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THE SYNTHESIS OF 1-METHYL-1-GERMAADAMANTANE

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Summary

The syntheses of 1-methyl-1-germaadamantane and 1-chloro-1-germaadamantane are described. Attempts to prepare the 1-methyl-1-stannaadamantane and the novel cage systems, 1-silatris-nor- and 1-silatris-homo-adamantanes are also described as well as the syntheses of a variety of Group IV 1,3,5-trisubstituted cyclohexanes.

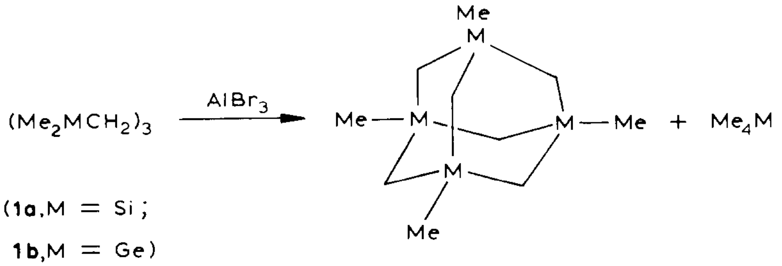
Introduction

The Lewis acid redistribution reaction has been a useful synthetic tool in organometallic chemistry with a particularly successful record in Group IV [1]. As indicated in eq. 1, the reaction leads to an equilibrium mixture of all possible combinations of R and R′ on the metal. Since the relative stability of the components determines the distribution of products, this route is most useful for preparing thermodynamically stable compounds.

$$R_4M + R'_4M \rightleftharpoons R_aR'_bM \ (a + b = 4) \qquad (1)$$

(R and R′ = alkyl, halogen, aryl, hydrogen, alkoxy, aryloxy; M = Si, Ge, Sn)

Using this approach, two 1,3,5,7-tetrametalloadamantyl (**2**) systems have been prepared in moderate yields from their respective trimetallocyclohexanes (**1**) and $AlBr_3$ (eq. 2) [2]. 1,1,3,3-tetramethyl-1,3-disilacyclobutane has also been used to synthesize (**2a**) [3].



(2)

(**1a**,M = Si ;
1b,M = Ge)

2a,M = Si ;
2b,M = Ge

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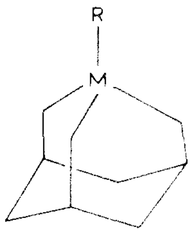
Prior to our synthesis of the 1-silaadamantyl system (**3**) [4], only two adamantane derivatives with one bridgehead metal atom had been reported. 1-Azaadamantane (**4**) was first prepared by Lukes, Galik, and Bauer [5] and the more recently prepared 1-boraadamantane was obtained as the pyridine complex (**5**) by Mikhailov and Smirnov [6]. In 1983, the synthesis of a fourth heteroadamantane, a derivative of 1-phosphaadamantane (**6**), was described by Bickelhaupt [7].



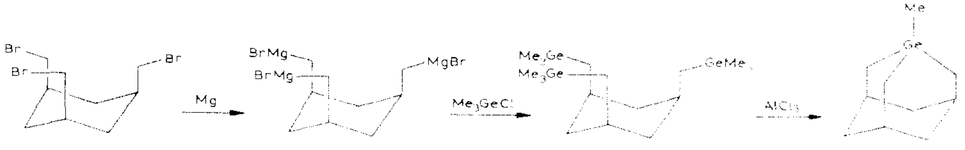
(**3**, M = Si, R = Me; **5**, M = B, R = pyridine;
4, M = N; **6**, M = P)

The potential for a new and interesting chemistry from organometallic compounds in which a metal atom is incorporated into the adamantane cage structure prompted us to try to extend the redistribution reaction to other metal atoms and to smaller and larger homologs of the silaadamantyl system. In this paper we report the results of our efforts to prepare germa- and stanna-adamantanes as well as silatris-nor- and silatris-homo-adamantanes. Also included are the details of the syntheses of a variety of new Group IV substituted cyclohexanes.

