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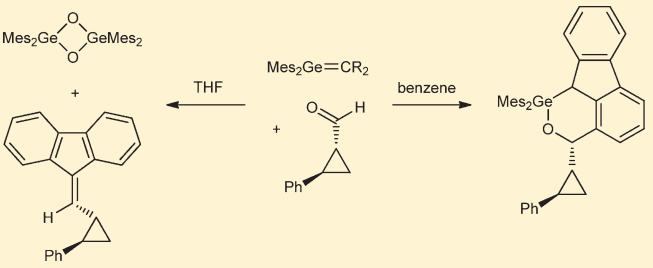
Addition of Aldehydes to Germenes: The Influence of Solvent

Christopher J. Allan, Crispin R. W. Reinhold, Laura C. Pavelka, and Kim M. Baines*

Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7

Supporting Information

ABSTRACT: The addition of *trans*-(2-phenylcyclopropyl)carboxaldehyde to dimesitylfluorenylidenegermane produced four diastereomers of a 1,2-oxagermin, **7a**−**d**, 2,2,4,4-tetramesityl-1,3-dioxadigermetane (**8**), and fluorenylidene(*trans*-2-phenylcyclopropyl)methane (**9**). The ratio of the products showed a strong dependence on the solvent: **7a**−**d** were formed almost exclusively when ether or benzene was used as the solvent for the reaction, whereas 1,3-dioxadigermetane **8** and alkene **9** were the major products formed in THF. A mechanism is proposed to account for the observations.



INTRODUCTION

Although the discovery of silenes[1−3] and germenes[4,5] took place over 40 years ago, the fundamental chemistry of these molecules remains an active area of interest,[6,7] as an understanding of their reactivity is critical for the development of potential applications of the chemistry (for example in organic synthesis[8] or in material sciences[9]). One of the most important reactions of the lighter group 14 metallenes ($R_2M{=}CR'_2$; M = Si, Ge) is the addition of carbonyl compounds. With nonenolizable, saturated ketones and aldehydes, metallaoxetanes (**1a**) are most often formed, although the four-membered ring often undergoes cleavage.[6,7] In contrast, the addition of unsaturated ketones and aldehydes usually leads to formal [4 + 2] adducts (**1b**), while ene adducts (**1c**) are often formed upon addition of ketones and aldehydes with an α-hydrogen (Scheme 1). The addition of the carbonyl compound to the metallene generally occurs cleanly in high yield, and thus, these reactions have been used extensively during the development of the chemistry of silenes and germenes to provide evidence for transient species.

We have utilized *trans*-(2-phenylcyclopropyl)carboxaldehyde (**2**) as a probe to examine the nature of any reactive intermediates that may form during the cycloaddition of aldehydes to a variety of group 14 (di)metallenes.[10−13] The probe is able to distinguish between biradical and cationic intermediates. Rapid and regioselective ring opening occurs upon the formation of an α-cyclopropyl radical (**2b**); in contrast, the analogous α-cyclopropyl cation (**2a**) does not rearrange (Scheme 2). The rate constant for the rearrangement of **2b** has been estimated to be greater than 2×10^{10} s^{-1}.[14−16] Thus, the isolation of ring-opened adducts of aldehyde **2** provides strong evidence for a biradical intermediate. The cyclopropyl ring would not be expected to open during a concerted cycloaddition, and thus, it is necessary to use other techniques to differentiate between a concerted reaction pathway and one involving a cationic intermediate.

Using this approach, we have found that the mechanistic pathway is highly dependent on the nature of the (di)metallene. For silenes, the addition of aldehydes to the naturally polarized neopentylsilene $Mes_2Si{=}CHCH_2t$-Bu proceeds via a zwitterionic intermediate.[13] In contrast, the addition of aldehydes to the relatively nonpolar Brook silene $(Me_3Si)_2Si{=}C(OSiMe_3)R$,[13] the nonpolar disilene $Mes_2Si{=}SiMes_2$,[10,11] or the relatively nonpolar germasilene $Mes_2Ge{=}SiMes_2$[10,11] proceeds by way of a biradical intermediate. The addition of the probe to the nonpolar digermene $Mes_2Ge{=}GeMes_2$, surprisingly, was found to proceed through a zwitterionic intermediate.[12] Although the mechanism of aldehyde addition has been investigated for many group 14 (di)metallenes, the mechanism of the addition of carbonyl compounds to germenes ($R_2Ge{=}CR_2$) has not yet been examined experimentally.

Mosey et al. have investigated the mechanism of formaldehyde addition to the parent (di)metallenes ($H_2M{=}EH_2$: M = Si, Ge; E = C, Si, Ge) using density functional theory.[17] In the addition of formaldehyde to the parent silene, disilene, germasilene, and digermene, the lowest energy reaction pathway found was the same as that determined through the experimental studies. In agreement with a previous computational study,[18] the addition of formaldehyde to germene followed a concerted reaction pathway; zwitterionic and biradical intermediates were not located as stationary points on the potential energy surface. The computational study did not consider the effect of substituents on the mechanism of the cycloaddition reaction. More recently, the addition of 1,4-benzoquinone to $H_2Ge{=}CH_2$[19] and the addition of α-ethylenic aldehydes and ketones to $HP{=}C{=}GeH_2$[20] have been examined using density functional computational methods. In each case, the one-step cycloaddition reaction of the carbonyl functionality to the germanium−carbon double bond was described

