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Catalytic Synthesis of Poly(arylmethylgermanes) by Demethanative Coupling: A Mild Route to σ-Conjugated Polymers

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Abstract: A variety of poly(arylmethylgermanes) have been synthesized from aryldimethylgermanes in high yield via mild catalytic demethanative coupling using tetrakis(trimethylphosphine)dimethylruthenium as a convenient catalyst precursor. Polymerizations of germanes Me_2GeArH (Ar = phenyl, *p*-tolyl, *p*-fluoro, *p*-trifluorotolyl, *p*-anisyl, and *m*-xylyl) proceed in neat monomer at room temperature. Catalyst removal can be effected by treatment of the reaction mixture with air, which gives polymer yields between 70% and 100%. Alternatively, separation of the catalyst by precipitation of the polymers from THF solution with methanol gives lower yields, but of somewhat higher molecular weight material. The new polygermanes are characterized by ^{1}H NMR and by gel permeation chromatography (GPC) using both polystyrene standards and light scattering methods. Molecular weights calculated by polystyrene analysis fall in the ranges of $M_\mathrm{w} = 3 \times 10^3$ to 7×10^3 and $M_\mathrm{n} = 2 \times 10^3$ to 6×10^3. Values obtained from light scattering are approximately 60% and 82% higher, respectively, resulting in M_w measured by SEC/LS in the range 5×10^3 to 1×10^4, with $M_\mathrm{w}/M_\mathrm{n} \sim 1.3$. The absorption spectra of the polygermanes exhibit λ_max in the range 326−338 nm. Comparison of the properties of poly(phenylmethylgermane) prepared by catalytic demethanative coupling and Wurtz coupling of $MePhGeCl_2$ with sodium revealed no significant differences.

Introduction

Polysilanes and polygermanes are inorganic polymers with interesting electronic and optical properties not normally associated with saturated polymers, arising from the delocalization of σ-electrons along the polymer backbone.[1,2] Although not as extensively studied as polysilanes, polygermanes also exhibit a red shift of λ_max with increasing chain length,[3] semiconductive behavior upon oxidative doping,[2c] and significant nonlinear optical behavior.[4] As in the case of polysilanes, polygermanes are thermochromic, exhibiting an abrupt increase in λ_max below a discrete temperature associated with changes in the polymer chain conformation.[5] One main difference between the Si and Ge backbone polymers is that the latter exhibits a smaller band gap.[6] Polysilanes fluoresce with high quantum efficiencies,[1a] and although the only reports of emission from polygermanes are found in the patent literature,[7] properties similar to those of the polysilanes can be expected. Potential industrial applications for these polymers include photoresists,[2a,3a,8] third-order nonlinear optical materials,[4] charge transport polymers,[9] photoconductors,[9b] microlithographic materials,[10] and photoinitiators.[2a]

The primary synthetic method for making polygermanes is via Wurtz coupling of diorganodichlorogermanes by alkali metals. Although a variety of alkyl and aryl derivatives can be used, there are severe limitations to this method. The high molecular weight polymers are only prepared in low yields, usually less than 25%,[3a,5,11] and the synthesis is not tolerant of many electronically active functional groups due to the harsh reaction conditions.[11] Other methods of preparation involve dehydrocoupling polymerization using early transition metal catalysts, which produces large amounts of cyclic oligomers,[12] and from certain organogermylenes, which polymerize to give

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moderate molecular weight products in yields up to 60%.[11] In addition, polygermanes have been synthesized in low yield by electrochemical reduction of chlorogermanes.[13]

We recently described a highly efficient ruthenium-catalyzed process, which gives high molecular weight polydimethylgermane under mild conditions (25 °C) in essentially quantitative yield.[14] In this demethanative coupling reaction, germanium−germanium bonds are produced with concurrent irreversible loss of methane. We now report that this synthetic method can be extended to produce a variety of poly(arylmethylgermanes) containing both electron-donating and electron-withdrawing functional groups on the phenyl ring. The polymerizations occur in high yield under mild reaction conditions.

Results and Discussion.

Monomer Syntheses. Unlike their silicon analogues, germane monomers of the form Me_2GeArH used in these polymerizations are not readily available. The obvious synthetic approach would be to selectively displace one chloride from dimethyldichlorogermane with an aryl group, using either the corresponding lithium or Grignard reagent. However, this approach does not give the desired selectivity and results in a mixture of mono- and disubstituted aryl products. Thus, the less direct, but high yield, route shown in eqs 1 and 2 was utilized.