Results

1-Methyl-1-germaadamantane (**7**) was obtained in ~ 37% yield by the aluminum chloride catalyzed redistribution of *cis*-1,3,5-tris(trimethylgermylmethyl)cyclohexane. The trigermyl compound was prepared from the reaction of trimethylchlorogermane with the tri-Grignard reagent [8] derived from *cis*-1,3,5-tris(bromomethyl)cyclohexane and magnesium in tetrahydrofuran (THF) (Scheme 1). Magnesium is known to reduce chlorogermanium compounds [9], doing so even in the presence of the tribromide, requiring that we prepare a solution of the tri-Grignard separately and follow with treatment with trimethylchlorogermane.

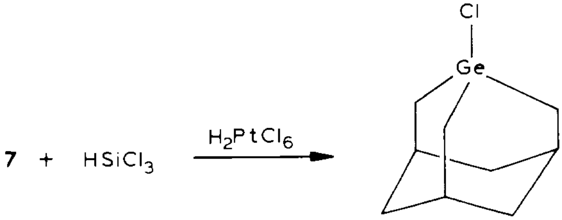
Functionalization of **7** was accomplished by using the chlorodemethylation procedure developed by Beck and Benkeser [10]. Thus, heating **7** in the presence of a



(7)

SCHEME 1

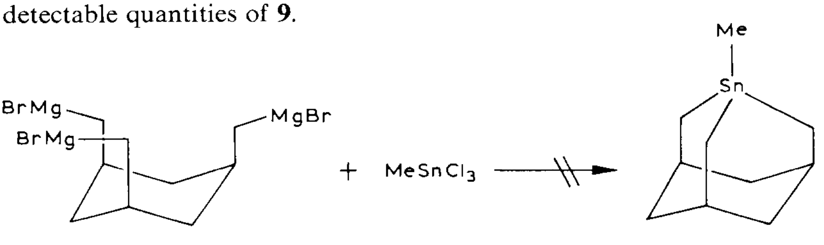
catalytic amount of chloroplatinic acid and excess trichlorosilane for 68 h gave 1-chloro-1-germaadamantane (**8**) in 36% yield (eq. 3).



(3)

(8)

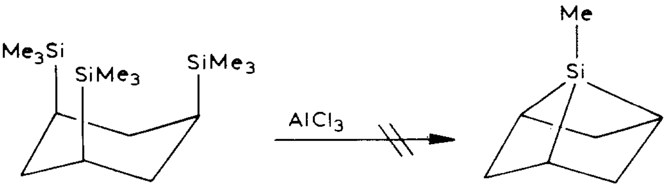
Attempts to prepare 1-methyl-1-stannaadamantane (**9**) by a route parallel to that in Scheme 1 failed. Aluminum chloride gave a white powder and viscous oils when treated with *cis*-1,3,5-tris(trimethylstannyl)cyclohexane. A "capping" reaction (eq. 4), similar to one used to prepare small quantities of **3** [8] also failed to generate detectable quantities of **9**.



(4)

(9)

Extension of the redistribution reaction to the synthesis of tris-nor (**10**) and tris-homo (**11**) analogs of 1-silaadamantane proved unsuccessful, leading, in both cases, to viscous oils and no detectable quantities of volatile products other than tetramethylsilane.



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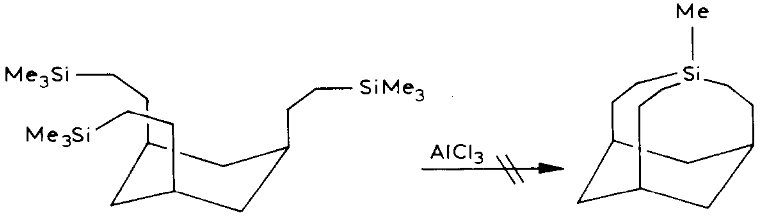
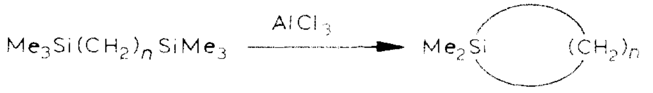


(11)

Discussion

The aluminum chloride catalyzed redistribution of *cis*-1,3,5-tris(trimethylsilylmethyl)cyclohexane to give 1-methyl-1-silaadamantane [4] in synthetically useful yields has been successfully applied to the germanium analogue. Moreover, 1-methyl-1-germaadamantane was converted to the chloro derivative by a second redistribution reaction involving trichlorosilane as a source of chlorine and chloroplatinic acid as the catalyst. The yields for the germanium redistribution reactions are only 50–60% of the yields for the silicon analogues.

