

Journal of Organometallic Chemistry 521 (1996) 417-419

Preliminary communication

Extension of the Benkeser reaction to the reductive trichlorosilylation of main group element chlorides ¹

Wolf-Walther du Mont^{*}, Lutz Peter Müller, Lars Müller, Sebastian Vollbrecht, Andreas Zanin

Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig, Germany

Received 14 February 1996

Abstract

Chlorophosphanes RR'PX 1 (1a: R, R' = i-propyl; 1b: R = t-butyl, R' = i-propyl; 1c: RR' = 3-methylphosphol-2-enyl) react with trichlorosilane and triethylamine to provide trichlorosilylphosphanes RR'PSiCl₃ 2a-c and triethylaminonium chloride in high yield. In the case of the reaction of dichlorophosphanes RPCl₂ 3 with trichlorosilane and triethylamine, double trichlorosilylation provides bis(trichlorosilyl)phosphanes RP(SiCl₃)₂ 4a-f (a: R = ⁱPr, b: R = ⁱBu, c: R = 1-adamantyl, d: R = (Me₃Si)₂CH, e: R = NEt₂, f: R = N(ⁱPr)₂). However, depending on the nature of R, reactions may also lead to cyclophosphanes (RP)_n 5 (thus 4a and 4e could not be isolated in a pure state) or to trichlorosilylphosphanes RP(H)SiCl₃ 6. With 3g (R = 2,4,6-ⁱBu₃C₆H₂), mixtures of 6g and 2,4,6-ⁱBu₃C₆H₂PH₂ are formed. Chlorotrimethylstannane 7 reacts with trichlorosilane and triethylamine providing the trichlorosilylstannane R₃SnSiCl₃ (R = CH₃) 8.

Keywords: Silyl stannane; Silyl phosphine; Group 14; Nuclear magnetic resonance; Group 15; Reductive silylation

1. Introduction

Trihalogenosilyl compounds are of general importance as trifunctional precursors for the synthesis of highly functionalised silicon compounds, like branched silicones and silasesquioxanes. Hexachlorodisilane is a useful reagent for the reductive trichlorosilylation of certain chlorophosphanes providing the corresponding trichlorosilylphosphanes [1-3]. The related cleavage of organotin phosphanes with hexachlorodisilane furnishes trichlorosilylphosphanes as well as the trichlorosilylstannanes [4]. Trichlorosilylstannanes and related germanes, being a kind of α -halogen(metal)silane, are most desirable precursors for further transformations. However, even on the "semi-catalytic" pathway according to Scheme 1 (including trichlorosilylphosphane recycling), the synthesis of Me₃SnSiCl₃ still requires Me₃SnCl, Si₂Cl₆ (which is quite expensive) and three equivalents of methyllithium [4] (Scheme 1).

The formation of trichlorosilylphosphanes from chlorophosphanes, and of trichlorosilylgermanes and -stannanes from germyl- and stannylphosphanes, with the help of hexachlorodisilane appears to be associated with latent trichlorosilyl anions. These latent trichlorosilyl anions are generated from one SiCl₃ group of Si₂Cl₆ when the other silicon atom is attacked by a phosphorus nucleophile [3]. By ³¹P and ²⁹Si NMR, a phosphanehexachlorodisilane 1:1 adduct has been detected as intermediate in the course of such a trichlorosilylation reaction of an alkyl(dialkylamino)chlorophosphane with hexachlorodisilane [3]. Latent trichlorosilyl anions are also the key precursors in reactions of trichlorosilane/triethylamine mixtures with various organic halides leading to products of reductive C-trichlorosilylations [5,6].

$$R(R'_{2}N)PCl + Si_{2}Cl_{6} \rightarrow R(R'_{2}N)(Cl)P - SiCl_{3} - SiCl_{3}$$
$$\rightarrow R(R'_{2}N)PSiCl_{3} + SiCl_{4} \quad (1)$$

[3]

$$RCl + HSiCl_3 + NEt_3 \rightarrow RSiCl_3 + Et_3NH^+Cl^-$$
(2)

$$Me_{3}SiOTf + HSiCl_{3} + NEt_{3}$$

$$\rightarrow Me_{3}SiSiCl_{3} + Et_{3}NH^{+}OTf^{-}$$
(3)

[7]

Therefore, it would be desirable to explore whether the easily accessible reagent of Benkeser's reactions

^{*} Corresponding author.