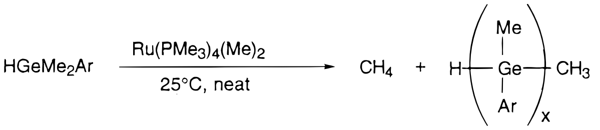
$$Me_2GeCl_2 + 2ArMgBr \xrightarrow[>95\%]{Et_2O} Me_2GeAr_2 \qquad \textbf{eq 1}$$

Ar = phenyl, *p*-tolyl, *p*-fluoro, *p*-trifluorotolyl, *m*-xylyl, *p*-anisyl

$$Me_2GeAr_2 \xrightarrow[70\text{-}93\%]{(1)\ 1.0\ HSO_3CF_3,\ neat \quad (2)\ LAH,\ Et_2O} \boxed{Me_2GeArH} \qquad \textbf{eq 2}$$

The diaryldimethylgermanes are prepared in >95% yield from dimethyldichlorogermane with excess Grignard reagent. These products are air- and water-stable and are easily isolated and purified. Selective cleavage of one aryl group with exactly 1 equiv of triflic acid[15] yields the aryldimethylgermyltriflate, which is not isolated but is reacted directly with LAH to provide the desired Me_2GeArH compound. The combined yield for these two steps is typically 70%−93%. The only monomer synthesis for which high yields were not obtained was the *meta*-xylyl derivative. Even when the mixture of Grignard reagent and dimethyldichlorogermane was refluxed for several hours, the yield of diaryldimethylgermane was only 62% and the combined yield for the triflic acid and reduction steps was only 56%. Mass spectrometry confirmed that a significant byproduct of the Grignard reaction was the coupling product, 3,3′,5,5′-tetramethylbiphenyl.

Demethanative Coupling of Me_2GeArH. Polymerization of the dimethylarylgermanes is accomplished by stirring ~1 mol % of $(PMe_3)_4RuMe_2$ in neat germane monomer at room temperature under a nitrogen atmosphere. We have previously shown that this ruthenium compound is a convenient and readily available precursor to the active catalytic species.[14] This precursor is easily prepared by the reaction of MeMgBr reagent with $(PMe_3)_4RuCl_2$, and although it is air- and water-sensitive, it is quite thermally stable. As shown in eq 3, the reaction



$$HGeMe_2Ar \xrightarrow[25°C,\ neat]{Ru(PMe_3)_4(Me)_2} CH_4 + H\!\left(\begin{array}{c} Me \\ | \\ Ge \\ | \\ Ar \end{array}\right)_{\!x}\!CH_3$$

Ar = Ph, *p*-tolyl, *p*-fluoro, *m*-xylyl, *p*-anisyl, *p*-trifluorotolyl

eq 3

proceeds with concurrent evolution of methane. Although the synthesis of poly(phenylmethylgermane) has been described in the literature,[2a,c,3c,4a,b,11,16] the substituted poly(arylmethylgermanes) reported herein have not been previously prepared. Preparations of polysilane analogues for all but the *m*-xylyl derivative are described in the literature, albeit in much lower yields.[17]

Table 1. Effect of Polymer Isolation Method on Molecular Weight

	methanol precipitation[a]				air workup[a]			
Ar−Ge	yield (%)	M_w	M_n	DP[b]	yield (%)	M_w	M_n	DP[b]
C_6H_5	52	7900	6500	40	68	6200	4300	25
p-C_6H_4F	51	10100	8800	48	82	5700	5000	27
p-$C_6H_4CH_3$	54	5500	4700	26	100	4600	3200	18

[a] Molecular weights determined by SEC/LS; values rounded to nearest 100 Da. [b] DP = M_n/(MW of repeat unit).

