

**Zur Reaktion von  $\text{PCl}_3$  mit  $\text{NaR}^*$ ,  $\text{KR}^*$  und  $\text{ZnR}_2^*$  ( $\text{R}^* = \text{Si}^t\text{Bu}_3$ ) [1]:**

**Bildung des Diphosphens  $\text{R}^*\text{P}=\text{PR}^*$ , Tetraphosphans  $\text{P}_4\text{R}_2^*$ ,**

**Tetraphosphanids  $\text{NaP}_4\text{R}_3^*$  sowie von Halogenphosphanen  $\text{R}_m^*\text{P}_n\text{Cl}_p$**

On the Reaction of  $\text{PCl}_3$  with  $\text{NaR}^*$ ,  $\text{KR}^*$  and  $\text{ZnR}_2^*$  ( $\text{R}^* = \text{Si}^t\text{Bu}_3$ ) [1]:

Formation of the Diphosphene  $\text{R}^*\text{P}=\text{PR}^*$ , Tetraphosphane  $\text{P}_4\text{R}_2^*$ , Tetraphosphanide  $\text{NaP}_4\text{R}_3^*$  as well as Halogenophosphanes  $\text{R}_m^*\text{P}_n\text{Cl}_p$

Nils Wiberg, Angelika Wörner, Hans-Wolfram Lerner und Konstantin Karaghiosoff\*

Department Chemie der Universität München, Butenandtstr. 5-13 (Haus D), D-81377 München  
\* NMR-Spektrensimulation

Sonderdruckenforderungen an Prof. Dr. N. Wiberg. E-mail: niw@cup.uni-muenchen.de

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The reaction of  $\text{PCl}_3$  at r. t. with an equimolar amount of  $\text{NaR}^*$  in heptane gives the colorless phosphane  $\text{R}^*\text{PCl}_2$  (**1**), the colorless diphosphane  $\text{R}^*\text{CIP-PClR}^*$  (**2**), the light green diphosphene  $\text{R}^*\text{P}=\text{PR}^*$  (**4**), the cyclotetraphosphane  $\text{R}_2^*\text{P}_4\text{Cl}_2$  (**6**) (not isolated), the light yellow bis(cyclotriphosphanyl)  $\text{P}_6\text{R}^*_{4}$  (**7**), the cyclotriphosphane  $\text{R}^*_2\text{P}_3\text{Cl}$  (**8**) (not isolated), and the colorless bicyclopophosphane  $\text{P}_4\text{R}^*_{2}$  (**9**). With a threefold molar amount of  $\text{NaR}^*$  in tetrahydrofuran the blue violet triphosphanide  $\text{NaP}_3\text{R}^*_{2}$  (**10**), the dark red tetraphosphanide  $\text{NaP}_4\text{R}^*_{3}$  (**11**), and the orange pentaphosphanediide  $\text{Na}_2\text{P}_5\text{R}^*_{3}$  (**12**) are formed from  $\text{PCl}_3$  besides the phosphanides  $\text{NaPR}^*_{2}$ ,  $\text{Na}_2\text{PR}^*$  (isolated),  $\text{NaP}_2\text{R}^*_{3}$  and  $\text{Na}_2\text{P}_2\text{R}^*_{2}$ . With a four-fold molar amount of  $\text{KR}^*$  in benzene  $\text{PCl}_3$  gives the green diphosphanediide  $\text{K}_2\text{P}_2\text{R}^*_{2}$  and the red phosphanediide  $\text{K}_2\text{PR}^*$ , and with an equimolar amount of  $\text{ZnR}^*_{2}$  in heptane the compounds **1**, **2**, **4**, **7** and **8** are obtained. The compound  $\text{R}^*\text{P}=\text{PR}^*$  (**4**), the first diphosphene with two silyl substituents, is formed in high yields from the action of Na on  $\text{R}^*\text{PCl}_2$  in heptane at 90 °C. It gives a [2+4] cycloadduct with 2,3-dimethylbutadiene and phosphanides ( $\text{Na}_2\text{P}_2\text{R}^*_{2}$  or  $\text{Na}_2\text{PR}^*$ ) with Na or  $\text{NaR}^*$ . Bicyclopophosphane  $\text{P}_4\text{R}^*_{2}$  (**9**) (structure: two  $\text{R}^*\text{P}_3$  rings with a common edge) is exclusively obtained from  $\text{Na}_2\text{P}_4\text{R}^*_{2}$  (formed quantitatively from  $\text{P}_4$  and 2  $\text{NaR}^*$ ) and TCNE. **9** may be reduced (Na, THF) with reformation of  $\text{Na}_2\text{P}_4\text{R}^*_{2}$  and reacts in the presence of  $\text{NaR}^*$  with formation of dark red  $\text{NaP}_4\text{R}^*_{3}$  (**11**) (structure:  $\text{P}_3$  ring with two  $\text{R}^*$  substituents in *trans* position and one  $\text{PNaR}^*$  substituent). Straightforward syntheses of halogenophosphanes include (i) reactions of  $\text{ZnR}^*_{2}$  with  $\text{PCl}_3$  or  $\text{PBr}_3$  (mole ratio 1 : 2) in heptane to form  $\text{R}^*\text{PCl}_2$  (**1**) or  $\text{R}^*\text{PBr}_2$ , and (ii) reaction of  $\text{R}^*_{2}$  with  $\text{R}^*\text{PCl}_2$  (mole ratio 1 : 2) without a solvent, or of  $\text{KR}^*$  and  $\text{PCl}_3$  (mole ratio 2 : 1) in benzene to form  $\text{R}^*\text{CIP-PClR}^*$  (**2**). The halogenophosphanes  $\text{R}_2^*\text{P}_3\text{Cl}$  (**8**) (structure:  $\text{P}_3$  ring with two  $\text{R}^*$  substituents in *trans* position and one Cl substituent) as well as  $\text{R}^*_2\text{P}_4\text{Cl}_2$  (**6**) (structure:  $\text{P}_4$  ring with alternating  $\text{R}^*$  and Cl substituents) have not been isolated. The  $^{31}\text{P}$ -NMR spectra and the pathways of formation of the phosphorus compounds are discussed.