Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

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To cite this article: Jeffrey A. Cooke, Craig E. Dixon, Matthew R. Netherton, Gerlinde M. Kollegger & Kim M. Baines (1996) Improved Synthesis of 1,2-Dichlorotetramesityldigermane and Other Mesitylgermanes, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 26:7, 1205-1217, DOI: 10.1080/00945719608004362

To link to this article: http://dx.doi.org/10.1080/00945719608004362

SYNTH. REACT. INORG. MET.-ORG. CHEM., 26(7), 1205–1217 (1996)

IMPROVED SYNTHESIS OF 1,2-DICHLOROTETRAMESITYLDIGERMANE AND OTHER MESITYLGERMANES

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ABSTRACT

An improved procedure for the synthesis of 1,2-dichlorotetramesityldigermane is reported.

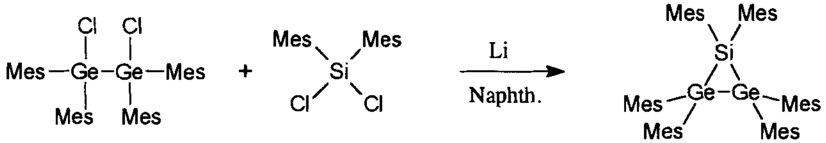
INTRODUCTION

The report on the synthesis and characterization of $Mes_2Si=SiMes_2$ (Mes = mesityl, 2,4,6-trimethylphenyl)[1] was significant for *two* reasons. Not only was it the first report of a stable, solid derivative of a disilene but it also introduced the bulky mesityl group as a kinetically-stabilizing substituent in the chemistry of low-coordinate Group 14 compounds.[2] This substituent has been extensively used in the areas of both kinetically-stabilized doubly-bonded silicon[3] and germanium[4] compounds. Since dimetallenes have become invaluable as starting materials for a variety of small ring organometallic compounds,[3,4] high yield syntheses of their precursors have become extremely important.

We have reported on the synthesis[5] and chemistry[6] of $Mes_2Ge{=}SiMes_2$. The germasilene is the end product of a seven-step synthetic sequence starting from commercially available $SiCl_4$ and $GeCl_4$.[5a] It is imperative that each step along the reaction sequence be as simple and as high yielding as possible. Since our original paper on the synthesis of hexamesitylsiladigermirane, the immediate precursor to the germasilene, we have improved the synthetic procedures for some of the starting materials, in particular the mesitylgermanes. In this paper we wish to describe these improved procedures such that they may become generally available, not only to those working in the area of germasilene chemistry, but also in the broader area of mesityl-stabilized germanium compounds.

RESULTS AND DISCUSSION

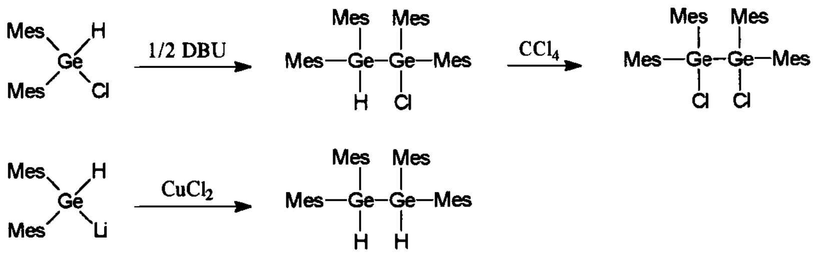
The synthesis of $SiGe_2Mes_6$ is outlined below.



Dichlorodimesitylsilane was readily prepared according to a procedure developed by West and co-workers.[7] First, mesityllithium was synthesized by reacting two equivalents of BuLi with MesBr. The lithium reagent was allowed to react with $SiCl_4$ to form the desired dichlorosilane.