The polymers have been isolated from the catalyst by two different methods. During all manipulations, the polygermane products must be protected from room light to prevent photodecomposition because these materials are very light-sensitive, especially in the presence of oxygen. In the first separation method, the reaction mixture is dissolved in tetrahydrofuran, then stirred in air (protected from room light) for ca. 30 min, during which the ruthenium catalyst decomposes to a fine black precipitate. The solution is filtered through a column of Celite, and removal of the solvent leaves a gummy solid in nearly quantitative yield. The second method involves dissolving the reaction mixture in tetrahydrofuran, then precipitating the polymer with a large excess of methanol. Interestingly, the ruthenium species remains soluble, even after the polymer is precipitated in air. Polygermanes obtained by this method are white powdery materials that are not tacky. Yields from methanol precipitation are generally in the 50%−60% range and tend to have higher molecular weights, reflecting the partial fractionation of the polymer based on solubility. For purposes of comparison, three monomers were polymerized, then split into equal portions for isolation by the two methods. The data from these experiments are illustrated in Table 1.

The GPC chromatograms for air and methanol treatments of the phenyl polygermane are shown in Figure 1, revealing the

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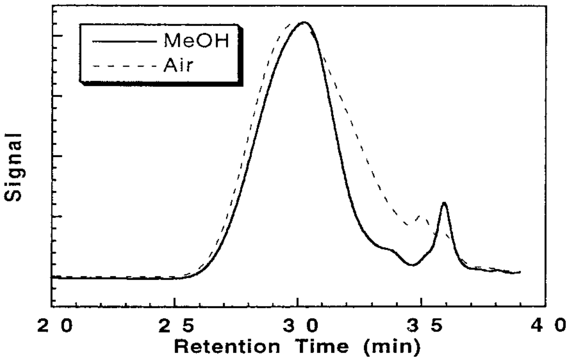

Figure 1. Influence of polymer isolation method on molecular weight distribution. Chromatograms of $(PhMeGe)_x$ purified by air workup (solid line) and polymer precipitated from THF/MeOH (dashed line).

Table 2. Effect of Time on MW and λ_{Max} for Poly(phenylmethylgermane) Polymerization

time	M_w[a]	M_n[a]	DP[b]	λ_{max}
1 h	5300	4000	24	326
1 day	6400	4900	30	328
1 week	6900	5100	31	330

[a] Air workup, molecular weights by SEC/LS; values rounded to nearest 100 Da. [b] DP = M_n/(MW of repeat unit).

Table 3. Details of Polymerization Reactions

Ar−Ge	mmol of monomer	mol % catalyst	reaction time[a]	yield[b] (%)
C_6H_5	5.53	0.7	5 weeks	52
p-C_6H_4F	1.49	0.9	2 weeks	51
p-$C_6H_4CF_3$	1.18	1.0	1 week	7[c]
p-$C_6H_4CH_3$	0.83	1.9	1 week	54
m-$C_6H_3(CH_3)_2$	1.54	1.0	1 week	61
p-$C_6H_4OCH_3$	0.90	1.0	2 weeks	19[d]

[a] Reactions performed at varied times showed similar results; see text. [b] Precipitated from tetrahydrofuran with methanol [c] Yield of air workup 44%. [d] Yield of air workup 95%.

decrease in the lower molecular weight fractions in material precipitated from methanol.

The influence of reaction time on polymer molecular weight and λ_{max} was investigated in the polymerization of dimethylphenylgermane. Aliquots were removed from the reaction mixture (1 mol % catalyst, 25 °C) after 1 h, 1 day, and 1 week. After 1 h, the aliquot was a viscous liquid with $M_w \sim 5300$, but after 1 day, the reaction mixture was a tacky solid exhibiting a 25% increase in M_w. Finally, only a modest gain of ~10% in M_w was observed in the material which was allowed to react for 1 week. Molecular weights (SEC/LS) and λ_{max} values (measured in THF solution) are shown in Table 2.

Typical polymerization data for all poly(arylmethylgermanes) are shown in Table 3. These experiments involve approximately 1 mol % of the ruthenium catalyst precursor and are allowed to proceed for 1−2 weeks before the polymers are precipitated with methanol. Note that the reaction times are unnecessarily long, as explained above, and similar results would be expected after only 1 day. The polymers exhibited ^{1}H NMR spectra consistent with the expected structures; methyl and aryl protons on the main chain showed broad resonances in the ranges δ 0.9 to −0.2 ppm and δ 7.8 to 6.3 ppm, respectively. A few very small sharper peaks rise slightly above the broad resonances. Tolyl protons exhibited a broad peak at δ 2.08, *m*-xylyl protons at δ 2.06, and anisyl protons at δ 3.32.

