ELSEVIER

Journal of Organometallic Chemistry 580 (1999) 378–381

Journal of Organo metallic Chemistry

Preliminary communication

Cp_2TiCl_2 catalyzed one-pot synthesis of *n*-Bu_3GeH from $GeCl_4$

Thomas J. Colacot *

Organometallic Chemicals and Catalysts Development, Precious Metals Division, Johnson Matthey, 2001 Nolte Drive, West Deptford, NJ 08066, USA

Received 9 October 1998

Abstract

The reaction of $GeCl_4$ with *n*-BuMgCl in presence of a catalytic amount of Cp_2TiCl_2 gives *n*-Bu_3GeH and *n*-Bu_4Ge in ca. 70 and 25% yield, respectively. This method provides an industrially feasible one-pot synthesis for Bu_3GeH and Bu_4Ge. The reaction temperature and stoichiometry seem to be important in the distribution of the products. Apart from elemental analysis these compounds have been characterized by comparing their boiling points, NMR spectral data and GC assay with that of the authentic samples. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: tri-*n*-Butylgermane; Cp_2TiCl_2 catalyst; $GeCl_4$; NMR; One-pot synthesis

---

1. Introduction

The usefulness of tri-*n*-butyltin hydride as a synthon [1] in organic chemistry has been explored for the past three decades especially for free radical inter- and intramolecular couplings [2], regio- and stereoselective syntheses [3], tertiary amine synthesis via hydrostannation of imines [4], reduction of CO groups [5] and selective dehalogenation reactions [1b, 6]. However, there are several limitations associated with this reagent. The use of tri-*n*-butyl germane, *n*-Bu_3GeH as an alternative reagent has been a clever approach as it behaves like *n*-Bu_3SnH in many cases, but gives fewer side reactions with improved selectivity [7]. Several advantages of Bu_3GeH over Bu_3SnH have been well documented in the literature [7,8]. The thermodynamic data suggest that the Ge–H bond is 8 kcal mol^{-1} stronger than that of the Sn–H bond, which is attributed to the slow hydrogen donating ability of Bu_3GeH and the minimum side reactions [7,9]. The bond dissociation energy suggest that germyl radicals are equal or better halogen abstractors in comparison to the stanyl radical [7,10].

Commercially available *n*-Bu_3GeH is about 10–40 times more expensive than *n*-Bu_3SnH. Although part of the reason is due to the high cost of Ge metal in comparison to that of Sn, the corresponding *n*-Bu_3SnH is synthesized by a one-pot route using commercially available starting materials [11]. In the case of the corresponding germane, so far no similar convenient one-pot syntheses are available. The commonly employed method involves a three step process where *n*-Bu_3GeH is produced by the $LiAlH_4$ reduction [12] of Bu_3GeCl, which is either isolated as one of the scrambling products [13] from the reaction of $GeCl_4$ with Bu_4Ge or obtained by alkylating [14] Bu_4Ge with $AlCl_3$. Bu_4Ge is generally obtained by the reaction between $GeCl_4$ and BuMgCl. Although the reported yield for the last step[12] is 85–90%, the overall yield could be much lower. GeO_2 has also been used as a starting material for the production of Bu_3GeH [15]. In this case GeO_2 was converted to $K_2[Ge(O_2C_6H_4)_3]$ by reacting with catechol in presence of MeOK. Reaction of

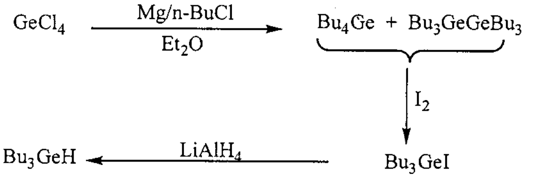
---

* Corresponding author.

E-mail address: colactj@jmusa.com (T.J. Colacot)

PII: S0022-328X(98)01172-3

$K_2[Ge(O_2C_6H_4)_3]$ with BuMgBr/Cp_2TiCl_2 was reported to yield 75% of the product. However, when we repeated the reaction several times on a 250–500 g scale, the yield was only 35–45%. We also observed that $K_2[Ge(O_2C_6H_4)_3]$ has a tendency to absorb the H_2O produced from the system. The presence of the water molecules seems to decrease the yield drastically and we had to dry $K_2[Ge(O_2C_6H_4)_3]$ at above 100°C for several days to get rid of the moisture before the reaction. Moreover, the acid hydrolyzed Grignard reaction mixture had to be extracted several times with dilute NaOH solution to get rid of the catechol completely from the system. Yet another route uses $GeCl_4$ as the starting material from which the germane has been isolated in 45% yield [7]. The essential steps are summarized below.