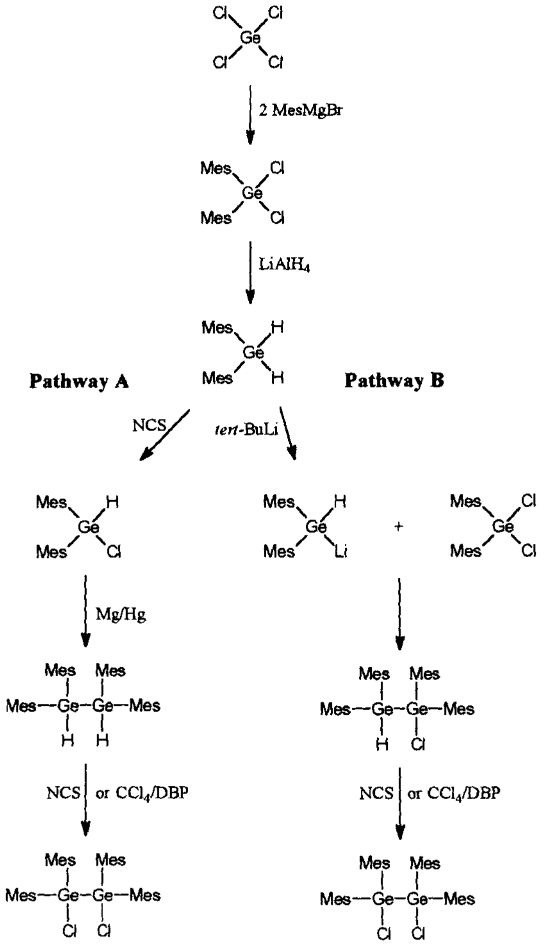
The synthesis of $Mes_4Ge_2Cl_2$, however, involved a more lengthy procedure. First, Mes_2GeCl_2 was prepared by reaction between two equivalents of mesitylmagnesium bromide, MesMgBr, and germanium tetrachloride, $GeCl_4$. The dichlorogermane was easily reduced to Mes_2GeH_2 with $LiAlH_4$ in THF.[8] From this point, two methods to the desired dichlorodigermane have been successfully employed, depicted in Pathways A and B in Scheme 1.

Pathway A was the route initially followed. After monochlorination of dimesitylgermane with N-chlorosuccinimide (NCS) in THF at 80°C in a Carius tube,[9] two equivalents of the chlorogermane were coupled using magnesium amalgam to form $Mes_4Ge_2H_2$, in addition to Mes_2GeH_2 presumably from reduction of the chlorogermane. The coupling was an adaptation of a procedure developed by Satgé for the formation of $Ph_4Ge_2H_2$ from Ph_2GeHCl.[10] This procedure consistently gave higher yields than the previously reported methods of coupling Mes_2GeHCl using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 51%)[11] or Mes_2GeHLi using $CuCl_2$ (66%).[12]



The components of the product mixture from the magnesium amalgam coupling could be fully chlorinated to give the dichlorodigermane and the dichlorogermane, which were easily separated by dry column flash chromatography.[13] The overall isolated yield of the dichlorodigermane averaged 40% from $GeCl_4$.

There were many problems with this route. First, the formation of Mes_2GeH_2, as described by Satgé,[8] was found to be quite unreliable. The Satgé procedure[8] produces a mixture of $MesGeH_3/Mes_2GeH_2/Mes_3GeH$. The yield of



Scheme 1

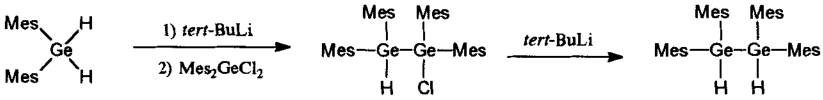
Mes_2GeH_2 would vary dramatically, from unacceptably low to moderately high. The crucial step in the reaction sequence appears to be the formation of the Grignard reagent: the concentration of the Grignard reagent has to be determined accurately. By doing so, the yield of Mes_2GeH_2 improved considerably at the expense of $MesGeH_3$ and Mes_3GeH: up to 88% of Mes_2GeH_2, in contrast to the

45% reported by Satgé.[8] In addition to dramatically improving the yield for this reaction, the modified method also yielded the germane more reproducibly. Furthermore, the coupling of Mes_2GeHCl with magnesium amalgam was difficult to accomplish consistently, with levels of the unwanted Mes_2GeH_2 ranging from $<10\%$ to 40%. The use of large amounts of mercury, heated with a Bunsen burner flame to form the amalgam, is also not recommended, both from a health and a waste disposal point of view. While Pathway A worked, and sometimes worked well, it was clear that a more dependable source of starting material was required.