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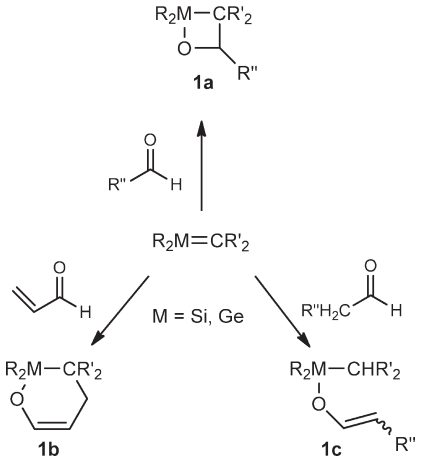
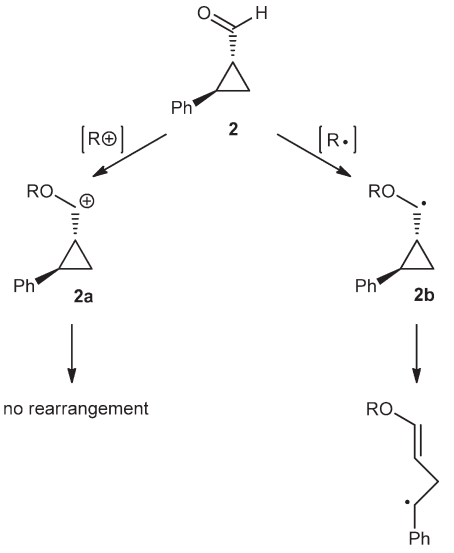
Scheme 1. Aldehyde Addition to a Metallene



Scheme 2. Reactivity of *trans*-(2-Phenylcyclopropyl)carboxaldehyde toward Radicals and Cations



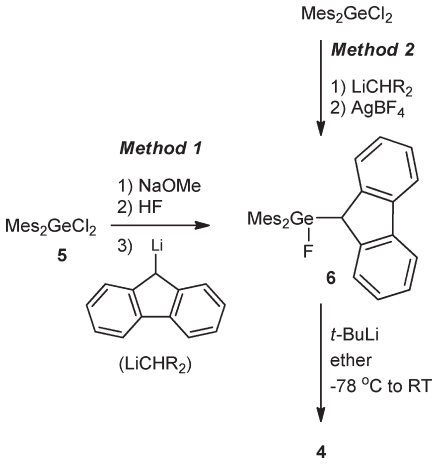
as being asynchronous, with Ge−O bond formation preceding C−C bond formation.

Herein, we now report on the addition of probe **2** to a stable germene to investigate the mechanism of this important reaction.[19−21] Two naturally polarized germenes were considered as substrates for this study: 1,1-dimesitylneopentylgermene[22] (**3**) and dimesitylfluorenylidenegermane (**4**).[5] Both germenes are stable in solution and can be readily synthesized. The addition of a number of aldehydes and ketones, including diketones and quinones, to germenes **3**[23] and **4**[19,21b,21d,21f,21g,24] has been reported. Given that the addition of carbonyl compounds to germene **3** often results in the formation of ene adducts,[23] germene **4** was chosen as the substrate for this study.

RESULTS AND DISCUSSION

Germene **4** was synthesized in four steps from dichlorodimesitylgermane, as outlined in Scheme 3 (method 1), with only minor modifications to the published procedure[5,25] (sodium methoxide

Scheme 3. Synthesis of Germene 4



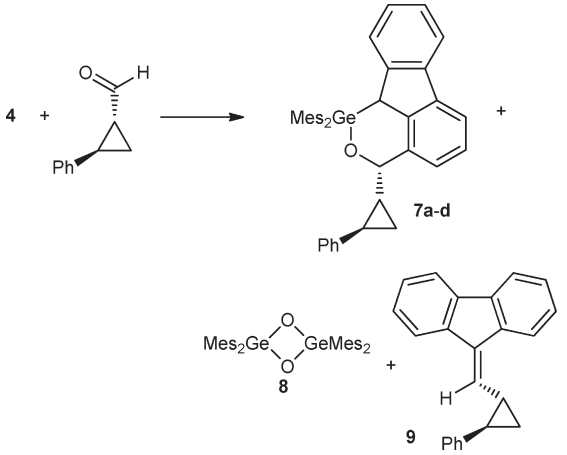
rather than methanol/triethylamine was used as the reagent in step 1). The purification of fluorofluorenyldimesitylgermane (**6**)[5] was problematic: sublimation of the crude product mixture was required to remove excess fluorene, followed by fluorination and subsequent chromatography of the residue to remove the hydrolysis byproducts of difluorodimesitylgermane. After purification, fluorogermane **6** was isolated in reasonable purity in 64% yield from Mes_2GeF_2 (41% yield from Mes_2GeCl_2). The yield of the fluorogermane **6** was greatly improved by the direct alkylation of Mes_2GeCl_2 with fluorenyllithium to give chlorofluorenyldimesitylgermane, which was isolated without an aqueous workup and readily purified by recrystallization. Treatment of the chlorogermane with $AgBF_4$ gave **6** in 75% yield (from Mes_2GeCl_2) after purification by chromatography (Scheme 3, method 2).

The NMR data of fluorogermane **6** clearly show the presence of the fluorine substituent: the signals assigned to the *o*-Me of the mesityl substituents in both the ^{13}C and the ^{1}H NMR spectra of **6** appear as doublets due to coupling to the fluorine. Furthermore, the signals assigned to the quaternary carbons of the fluorenyl substituent and the ipso carbon of the mesityl substituents in the ^{13}C NMR spectrum of the fluorogermane **6** are also doublets, again, due to coupling with the fluorine. The molecular structure of **6** was determined by X-ray crystallography; all bond lengths and angles fall within normal ranges (see Figure S1 in the Supporting Information).[26]

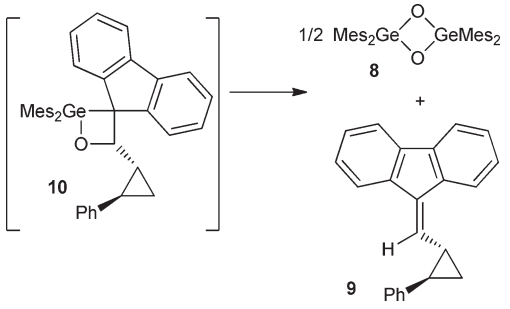
Treatment of fluorogermane **6** with 1 equiv of *t*-BuLi in diethyl ether gives germene **4** in quantitative yield by NMR spectroscopy. Accordingly, the signals in the ^{1}H and the ^{13}C NMR spectra of germene **4** in deuterated benzene show no evidence of coupling to fluorine and the ^{19}F NMR spectrum of the germene shows only a weak signal due to residual fluorogermane **6**.

