the related trichlorosilylphosphane i-Pr(t-Bu)PSiCl₃ provided a mixture of SiCl₄, 1c, 3c, 5c and 7c. 3a and 3c have been trapped as inert molybdenum complexes (CO)₄Mo(μ-PRR')₃GeCl₂ 6a and 6c from equilibrilia containing 1a / 2a / 3a and 3c / 4c/ 5c / 7c respectively.

Ring - ring transformations can easily be followed by ³¹P NMR, when dichlorogermylene inserts into P-P bonds of cyclophosphanes (RP), (R= 1-Bu, i-Pr). Triphosphagermetanes 8 are clearly the primary products, but subsequently, formation of triphosphadigermolanes 9 and tetraphosphagermolanes 10 can be observed.

X-ray crystal structure determinations on compounds **6a**, **8**, **9** [(t-BuP)₃(GeCl₂)_a, n= 1, 2)] and (t-BuP)₃PGeCl₃[3] reveal, that P-Ge^{IV} bond lengths are very susceptible to the degree of chlorine substitution at germanium.

Insertion of dichlorogermylene into the P-P bond of the new P-phosphanylphosphankene $(Me_3Si)_2C=PP-i-Pr_1$ (11) [4] is followed by a rearrangement leading to a transient unsymmetric diphosphene with a Cl-Ge-C-P=P-C-Ge-PR₂ backbone. Loss of i-Pr₂PCl from this diphosphene provides an unusual diphosphane $\{P_2[C(SiMe_3)_2]_2(GeCl_2)\}$ (12) which apparently (NMR) adopts a bicylic structure.

References

- C. Druckenbrodt, W.-W. du Mont, F. Ruthe, P.G. Jones, Z. Anorg. Allg. Chem. 1998, 624, 590.
- [2] W.-W. du Mont, M. Karnop, J. Mahnke, R. Martens, C., Druckenbrodt, J. Jeske, P.G. Jones, Chem. Ber. /Recueil 1997, 130, 1619.
- [3] M. Karnop, W.-W. du Mont, P. G. Jones, J. Jeske, , Chem. Ber. /Recueil 1997, 130, 1611.
- [4] J. Mahnke, A. Zanin, W.-W. du Mont, F. Ruthe, P. J. Jones, Z. Anorg. Allg. Chem. 1998, 624, 1447.