Pathway B was found to be a more satisfactory route, eliminating the difficult Carius tube chlorination and magnesium amalgam coupling reactions, replacing them with quicker, easier, and more reproducible chemistry. First, dichlorodimesitylgermane was prepared by chlorination of Mes_2GeH_2 in CCl_4 with dibenzoyl peroxide (DBP) as a radical initiator. This reaction can be completed in six hours, with no workup necessary except for removal of the solvent. This procedure resembles the synthesis of Mes_2GeCl_2 as reported by Satgé and co-workers,[14] differing simply by the use of dibenzoyl peroxide as an initiator rather than azoisobutyronitrile (AIBN) and by refluxing the reaction mixture for six hours rather than heating in a Carius tube at 90 °C for two hours. Alternatively, the addition of exactly two equivalents of mesitylmagnesium bromide to $GeCl_4$ yields Mes_2GeCl_2 that can be isolated after trituration with hexanes in pure form and acceptable yield (54-62%) from the reaction mixture eliminating two synthetic steps (that is, reduction and chlorination). Although, it has been reported that Mes_2GeHLi does not yield $(Mes_2GeH)_2$ when reacted with Mes_2GeHCl,[12] Mes_2GeHLi (formed by treatment of Mes_2GeH_2 with *t*-BuLi)[15] reacts with Mes_2GeCl_2 to give Mes_4Ge_2HCl in a manner analogous to the formation of $Mes_2GeHSiClMes_2$.[16] This simple reaction provided the chlorodigermane in consistently excellent yields. Simple acidic workup of the reaction mixture was all that was required, with no difficult removal/disposal of elemental mercury or dissolved mercury salts. The only side product of the reaction was a small amount of dimesitylgermane, most likely formed by quenching of unreacted germyllithium reagent with aqueous acid. Even though this route to the digermane gives the same unwanted Mes_2GeH_2 as the magnesium amalgam route described in Pathway A, the amount of germane formed is consistently very low, rarely exceeding 5-10%. The Mes_2GeH_2 is simply carried along with the desired chlorodigermane and separated after the next step in the reaction sequence.

Chlorination of Mes_4Ge_2HCl[11] (and Mes_2GeH_2) can be completed using either CCl_4/DBP or NCS. Separation and purification of the product is possible either by chromatographic techniques or by recrystallization with hexane/methylene chloride or toluene. While the yield is generally comparable regardless of the chlorination or purification method, the CCl_4/DBP method followed by chromatography is preferred, despite the fact that it requires a longer reaction time, since the reaction is simpler to perform. The overall yield of the dichlorodigermane from $GeCl_4$ via Pathway B averaged 60%.

If the parent 1,1,2,2-tetramesityldigermane is required, reduction of $Mes_2GeHGeClMes_2$ by $LiAlH_4$, as reported in the literature,[11] is unsatisfactory since it also leads to significant cleavage of the central Ge-Ge bond. $Mes_2GeHSiClMes_2$ can easily be reduced to $Mes_2GeHSiHMes_2$ using *tert*-BuLi.[15] The chlorodigermane can be reduced using the same reagent. This reaction can conveniently be carried out in one-pot starting from dimesitylgermane. The yield of 1,1,2,2-tetramesityldigermane (82%) is greater than that reported in the literature for the coupling of Mes_2GeHLi using $CuCl_2$ (66%).[12]



EXPERIMENTAL

All experiments requiring a dry/inert atmosphere were carried out in oven or flame-dried glassware under an atmosphere of argon. THF and Et_2O were distilled from sodium/benzophenone ketyl prior to use. *tert*-BuLi was used as received from Aldrich Chemical Co. $GeCl_4$ was used as received from Toronto Research Co.