The addition of *trans*-(2-phenylcyclopropyl)carboxaldehyde (**2**) to germene **4** yielded diastereomers **7a**−**d** and/or 2,2,4,4-tetramesityl-1,3-dioxadigermetane (**8**) and alkene **9**, depending on the solvent of the reaction (Scheme 4). Chromatographic separation of the crude product mixture allowed for the isolation of a mixture of diastereomers **7a**,**b**, diastereomer **7c**, diastereomer **7d**, and a mixture of 1,3-dioxadigermetane **8**[27] and alkene **9**. Diastereomers **7a**−**d** and **9** were identified by ^{1}H, gCOSY, $^{1}H-^{13}C$ gHMBC, and $^{1}H-^{13}C$ gHSQC NMR spectroscopy and mass spectrometry. Given the critical role the structures of the adducts play in the mechanistic interpretation, we include a

Scheme 4. Addition of Aldehyde 2 to Germene 4



Scheme 5. Conversion of Oxagermetane 10 to Dioxadigermetane 8 and Alkene 9



brief discussion of the salient features of the spectroscopic data that lead to the unequivocal identification of the products.

The spectral features of all diastereomers of **7** are similar, and thus, only the spectral identification of **7d** is presented here. The highest mass ion in the mass spectrum of **7d** was observed at m/z 622, which corresponds to a 1:1 adduct of the aldehyde and the germene. The ^{1}H NMR spectrum of diastereomer **7d** contained signals in three regions: 1.03−2.54, 4.26−4.79, and 6.29−7.76 ppm. The ^{1}H−^{1}H gCOSY NMR spectrum of diastereomer **7d** showed correlations between the ^{1}H signals at 2.2,[28] 1.67 (dddd), 1.28 (ddd), and 1.03 ppm (ddd). On the basis of the observed correlations, multiplicities, and chemical shifts of the signals, these signals were assigned to the ^{1}H nuclei of an intact cyclopropyl ring. Furthermore, on the basis of the magnitude of the coupling constants, the stereochemistry of the two substituents on the cyclopropyl ring was determined to be trans. A correlation between the ^{1}H signal at 4.79 ppm (d) and the ^{1}H signal at 1.67 ppm, assigned to a cyclopropyl ^{1}H, was also apparent. On the basis of the chemical shift of the signal at 4.79 ppm, the signal was assigned to the former aldehydic ^{1}H of the probe. Signals were also apparent in the ^{1}H NMR spectrum of **7d**, which were consistent with two nonequivalent mesityl substituents and a phenyl group. In addition, two separate spin systems were observed in the aromatic region of the ^{1}H NMR spectrum of **7d** at 7.76 (d), 7.58 (d), 7.24 (t), and 7.2 ppm[28] and at 7.70 (d), 7.50 (d), and 7.28 ppm (t). The signal at 4.26 ppm (s) showed correlations to the ^{13}C signals of both aromatic spin systems in the ^{1}H−^{13}C gHMBC spectrum of **7d** and, thus, is assigned to a doubly benzylic ^{1}H. Taken together, these data lead to the assignment of the structure shown in Scheme 4. Notably, the stereochemistry of the cyclopropyl rings was determined to be trans in each stereoisomer of **7** (see Figure S2 in the Supporting Information).

Attempted isolation of **9** by chromatography yielded a sample contaminated with 1,3-dioxadigermetane **8**.[29] Purification of **9** was achieved by fluorination of the dioxadigermetane, followed by chromatographic separation of the products. The highest mass ion in the mass spectrum of **9** was observed at m/z 294, corresponding to the molecular ion; notably, the isotopic pattern typical of germanium was absent. The ^{1}H−^{1}H gCOSY spectrum of the isolated compound showed a correlation between the signal at 6.11 ppm, assigned to a vinylic ^{1}H, and the signal at 2.54 ppm. The gCOSY spectrum also showed two aromatic spin systems that each integrated for 4H. These signals were assigned to a fluorenyl system. Total correlation spectroscopy (TOCSY) was performed on the sample. Irradiation of the signal at 6.11 ppm showed enhancement of the ^{1}H signals at 0.97, 1.29, 1.97, and 2.54 ppm. On the basis of the splitting patterns and chemical shifts, these signals were assigned to a 1,2-disubstituted cyclopropyl ring with a trans orientation of the substituents. All data are in agreement with the structure assigned to alkene **9**.

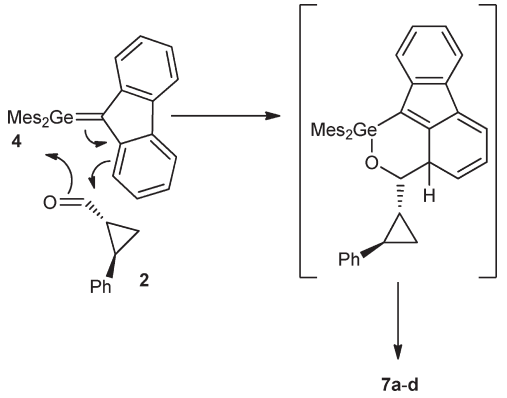
The solvent of the reaction greatly influences the product distribution (see Table 2 in the Experimental Section). When the aldehyde was added to the germene formed in situ in Et_2O, oxagermins **7a**−**d** were the major products (91% of the adducts). In contrast, when the reaction was carried out in THF under identical conditions, **8** and **9** were formed in quantitative yield.