Since we have been interested in an industrially feasible process for the simultaneous production of Bu_3GeH and Bu_4Ge, we choose to use the readily available $GeCl_4$ starting material. Herein we report a Cp_2TiCl_2 catalyzed convenient one-pot synthesis for Bu_3GeH and Bu_4Ge from $GeCl_4$.

2. Experimental

All the reactions and subsequent work-up were performed under N_2 atmosphere using the Schlenk technique in conjunction with a glove box (Vacuum Atmospheres Model HE-493/MO-5). The starting materials such as $GeCl_4$, Cp_2TiCl_2 and n-BuMgCl were purchased from Alfa–Asear, a Johnson Matthey company. Proton and ^{13}C-NMR spectral data were recorded using a Varian XL-300 FTNMR spectrometer operating at 300.1 and 75.5 MHz, respectively. GC analyses were performed on a Shimadzu GC-14A. The elemental assays were done at E and R Microlab, Corona, NY and Robertson Microlit, NJ.

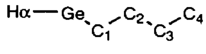
2.1. Reaction of $GeCl_4$ with n-BuMgCl in presence of Cp_2TiCl_2

Germanium tetrachloride (35 g, 0.16 mol) was loaded into a precooled (dry ice/acetone) three necked flask (3 l capacity) containing anhydrous diethyl ether (1 l) and Cp_2TiCl_2 (3 g). To this, a 2 M solution of n-BuMgCl (400 ml, 0.80 mol) in Et_2O was added over a period of 1 h with stirring. Once the addition was over, the slush bath was removed and the contents of the flask were slowly allowed to warm to r.t. It was then refluxed overnight. The mixture was hydrolyzed by carefully adding 2 M HCl (400 ml) at 0°C over a period of 1 h. The organic layer was separated while the aqueous phase was extracted with ether (200 ml × 3) and the washings were collected along with the organic layer. The organic layer was dried by treating with anhydrous $MgSO_4$ for about 3 h. It was then filtered and solvent was removed using a rotavap under reduced pressure. The resulting crude was then filtered to remove a small amount of an orange–red solid, presumably a Cp_2Ti-based complex (not characterized). GC analysis of the crude showed mainly two peaks at 3.18 (major) and 7.10 (minor) retention time due to Bu_3GeH and Bu_4Ge, respectively. These two products were then separated by careful distillation under reduced pressure to give Bu_3GeH (27.5 g, 69%. Found: C, 58.87; H, 11.23. Anal. Calc. for $C_{12}H_{28}Ge$: C, 58.87; H, 11.40) and n-Bu_4Ge (12.6 g, 26%. Found: C, 63.86; H, 12.07. Anal. Calc. for $C_{16}H_{36}Ge$: C, 63.88; H, 11.97) at 85°C/7–8 mbar (61–63°C/0.3 torr [12a]) and at 115°C/6–7 mbar (160–161°C/22.7 hPa [15]), respectively. Detailed NMR spectra of these two complexes are listed in Table 1.

3. Results and discussion

An ether solvent-mediated reaction of $GeCl_4$ with 4–5 mols of n-BuMgCl carried out at − 78°C to r.t., in the presence of a catalytic amount of Cp_2TiCl_2 reacted cleanly to give n-Bu_3GeH as the major product. In-

Table 1
^1H- and ^{13}C-NMR spectral data of n-Bu_3GeH and n-Bu_4Ge recorded in $CDCl_3$ using TMS reference



Numbering of atoms [a,b]	n-Bu_3GeH (δ PPM)	n-Bu_4Ge (δ PPM)
α^c	3.68	–
H-1($J_{\alpha,1}$)	0.85 (3.0 Hz)	0.69
C-1	12.0	12.50
H-2 ($J_{1,2}$)	1.2–1.4	1.31(8.1 Hz)
C-2	28.72	27.50
H-3 ($J_{3,4}$)	1.2–1.4 (6.8 Hz)	1.31(7.1Hz)
C-3	26.31	26.60
H-4	1.08	0.87
C-4	13.83	13.70

[a] Proton spectra are high order, virtually coupled.