NMR spectra were recorded on a Gemini 200 (200.1 MHz for ^1H) or a Gemini 300 (299.9 MHz for ^1H) NMR spectrometer using deuterated benzene as solvent and are reported in parts per million (ppm). Melting points are corrected.

Unless otherwise specified, water and brine washes were completed using approximately the same quantity of the aqueous wash as the organic extract.

Mes_2GeH_2 and Mes_2GeCl_2, Modified Procedure[8]

MesBr (78 g, 0.4 mol) was dissolved in THF (50 mL) and added dropwise to Mg (19.2 g, 0.79 mol) in THF (150 mL) over a 1/2 h period. The reaction was initiated after approximately 1/4 of the solution was added by breaking up the Mg with a glass rod. The reaction mixture refluxed during the addition of bromomesitylene. Once the addition was complete, an additional 200 mL of THF was added to the brown/black reaction mixture. Although this may seem like a large amount of solvent, this much is required to prevent stirring problems later in the experiment. The reaction mixture was refluxed for 3 h and then the concentration of the Grignard reagent was determined by back titration to be 0.87 M.[17]

A three-neck round bottom flask was equipped with a condenser, a magnetic stirrer and a 250 mL pressure equalizing dropping funnel. The apparatus was flame dried twice and put under a steady stream of argon.

MesMgBr (197 mL, 0.87 M, 0.17 mol) was added dropwise to a solution of $GeCl_4$ (10 mL, 0.086 mol) in Et_2O (85 mL). A white precipitate was seen as soon as the first drops of mesitylmagnesium bromide were added. The reaction mixture became increasingly cloudy and white as the MesMgBr was added. After approximately 100 mL of the Grignard reagent was added, it became necessary to cool the reaction mixture and to add an additional 60 mL of ether.

After 6 h of stirring, a small aliquot of the reaction mixture was worked up with 6 M HCl to determine the extent of reaction. At this point, the only identifiable halogermane present was Mes_2GeCl_2. The procedure now varies depending on the desired product.

For Mes_2GeCl_2 The reaction mixture was quenched with 6 M HCl (approximately 100 mL). Ice should be available during this procedure. The two layers were diluted with ether (approximately 20 mL) and separated. The water layer was washed with 100 mL of ether (divided out over three extractions). The combined ether layers were yellow. The ether extracts were dried using anhydrous $MgSO_4$, filtered and the solvent removed under vacuum. Hexanes were added to triturate the pale yellow residue. The resulting white crystalline compound was removed by filtration and dried to give a 54-62% (17.7-20.4 g) yield of Mes_2GeCl_2 (mp 142-3 °C; lit.[14] 142-3 °C) which could be used without further purification.

For Mes_2GeH_2 $LiAlH_4$ (3.6 g; 5.1 mmol) was slowly added to the reaction mixture which was cooled in an ice bath. The reaction mixture was stirred overnight and then worked up with 1 M HCl. The water layer was extracted with diethyl ether. The ether layers were combined and extracted with water, saturated NaCl, and then dried over anhydrous $MgSO_4$. The ether was removed under vacuum. A ^1H NMR spectrum of the residue was taken to determine if purification of Mes_2GeH_2 (from $MesGeH_3$/Mes_3GeH) was required. If required, the reaction mixture was distilled through a short path distillation apparatus. A low boiling fraction ($MesGeH_3$) was removed at 36-43 °C (0.05 mm Hg). The pot residue consisted of 23.17 g of pure Mes_2GeH_2 (86%; mp 118-20 °C; lit.[8] 118-20 °C).

