

STANNYLENE AND GERMYLENE AS POWERFUL DECHLORINATED REAGENTS.  
 NEW ROUTE TO DIPHOSPHERE.

Michael VEITH and Volker HUCH

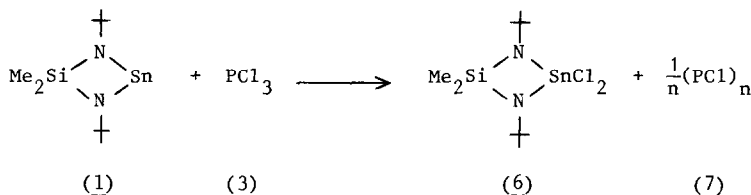
Institut für Anorganische und Analytische Chemie der TU, Pokelsstr. 4,  
 D-3300 Braunschweig F.R.G.

Jean-Pierre MAJORAL<sup>a</sup>, Guy BERTRAND<sup>b</sup> and Georges MANUEL<sup>b</sup>

<sup>a</sup> ERA 926, <sup>b</sup> ERA 829, Université Paul Sabatier, 118 route de Narbonne,  
 31062 Toulouse cedex, France

Summary : Dichlorophosphines  $\text{RPCl}_2$  [ $\text{R}=\text{Cl}$  (3), Ph (4) and 2,4,6- $\text{Bu}_3\text{C}_6\text{H}_2$  (5)] are reduced to the corresponding phosphorus-I compounds by the stannylene  $\text{Me}_2\text{Si}(\text{NBu}^t)_2\text{Sn}$ : (1) or by the germylene  $\text{GeI}_2$  (2) ; in the case of the reaction of (5) with (1), bis(2,4,6-tri-tert-butyl-phenyl)-diphosphene (9) is obtained with a 65 % yield.

In the search of a new, mild and general route to compounds possessing multiple bonds between the heavier main group elements<sup>1-3</sup> we investigated the action of 1,3-di-tert-butyl-2,2-dimethyl-1,3,2,4  $\lambda^2$  diazasilastannetidine (1)<sup>4</sup> or diiodogermylene (2) on various dichlorinated organometallic derivatives. Here we wish to report our first results observed in the phosphorus series. We found that the tin-II compound (1) reacts spontaneously in benzene, at room temperature with equimolecular amounts of phosphorus trichloride (3) or phenyldichlorophosphine (4) giving the dichlorostannane (6)<sup>5</sup>. After sublimation of the residue at  $60^\circ\text{C}/10^{-3}$  Torr (6) was obtained with a 95 % yield (mass spectrum :  $375 (\text{M}-15)^+$  ; anal. calcd. for  $\text{C}_{10}\text{H}_{24}\text{N}_2\text{SiSnCl}_2$  : C, 30.80 ; H, 6.20 ; N, 7.18 ; Cl, 18.18. Found : C, 30.75 ; H, 6.23 ; N, 7.01 ; Cl, 17.90). In the case of (3) the phosphorus-containing product consists of a yellow amorphous, insoluble (presumably polymeric) powder of  $(\text{PCl})_n$  (7) composition. Pentaphenylcyclopentaphosphane (8) [ $^{31}\text{P}$  NMR (THF,  $\delta$ ) : 4.7 ppm ; mass spectrum :  $540 (\text{M}^+)$ ] is similarly obtained from (4)





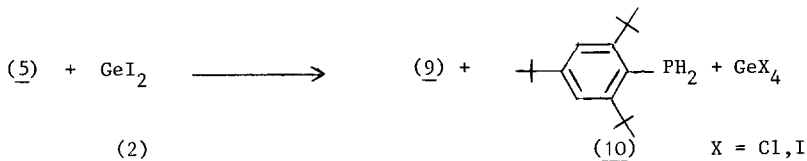
These results suggest that phosphorus-I compounds  $\text{RP}^{\text{I}}$  ( $\text{R}=\text{Cl}, \text{Ph}$ ) are formed as transient intermediates in the course of the reactions. Since it has recently been demonstrated that the use of ligands with large steric bulk permitted the isolation of the dimers of silylene<sup>2</sup>, germylene<sup>3</sup> and phosphinidenes<sup>1</sup> - compounds possessing a double bond between two heavier main group elements - we reacted (1) with 2,4,6-tri-tert-butylphenyldichlorophosphine (5).



In a typical experiment, a mixture of (5) (0.5 g, 1.5 mMole), stannylene (1) (0.4 ml, 1.5 mMole) and 10 ml of benzene was stirred at 40°C under a nitrogen atmosphere for half an hour. After condensation of the benzene in a cooled trap 0.27 g (65 % yield) of (9) was recrystallized from hexane as an orange-red solid which was identified by single X-ray diffraction<sup>1a</sup>. After evaporation of the hexane solution and sublimation (6) was obtained in 78 % yield.