[b] Carbon in $CDCl_3$ are identified from DEPT, HETCOR spectra and from T1 relaxation data.

[c] Septet pattern was observed due to $Ge(CH_2\text{–})_3$ coupling. T1's for carbons in seconds are C-1: 2.7 s, 2.3 s; C-2: 3.6 s, 3.1 s; C-3: 4.4 s, 3.6 s; C-4: 5.1 s, 4.1 s respectively for n-Bu_3GeH and n-Bu_4Ge.

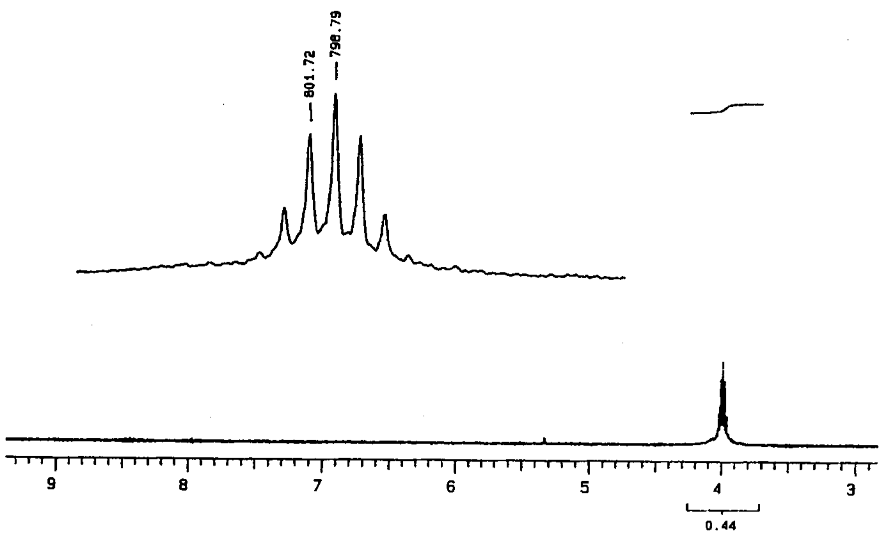


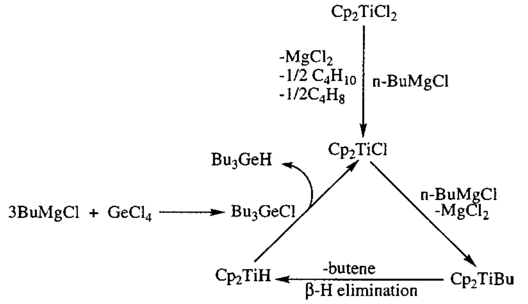
Fig. 1. Proton NMR spectrum showing the septet pattern of Ge–H due to coupling wih the three identical CH_2 groups.

order to insure that the reaction was complete, it was refluxed overnight. The byproduct, Bu_4Ge has also been isolated to analytical purity.

$$GeCl_4 + 5n\text{-}BuMgCl \xrightarrow{Cp_2TiCl_2} n\text{-}Bu_3GeH + n\text{-}Bu_4Ge$$

No other major products have been detected or isolated from the study. However, when the reaction was conducted at r.t., it was very vigorous with considerable gas evolution occuring, and the yield of Bu_3GeH decreased to 35–45% along with the formation of Bu_4Ge. In addition to these two products, sizable quantities of a high boiling residue was also observed in the flask. Although no optimization work has been done, we feel that the reaction temperature, stoichiometry, anhydrous reaction conditions and the order of addition of the reagents may be important in the distribution of the products.

Apart from the satisfactory elemental assay, these two products have been well characterized by comparing their boiling points, GC retention time and NMR spectral data with that of authentic samples. We have also carried out a detailed NMR spectral analysis including HETCOR and DEPT to assign all the protons and carbons unambiguously. It is interesting to note that the proton attached to the Ge in Bu_3GeH gave a text book example of a septet (Fig. 1) at 3.68 ppm in $CDCl_3$ (3.99 ppm neat) due to three bond coupling with the three CH_2 groups through Ge.



Scheme 1. Proposed mechanism for the Cp_2TiCl_2 catalyzed reaction of $GeCl_4$ with n-BuMgCl to produce Bu_3GeH.

The exact mechanism of the above process is not clearly understood. However the following mechanism is proposed (Scheme 1) based on Corriu's studies [15,16].

