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Oligomerization of phenylgermanes by catalytic dehydrocoupling

Clare Aitken, John F. Harrod, Abdul Malek
Chemistry Department, McGill University, Montreal, H3A 2K6 (Canada)

and Edmond Samuel
Ecole Nationale Supérieure de Chimie de Paris (France)

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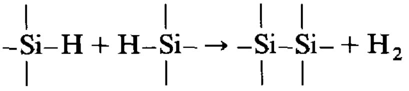
Abstract

Phenylgermane and diphenylgermane both show greater activity towards dehydrocoupling with a dimethyltitanocene catalyst than do their silane analogues. Phenylgermane polymerizes to a three-dimensional gel with dimethyltitanocene as catalyst and undergoes stepwise oligomerization with a vanadocene catalyst. Diphenylgermane is selectively dimerized to tetraphenyldigermane with a dimethyltitanocene catalyst. Reaction of diphenylgermane and dimethyltitanocene in equimolar ratio gives a purple product with properties similar to those exhibited by silyltitanocene(III) complexes reported earlier. This purple product is a powerful catalyst for the oligomerization of diphenylgermane and of tetraphenyldigermane to an oligomer consisting mainly of octaphenyltetragermane.

Introduction

We recently reported a novel catalysis for the oligomerization of primary silanes to organopolysilanes of ca. 10 to 20 Si atoms [1a–1d]. By suitable modification of the catalysts di-, tri- and cyclohexa-silanes have also been made with high selectivity, using the same methodology [1d,2]. The methodology involves the intermolecular elimination of molecular H_2 between two Si–H containing molecules (dehydrocoupling), according to eq. 1. The dialkylmetallocenes of Ti and Zr exhibit unique activities as catalysts for these reactions.



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{H} + \mathrm{H}-\overset{|}{\underset{|}{\mathrm{Si}}}- \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\overset{|}{\underset{|}{\mathrm{Si}}}- + \mathrm{H}_2 \tag{1}$$

Given the similarities that exist between the chemistries of Si and Ge, an obvious extension was to study the scope of this type of catalysis for the synthesis of Ge–Ge

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bonds. As with Si, the number of synthetic methods for the formation of Ge–Ge bonds is quite limited. The more commonly used routes are Wurtz–Fittig type coupling of halides, or pseudohalides, with group 1 metals [3], the insertion of germylenes into Ge–X bonds (X is most commonly H or another group 14 atom) [4], and the reaction of germyllithiums with germyl halides [5]. The Wurtz–Fittig coupling generally leads to cyclic oligogermanes, but recently has been applied to the synthesis of high molecular weight polymers [6,7]. The germylene insertion method provides an elegant one pot synthesis of aryloligogermanes with 2, 3 and 4 germanium atoms in the chain [4].

To our knowledge, the only previous report of the use of catalytic dehydrocoupling for the formation of oligogermanes involved the decomposition of Et_2GeH_2 over steel wool at ca. 75 °C to give $H[Et_2]_nH$, $n = 2$, 3 and 4 [8].

Results and discussion

Polymerization of phenylgermane. In the presence of catalytic amounts of dimethyltitanocene, phenylgermane undergoes a reaction which is in most respects analogous to that of phenylsilane. Provided the catalyst concentration is low enough (typically < 1 mole% based on substrate; 1/1 phenylgermane/toluene mixture), there is a brief induction period during which no observable reaction occurs. The end of the induction period is signalled by the onset of gas evolution and a sudden change in color of the solution from pale yellow to intense purple. The germane reaction differs from that of the silane in one important respect, in that gel formation occurs quite soon after the onset of polymerization of the germane, while neither gels nor evidence for branching have ever been observed in the silane polymerization. At higher catalyst and monomer concentrations, the germane polymerization can be quite violent and gelation is almost instantaneous. In addition to the visible change of the medium from a mobile liquid to a rigid gel, the onset of gelation is evident from the change in the ESR signals of the solution from typical solution to typical solid signals.

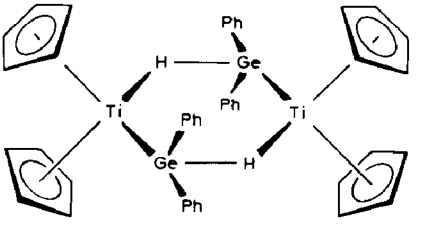
Vanadocene is a very poor catalyst for the dehydrocoupling of silanes [9]. It does however effect the stepwise oligomerization of phenylgermane at reasonable rates at 50 °C. The appearance and disappearance of the intermediate di- and tri-germanes are easily followed by ^1H NMR. The di- and tri-germanes are eventually converted into a mixture of higher oligogermanes whose composition and structures have not been determined.