Polymers containing *p*-trifluorotolyl and *p*-anisyl substituents were obtained in significantly lower yield following precipitation with methanol, and a larger, lower molecular fraction remained in solution ($M_n < 1000$). It thus appears that either the coupling of these monomers is particularly sluggish or the catalyst lifetime is unusually short in these cases. Attempts to optimize the polymerization of these monomers is continuing.

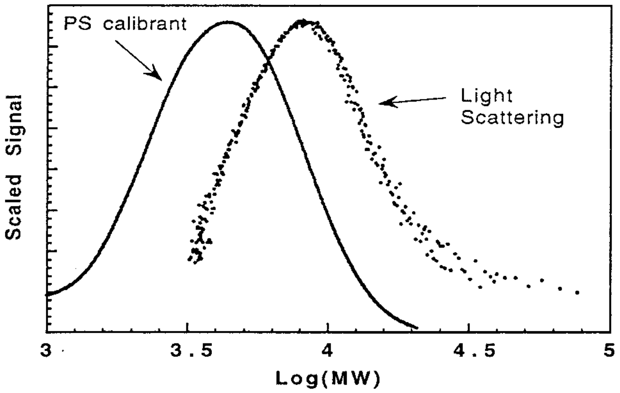

Figure 2. Comparison of GPC peaks determined by polystyrene and light scattering analyses. Solid line denotes molecular weight determined relative to polystyrene; dots indicate molecular weight measured by light scattering.

Molecular Weights Determined by Polystyrene and Light Scattering Methods. It has been reported that molecular weights for polysilanes as determined relative to polystyrene standards can differ by as much as a factor of 2−3 from more absolute values obtained with techniques such as light scattering[1a,18] and viscometry.[14] It is therefore useful to compare the molecular weights obtained relative to polystyrene with those measured using a multiangle light scattering detector. Static light scattering is an absolute characterization method allowing one to determine the molecular weight and size (root mean square radius) of a macromolecule without reference to an external standard.[19] The only property which must be known for each type of polymer to be studied is the refractive index increment with concentration, d*n*/d*c*. This value was measured for poly(phenylmethylgermane) in tetrahydrofuran to be 0.190 ± 3% mL/g[20] using standard procedures[21] and taken as constant for the other aryl derivatives. The degree of anisotropy of a macromolecule can also affect light scattering, but the polygermanes under consideration are sufficiently small ($M_w < 10\,000$) that isotropic scattering can be safely assumed.

Sample GPC traces are shown in Figure 2, incorporating molecular weights determined by light scattering and relative to polystyrene calibrant.

Molecular weights as determined by the two methods are tabulated in Table 4. For comparison, a sample of poly(phenylmethylgermane) prepared by Wurtz coupling is included. For all but the trifluorotolyl polymer, the conjugation lengths as determined by light scattering are significantly higher than those calculated relative to polystyrene. This may reflect a deviation in d*n*/d*c* for the fluorinated material. Ignoring the trifluorotolyl derivative, the average ratio PS/LS for M_w is 0.63 and 0.55 for M_n.

Electronic Properties. The absorption spectrum for each of the polymers was measured in dilute solution (1−2 mg/50

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Table 4. Molecular Weights of Poly(arylmethylgermanes) as Determined by GPC/LS and against Polystyrene Calibrant

Ar−Ge	$M_{w\ PS}$[a]	$M_{n\ PS}$	DP_{PS}[b]	$M_{w\ LS}$[a]	$M_{n\ LS}$	DP^{b}_{LS}	$M_{w\ PS}/M_{w\ LS}$	$M_{n\ PS}/M_{n\ LS}$
C_6H_5−Wurtz[c]	*6000*	*4300*	*26*	*8500*	*7100*	*43*	*0.70*	*0.61*
C_6H_5	5400	3600	22	7900	6500	40	0.69	0.54
p-C_6H_4F	6500	4900	27	10100	8800	48	0.65	0.56
p- $C_6H_4CF_3$	7000	6100	26	6900	6100	26	1.01	0.99
p-$C_6H_4CH_3$	3400	2700	15	5500	4700	26	0.62	0.58
m-$C_6H_3(CH_3)_2$	4200	3000	15	6000	4900	25	0.70	0.61
p-$C_6H_4OCH_3$	3000	2500	13	6000	5500	28	0.50	0.46

[a] "PS" denotes calibration against polystyrene; "LS" indicates determination of molecular weight by GPC/light scattering. [b] DP = M_n/(MW of repeat unit). [c] $(PhMeGe)_x$ prepared by reduction of $PhMeGeCl_2$ with sodium.