1-Methyl-1-stannaadamantane could not be isolated by this approach, however, and the production of polymeric materials suggests that our conditions are too vigorous. The greater sensitivity of the tin system may be due to the size of the tin atom which has a covalent radius of 140 pm [11]. The molecular structures of the sila- and germa-adamantanes [12] show covalent radii of 115 and 121 pm for silicon and germanium, respectively. Thus, should the cage structure form, angle strain in the stannaadamantane system would be expected to be considerably greater than for the smaller atoms and increase its reactivity toward Lewis acids. Ring strain may also explain our failure to isolate 1-methyl-1-silatrisnoradamantane (**10**) by this method. Lewis acids are notoriously reactive toward small silacycles [13] and it is likely that **10**, or strained intermediates formed en route to **10** will react very quickly with aluminum chloride. It should be noted however, that, while small rings containing silicon react with aluminum chloride, the redistribution reaction has been successfully employed to prepare them (eq. 5) in modest to good yields [14].



(5)

n = 3-6

We were surprised by the failure of the redistribution reaction to produce 1-methyl-1-silatrishomoadamantane (**11**). However, examination of molecular models indicated that once one of the seven-membered rings had formed subsequent reaction to form the second ring system would be sterically inhibited.

Experimental

cis-1,3,5-Tris(trimethylgermylmethyl)cyclohexane from the tri-Grignard of cis-1,3,5-Tris(bromomethyl)cyclohexane

cis-1,3,5-Tris(bromomethyl)cyclohexane (4.74 g, 13.1 mmol) in dry THF (50 ml) was slowly added dropwise to rapidly stirred magnesium turnings (2.0 g, 82.3 mmol) in dry THF (50 ml) at room temperature under a dry nitrogen atmosphere. The magnesium turnings had been cleaned by adding 1,2-dibromoethane (0.74 g, 3.92 mmol) before the addition of the tribromide. The tri-Grignard was stirred at room temperature for 2 h, refluxed for 14 h, and then transferred by means of a double-tipped needle into another flask under a dry nitrogen atmosphere. The excess magnesium turnings were washed with dry THF (1 × 50 ml), and the washing added to the grey-black tri-Grignard solution. Trimethylgermanium chloride (6.0 g, 39.2 mmol) in dry THF (20 ml) was slowly added dropwise to the rapidly stirred tri-Grignard solution at 0°C. The mixture was stirred at 0°C for 2 h, at room temperature for 2 h, and at reflux temperature for 15 h. 150 ml of THF was removed from the reaction mixture by distillation. The pot residue was taken up in ether (100 ml) and washed with a solution of saturated NH_4Cl (50 ml). The aqueous portion was washed with ether (50 ml) and the combined ethereal solutions washed once more with a solution of saturated NH_4Cl (50 ml). The ethereal solution was dried over anhydrous $MgSO_4$ and filtered. Removal of the solvent under reduced pressure gave a slightly fluorescent green oil. The oil was pre-adsorbed onto silica gel (10 g) and placed on a silica gel column measuring 4 × 16 cm. Elution with pentane (400 ml) as one fraction gave 3.09 g of a clear, water white liquid. GLC (6′ × 1/4″ 10% SE-30 on Chromosorb W) analysis of the liquid gave three peaks corresponding to *cis*-1,3-dimethyl-5-(trimethylgermylmethyl)cyclohexane, *cis*-1-methyl-3,5-bis(trimethylgermylmethyl)cyclohexane, and *cis*-1,3,5-tris(trimethylgermylmethyl)cyclohexane by analogy to the retention times from the *cis*-1,3,5-tris(trimethylsilylmethyl)cyclohexane system. The amounts of each compound estimated from the chromatogram were 0.01 g, 0.19 g, and 2.89 g (47%), respectively. An analytically pure sample of *cis*-1,3,5-tris(trimethylgermylmethyl)cyclohexane was obtained by standard GLC preparation methods. m.p. 43°C. IR (CCl_4) cm^{-1}: 2950 and 2875 (C–H), 1230 (Ge–CH_3). NMR (CCl_4, benzene): 0.14 (s, 27H, Ge-CH_3), 0.40–0.84 and 1.20–1.81 (two-m, 15H, $CCH_2\text{–}\overset{\overset{H}{|}}{\underline{C}}\text{–}CH_2Ge$).