¹ Dedicated to Professor R.J. Corriu on the occasion of his 62th birthday.

R ₂ PSiCl ₃ + 3 MeLi	••••>	R ₂ PSiMe ₃ + 3 LiCi
$R_2PSiMe_3 + Me_3SnCl$	>	R ₂ PSnMe ₃ + Me ₃ SiCl
$R_2PSnMe_3 + Si_2Cl_6$	>	R2PSiCl3 + Me3SnSiCl3

 $Me_3SnCl + Si_2Cl_6 + 3 MeLi ---> Me_3SnSiCl_3 + Me_3SiCl + 3 LiCl Scheme 1.$

would also be useful as a synthetic alternative to hexachlorodisilane as precursor for various main group element trichlorosilyl compounds. By use of trimethylsilyltriflate as a starting material, the trichlorosilane/triethylamine reagent had been successfully used for Si-Si bond formation providing Me₃SiSiCl₃ [7]. The trichlorosilane/triethylamine reagent is known to reduce .hlorophosphanes R₂PCl and RPCl₂ to phosphanes R₂PH and RPH₂ [8]. Recently, in the course of such a reaction, the formation of a trichlorosilylphosphane Ph₃CP(SiCl₃)H had been recognised by ³¹P NMR [9]; subsequently, alkyl(diorganylamino)chlorophosphanes were straightforwardly transformed into the corresponding trichlorosilylphosphanes with help of the trichlorosilane/triethylamine reagent [3].

As a probe for the generalisation of the Benkeser-type reductive trichlorosilylation of mono- and bifunctional main group element halides, we chose the reactions of various dialkylchlorophosphanes, alkyldichlorophosphanes, dialkylaminodichlorophosphanes and of chlorotrimethylstannane with the trichlorosilane/triethylamine reagent.

2. Results and discussion

The reactions of chlorophosphanes 1 and 3 with the trichlorosilane/triethylamine reagent in aprotic solvents were followed by ^MP NMR (Eqs. (4)-(7), Table 1). With moderately bulky di-i-propylchlorophosphane 1a and t-butyl-i-propylchlorophosphane 1b the trichlorosilane/triethylamine reagent provides, under mild conditions within a few hours, the trichlorosilylphosphanes **2a,b** in excellent yields. Depending on the reaction conditions, 2a and 2b are accompanied by small amounts of tetra-i-propyldiphosphane and 1,2-di-t-butyl-1,2-di-ipropyldiphosphane. Phospholene 1c is also straightforwardly reduced by the trichlorosilane/triethylamine reagent: addition of the phospholene to a slight excess of the trichlorosilane/triethylamine reagent provides mainly the trichlorosilylphosphane 2c; with half an equivalent of the trichlorosilane/triethylamine reagent, a mixture of diastereomers (meso/rac) of 3,3'-dimethyl-[1,1']-bisphosphol-2-en is formed. 2a-c can be separated from the diphosphanes by distillation. The reactions of 1a with 2a or 1c with 2c can be used as simple syntheses of the diphosphanes.

Moderately bulky alkyldichlorophosphanes and dialkylaminodichlorophosphanes **3a-f** also react under very mild conditions with the trichlorosilane/triethylamine reagent, furnishing alkyl- and dialkyl-bis(trichlorosilyl)phosphanes. The reaction is sometimes accompanied by cyclophosphane formation, but alkylbis(trichlorosilyl)phosphanes **4b-d** and dialkylaminodichlorophosphane **4f** could be isolated in fair yields from the reaction mixtures. Cyclophosphane formation in the course of the silylation reactions can be explained by decomposition of intermediate unstable chloro(silyl)phosphanes [10].