Alternate Mes_2GeCl_2 Synthesis

Mes_2GeH_2 (7.5 g, 0.024 mol) was dissolved in CCl_4 (250 mL). Dibenzoyl peroxide (75 mg) was added and the reaction mixture refluxed for 6 h. The solvent was evaporated to give 9.02 g of crude Mes_2GeCl_2 (98%) as a yellow solid which was used without further purification.

Synthesis of $Mes_4Ge_2H_2$, Pathway A

Magnesium amalgam was prepared by heating Hg (103.48 g, 515.9 mmol) and Mg (1.01 g, 41.5 mmol) in a round bottom flask under Ar with a Bunsen burner flame. The formation of the amalgam was deemed complete when all of the magnesium had been incorporated into the mercury, yielding a grey metallic semisolid. Once the amalgam had cooled, a solution of Mes_2GeHCl[9] (13.24 g, 38.1 mmol) in dry THF (60 mL) was added dropwise with vigorous stirring to the amalgam over a period of 20 minutes. This mixture was refluxed for 20 h. Usual workup consisting of HCl quench (50 mL, ~ 1 M), diethyl ether extraction (3x, 130 mL total), water wash, brine wash, and $MgSO_4$ drying of the combined extracts yielded a clear, colorless solution. Removal of the solvent yielded an off-white solid (13.5 g) consisting of $Mes_4Ge_2H_2$ (90%) and Mes_2GeH_2 (10%) as determined by ^1H NMR spectroscopy, which was used without further purification.

Synthesis of Mes_4Ge_2HCl, Pathway B

To a cold (-20 °C) solution of Mes_2GeCl_2 (7.4 g, 19.1 mmol) in dry THF (40 mL), a yellow-orange solution of Mes_2GeHLi[15] (prepared from Mes_2GeH_2 (6 g, 19.2 mmol) and *t*-BuLi (27.2 mmol) at -20 °C) in dry THF (80 mL), was added dropwise over a period of 30 minutes. The solution was allowed to warm to room temperature and stirred overnight. Workup with HCl (60 mL, ~ 1M) followed by ether extraction (3x, 150 mL total), water and brine washes of the combined extracts, $MgSO_4$ drying and solvent removal yielded a light yellow solid identified as a mixture of Mes_4Ge_2HCl (92%), Mes_2GeH_2 (5%) and $Mes_4Ge_2H_2$ (3%) as determined by ^1H NMR spectroscopy.

Synthesis of $Mes_4Ge_2Cl_2$ (CCl_4 Chlorination of Mes_4Ge_2HCl), Pathway B

A solution of Mes_4Ge_2HCl[18] (12.7 g, 19.3 mmol) and dibenzoyl peroxide (~20 mg) in CCl_4 (approximately 100 mL) was refluxed for *up to* 5 days. The progress of the reaction is monitored every 24 hrs by ^1H NMR spectroscopy by following the disappearance of the Ge-H signal. During the reflux period, the color of the solution changed from pale yellow to a deep yellow. Additional dibenzoyl peroxide was added (~20 mg) approximately every 2 days until the reaction was complete. Following drying ($MgSO_4$) of the solution and solvent removal, the yellow solid residue was purified by flash chromatography[13] through a 6" dry silica gel column using a 1:1 mixture of hexane/CH_2Cl_2 as the eluent to give $Mes_4Ge_2Cl_2$ (8.8 g, 12.7 mmol, 66%) as a white solid (mp dec 258-266 °C; lit.[11] dec 235-250 °C). Further purification, if required, can be achieved by recrystallization from hexane/CH_2Cl_2 (approximately 20/1).

Synthesis of $Mes_4Ge_2Cl_2$ (NCS Chlorination of Mes_4Ge_2HCl), Pathway B

A solution of NCS (1.0 g, 7.5 mmol) and Mes_4Ge_2HCl[18] (2.63 g, 4 mmol) in dry THF (50 mL) was refluxed for 2 days. After drying ($MgSO_4$) the solution, the solvent was removed under vacuum and the yellow solid residue was separated by dry column flash chromatography[13] using a 1:1 mixture of hexane/CH_2Cl_2 as the eluent. Recrystallization from hexane/CH_2Cl_2 (approximately 20/1) yielded $Mes_4Ge_2Cl_2$ (1.55 g, 2.2 mmol, 55%) as a white solid.