MS (*m/e*): 476 (parent), 343, 211, 118 (base). The peaks in the mass spectrum appear as clusters due to the numerous stable isotopes of germanium. ^{73}Ge was used to calculate molecular weight.

Anal. Found: C, 45.46; H, 8.93. $C_{18}H_{42}Ge_3$ calcd.: C, 45.39; H, 8.89%.

1-Methyl-1-germaadamantane (7).

A rapidly stirred mixture of *cis*-1-3-dimethyl-5-(trimethylgermylmethyl)cyclohexane (0.01 g, 0.04 mmol), *cis*-1-methyl-3,5-bis(trimethylgermylmethyl)cyclohexane (0.18 g, 0.50 mmol) and *cis*-1,3,5-tris(trimethylgermylmethyl)cyclohexane (2.69 g, 5.7 mmol) was refluxed in dry benzene (5 ml) with freshly sublimed anhydrous aluminum chloride (0.3 g, 2.2 mmol) for 15 h under a dry nitrogen atmosphere. All volatile material (0.57 g) between 25–55°C was removed by distillation from the clear light brown reaction mixture. The pot residue was cooled to room temperature, benzene (5 ml) and wet acetone (2 ml) added, and the mixture stirred for 30 min. Benzene (10 ml) was added to the mixture and the benzene solution washed with a 10% HCl solution (10 ml) and with distilled H_2O (10 ml). Drying of the benzene solution over anhydrous $MgSO_4$, followed by filtration and concentration under reduced pressure gave a yellow oil. The oil was pre-adsorbed onto silica gel (5 g) and placed on a 2.5 cm × 18 cm silica gel column. Elution with pentane (200 ml) as one fraction gave 0.45 g of a clear, water-white oil. GLC analysis (6′ × 1/4″ 10% SE-30 on Chromosorb W) of the oil showed it to contain 95% 1-methyl-1-germaadamantane. This corresponds to an overall yield of 37% of theoretical. An analytical sample of 1-methyl-1-germaadamantane was obtained by standard preparative GLC methods. The molecular structure of 7 was determined by gas phase electron diffraction methods [13b]. IR (neat) cm^{-1}: 2860 (C–H), 1190 (Ge–CH_3), 1180 (Ge–CH_5).

NMR (CCl_4, benzene): 0.11 (s, 3H, Ge-CH_3), 1.06 (d, 6H (*J* 4.3 Hz), Ge–CH_2–C), 1.69 (single peak with small broad signals located at 1.56 and 1.87, 6H, C–CH_2–C), 2.38 (broad single peak, 3H, C–$\overset{\overset{\text{H}}{|}}{C}$–C). MS (*m/e*): 211 (parent), 196, 123, 109.

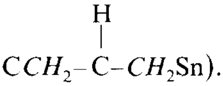
*1-Chloro-1-germaadamantane (**8**).*

1-Methyl-1-germaadamantane (**7**) (160 mg, 0.76 mmol), trichlorosilane (201 mg, 1.5 mmol), and chloroplatinic acid (~ 5 mg) were heated at 150°C in a sealed tube for 24 h. The contents of the tube were filtered through a glass wool plug under a dry nitrogen blanket and the excess trichlorosilane removed under reduced pressure to afford an oil. Analysis by GLC (6′ × 1/4″ 10% SE-30 Chromosorb W) showed the reaction to be 50% complete. The concentrated material along with trichlorosilane (537 mg, 4 mmol) and chloroplatinic acid (~ 5 mg) were heated in another sealed tube at 150°C for 44 h. The above work-up procedure was repeated and GLC analysis of the residue showed it to contain 1-chloro-1-germaadamantane (**8**) and some higher molecular weight material. 1-Chloro-1-germaadamantane (**8**) (63 mg, 36%) was obtained as a white crystalline material by standard preparative GLC methods. M.p. (sealed tube) 128–130°C. IR (CCl_4) cm^{-1}: 2890 (C–H), 1180 (Ge–CH_2). NMR (CCl_4, benzene): 1.60 (d, (*J* 4.1 Hz)) and 1.71 (single peak) (overlapping peaks, total 12H, C–CH_2–Ge and C–CH_2–C), 2.63 (broad single peak, 3H, C–$\overset{\overset{\text{H}}{|}}{C}$–C). MS (*m/e*): 231 (parent), 196, 108.

