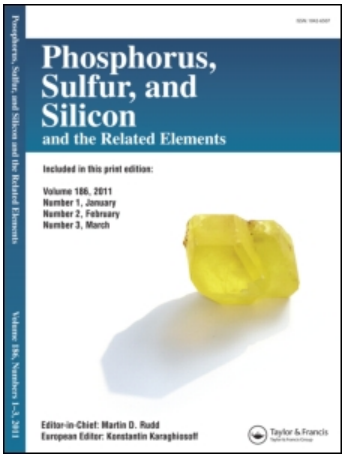

Phosphorus, Sulfur, and Silicon and the Related Elements

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]
[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

Phosphorus, Sulfur and Silicon, 1999, Vol. 147, pp. 77-77
Reprints available directly from the publisher
Photocopying permitted by license only

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 $GeCl_2$-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 $GeCl_2$. 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)$PGeCl_3$ **7c** [2] with the related trichlorosilylphosphane i-Pr(t-Bu)$PSiCl_3$ provided a mixture of $SiCl_4$, **1c**, **3c**, **5c** and **7c**. **3a** and **3c** have been trapped as inert molybdenum complexes $(CO)_4Mo(\mu\text{-}PRR')_2GeCl_2$ **6a** and **6c** from equilibrilia containing **1a / 2a / 3a** and **3c / 4c / 5c / 7c** respectively.

Ring - ring transformations can easily be followed by ^{31}P NMR, when dichlorogermylene inserts into P-P bonds of cyclophosphanes $(RP)_3$ (R= t-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** $[(t\text{-}BuP)_3(GeCl_2)_n$, n= 1, 2)] and (t-BuP)$_3PGeCl_3$ [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*-phosphanylphosphaalkene $(Me_3Si)_2C{=}PP\text{-}i\text{-}Pr_2$ (**11**) [4] is followed by a rearrangement leading to a transient unsymmetric diphosphene with a Cl-Ge-C-P=P-C-Ge-PR_2 backbone. Loss of $i\text{-}Pr_2PCl$ 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

[1] 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.