One-pot Synthesis of $Mes_4Ge_2H_2$

tert-BuLi (34.6 mL, 1.7 M in pentane, 0.06 mol) was added in one portion to a solution of Mes_2GeH_2 (7.38 g, 23.6 mmol) in dry THF (95 mL) cooled to -23 °C (dry ice/CCl_4). The yellow reaction mixture was stirred at -23 °C for 5 h and then transferred to a pressure-equalizing addition funnel and added dropwise over 25 min to a solution of Mes_2GeCl_2 (9.0 g, 23.6 mmol) in THF (45 mL) at -23 °C. The color of the reaction mixture darkened during the addition. The reaction mixture was kept at -23 °C for 2 h and then allowed to warm to room temperature

TABLE I ^1H NMR Data of Mesitylgermanes (δ ppm)

Compound	Solvent	Mes-H	Ge-H	*o*-Me	*p*-Me	Ref.
Mes_2GeCl_2	C_6D_6	6.55		2.49	1.96	
Mes_2GeH_2	C_6D_6	6.72	5.27	2.33	2.09	
Mes_4Ge_2HCl	C_6D_6	6.70; 6.63	6.09	2.42; 2.39	2.07; 2.04	11
$Mes_4Ge_2Cl_2$	C_6D_6	6.65		2.49 (broad)	2.04	11
$Mes_4Ge_2H_2$	C_6D_6	6.68	5.92	2.35	2.07	11, 12

and stirred overnight, by which time the reaction mixture was orange in color. The reaction mixture was cooled to -23 °C and a second aliquot of *tert*-BuLi (20.0 mL, 1.7 M in pentane, 0.03 mol) was added in one portion. The color of the reaction mixture immediately darkened. The solution was kept at -23 °C for 1/2 h and then allowed to warm to room temperature and stirred overnight. The yellow reaction mixture was added to an aqueous solution of HCl (6 M), the aqueous layer was extracted 4 times with Et_2O and the combined organic layers were washed with a saturated NaCl solution. The organic phase was dried over $MgSO_4$. After filtration, the ether was removed under vacuum to give $Mes_4Ge_2H_2$ (12.0 g, 19.2 mmol; 82%) as a white powder (mp 208-10 °C; lit.[12] 208 °C).

ACKNOWLEDGMENTS

We would like to thank NSERC of Canada for financial support of this work in the form of a grant (to KMB) and a Summer Research Assistantship (to MRN). Financial assistance in the form of an E. Schrödinger International Fellowship (to GMK) is also acknowledged. We would like to thank Kyle Fujdala for technical assistance.

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17. It is important to determine accurately the concentration of the Grignard reagent in each reaction. The amount of Grignard reagent/$GeCl_4$ is adjusted each time to give exactly a 2:1 ratio of MesMgBr:$GeCl_4$.

18. The composition of the reaction mixture from the Mes_2GeHLi/Mes_2GeCl_2 coupling reaction can vary depending on the quality of the *tert*-BuLi used to generate the germyllithium reagent. If the mixture consists of $Mes_4Ge_2HCl/Mes_2GeH_2/Mes_4Ge_2H_2$, the

quantity of reagents for chlorination is adjusted based on the Mes_4Ge_2HCl/Mes_2GeH_2/$Mes_4Ge_2H_2$ ratio as determined by ^1H NMR spectroscopy. If the mixture consists of Mes_4Ge_2HCl/Mes_2GeCl_2, flash chromatography through a 6" silica gel column can be performed at this stage to give pure Mes_4Ge_2HCl before chlorination.

Received: 8 November 1995
Accepted: 11 April 1996
Referee I: P. Boudjouk
Referee II: M. Denk