Anal. Found: C, 44.79; H, 6.14. $C_9H_{15}GeCl$ calcd.: C, 46.74; H, 6.54%.

cis-1,3,5-Tris(trimethylstannylmethyl)cyclohexane from the tri-Grignard of cis-1,3,5-tris(bromomethyl)cyclohexane

cis-1,3,5-Tris(bromomethyl)cyclohexane (6.07 g, 16.7 mmol) in dry THF (25 ml) was slowly added dropwise to rapidly stirred magnesium turnings (2.56 g, 110 mmol) in dry THF (50 ml) at room temperature under a dry nitrogen atmosphere. The magnesium turnings had been cleaned with 1,2-dibromomethane (940 mg, 5.0 mmol) in dry THF (10 ml). The tri-Grignard was stirred at room temperature for 2 h, refluxed for 22 h, and then transferred by means of a double-tipped needle into an equal pressure addition funnel under a dry nitrogen atmosphere. The excess magnesium turnings were washed with dry THF (2 × 10 ml), and the washings added to the grey-black tri-Grignard solution. The tri-Grignard was slowly dripped into a rapidly stirred solution of trimethyltin(IV) chloride (10.0 g, 50.2 mmol) in dry THF (35 ml) at room temperature. The addition funnel was rinsed with dry THF (10 ml) and the mixture refluxed for 43 h. A 115 ml portion of THF was removed from the reaction mixture by distillation. The pot residue was taken up in diethyl ether (150 ml) and washed with a solution of saturated NH_4Cl (50 ml). The aqueous portion was washed with ether (2 × 50 ml). The combined ethereal extracts were dried over anhydrous Na_2SO_4 and filtered. Removal of the solvent under reduced pressure gave 11.21 g of yellow oil. The oil was pre-adsorbed onto silica gel (15 g) and placed on a silica gel column measuring 4 × 20 cm. Elution with pentane (650 ml) as one fraction gave 6.41 g of a clear, water-white liquid. GLC (6′ × 1/4″ 10% SE-30 on Chromosorb W) analysis of the liquid gave three peaks corresponding to *cis*-1,3-dimethyl-5-(trimethylstannylmethyl)cyclohexane, *cis*-1-methyl-3,5-bis(trimethylstannylmethyl)cyclohexane, and *cis*-1,3,5-tris(trimethylstannylmethyl)cyclohexane by analogy to the retention times from the *cis*-1,3,5-tris(trimethylsilylmethyl)cyclohexane system. The amount of each compound calculated from the chromatogram was 0.05, 0.73, and 5.63 g (55%), respectively. An analytically pure sample of *cis*-1,3,5-tris(trimethylstannylmethyl)cyclohexane was obtained by standard GLC preparative methods. M.p. 38–40°C. Attempts to trap the tri-Grignard in situ with Me_3SnCl gave only an amorphous black powder and a viscous oil. IR (CCl_4) cm^{-1}: 2960 and 2875 (C–H), 1190 ($Sn-CH_3$). NMR (CCl_4, benzene): 0.12 with two satellites at −0.16 and 0.40 (s, 27H, $Sn-\mathit{CH}_3$), 0.45–0.99 and 1.08–1.82 (two-m, 15H, $C\mathit{CH}_2-\overset{\displaystyle H}{\overset{|}{C}}-\mathit{CH}_2Sn$). MS (*m/e*): 614 (parent), 435, 257, 164 (base).



Anal. Found: C, 35.56; H, 6.50. $C_{18}H_{42}Sn_3$ calcd.: C, 35.18; H, 6.89%.

Attempted synthesis of 1-methyl-1-stannaadamantane (9)

A mixture of *cis*-1,3,5-tris(trimethylstannylmethyl)cyclohexane (2.64 g, 4.3 mmol), *cis*-1-methyl-3,5-bis(trimethylstannylmethyl)cyclohexane (233.4 mg, 0.08 mmol) were dissolved in dry benzene (10 ml). Anhydrous $AlCl_3$ (300 mg, 2.2 mmol) was added and the mixture stirred and refluxed for 24 h. An insoluble solid formed during the reaction. The mixture was cooled to room temperature and a solution of 10% HCl (10 ml) added. Benzene (15 ml) was added and the solid filtered from the mixture and air dried. The solid was extracted with diethyl ether and concentrated to dryness under reduced pressure. The ether contained no detectable material.