To determine that germene **4** is the reactive species and not $Mes_2GeFCLiR_2$ (the immediate precursor to germene **4**; CR_2 = fluorenylidene), the germene was isolated and purified by trituration prior to the addition of the aldehyde. Addition of aldehyde **2** to the isolated germene **4** in benzene (a weakly coordinating solvent) gave almost exclusively oxagermins **7a**−**d**, whereas the addition of aldehyde **2** to the isolated germene **4** in THF gave **8** and **9** as the major products (77% of the adducts).

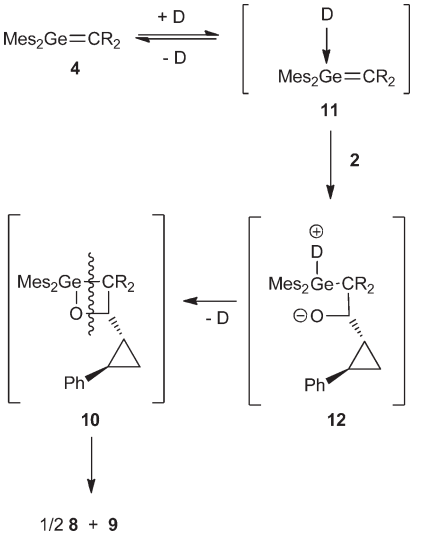
Alkene **9** is likely formed by the decomposition of the intermediate oxagermetane **10** (Scheme 5). Compound **9** was observed in the crude reaction mixture before exposure to air, moisture, or chromatography, and thus, it is probable that cycloadduct **10** spontaneously decomposes. The isolation of 1,3-dioxadigermetane **8** provides further evidence for the formation of the intermediate oxagermetane.

The absence of products derived from ring opening of the cyclopropyl substituent of the aldehyde demonstrates that no radical developed at the cyclopropyl carbinyl position during the formation of **7a**−**d** or oxagermetane **10** (or the subsequent cleavage of **10** to give **8** and **9**). The absence of a cyclopropyl carbinyl radical is further evidenced by the formation of only four diastereomers of oxagermin **7**; if the cyclopropyl ring were to open during the reaction, scrambling of the stereochemistry of the cyclopropyl substituents would be expected to produce up to eight diastereomers (see Figure S2 in the Supporting Information). These results, together with the results of the computational studies which indicate the absence of any intermediates,[17−20] suggest that the addition of aldehyde **2** to germene **4** partitions between two pathways: a concerted [4 + 2] cycloaddition followed by a hydrogen transfer to give **7a**−**d** and a concerted [2 + 2] pathway to give **10**. However, it is difficult to reconcile the dramatic influence of the solvent on the product distribution if all products are derived from (at least initially)

Scheme 6. Proposed Mechanism for the Formation of 7a−d



Scheme 7. Proposed Mechanism for the Formation of 8 and 9



concerted reaction pathways. Thus, we propose that the two types of products (**7a−d** and **8**/**9**) are derived from two different species. We believe that the formation of diastereomers **7a−d** occurs by way of a concerted [4 + 2] cycloaddition between germene **4** and aldehyde **2**, where the aldehyde acts as the dienophile and the germene as the diene, followed by a hydrogen transfer (Scheme 6). The reaction is completely regioselective, presumably due to the formation of the energetically favorable Ge−O bond and the polarities of the C═O and the Ge═C bonds. Alternatively, *nucleophilic* addition of a donor complex of the germene (**11**) to aldehyde **2** gives oxagermetane **10** (perhaps via the zwitterion **12**), which spontaneously decomposes to **8** and **9** (Scheme 7).

There are two plausible candidates for donors: the solvent molecules and/or fluoride ion. Both THF and diethyl ether have been reported to form adducts with germene **4**;[5a] coordination with the solvent would increase the nucleophilicity of the germenic carbon. In support of this hypothesis, the relative amount of **9** increases with increasing donor abilities of the solvents: THF > Et_2O ≫ benzene.[30,31] On the other hand, the molecular structures of the proposed THF or Et_2O adducts of germene **4** were not determined;[5a] the crystals isolated by Couret et al. may have been solvates of the germene rather than discrete complexes. Furthermore, we did not observe the formation of solvates/donor complexes of germene **4**. Despite an earlier report which stated that $Ph_2Ge{=}CH_2$ may complex weakly with THF,[32] Leigh reported that the λ_{max} values of the UV/vis spectra of bis(*p*-trifluoromethylphenyl)germene[21c] and a germahexatriene[21e] (microsecond lifetimes) are unaffected upon varying the solvent from hexanes to THF. Thus, the evidence for the complexation of germene **4** by solvent is somewhat ambiguous.

One equivalent of LiF is formed during the synthesis of **4**.[33] The solubility of LiF in THF or benzene is known (0.09 mM and 0.011 mM, respectively);[34] however, the solubility of LiF in diethyl ether has not been reported to our knowledge. Et_2O is comparable in polarity to benzene but is a much better donor.[30] Possibly, the different solubilities of LiF in THF and in Et_2O account for the different results observed when the germene is generated and used in situ in either THF or Et_2O. The addition of a few milligrams of LiF and aldehyde **2** to the isolated germene **4** redissolved in THF did result in a small increase in the amount of alkene **9** relative to oxagermins **7a−d**; however, a significant increase in the amount of hydrolysis products was also observed under these conditions and it is difficult to separate the influence of added LiF from that of adventitious water. Given that the relative amount of **9** correlates to the donor ability of the solvent and the fact that we observe the formation of **8**/**9** in THF after attempts to remove fluoride, we favor a solvent-donor complex of germene **4** as the reactive species; however, we cannot rule out that fluoride may catalyze the reaction.