With i-propyldichlorophosphane 3a as starting material, formation of tetra-i-propylcyclotetraphosphane and of cyclic silvlphosphanes like (¹Pr, P)₃(SiCl₂), and $({}^{1}Pr_{2}P)_{4}(SiCl_{2})$ in the course of the distillation prevented the isolation of 4a in a pure state. Using the extremely bulky aryldichlorophosphane 2,4,6-¹Bu₃C₆-H₂PCl₂, 3g as starting material, the trichlorosilane/triethylamine reagent led to a mixture of the mono-trichlorosilylphosphane 6g and the primary phosphane 2,4,6- $^{1}Bu_{3}C_{6}H_{2}PH_{2}$; with increasing reaction time; the amount of 6g in the reaction mixture decreases in favour of the primary phosphane (Eq. (7)). Protolytic cleavage of the P-Si bonds of 6g (and of hypothetic 4g $[2,4,6-'Bu_3C_6H_2P(SiCl_3)_2]$) might be due to the presence of triethylammonium chloride; this question is at present under investigation. Further small-scale experiments followed by ³¹P NMR indicating the straightforformation of $Ph_2CHP(SiCl_3)_2$ and ward $Ph(Me_3Si)CHP(SiCl_3)_2$ confirm that the bis-silylation of dihalogenophosphanes with HSiCl₃/NEt₃ is a synthetic method of wide applicability.

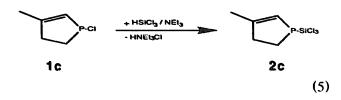
 $RR'PCl + HSiCl_{3} + NEt_{3} \rightarrow RR'PSiCl_{3} + HNEt_{3}Cl$ 1a R, R' = Pr 2a 1b R = Bu, R' = Pr 2b (4)

 Table 1
 1

 ³¹ P and ²⁹ Si NMR data of trichlorosilylphosphanes
 1

and a second	ie entre sont	δ ³⁴ Ρ (ppm)	δ ²⁹ Si (ppm)	¹ J (³¹ P, ²⁹ Si) (Hz)
¹ Pr ₂ PSiCl ₃	2a [1]	- 19.2	+ 16.7	104.3
¹ Bu(¹ Pr)PSiCl ₃	2b	+ 6.5	+11.8	116.20
P-tuCia	2c	- 32.2	+13.5	122.3
¹ PeP(SiCL ₂) ₂	4a	- 78.0	+ 8.0	72.7
¹ BuP(SiCL),	4b [3]	- 55.3	+ 7	77.3
1-AdaP(SiCL)	4c	- 56.1	+ 7.2	79.8
(Me ₃ Si) ₂ CHP(SiCl ₃) ₂	4d	- 82.8	+ 6.2	85.1
Ph(Me ₁ Si)CHP(SiCL)		- 82.6		79.8
Ph ₂ CHP(SiCL) ₂		- 85.5		75.3
Et, NP(SiCl ₁),	4e	+ 11.7	+ 1.8	75
'Pr, NP(SiCL),	41	- 9.3	+ 1.8	70,9
2.4.6-'Bu (C6H, P(H)(SiCI,)	6g	- 103.8	+14.8	88.5
· · · · ·	•			221.1 ^a

^{a 1}J(PH).



 $RPCl_{2} + 2HSiCl_{3} + 2NEt_{3}$ $\rightarrow RP(SiCl_{3})_{2} + 2HNEt_{3}Cl$ 3a-3f $4a: R = {}^{i}Pr$ $4b: R = {}^{i}Bu$

4c:
$$R = 1$$
-Adamantyl
4d: $R = (Me_3Si)_2CH$
4e: $R = NEt_2$
4f: $R = N \cdot Pr_2$
(6)

$$2,4,6-{}^{'}Bu_{3}C_{6}H_{2}Cl_{2} + 2HSiCl_{3} + NEt_{3}$$

$$\rightarrow HNEt_{3}Cl + SiCl_{4}$$

$$+ 2,4,6-{}^{'}Bu_{3}C_{6}H_{2}P(H)\left(SiCl_{3}\right)$$

$$+ 2,4,6-{}^{'}Bu_{3}C_{6}H_{2}PH_{2}$$
(7)

 $Me_{3}SnCl + HSiCl_{3} + NEt_{3} \rightarrow Me_{3}SnSiCl_{3}$ $7 \qquad 8$ $+ HNEt_{3}Cl \qquad (8)$

Silylation of the P-chlorophosphaalkene $(Me_{3}Si)_{2}C=PCl$ with the trichlorosilane/triethylamine reagent (attempted synthesis of $(Me_{3}Si)_{2}C=PSiCl_{3}$) [11]) is accompanied by hydrosilylation of the P=C double bond. The main product of this reaction is the stable bis(trichlorosilyl)phosphane $(Me_{3}Si)_{2}CHP(SiCl_{3})_{2}$ 4d.