The filtrate was transferred to a separatory funnel and the benzene layer removed from the aqueous portion. The benzene solution was washed with distilled H_2O (2 × 20 ml), dried over anhydrous $MgSO_4$, and filtered. A small amount of a clear, yellow syrup was obtained after the benzene was removed under reduced pressure. Analysis of the syrup by GLC (6′ × 1/4″ 10% SE-30 on Chromosorb W) showed only high molecular weight material to be present.

Attempted synthesis of 1-methyl-1-stannaadamantane (9) by redistribution of cis-1,3,5-tris(trimethylstannylmethyl)cyclohexane on Al_2O_3

A mixture of *cis*-1,3,5-tris(trimethylstannylmethyl)cyclohexane (878 mg, 1.43 mmol), *cis*-1-methyl-3,5-bis(trimethylstannylmethyl)cyclohexane (114 mg, 0.25 mmol), and *cis*-1,3-dimethyl-5-(trimethylstannylmethyl)cyclohexane (7.8 mg, 0.03 mmol) were dissolved in dry benzene (25 ml). Neutral alumina (1.5 g) was added and the mixture refluxed for 24 h. The reaction was cooled to room temperature and filtered. A clear, water-white oil was obtained after the filtrate was concentrated. GLC (6′ × 1/4″ 10% SE-30 on Chromosorb W) analysis showed only the starting stannanes and higher molecular weight material to be present.

Attempted synthesis of 1-methyl-1-stannaadamantane (9) by reaction of the tri-Grignard of cis-1,3,5-tris(bromomethyl)cyclohexane and methyltrichlorostannane.

cis-1,3,5-Tris(bromomethyl)cyclohexane (3.78 g, 10.4 mmol) in dry THF (25 ml) was slowly added dropwise to rapidly stirred magnesium turnings (1.59 g, 66.6 mmol) in dry THF (20 ml) at room temperature under a dry nitrogen atmosphere. The magnesium turnings had been cleaned with 1,2-dibromoethane (590 mg, 3.1

mmol) in dry THF (10 ml). The tri-Grignard was stirred at room temperature for 20 h, refluxed for 3 h, and then cooled back to room temperature. The grey-black solution of was transferred by means of a double-tipped needle into an equal pressure addition funnel under a dry nitrogen atmosphere. The excess magnesium turnings were washed with dry THF (2 × 10 ml) and the washings added to the tri-Grignard solution. Methyltrichlorostannane (2.5 g, 10.4 mmol) in dry THF (60 ml) and the solution of were slowly added simultaneously a drop at a time to stirring and refluxing THF (35 ml). Both solutions were completely added after 8 h. The reaction mixture was refluxed for 15 h, cooled to 0°C and slowly hydrolyzed with ice (4 g). The mixture was concentrated under reduced pressure and diethyl ether (50 ml) added to the residue. The ethereal solution and the magnesium salts were placed in a separatory funnel and washed (2 × 50 ml) with a saturated sodium chloride solution. The ethereal solution was dried over anhydrous $MgSO_4$ and filtered. Removal of the solvent under reduced pressure gave a small amount of a clear yellow oil. The oil was shown to contain only high molecular weight material by GLC (6′ × 1/4″, 10% SE-30 on Chromosorb W) analysis.