Reactions of diphenylgermane. Since diphenylgermane can only couple in a linear manner, its reactions are much easier to monitor by conventional high resolution NMR spectroscopy. In a typical catalytic reaction, with carefully recrystallized dimethyltitanocene (0.02 M) and phenylgermane (0.7 M) in toluene-d_8, no observable reaction occurs at room temperature. Warming the reaction mixture to 50 °C, without agitation, results in an accelerating evolution of hydrogen and near-quantitative conversion of the diphenylgermane to tetraphenyldigermane in the course of a few minutes. When the consumption of substrate approaches completion the solution suddenly changes color from yellow to purple and there is a short surge in hydrogen evolution. During catalytic dimerization, the yellow solution shows marked instability if agitated, particularly if the dimethyltitanocene was not carefully purified before use. This instability is manifest by the sudden appearance of dark purple streaks which rapidly suffuse the whole solution. The color change is accompanied by a violent evolution of gas. If this transformation occurs before the complete conversion of diphenylgermane to tetraphenyldigermane, further reaction gives a complex mixture of oligogermanes, rather than the digermane.

The dark purple solutions described above have a completely different catalytic activity from the yellow species which selectively produces tetraphenyldigermane. The dark purple product may be generated directly by heating a 1/1 molar mixture of dimethyltitanocene and diphenylgermane to about 50 ° C, or by UV irradiation of such a mixture. With slightly aged dimethyltitanocene, the appearance of the purple product is almost instantaneous. With freshly recrystallized dimethyltitanocene, the appearance of the purple color may take as long as ten minutes. Addition of an excess of diphenylgermane to such a catalyst leads to copious hydrogen evolution and the formation of a mixture of oligodiphenylgermylenes, the major component of which is octaphenyltetragermane.

Attempts to obtain crystalline germyltitanocene(III), or germyltitanocene(IV) complexes, analogous to those resulting from similar reactions of phenylsilane [1b], or of triphenylgermane [10], from the equimolar reaction of diphenylgermane and dimethyltitanocene did not succeed. However, ^{1}H NMR observations provide strong indications of the progress of the reaction and the nature of the products. If the 1/1 molar reaction mixture is heated for a few minutes and quenched to room temperature before the appearance of purple color, the ^{1}H NMR spectrum shows the partial disappearance of the Cp (5.67 ppm) and Me (0.005 ppm) of dimethyltitanocene and the appearance of new Cp (5.56 ppm) and Me (0.17 ppm) resonances in the ratio of 10/3. These resonances are almost certainly due to the production of $Cp_2TiMe(GeHPh_2)$ (**1**), in a reaction strictly analogous to that observed with triphenylgermane [10].

Just after the appearance of the purple color, dimethyltitanocene is no longer detectable in the mixture, but the resonances of compound **1** are still prominent. In addition, two new Cp resonances of equal intensity, and of similar total intensity to the Cp resonance of **1**, are seen at 5.92 and 5.80 ppm and a high field hydride (sharp singlet) at -7.64 ppm. The Cp and hydride resonances are in the ratio of 10/1. With the passage of time, or on mild heating all of these resonances disappear and the only sharp signals that remain are due to the phenyl and Ge–H groups of di- and tri-germanes. We attribute the Cp and hydride resonances to a compound with the structure shown in **2**, by analogy with the previously reported $[Cp_2TiSiH_2Ph]_2$ [1b]. This structure fits the NMR observations, provided the $Ge_2Ti_2H_2$ ring is not planar, and the two Cp groups on each Ti are diastereotopic.



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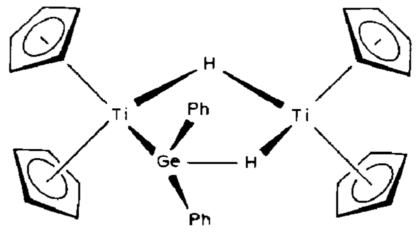

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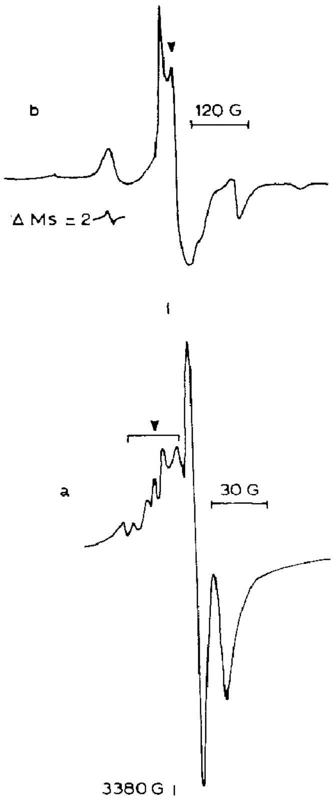

Fig. 1. ESR spectra of the purple solution resulting from reaction of diphenylgermane and dimethyltitanocene in equimolar ratio. (a) Room temperature, (b) frozen toluene solution. The features marked with an arrow are due to $[Cp_2TiH]_2H$ [1b].