Table 5. Absorption Data for Substituted Poly(arylmethylgermanes)

Ar−Ge	DP (LS)	λ_{max} (nm)	ϵ/Ge−Ge (L mol^{-1} cm^{-1})
C_6H_5−Wurtz[a]	*43*	*332*	*5600*
C_6H_5	40	332	8000
p-C_6H_4F	48	336	5100
p-$C_6H_4CF_3$	26	332	3000
p-$C_6H_4CH_3$	26	326	7500
m-$C_6H_3(CH_3)_2$	25	330	7100
p-$C_6H_4OCH_3$	28	338	10100

[a] $(PhMeGe)_x$ prepared by reduction of $PhMeGeCl_2$ with sodium.

mL); λ_{max} values and corresponding extinction coefficients are listed in Table 5. Poly(arylmethylgermanes) as synthesized by demethanative coupling exhibit λ_{max} between 326 and 338 nm; there is no convincing trend in the effect of electron-donating or -withdrawing ability on λ_{max}.

The molecular weight and λ_{max} of poly(phenylmethylgermane) prepared by demethanative coupling are consistent with those of similar materials synthesized by Wurtz condensation as described in the literature[2a,c,3c,4a,11,16a] and as performed in our laboratory.

Mechanistic Considerations. We have previously proposed a mechanism for the demethanative coupling in which Ge−C bond cleavage and Ge−Ge bond formation are accomplished by sequential α-CH_3 and germyl to germylene migration steps.[14] This process is easily adapted for the polymerization of Me_2GeArH monomers, as illustrated in Scheme 1. Initially, reaction of $(PMe_3)_4RuMe_2$ is believed to yield $P_nRu(GeMe_2Ar)_2$ ($n = 3$ or 4) and CH_4. Although the active bis(germyl) complex is not directly observed in this case, $(PMe_3)_4Ru(GeMe_3)_2$, isolated from the analogous reaction with $GeMe_3H$, has been shown to be the active catalyst in the polymerization of Me_3GeH.[14]

Considering this proposed mechanism, it is possible that the aryl group, rather than the methyl group, migrates from the germanium to the ruthenium center. This migration might ultimately lead to the elimination of arene. However, in a study of the polymerization of Me_2GePhH, analysis by ^{1}H NMR and GC shows no evidence for benzene evolution during the course of the polymerization. In addition, ^{1}H NMR integrations indicate that the polymer contains equal numbers of phenyl and methyl groups. However, this observation does not rule out the possibility of a *reversible* α-aryl migration to ruthenium, but merely indicates that aryl-H reductive elimination does not ultimately occur. Investigation of the polymer microstructure is needed to determine whether there is redistribution of the aryl and methyl groups occurring along the polymer chain.

Polymer Microstructure. The mechanism of demethanative coupling allows for the possibility of either linear or branched chains, depending on whether the methyl group migrates from a group containing one or more Ge groups. Analysis of poly(dimethylgermane) synthesized by demethanative coupling has proven that the backbone is indeed branched. Qualitative evidence includes greater solubility compared with the linear analogue, as well as low intrinsic viscosity and small hydrodynamic diameter.[14] More recently, the degree of branching was quantitatively determined by digesting the polygermane with bromine, which cleaves all Ge−Ge bonds while leaving Ge−Me bonds intact. Analysis of the resulting monogermane fragments revealed that ~60% of the backbone is made up of the expected $-GeMe_2-$ units. The remaining 40% is equally distributed between $-GeMe-$ and $-GeMe_3-$ groups, the latter arising from redistribution or branching.[22] Unfortunately, it was not possible to utilize a similar method to digest the aryl polygermanes because bromine cleaves germanium−aryl bonds as well as Ge−Ge bonds. Iodine was found to be similarly unselective. In addition, the radii of the polymers are not large enough to permit accurate determination of branching by light scattering methods.