Although solvent effects are common in many areas of chemistry, our results represent a rare example of where the solvent dramatically influences the product distribution of a reaction of a (di)metallene. In 1996, Ishikawa noted that donor solvents (THF, CH_3CN) influenced the diastereoselectivity of the products derived from the addition of acetone to a silatriene.[35] The authors attributed the effect to coordination of the solvents to the silene. In 2006, Oehme reported that the product ratios of the aldehyde adducts of an intramolecularly stabilized silene vary on changing the solvent from heptane to THF; however, they concluded that this was not the result of a change in mechanism, but rather a consequence of the stabilization of the proposed zwitterionic intermediates by solvent.[36]

Interestingly, in no other study of the reactivity of germene **4** toward carbonyl compounds[19,21b,21d,21f,21g,24] did the germene act as the 4π component in a cycloaddition reaction with the carbonyl group. With our results, a direct comparison can be made between the addition of germene **4** to two different aldehydes: benzaldehyde and *trans*-(2-phenylcyclopropyl)carboxaldehyde (**2**). Both reactions were carried out in diethyl ether. When PhCHO was added to germene **4**, a stable [2 + 2] adduct was isolated,[24a] and when **2** was added, a product derived from [4 + 2] cyclization was obtained (i.e., **7a−d**) with the germene acting as the diene. Furthermore, the [2 + 2] adduct between germene **4** and aldehyde **2** (**10**) does not appear to be stable. Perhaps there are favorable interactions between the aromatic aldehyde and the fluorenyl substituent in the transition state of the addition of PhCHO to **4**, which leads to the [2 + 2] cycloadduct. A detailed understanding of the factors influencing the different modes of addition between carbonyl compounds and germene **4** requires more study.

In summary, the addition of *trans*-(2-phenylcyclopropyl)-carboxaldehyde (**2**) to dimesitylfluorenylidenegermane (**4**) yields both six-membered and four-membered rings. In both instances,

the probe **2** did not rearrange, and thus, a biradical intermediate can be ruled out. We favor a two-step reaction pathway, a [4 + 2] cycloaddition followed by a hydrogen transfer, for the formation of the oxagermins on the basis of the results of a computational study of a similar reaction.[37] The solvent of the reaction dramatically influences the outcome of the reaction: in diethyl ether or benzene, oxagermins **7a**−**d** are the major products, whereas in THF, **8** and **9** are the major products observed. The change in product distribution can be readily understood in terms of the different coordination abilities of the solvents. THF strongly coordinates to the Ge of the germene; the complex then acts as a nucleophile toward the aldehyde, which ultimately results in the formation of dioxadigermetane **8** and alkene **9**. Ether does not coordinate as strongly, and hence, less alkene is formed during reactions in ether. Benzene does not coordinate, and accordingly, oxagermins **7a**−**d** are formed in quantitative yield. We acknowledge that the methods used to remove fluoride from the reaction mixture may not have been sufficient and fluoride may be the catalyst in the reaction. The results presented here illustrate, for the first time, the dramatic effect that the solvent and/or a donor can play on the outcome of the reactions of germenes.

EXPERIMENTAL SECTION

All experiments were carried out in flame-dried glassware under an atmosphere of argon using a Schlenk line or in a nitrogen-filled glovebox. All solvents were dried by passing through an alumina column and purged with nitrogen, with the exception of solvents used for chromatographic separations. NMR spectra were recorded on an Inova 400 or 600 MHz spectrometer. ^{1}H NMR spectra are referenced to C_6D_5H at 7.15 ppm, ^{13}C NMR spectra are referenced to C_6D_6 at 128.00 ppm and CF_3Ph as an external standard (−63.9 ppm against $CFCl_3$) for ^{19}F NMR spectra. *trans*-(2-Phenylcyclopropyl)carboxylic acid was reduced with lithium aluminum hydride in diethyl ether to give the corresponding alcohol,[38] which was subsequently oxidized using Swern conditions to *trans*-(2-phenylcyclopropyl)carboxaldehyde.[39]

Synthesis of Chlorofluorenyldimesitylgermane. A solution of fluorene (1.31 g, 7.9 mmol) dissolved in THF (25 mL) was cooled to −78 °C. *t*-BuLi (5.2 mL, 1.5 M in pentane, 7.9 mmol) was added slowly to the solution, which became bright orange. After the mixture was stirred for 1.5 h, a solution of dichlorodimesitylgermane (3.0 g, 7.9 mmol) dissolved in THF (25 mL) was added slowly to the reaction mixture. The solution was stirred for 3 h at −78 °C and then warmed to room temperature and stirred overnight. The solvent was removed in vacuo; hexanes were added to the residue to give a suspension. The solids were removed by filtration, and the solvent was removed in vacuo to give a residue which was recrystallized from hexanes to yield a colorless solid (3.5 g, 6.8 mmol, 87%). Mp: 202−204 °C. ^{1}H NMR (C_6D_6): δ 7.75 (br d, 1H, fluorenyl, J_{HH} = 7.6 Hz), 7.69 (d, 1H, fluorenyl, J_{HH} = 7.6 Hz), 7.20 (tt, 1H, fluorenyl, J_{HH} = 7.6, 0.9 Hz), 7.02 (dt, 1H, fluorenyl, J_{HH} = 1.0, 7.6 Hz), 6.58 (s, 4H, Mes H), 5.00 (s, 1H, GeCH), 2.12 (s, 12H, Mes *o*-CH_3), 1.97 (s, 6H, Mes *p*-CH_3). ^{13}C NMR (C_6D_6): δ 143.84 (fluorenyl C), 142.99 (Mes *o*-C), 142.05 (fluorenyl C), 139.87 (Mes *p*-C), 136.02 (Mes *i*-C), 130.04 (Mes CH), 127.76 (fluorenyl CH), 126.99 (fluorenyl CH), 125.20 (fluorenyl CH), 120.07 (fluorenyl CH), 48.49 (GeCH), 24.12 (Mes *o*-CH_3), 20.86 (Mes *p*-CH_3). High-resolution EI-MS for $C_{31}H_{31}{}^{70}Ge^{35}Cl$ (M^+): *m*/*z* calcd 508.1357, found 508.1336. Anal. Calcd for $C_{31}H_{31}GeCl$: C, 72.77; H, 6.11. Found: C, 71.38; H, 6.00.

