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

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

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Insertion of dichlorogermylene (from  $\text{GeCl}_2$ -dioxane) into the P-P bonds of tetraalkyldiphosphanes  $(\text{PRR}')_2$  (**2a**:  $\text{R}, \text{R}' = \text{i-Pr}$ ; **2b**:  $\text{R} = \text{t-Bu}$ ,  $\text{R}' = \text{i-Pr}$ ; **2c**:  $\text{R}, \text{R}' = \text{t-Bu}$ ) 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  $\text{GeCl}_2$ . Subsequently **3b** and **3c** undergo  $\alpha$ -eliminations to dialkylchlorophosphanes **5b** and **5c** and the dimeric phosphanylgermylenes  $(\text{RR}'\text{PGeCl})_2$ , **4b** and **4c** [1]. Similar to the above (but in absence of dioxane), reacting the trichlorogermylphosphane  $\text{i-Pr}(\text{t-Bu})\text{PGeCl}_3$ , **7c** [2] with the related trichlorosilylphosphane  $\text{i-Pr}(\text{t-Bu})\text{PSiCl}_3$  provided a mixture of  $\text{SiCl}_4$ , **1c**, **3c**, **5c** and **7c**. **3a** and **3c** have been trapped as inert molybdenum complexes  $(\text{CO})_5\text{Mo}(\mu\text{-PRR}')_2\text{GeCl}_2$ , **6a** and **6c** from equilibria containing **1a** / **2a** / **3a** and **3c** / **4c** / **5c** / **7c** respectively.

Ring - ring transformations can easily be followed by  $^{31}\text{P}$  NMR, when dichlorogermylene inserts into P-P bonds of cyclophosphanes  $(\text{RP})_3$  ( $\text{R} = \text{t-Bu}$ ,  $\text{i-Pr}$ ). 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** [ $(\text{t-BuP})_3(\text{GeCl}_2)_n$ ,  $n = 1, 2$ ] and  $(\text{t-BuP})_3\text{PGeCl}_3$  [3] reveal, that P-Ge<sup>IV</sup> 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  $(\text{Me}_2\text{Si})_2\text{C}=\text{PP-i-Pr}_2$  (**11**) [4] is followed by a rearrangement leading to a transient unsymmetric diphosphene with a  $\text{Cl-Ge-C-P}=\text{P-C-Ge-PR}_2$  backbone. Loss of  $\text{i-Pr}_2\text{PCl}$  from this diphosphene provides an unusual diphosphane  $\{\text{P}_2[\text{C}(\text{SiMe}_3)_2](\text{GeCl}_2)\}$  (**12**) which apparently (NMR) adopts a bicyclic structure.

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