To qualitatively probe the issue of branching in the aryl-substituted polygermanes, the spectroscopic and electronic properties of poly(phenylmethylgermane) prepared by demethanative coupling were compared with those of the linear analogue, synthesized by Wurtz condensation of $MePhGeCl_2$. The molecular weights of the two polymers are comparable, (M_w = 7900 and 8500). The ^{1}H NMR spectra of the two polymers are very similar, and their absorption spectra nearly identical (Table 5). The tentative conclusion suggested by these data is that there is no significant branching in the aryl polygermanes as synthesized by demethanative coupling. Branching would be expected to broaden the absorption peak due to increased σ-conjugation in more than one direction.[23]

Conclusions

The method of demethanative coupling has been shown to be useful for the synthesis of a variety of substituted poly(arylmethylgermanes). These polymers exhibit the anticipated absorbance spectra associated with σ-conjugation. Polymers were characterized by GPC using both light scattering methods and polystyrene standards. Light scattering values were shown to be ca. 70% greater than those determined relative to polystyrene. Comparison of poly(phenylmethylgermane) prepared by demethanative coupling with a sample from a typical Wurtz condensation reveals that the two polymers are nearly identical in all respects.

Experimental Section

Materials and Procedures. All manipulations were carried out in dried glassware under a N_2 atmosphere in a drybox or using standard Schlenk and high vacuum line techniques. Solvents were dried over sodium benzophenone ketal and then refluxed and distilled under nitrogen prior to use. Benzene-d_6 was dried over Na/K alloy. Phenyl,

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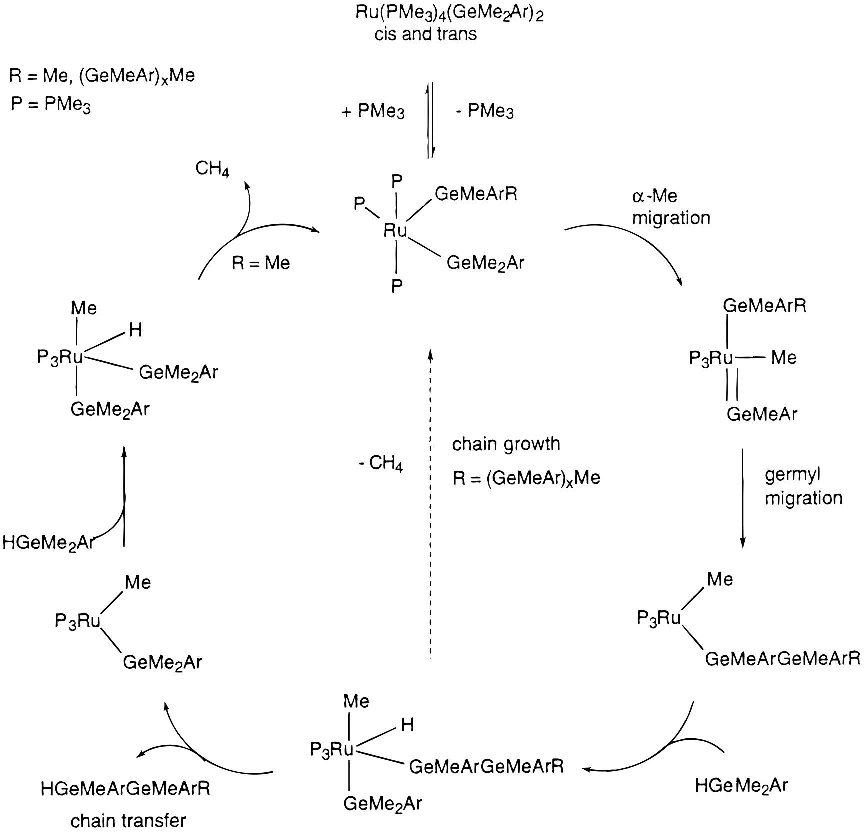
Scheme 1. Proposed Mechanism for Demethanative Coupling



p-tolyl, and *p*-fluorophenyl Grignard reagents were purchased from Aldrich. Bromoaryl compounds were purchased from Aldrich, then dried over calcium hydride before use and purity checked by NMR. Dimethyldichlorogermane was synthesized by the direct reaction of germanium metal with methyl chloride[24] and purified by spinning band distillation. The literature procedures for preparing $(PMe_3)_4RuMe_2$[25] from $(PMe_3)_4RuCl_2$ were followed. Wurtz coupling of $PhMeGeCl_2$ was performed as reported in the literature.[11]

Spectra. ^{1}H NMR spectra were obtained on a Bruker AC-200 spectrometer. NMR spectra were obtained at room temperature using benzene-d_6 as a solvent. Chemical shifts are reported relative to tetramethylsilane. Mass spectra were recorded on a VG ZAB-E spectrometer using CH_4 CI. Gas chromatography was performed on a Hewlett-Packard 5890A gas chromatograph equipped with a flame ionization detector. The column employed was an Alltech Econo-Cap capillary column (30 m length, 0.32 mm i.d., film 0.25 μm, packed with cross-linked poly(dimethylsiloxane)).