The reaction of chlorotrimethylstannane 7 with the trichlorosilane/triethylamine reagent was monitored by ¹¹⁹Sn and ²⁹Si NMR. Within 3 days at room temperature in pentane, about 25% of chlorotrimethylstannane (in the reaction mixture in the presence of triethylamine: $\delta^{119}Sn = +117$ ppm) were converted into trichlorosilyltrimethylstannane **8** ($\delta^{119}Sn = -53$ ppm [4]). After separation of the solution from the triethylammonium chloride residue, recrystallisations from dichloromethane allowed enrichment of **8** close to analytical purity [4].

At present, further experiments meant to extend and vary our novel mild access to trihalogenosilyl derivatives of main group elements with help of the trichlorosilane/triethylamine reagent are under the way.

3. Experimental

All experiments were carried out under exclusion of air and moisture. Solvents were dried according to standard procedures. NMR spectra were determined with Bruker AC 200 instruments (200 MHz for ¹H, 81 MHz for ³¹P and 39.8 MHz for ²⁹Si); shifts are given relative to TMS (¹H, ²⁹Si) and 85% H₃PO₄ (³¹P).

Preparation of 4d: 1.16g (11.5 mmol) triethylamine were added to a solution of 1.2g (5.7 mmol) dichlorobis(trimethylsilyl)methylphosphane 3d and 1.5g (11.5 mmol) trichlorosilane in 30 ml hexane at 0°C. The mixture warmed up to room temperature and was further stirred for 1 day. A ³¹P NMR-spectrum confirmed complete consumption of the chlorophosphane 3d. After separation from the precipitate, the solvent was removed under reduced pressure. Distillation of the residue at 97 °C/0.01 mbar provided 1.85 g (70%) bis(trimethylsilyl)methylbis(trichlorosilyl)phosphane 4d as oily liquid. C₇H₁₉Cl₆PSi₄ (458.7). EI-MS: 458(1%, M⁺), 443(1%, M⁺-CH₃), 192(17%, M⁺-2SiCl₃), base peak 73(Me₃Si⁺). Calc. C, 18.30; H, 4.1%. Found: C, 18.27; H 4.1%.

New trichlorosilylphosphanes **2b**, **2c** (distillable liquids like known **2a** [1]) and bis(trichlorosilyl)phosphanes **4c** (colourless solid, 60%, after evaporation of the solvent) and **4f** (colourless crystals, f.p. $62^{\circ}C$, 50% after distillation at $92^{\circ}C/0.01$ mbar) were prepared in a similar fashion.

Acknowledgements

We thank the Deutschen Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

References

- [1] R. Martens, W.-W. du Mont and L. Lange, Z. Naturforsch. Teil B:, 46 (1991) 1609.
- [2] R. Martens and W.-W. du Mont, Chem. Ber., 125 (1992) 657.
- [3] L.-P. Müller, W.-W. du Mont, J. Jeske and P.G. Jones, *Chem. Ber.*, 128 (1995) 615.
- [4] R. Martens and W.-W. du Mont, Chem. Ber., 126 (1993) 1115.
- [5] R.A. Benkeser, Acc. Chem. Res., 4 (1971) 94.
- [6] R.A. Benkeser, K.M. Foley, J.B. Grutzner and W.E. Smith, J. Am. Chem. Soc., 92 (1970) 697.
- [7] W. Uhlig and A. Tzschach, Z. Chem., 29 (1989) 335.
- [8] H. Fritzsche and U. Hasserodt, Chem. Ber., 98 (1965) 1681.
- [9] V. Plack, J.R. Goerlich, A. Fischer, H. Thönessen, P.G. Jones and R. Schmutzler, Z. Anorg. Allg. Chem., 621 (1995) 1080.
- [10] R. Appel and W. Paulen, Angew. Chem., 93 (1981) 902.
- [11] A. Zanin, M. Karnop, J. Jeske, P.G. Jones and W.-W. du Mont, J. Organomet. Chem., 475 (1994) 95.