The first step of the reaction could be the formation of Bu_3GeCl from the reaction of $GeCl_4$ with BuMgCl. This is reduced by 'Cp_2TiH' produced in situ by the reaction of Cp_2TiCl_2 with BuMgCl. The presence of a β-hydrogen in the butyl group seems to be important in obtaining the R_3GeH. The generality of this route to other germanes with particular emphasis on the optimization of the process, the influence of β-hydrogen and the use of Cp_2TiCl instead of Cp_2TiCl_2 will be verified in a future publication.

Acknowledgements

Dr R.A. Teichman and Dr W.H. Tamblyn are acknowledged for their encouragement in this work. Thanks are also due to Dr E.S. Gore for useful discussions.

References

[1] (a) R.F. Bennett, Camb. Environ. Chem. Ser. 8 (1996) 21. (b) W.P. Neumann, Synthesis (1987) 665. (c) E. Lacôte, P. Renaud, Angew. Chem. Int. Ed. Engl. 37 (1998) 2156.
[2] D.S. Hays, G.C. Fu, J. Org. Chem. 61 (1996) 4.

[3] (a) T. Tokoroyama, T. Aoto, J.Org. Chem. 63 (1998) 4151. (b) M. Brakta, P. Lhoste, D. Sinou, J.Org. Chem. 54 (1989) 1890. (c) J.J. Tufariello, A.D. Dyszlewski, J. Chem. Soc. Chem. Commun. (1987) 1138.
[4] T. Kawakami, T. Sugimoto, I. Shibata, N. Sonoda, J. Org. Chem. 60 (1995) 2677.
[5] (a) M. Degueil-Casaing, A. Rahm, N. Dahan, J. Org. Chem. 51(1986) 1672. (b) B.A. Narayanan, C. Amatore, J.K. Kochi, Organometallics 5 (1986) 926.
[6] (a) G. Wurm, H.A. Gurka, Arch. Pharm. (1986) 190. (b) A. Holy, Nucl. Acid Chem. 2 (1978) 1007.
[7] M.J. Tolteben, Ph.D. Dissertation, University of Pittsburg, PA, USA, 1992, pp. 169. (b) M.J. Tolteben, Diss. Abstr. Int. B 53 (1992) 2879.
[8] (a) S. Tsunoi, I. Ryu, S. Yamasaki, H. Fukushima, M. Tanaka, M. Komatsu, N. Sonoda, J. Am. Chem. Soc. 118 (1996) 10670. (b) P. Pike, S. Hershberger, J. Hershberger, Tetrahedron Lett. 26 (1985) 6289. (c) P. Pike, S.Hershberger, J. Hershberger, Tetrahedron Lett. 44 (1988) 6295. (d) L. Geng, X. Lu, J. Organomet. Chem. 376 (1989) 41. (e) W.R. Dolbier, Jr., X.X. Rong, B.E. Smart, Z-Y. Yang, J. Org. Chem. 61 (1996) 4824. (f) A.L.J. Beckwith, D.H. Roberts, C.H. Schiesser, A. Wallner, Tetrahedron Lett. 26 (1985) 3349.
[9] H. Mayr, N. Basso, Angew. Chem. Int. Ed. Engl. 31 (1992) 1046.
[10] K.B. Clark, D. Griller, Organometallics 10 (1991) 746.
[11] J. Szammer, L. Otvos, Chem. Ind. (1998) 764.
[12] (a) P.J. Stang, M.R. White, J. Am. Chem. Soc. 103 (1981) 5429. (b) J.W. Wilt, J. Lusztyk, M. Peeran, K.U. Ingold, J. Am. Chem. Soc. 110 (1988) 281.
[13] (a) K.V. Pavlov, I.P. Shvedov, Z. Obshch. Khim. 64 (1994) 160. (b) F. Rijkens, E.J. Bulten, W. Drenth, G.J.M. Van der Kerk, Recueil 85 (1966) 1233.
[14] M. Lesbre, P. Mazerolles, J. Satge, in: D. Seyferth (Ed.), The Organic Compounds of Germanium, Wiley, New York, 1971.
[15] G. Cerveau, C. Chuit, R.J.P. Corriu, C. Reye, Organometallics 10 (1991) 1510.
[16] E. Colomer, R. Corriu, J. Organomet. Chem. 82 (1974) 367.