Analogous experiments were conducted with diiodogermylene (2)<sup>6</sup> instead of (1). White crystals of (8) were obtained in almost quantitative yield from the 1:1 reaction of (4) with (2) in benzene at 110°C in a sealed tube (50 h).

In an attempt to prepare the diphosphene (9), the dichlorophosphine (5) in benzene was allowed to react with (2) at 60°C (10 h). Beside (9) (40 % yield), the phosphine (10) arising from the thermal decomposition of (9)<sup>1b</sup> was also formed.



Since the dechlorination reaction by stannylene (1) or diiodogermylene (2) is not

sensitive to steric hindrance, it should be possible to extrapolate such a method for the synthesis of various stable  $\pi$  bonded organometallic species.

Acknowledgment. We gratefully acknowledge support of this work by the CNRS (A.T.P. Concepts Nouveaux de l'objectif chimie fine).

#### REFERENCES

- <sup>1</sup>
- (a) M. YOSHIFUJI, I. SHIMA, N. INAMOTO, K. HIROTSU and T. HIGUCHI, *J. Amer. Chem. Soc.*, 103, 4587 (1981).
  - (b) G. BERTRAND, C. COURET, J. ESCUDIE, S. MAJID and J.P. MAJORAL, *Tetrahedron Lett.*, 23, 3567 (1982).
  - (c) A.H. COWLEY, J.E. KILDUFF, T.M. NEWMAN and M. PAKULSKI, *J. Amer. Chem. Soc.*, 104, 5820 (1982).
  - (d) B. CETINKAYA, A. HUDSON, M.F. LAPPERT, H.J. GOLDWHITE, *J. Chem. Soc. Chem. Commun.*, 609 (1982).
  - (e) B. CETINKAYA, P.B. HITCHCOCK, M.F. LAPPERT, A.J. THORNE and H. GOLDWHITE, *J. Chem. Soc. Chem. Commun.*, 691 (1982).
  - (f) C. COURET, J. ESCUDIE and J. SATGE, *Tetrahedron Lett.*, 23, 4941 (1982).
  - (g) E. NIECKE and R. RÜGER, *Angew. Chem., Int. Ed. Engl.*, 95, 154 (1983).
  - (h) C.N. SMIT, Th.A. VAN DER KNAAP, F. BICKELHAUPT, *Tetrahedron Lett.*, 24, 2031 (1983).
  - (i) M. YOSHIFUJI, K. ANDO, K. TOYOTA, I. SHIMA and N. INAMOTO, *J. Chem. Soc. Chem. Commun.*, 419 (1983).
  - (j) A.H. COWLEY, J.E. KILDUFF, M. PAKULSKI and C.A. STEWART, *J. Amer. Chem. Soc.*, 105, 1655 (1983).
  - (k) M. YOSHIFUJI, K. SHIBAYAMA, N. INAMOTO, T. MATSUSHITA and K. NISHIMOTO, *J. Amer. Chem. Soc.*, 105, 2495 (1983).
  - (l) A.H. COWLEY, J.E. KILDUFF, S.K. MEHROTRA, N.C. NORMAN and M. PAKULSKI, *J. Chem. Soc. Chem. Commun.*, 528 (1983).
- <sup>2</sup>
- (a) R. WEST, M.J. FINK and J. MICHL, *Science*, 214, 1343 (1981).
  - (b) S. MASAMUNE, Y. HANZAWA, S. MURAKAMI, T. BALLY and J.F. BLOUNT, *J. Amer. Chem. Soc.*, 104, 1150 (1982).
  - (c) P. BOUDJOUK, B.H. HAN and K.R. ANDERSON, *J. Amer. Chem. Soc.*, 104, 4992 (1982).

- <sup>3</sup> S. MASUMUNE, Y. HANZAWA and D.J. WILLIAMS, *J. Amer. Chem. Soc.*, 104, 6136 (1982).
- <sup>4</sup> M. VEITH, *Angew. Chem.*, 87, 287 (1975) ; *Angew. Chem., Int. Ed. Engl.*, 14, 260 (1975).
- <sup>5</sup> M. VEITH, O. RECKTENWALD and H. HUMPFER, *Z. Naturforsch.*, 33b, 14 (1978).
- <sup>6</sup> G. MANUEL, Thesis n° 390, 1970, University of Toulouse.

(Received in France 24 July 1983)