Synthesis of Fluorofluorenyldimesitylgermane (6). $AgBF_4$ (240 mg, 1.23 mmol) was added to a solution of chlorofluorenyldimesitylgermane (154 mg, 0.30 mmol) dissolved in DCM (10 mL) to give a heterogeneous mixture. After the mixture was stirred for 1 h at room temperature, the solids were removed by decantation and the solvent was removed in vacuo. The residue was purified by preparative thin-layer chromatography (SiO_2, $CHCl_3$) to give a colorless solid (128 mg, 0.26 mmol, 86%) identified as fluorogermane **6**. The spectral data agreed well with the published values[5a] (^{1}H NMR chemical shifts, ±0.05 ppm; ^{19}F NMR chemical shifts, ±2.5 ppm). ^{13}C NMR (C_6D_6): δ 143.59 (d, fluorenyl C, J_{CF} = 2.3 Hz), 143.30 (Mes *o*-C), 141.96 (d, fluorenyl C, J_{CF} = 0.9 Hz), 140.12 (Mes *p*-C), 134.21 (d, Mes *i*-C, J_{CF} = 9.9 Hz), 129.60 (Mes CH), 127.19 (fluorenyl CH), 126.79 (fluorenyl CH), 124.88 (d, fluorenyl CH, J_{CF} = 1.8 Hz), 120.14 (fluorenyl CH), 46.71 (d, fluorenyl CH, J_{CF} = 12.8 Hz), 23.09 (d, Mes *o*-CH_3, J_{CF} = 4.1 Hz), 20.95 (Mes *p*-CH_3).

A translucent colorless blocklike crystal of $C_{31}H_{31}FGe$, approximate dimensions 0.07 mm × 0.08 mm × 0.11 mm, was used for X-ray crystallographic analysis. Data were collected at low temperature (−123 °C) on a Bruker Apex II CCD X-ray diffractometer (Mo Kα radiation, λ = 0.710 73 Å, 50 kV/30 mA). The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97.[40] Data were corrected for absorption effects using the multiscan method (SADABS). The crystallographic parameters are given in Table 1.

Table 1. Crystallographic Parameters for 6

empirical formula	$C_{31}H_{31}GeF$
formula wt	496.15
cryst syst	monoclinic
space group	$P1_21/n1$
a (Å)	8.8747(12)
b (Å)	9.2127(11)
c (Å)	30.870(4)
α (deg)	90
β (deg)	90.004(7)
γ (deg)	90
V (Å^3)	2523.9(5)
Z	4
no. of data/restraints/params	6018/0/304
goodness of fit	1.014
R ($I > 2\sigma(I)$)	0.0480
wR2 (all data)	0.0978
largest diff peak, hole (e Å^{-3})	0.445, −0.457

Typical Procedure for the Synthesis of Germene 4. Fluorogermane **6** (45 mg, 0.09 mmol) was dissolved in diethyl ether (10 mL); the solution was cooled in a dry ice/acetone bath. *tert*-Butyllithium (0.05 mL, 1.7 M in pentane, 0.09 mmol) was added slowly, and then the solution was warmed to room temperature. During this time, the clear solution changed from yellow to dark orange. After 1 h at room temperature, the ether was removed in vacuo. The residue was triturated with C_6D_6 and then centrifuged. The supernatant was analyzed by ^{1}H NMR spectroscopy and was found to contain germene **4** (88%), $[Mes_2Ge(fluorenyl)]_2O$[24a] (9%), residual fluorogermane **6** (3%), and traces of $Mes_2GeH(fluorenyl)$[5a] (<1%). No evidence for the Et_2O adduct of the germene was observed.[5a] ^{1}H NMR[5a] (C_6D_6): δ 7.88 (dt, 1H, fluorenyl, J_{HH} = 7.4, 0.9 Hz), 7.74 (dt, 1H, fluorenyl, J_{HH} = 7.6, 0.8 Hz), 7.19 (td, 1H, fluorenyl, J_{HH} = 7.4, 1.0 Hz), 7.10 (td, 1H, fluorenyl, J_{HH} = 7.4, 1.1 Hz), 6.73 (s, 4H, Mes H), 2.39 (s, 12H, Mes *o*-CH_3), 2.06 (s, 6H, Mes *p*-CH_3). ^{13}C NMR (C_6D_6): δ 143.45 (fluorenyl C), 143.12 (Mes *o*-C), 141.03 (Mes *p*-C), 136.53 (Mes *i*-C), 135.78 (fluorenyl C), 133.56 (Ge=C), 129.14 (Mes CH), 126.12 (fluorenyl CH), 124.16 (fluorenyl CH), 121.23 (fluorenyl CH), 120.02 (fluorenyl CH), 24.01 (Mes *o*-CH_3), 21.19 (Mes *p*-CH_3). ^{19}F NMR (C_6D_6): δ no significant signals observed; −173 (residual **6**).