The disappearance of the resonances of groups attached to the Ti is due to decomposition to paramagnetic species. ESR spectra of the purple product(s) are shown in Fig. 1. These spectra exhibit a remarkable resemblance to those previously attributed to the complex **3** [1b]. In the case of the diphenylgermyl analogue, it seems that the triplet state which gives rise to this ESR spectrum is sufficiently highly populated to render the NMR spectrum unobservable even at low temperature. The near identity of the spectral parameters for the Si and Ge compounds is not surprising since these parameters are largely determined by the Ti–Ti distance in the molecule [11] and the radii of Si and Ge are very similar (117 and 122 pm respectively).

The structure and composition of the polymer. Despite the high reactivity of the monomer, diphenylgermane only yields an oligomer of modest degree of polymerization. All of the physical data indicate that the oligomer is predominantly the linear tetramer with Ge–H end groups. We have not succeeded in crystallizing the oligomer, although it does precipitate as a white powder from cold hexane/toluene solutions.

The narrow GPC bands indicate a near-monodisperse material. The highest observed MS peak corresponds to the tetramer, minus two molecules of benzene. The ^{13}C NMR spectrum is very similar to that of 1,4-dichlorooctaphenyltetragermane [4]. Of particular relevance is the fact that the two resonances assigned to the

2,6-carbon atoms of the inner and terminal phenyl groups are of roughly equal intensity.

The intensity of the ν(Ge–H) band in the oligomer, relative to the ν(C=C) at 1480 cm^{-1}, is 0.54, compared to 0.92 for tetraphenyldigermane and 1.40 for diphenylgermane. This also provides strong support for the assignment of a linear tetramer structure.

A comparison of the germane and silane reactions

The reactions of arylgermanes and arylsilanes under the influence of titanocene-based catalysts are qualitatively very similar. The reactivity of the germanes is much higher than that of the corresponding silanes, as manifest by (1) the crosslinking of polyphenylgermylene and the absence of crosslinking in polyphenylsilylene and (2) the oligomerization of diphenylgermane and the absence of reaction of diphenylsilane. The selective dimerization of diphenylgermane under the influence of dimethyltitanocene is probably also a reflection of the greater reactivity of the germane with dimethyltitanocene. This catalysis seems to involve a reaction between the germane and dimethyltitanocene which does not lead to any gross change in the oxidation state of the titanium. The only new titanocene derivative detected by NMR during this catalytic dimerization is the putative $Cp_2Ti(CH_3)(GeHPh_2)$ described above. It thus seems likely that this compound is implicated in the formation of the dimer.

The appearance of the dark purple color is accompanied by a sudden disappearance of the dimethyltitanocene and the appearance of reduced titanium compounds. The compound **1** present in the solution at this point is not subject to the same sudden reduction. We believe that the catastrophic reduction reaction, also observed in the case of silane reactions with dimethyltitanocene and described in detail elsewhere [1b], is a branched chain reaction which depends on adventitious factors, such as radical initiator impurities and light, for its initiation. In the case of diphenylgermane this reaction seems to occur independantly of the reaction leading to **1**.

The reduced germyltitanocene species catalyze the oligomerization of diphenylgermane with the production of only small amounts of intermediate di- and tri-germanes. Such behavior is reminiscent of that observed for the dimethyltitanocene catalyzed polymerization of primary silanes [1a,b]. We speculated earlier that the failure of dimethyltitanocene to catalyze the polymerization of secondary silanes might be due to the need for a step involving α-hydride transfer from a homologated silyl ligand to titanium [1c,d], a process which is not possible if the ultimate silicon has two organic and one silyl substituent. Since it is highly likely that the diphenylgermane polymerization is proceeding by the same mechanism, the α-hydride transfer hypothesis no longer seems tenable. The high selectivity for the linear polymerization of primary silanes and the lack of reactivity of secondary silanes must therefore be due to large differences in reaction rates for primary, secondary and tertiary Si–H, rather than to a mechanistic selectivity.