1,3,5-Tris(trimethylsilyl)benzene

A solution of 1,3,5-trichlorobenzene (30.0 g, 0.17 mol) in dry THF (50 ml) was slowly added dropwise to a stirred mixture of cleaned magnesium turnings (14.46 g, 0.60 g, 0.60 mol) and trimethylchlorosilane (72.07 g, 0.66 mol) in dry THF (200 ml). The reaction temperature was maintained at 25°C throughout the addition. The magnesium turnings were cleaned with 1,2-dibromoethane (8.72 g, 0.05 mol) in dry THF (100 ml). The reaction mixture was stirred at room temperature for 4 h and refluxed for 20 h. The mixture was chilled in ice, filtered by suction, and the salts washed with ether (50 ml). The volatile material was then removed under reduced pressure. The oily residue was dissolved in ether (250 ml) and washed with a solution of saturated NH_4Cl (1 × 100 ml) and with distilled H_2O (1 × 100 ml). The ethereal solution was dried over anhydrous $MgSO_4$, filtered, and the solvent removed under reduced pressure. Distillation of the slightly yellow oil gave 34.06 g (70%) of 1,3,5-tris(trimethylsilyl)benzene as a water white liquid, b.p. 106°C/1.5 mmHg (lit. [16] 80°C/0.4 mmHg). IR (neat) cm^{-1}: 2915 (C–H), 1240 ($Si{-}CH_3$), 1135, 860, 750, 685. NMR (CCl_4, cyclohexane): 0.30 (s, 27H, $Si{-}CH_3$), 7.63 (s, 3H, Ar–H).

cis-1,3,5-Tris(trimethylsilyl)cyclohexane and trans-1,3,5-Tris-(trimethylsilyl)cyclohexane

A solution of 1,3,5-tris(trimethylsilyl)benzene (15.00 g, 51 mmol) in methylcyclohexane (30 ml) was hydrogenated using as catalyst 10% palladium on carbon (0.5 g). The hydrogenation was performed at 1000 psi in a Parr Bomb with stirring for 3 days. The catalyst was filtered from the otherwise homogeneous solution and the filtrate concentrated under reduced pressure leaving an oily white solid. The oil was removed from the solid by washing with acetone, filtering, and air drying. Recrystallization of the solid from hot methanol gave 3.75 g (24%) of *cis*- and *trans*-1,3,5-tris(trimethylsilyl)cyclohexane as white leaflets. M.p. (sealed tube) 94–96°C. IR (CCl_4) cm^{-1}: 2935, 2880, and 2820 (C–H), 1240 ($Si{-}CH_3$), 1115.

NMR (CCl_4, CH_2Cl_2): −0.07 (s, 27H, $Si{-}CH_3$), 0.26–1.16 (m), and 1.69 (d, (J 11 Hz)) (9H, $C{-}\overset{\overset{\displaystyle H}{|}}{\underline{C}}{-}CH_2C$). MS (*m/e*): 300 (parent), 152, 78, 73 (base). Anal. Found: C, 59.81; H, 11.98. $C_{15}H_{36}Si_3$ calcd.: C, 59.91; H, 12.07%.

*Attempted synthesis of 1-methyl-1-silatrisnoradamantane (**10**)*

A mixture of *cis*- and *trans*-1,3,5-tris(trimethylsilyl)cyclohexane (1.0 g, 3.3 mmol) and anhydrous $AlCl_3$ (100 mg, 0.75 mmol) in dry benzene was rapidly stirred and refluxed for 6 h. Wet acetone (2 ml) and a solution of 10% HCl (2 ml) were added to the reaction mixture after it was cooled to room temperature. The benzene solution was separated and washed with distilled H_2O (2 × 5 ml). After drying over anhydrous $MgSO_4$, filtering, and concentrating under reduced pressure, a very viscous oil was obtained. GLC (6′ × 1/4″ 10% SE-30 on Chromosorb W) analysis showed only the presence of high molecular weight material.

cis-1,3,5-Tris(iodomethyl)cyclohexane

Anhydrous sodium iodide (20.44 g, 136.4 mmol) and *cis*-1,3,5-tris(bromomethyl)cyclohexane (15.00 g, 41.3 mmol) were dissolved in dry acetone (150 ml) with stirring at room temperature under a dry nitrogen atmosphere. The mixture was stirred at room temperature for 2 h, then refluxed for 24 h. The reaction remained homogeneous for 30 minutes then sodium bromide began to precipitate. The acetone was removed under reduced pressure and distilled water (100 ml) added to the solid residue. Extraction with ether (3 × 50 ml) followed by removal of the solvent under reduced pressure gave a yellow solid. The solid was pre-adsorbed onto alumina (50 g) and placed on a 4 cm × 20 cm column of alumina. Elution with a 10% ether/pentane (1.2 l) mixture gave *cis*-1,3,5-tris(iodomethyl)cyclohexane as white crystals. Recrystallization from hot methanol gave 14.82 g (71%). M.p. 83–85°C. IR (CCl_4) cm^{-1}: 2865 (C–H), 1190. NMR ($CDCl_3$, TMS): 0.71 (q, 3H ($J = 12.1$ Hz), C–CH_2–C (axial)), 1.33–1.85 (broad-m, 3H, $C{-}\overset{H}{\overset{|}{C}}{-}C$), 2.02 (broad-d, 3H ($J$ 12.2 Hz), C–CH_2–C (equitorial)), 3.17 (d, 6H (J 5.9 Hz), CH–CH_2–I). MS (m/e): 504 (parent), 377, 250, 120.