Absorption and Emission Spectroscopy. All measurements were performed in spectrophotometric-grade tetrahydrofuran in a fused quartz cell with a path length of 1 cm. Absorption spectra were measured using an HP8452A diode array spectrophotometer connected to a microcomputer. Analyses were performed on fresh solutions, and samples were protected from room light to prevent photodecomposition.

Gel Permeation Chromatography. Molecular weights were determined by gel permeation chromatography, using both polystyrene standards and by using an in-line light scattering detector in conjunction with an RI detector. The GPC-LS instrument consists of a Rainin HPXL solvent delivery system connected to a Shodex GPC KF-801 column and three Waters Ultrastyragel columns of pore size 500, 10^3, and 10^4 Å maintained at 40 °C. Three in-line detectors are connected in series: a Rainin Dynamax UV-1 absorbance detector, a Wyatt Optilab 903 interferometric refractometer, and a Wyatt Technology Corp. mini-DAWN multiangle light scattering detector with a 690-nm laser light source. Tetrahydrofuran used as the mobile phase was dried, filtered, and degassed in-line (Degasys DG-1210) prior to delivery to the GPC pump. During measurements, the flow rate was 1 mL/min. Polymer solutions were approximately 8−15 mg/mL in tetrahydrofuran; a loop size of 100 μL was employed, making each injection size 0.8−1.5 mg. The signals from the in-line detectors were sent to a Pentium microcomputer and analyzed using Astra 4.5 software from Wyatt Technology Corp. The d*n*/d*c* value (refractive index increment with concentration) was determined for poly(phenylmethylgermane) to be 0.190 mL/g in THF at 690 nm and 22 °C using DNDC software from Wyatt Technology Corp. and assumed to be constant for all aryl derivative polygermanes. Upon processing the data, a zero- or first-order line fit was chosen to best fit the data from the three light scattering detectors. Calculated experimental errors in M_w and M_n ranged from 2% to 10%.

Me_2GeArH Monomer Syntheses. For three of the monomers prepared (Ar = phenyl, *p*-tolyl, and *p*-fluoro), the diaryldimethylgermanes were synthesized from commercially available Grignard reagents and Me_2GeCl_2. For the remaining three derivatives (*p*-trifluorotolyl, *p*-anisyl, and *m*-xylyl), the Grignard reagents were prepared from the corresponding para-brominated arenes. A typical monomer synthesis is described below. Yields for the diaryldimethylgermanes ranged from 95 to 99%, except for the *m*-xylyl, for which the yield was 62%. Combined yields for the triflic acid and reduction steps were in the range of 70%−93%, except for the *m*-xylyl, which was 56%. Prior to polymerization, Me_2GeArH monomers were dried over sodium chips or molecular sieves.

Bis(4-trifluorotolyl)dimethylgermane. 4-Trifluorotolylmagnesiumbromide was prepared from 15.338 g (68.17 mmol) of *p*-bromotrifluorotoluene (Aldrich) in 35 mL of dry ether and 2.358 g (97.02 mmol) of Mg turnings. This solution was added using a double-tipped needle to a 0 °C solution of 4.42 g (25.47 mmol) of dimethyldichlorogermane in 8 mL of dry ether in a two-neck flask equipped with a gas inlet and rubber septum. The resulting dark red solution was allowed to stir for 1 h at 0 °C, then warmed to room temperature and stirred overnight. Methanol was added to kill the excess Grignard; the solution was then

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[24] Lee, M. E.; Bobbitt, K. L.; Lei, D.; Gaspar, P. P. *Synth. React. Inorg. Met.-Org. Chem.* **1990**, *20*, 77−81.