Table 2. Relative Ratios of Products[a] Obtained under Varying Conditions

method	solvent	7a,b	7c	7d	9
A	Et_2O	58	19	14	9
A	THF	0	0	0	100
B	benzene	50	25	24	1
B	THF	10	7	6	77

[a] The ratios are an average of two to five runs, and values vary typically by ±3%, except for method B (THF), where greater variability was noted.

Procedures for the Addition of *trans*-(2-Phenylcyclopropyl)carboxaldehyde (2) to Dimesitylfluorenylidenegermane (4). *Method A.* Fluorogermane **6** (100 mg, 0.2 mmol) was dissolved in diethyl ether (or THF) (3 mL); the solution was cooled in a dry ice/acetone bath. *tert*-Butyllithium (0.1 mL, 1.7 M in pentane, 0.19 mmol) was added slowly. The solution was warmed to room temperature. During this time, the clear solution changed from yellow to dark orange. *trans*-(2-Phenylcyclopropyl)carboxaldehyde (29 mg, 0.2 mmol) dissolved in ether (or THF) (1 mL) was added slowly. The mixture was stirred for 1 h, during which time the solution decolorized. The solvent was removed in vacuo and the residue analyzed by ^{1}H NMR spectroscopy. Product ratios, as determined by ^{1}H NMR spectroscopy, are given in Table 2. The products were purified by preparative thin-layer chromatography on silica gel using hexanes/dichloromethane as the eluent (50:50 ratio for reactions done in ether and 70:30 for reactions done in THF). The bands were removed from the plate and suspended in dichloromethane. The solid was removed by filtration, and the solvent was removed under vacuum.[41,42] Dioxadigermetane **8**[29] and alkene **9** were isolated as a mixture from the reaction in THF. The mixture was dissolved in THF (20 mL). HF (48%; 1 mL) was added to the solution, which was then stirred for 1 h. The reaction was quenched with sodium sulfate. The solids were removed by filtration and washed with hexanes. After removal of the solvents, the residue was passed through a silica plug. If necessary, the residue was purified by preparative thin-layer chromatography (silica gel; 70:30 hexanes/dichloromethane) to give alkene **9**.

Method B. A solution of germene **4** was prepared using the typical procedure (see above). A benzene solution of *trans*-(2-phenylcyclopropyl)carboxaldehyde (1 equiv) was added to the germene. After the mixture was stirred for 1 h, the solvent was removed under vacuum and the residue was analyzed by ^{1}H NMR spectroscopy. Alternatively, the solvent (C_6D_6) was removed in vacuo from the solution of germene **4**, prepared using the typical procedure (see above). The residue was then dissolved in THF, and *trans*-(2-phenylcyclopropyl)carboxaldehyde (1 equiv), also dissolved in THF, was added to the solution. Because of the numerous manipulations of the germene, $[Mes_2Ge(fluorenyl)]_2O$[24a] and/or $Mes_2Ge(OH)(fluorenyl)$[5a] were often present as byproducts in varying amounts in the product mixtures produced. The presence of the hydrolysis products did not significantly influence the ratios of **7a**−**d** and **9**.

7a,b: pale yellow oil, 50:50 mixture of two diastereomers; ^{1}H NMR (C_6D_6) δ 7.75 (d, 1H, fluorenyl, J_{HH} = 7.2 Hz), 7.74 (d, 1H, fluorenyl, J_{HH} = 7.8 Hz), 7.64 (d, 1H, fluorenyl, J_{HH} = 7.8 Hz), 7.60 (d, 1H, fluorenyl, J_{HH} = 7.2 Hz), 7.52 (d, 1H, fluorenyl, J_{HH} = 7.8 Hz), 7.51 (d, 1H, fluorenyl, J_{HH} = 7.2 Hz), 7.23 (t, 3H, fluorenyl, J_{HH} = 7.5 Hz), 7.18 (t, 2H, fluorenyl, J_{HH} = 7.2 Hz), 6.94−7.15 (fluorenyl, phenyl), 6.79 (s, 2H, Mes H), 6.73 (s, 2H, Mes H), 6.40 (s, 2H, Mes H), 6.39 (s, 2H, Mes H), 4.89 (d, 1H, OCH, J_{HH} = 6.0 Hz), 4.64 (s, 1H, GeCH), 4.63 (d, 1H, J_{HH} = 7.8 Hz, OCH), 4.59 (s, 1H, GeCH), 2.59 (br s, 6H, Mes *o*-CH_3), 2.51 (br s, 6H, Mes *o*-CH_3), 2.21 (ddd, 1H, cyclopropyl, J_{HH} = 4.8, 4.8, 9.0 Hz), 2.13 (s, 3H, Mes *p*-CH_3), 2.11 (s, 3H, Mes *p*-CH_3), 2.09 (ddd, 1H, cyclopropyl, J_{HH} = 4.8, 4.8, 9.0 Hz), 1.88 (br s, 12H, Mes *o*-CH_3), 1.83 (s, 3H, Mes *p*-CH_3), 1.82 (s, 3H, Mes *p*-CH_3), 1.74−1.78 (m, 1H, cyclopropyl), 1.61−1.66 (m, 1H, cyclopropyl), 1.27 (ddd, 1H, cyclopropyl, J_{HH} = 4.8, 5.4, 8.4 Hz), 1.06 (ddd, 1H, cyclopropyl, J_{HH} = 4.2, 4.2, 9.6 Hz), 0.93 (ddd, 1H, cyclopropyl, J_{HH} = 4.8, 4.8, 9.6 Hz), 0.90 (ddd, 1H, cyclopropyl, 4.8, 4.8, 9.0 Hz); ^{13}C NMR (C_6D_6) δ 144.46 (fluorenyl C), 143.45 (phenyl), 143.41 (phenyl), 143.22 (Mes *o*-C), 143.13 (Mes *o*-C), 142.86 (Mes *o*-C), 142.79 (Mes *o*-C), 141.95 (fluorenyl C), 141.90 (fluorenyl C), 141.55 (fluorenyl C), 141.54 (fluorenyl C), 139.71 (fluorenyl C), 139.54 (fluorenyl C), 139.37 (Mes *p*-C), 139.32 (Mes *p*-C), 139.18 (fluorenyl C), 139.09 (Mes *p*-C), 139.06 (Mes *p*-C), 135.21 (Mes *i*-C), 135.03 (Mes *i*-C), 134.43 (Mes *i*-C), 134.20 (Mes *i*-C), 129.87 (Mes CH), 129.82 (Mes CH), 129.02 (Mes CH), 128.99 (Mes CH), 128.53 (phenyl), 128.51 (phenyl), 126.90 (fluorenyl CH), 126.86 (fluorenyl CH), 126.79 (fluorenyl CH), 126.71 (fluorenyl CH), 126.63 (phenyl), 126.44 (phenyl), 125.63 (fluorenyl CH), 125.56 (fluorenyl CH), 124.79 (fluorenyl CH), 124.73 (fluorenyl CH), 124.51 (fluorenyl CH), 124.44 (fluorenyl CH), 120.65 (fluorenyl CH), 118.55 (fluorenyl CH), 118.47 (fluorenyl CH), 79.95 (OCH), 78.11 (OCH), 44.15 (GeCH), 43.91 (GeCH), 32.27 (cyclopropyl), 31.94 (cyclopropyl), 23.95 (Mes *o*-CH_3), 23.84 (Mes *o*-CH_3), 22.43 (Mes *o*-CH_3), 22.31 (Mes *o*-CH_3), 22.10 (cyclopropyl), 21.59 (cyclopropyl), 21.05 (Mes *p*-CH_3), 20.74 (Mes *p*-CH_3), 14.00 (cyclopropyl), 13.32 (cyclopropyl); high-resolution EI-MS for $C_{41}H_{40}{}^{74}GeO$ (M^+) *m*/*z* calcd 622.2300, found 622.2311.