Anal. Found: C, 21.60; H, 3.05. $C_9H_{15}I_3$ calcd.: C, 21.45; H, 3.00%.

cis-1,3,5-Tris(2-trimethylsilylethyl)cyclohexane

Chloromethyltrimethylsilane (9.82 g, 80 mmol) in dry THF (10 ml) was slowly added dropwise to rapidly stirred magnesium turnings (4.8 g, 168 mmol) in dry refluxing THF (100 ml). The magnesium turnings were cleaned with 1,2-dibromoethane (1.5 g, 8.0 mmol) in dry THF (15 ml). The mixture was refluxed for 20 h to insure complete Grignard formation. The Grignard solution was cooled to 0°C and the solution separated from the excess magnesium turnings with the aid of a double tipped transfer needle. The cold Grignard solution was added to a solution of *cis*-1,3,5-tris(iodomethyl)cyclohexane (10.07 g, 20 mmol) in dry THF (50 ml) at 0°C. The excess of magnesium turnings were washed with cold, dry THF (2 × 25 ml) and the washings added to the cold reaction mixture. Kochi's reagent, dilithium tetrachlorocuprate, [15] (10 ml) was added, then the mixture stirred at 0°C for 3 h and at room temperature for 22 h. A solution of saturated NH_4Cl (50 ml) was added and the mixture extracted with pentane (3 × 50 ml). The combined extracts were washed with distilled H_2O (2 × 25 ml) and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave 7.95 g of a yellow oil which, upon standing, partially solidified. The oil was removed by suction filtration and the solid recrystallized from hot methanol. *cis*-1,3,5-Tris(2-trimethylsilylethyl)cyclohexane was obtained in 86% (6.63 g) as white needles. M.p. 60–62°C. IR (CCl_4) cm^{-1}: 2870 (C–H), 1240 (Si–CH_3).

NMR (CCl_4, benzene): 0.03 (s 27H, Si–*CH_3*), 0.30–0.73 (broad-m, 9H), 1.00–1.43 (broad-m, 9H), 1.83 (broad-d, 3H) signals from 0.30–1.83 due to $CH_2-\overset{\overset{H}{|}}{C}-C$ and C–*CH_2CH_2*–Si. MS (*m/e*): 384 (parent), 369, 296, 282, 208, 180, 101, 73 (base).

Anal. Found: C, 65.54; H, 12.55. $C_{21}H_{48}Si_3$ calcd.: C, 65.54; H, 12.57%.

*Attempted synthesis of 1-methyl-1-silatrishomoadamantane (**11**)*

A mixture of *cis*-1,3,5-tris(2-trimethylsilylethyl)cyclohexane (2.0 g, 5.2 mmol) and anhydrous $AlCl_3$ (1.5 g, 11.2 mmol) in dry benzene (40 ml) were rapidly stirred and refluxed for 6 h. The TMS (0.48 g, 52%) liberated from the reaction was trapped in a received cooled in a dry ice/isopropanol slush. Wet acetone (5 ml) and a solution of 10% HCl (5 ml) were added to the reaction mixture after it was cooled to room temperature. The organic layer was separated, washed with a solution of 10% HCl (2 × 20 ml), and then washed with distilled H_2O (2 × 20 ml). Drying of the benzene solution over anhydrous $MgSO_4$, filtering, and concentrating under reduced pressure afforded 6 g of a pale yellow solid. The solid was pre-adsorbed onto silica gel (15 g) and placed on a silica gel column measuring 3.5 cm × 10 cm. Elution with pentane (200 ml) as one friction gave a very small amount of a clear water white oil. GLC (6′ × 1/4″ 10% SE-30 on Chromosorb W) analysis of the oil showed it to contain only high molecular weight material and none of the expected product **11**.

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