[25] Statler, J. A.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 1731−1738.

extracted with an aqueous NaCl solution. After washing the organic layer three times, it was dried over magnesium sulfate and filtered. Removal of the solvent in vacuo yielded a dark red oil, yield 99.4%. ^{1}H NMR (C_6D_6): δ 7.36 (d, 4H, aryl), 7.15 (d, 4H, aryl), 0.36 (s, 6H, GeCH_3).

(4-Trifluorotolyl)dimethylgermane. Triflic acid (2.0 mL, 22.60 mmol) was slowly added via a gastight syringe to 9.3769 g (23.87 mmol) of neat bis(4-trifluorotolyl)dimethylgermane in an ice bath. The solution immediately turned purple-black. The solution was warmed to room temperature after the addition, then stirred for 2 h. No further color change was observed. The volatiles were removed in vacuo to yield a dark gray solid, (4-trifluorotolyl)dimethylgermyltriflate. This compound (8.8 g, 22.2 mmol) was slowly added to a solution of 0.90 g (23.7 mmol) of lithium aluminum hydride in dry ether. The solution was degassed and stirred overnight, turning greenish-yellow in color. After the reaction mixture was immersed in an ice bath, a 10% aqueous ammonium chloride solution was added dropwise to kill the excess lithium aluminum hydride. The solution was then filtered to remove the salts and the filtrate was extracted with three portions of ammonium chloride solution. The bright yellow organic layer was separated and dried over magnesium sulfate. Filtration and removal of the volatiles in vacuo left a bright yellow liquid in 95% yield. ^{1}H NMR (C_6D_6): δ 7.37−7.33 (d, 2H, aryl), 7.19−7.15 (d, 2H, aryl), 4.53 (m, 1H, Ge-*H*), 0.21 (d, 6H, GeCH_3).

Polymerization Reactions. NMR-Tube Scale. Poly(*m*-xylylmethylgermane) is given as a representative reaction. In a sealed tube, 32 mg (0.153 mmol) *m*-xylyldimethylgermane was combined with 35 μL of a stock solution made up of 5 mg of $(PMe_3)_4RuMe_2$ in 200 μL of benzene-d_6 (2.0×10^{-3} mmol, 1.3 mol % catalyst). Hexamethylbenzene was added as an internal standard, and the reaction was monitored by ^{1}H NMR. After an induction period of 20 min, methane evolution could be detected, and within 2 h, the spectrum clearly indicated the presence of polymer peaks. After 9 h, monomer resonances could no longer be detected. The polymer was isolated by removal of the benzene, followed by stirring the mixture in tetrahydrofuran in air to decompose the ruthenium catalyst. Filtration of the solution through a column of Celite to remove the ruthenium and removal of the solvent in vacuo left a sticky solid. ^{1}H NMR (C_6D_6): δ 7.4−6.5 (Ar), 2.06 (Ar−CH_3), 0.8−0.1 (Ge−CH_3).

Bulk Polymerization Reactions. Poly(phenylmethylgermane) is given as a representative example. Phenyldimethylgermane (1.00 g, 5.53 mmol) was reacted with 0.017 g (0.039 mmol, 0.70 mol %) of $(PMe_3)_4RuMe_2$ in a Wheaton vial under nitrogen at room temperature. The colorless solution initially turned reddish-purple with vigorous bubbling, then turned yellow and solid within 12 h. No further visible change was observed. After ca. 4 weeks, the polymer was dissolved in tetrahydrofuran and split into two equal portions. Note that subsequent studies (vide supra) indicate that the majority of polymerization is complete after 1 day and that almost no change in molecular weight is observed after 7 days. One portion of the polymer solution was stirred in air for 2 h to decompose the catalyst and filtered through Celite, and the solvent was removed in vacuo to yield 0.309 g (68%) of a tacky white solid (GPC/LS: $M_w = 6200$, $M_n = 4300$.) Note that the yield in this specific case is lower than generally observed due to accidental loss of material during workup. The second portion of polymer solution was treated with methanol (ca. 40 volumes) under nitrogen. The precipitate was collected by filtration and dried under vacuum to yield 0.236 g (52%) of a white powder (GPC/LS: $M_w = 7900$, $M_n = 6500$.). ^{1}H NMR (C_6D_6): δ 7.6−6.7 (Ge−C_6H_5), 0.7−0.2 (Ge−CH_3). Additional, lower weight polymer can be obtained by removing solvents from the filtrate in vacuo.

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