In conclusion, we draw attention to the fact that, despite the apparently higher reaction rates of the germanes relative to the silanes, the degrees of polymerization are still lower than the values obtained with primary silanes. In the case of diphenylgermane, the polymer produced by the purple catalyst solution has a limiting average degree of polymerization of ca. 4. Thus, the chain termination reactions are also very fast for the germanes. Remarkably, tetraphenyldigermane also dimerizes to octaphenyltetragermane, but no further chain growth has been achieved. We presently have no explanation for this behavior, beyond that fact that there may be several different mechanisms operating e.g. one that leads to rapid oligomerization and another which is specific for dimerization. Which processes dominate could well be substrate dependant.

Experimental

All manipulations were carried out under argon using standard Schlenk techniques. Solvents were distilled from Na/benzophenone prior to use. Melting points were measured under argon and are uncorrected.

Phenyltrichlorogermane and diphenyldichlorogermane were obtained from Strem Chemical Co. and used without further purification. Phenylgermane and diphenylgermane were prepared by reactions of the halides with $LiAlH_4$ in diethyl ether according to a combination of literature procedures [12]. Dimethyltitanocene was prepared according to the method of Claus and Bestian [13].

Catalytic dimerization of diphenylgermane. Diphenylgermane (1.0 g) was added to a solution of dimethyltitanocene (0.02 g) in toluene (5 ml). The mixture was warmed to about 50 ° C to initiate the reaction. The onset of reaction was signalled by the appearance of a slow stream of hydrogen bubbles. The gas evolution became increasingly vigorous until a violent burst and a change of color to violet signalled the end of the dimerization reaction. The reaction mixture was passed through a 1 × 5 cm column of Florisil to remove the catalyst and the column was washed with hexane. Evaporation of the eluate gave a white crystalline solid (0.9 g; 90%). Analysis: Found: C, 62.95; H, 4.87. $C_{24}H_{22}Ge_2$ calcd.: C, 63.27; H, 4.83%. m.p.: 85–90 ° C. IR: 2010 cm^{-1} (ν(Ge–H); intensity ratio of 2010/1480 peaks 0.92. ^1H NMR: δ 5.66 (Ge–H) ppm. MS (mass (abundance)): 305 (100), 456 (0.43). Lowest energy UV absorption max. 243 nm.

Catalytic oligomerization of Ph_2GeH_2. An NMR tube was charged with toluene-d_8 ((0.70 ml), dimethyltitanocene (0.02 g) and diphenylgermane (0.03 ml). The tube was warmed to 70 ° C until the solution turned dark purple. The catalyst solution was cooled to room temperature and diphenylgermane (0.5 ml) was added slowly enough to avoid loss of material from the tube due to excessive gas evolution. After the addition was complete, the rate of gas evolution rapidly subsided to a steady stream. After 1 h the ^1H NMR spectrum was recorded. The spectrum showed that all of the monomer had been consumed and a weak, broad complex of peaks due to GeH in polygermane was observed at δ 5.2–5.5. These peaks were too weak and broad to integrate successfully, but were in the range of 2 to 3% of the phenyl protons. After several days, the reaction mixture was passed through a 1 × 5 cm Florisil column to remove catalyst and evaporated to dryness under vacuum to give a white glassy solid (0.35 g). m.p.: softened at ca. 70 ° C. IR: ν(Ge–H) 2010 cm^{-1}; intensity ratio of 2010/1480 peaks 0.54. ^{13}C NMR (δ): C(1), 136.4; C(2,6) [Ge(2,3)], 136.1; C(2,6)[Ge(1,4)], 135.5; C(4), 128.5; C(3,5), 127.9 ppm. (^{13}C assignments by analogy with $Ph_8Ge_4Cl_2$ [4]). MS (mass (abundance)): 754 (1.00), 679 (2.7), 604 (2.4), 529 (3.4), 454 (15), 303 (100). Lowest energy UV absorption max. 300 nm.

The oligomer eluted from an Ultrastyragel GPC column with approximately the same retention time and half height peak width (516 s and 30 s) as a calibrant polystyrene of $\overline{M}_n = 950$; $\overline{M}_w/\overline{M}_n = 1.13$ (515 s and 24 s). Tetraphenyldigermane had a retention time of 540 s and a peak width of 24 s on the same column.

Oligomerization of tetraphenyldigermane. A Schlenk tube was charged with dimethyltitanocene (0.02 g), diphenylgermane (0.03 g) and toluene (3.0 ml) and heated at 65 °C. After the initial vigorous reaction had subsided and the purple color had appeared, the solution was cooled to room temperature and tetraphenyldigermane (0.4 g) was added. The mixture was heated to 65 °C for 5 h. After the product had been passed through a 1 × 5 cm Florisil column to remove catalyst, the solution was evaporated to dryness to give a glassy solid (0.3 g; 75%). This product had identical physical parameters to those cited above for the oligomer produced from diphenylgermane.

Acknowledgements

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