7c: pale yellow oil, contaminated with starting material; ^{1}H NMR (C_6D_6) δ 7.75 (d, 1H, fluorenyl, J_{HH} = 7.8 Hz), 7.63 (d, 1H, fluorenyl, J_{HH} = 7.2 Hz), 7.59 (d, 1H, fluorenyl, J_{HH} = 7.2 Hz), 7.46 (d, 1H, fluorenyl, J_{HH} = 7.2 Hz), 7.24 (t, 1H, fluorenyl, J_{HH} = 7.5 Hz), 7.2[28] (fluorenyl), 7.08−7.06 (m, 1H, phenyl), 7.03−7.00 (m, 2H, phenyl), 6.84 (s, 2H, Mes H), 6.36 (s, 2H, Mes H), 4.62 (d, 1H, OCH, J_{HH} = 7.8 Hz), 4.26 (s, 1H, GeCH), 2.56 (s, 6H, Mes *o*-CH_3), 2.17 (s, 3H, Mes *p*-CH_3), 2.04 (m, 1H, cyclopropyl), 1.87 (s, 6H, Mes *o*-CH_3), 1.82 (s, 3H, Mes *p*-CH_3), 1.79−1.75 (m, 1H, cyclopropyl), 1.22 (ddd, 1H, cyclopropyl, J_{HH} = 4.8, 4.8, 9.6 Hz), 1.04 (ddd, 1H, cyclopropyl, J_{HH} = 4.8, 4.8, 9.0 Hz); ^{13}C NMR (C_6D_6) δ 144.40 (fluorenyl C), 143.29 (phenyl), 142.61 (fluorenyl C), 142.52 (Mes *o*-C), 142.27 (Mes *o*-C), 141.24 (fluorenyl C), 140.26 (fluorenyl C), 140.03 (fluorenyl C), 139.24 (Mes *p*-C), 138.92 (Mes *p*-C), 137.50 (Mes *i*-C), 136.30 (Mes *i*-C), 129.88 (Mes CH), 128.86 (Mes CH), 128.73 (phenyl), 126.91 (fluorenyl CH), 126.75 (fluorenyl CH), 126.49 (fluorenyl CH), 126.12 (phenyl), 125.80 (phenyl), 124.72 (fluorenyl CH), 123.46 (fluorenyl CH), 120.87 (fluorenyl CH), 119.09 (fluorenyl CH), 76.02 (OCH), 42.93 (GeCH), 24.05 (Mes *o*-CH_3), 23.09 (Mes *o*-CH_3), 22.98 (cyclopropyl), 21.57 (cyclopropyl), 21.08 (Mes *p*-CH_3), 20.72 (Mes *p*-CH_3), 14.75 (cyclopropyl); high-resolution EI-MS for $C_{41}H_{40}{}^{74}GeO$ (M^+) *m*/*z* calcd 622.2300, found 622.2287.

7d: pale yellow oil, contaminated; ^{1}H NMR (C_6D_6) δ 7.76 (d, 1H, fluorenyl, J_{HH} = 7.2 Hz), 7.70 (d, 1H, fluorenyl, J_{HH} = 7.8 Hz), 7.58 (d, 1H, fluorenyl, J_{HH} = 7.8 Hz), 7.50 (d, 1H, fluorenyl, J_{HH} = 7.2 Hz), 7.28 (t, 1H, fluorenyl, J_{HH} = 7.8 Hz), 7.24 (t, 1H, fluorenyl, J_{HH} = 7.8 Hz), 7.2[28] (fluorenyl), 7.0−7.2 (m, phenyl), 6.82 (s, 2H, Mes H), 6.29 (s, 2H, Mes H), 4.79 (d, 1H, J_{HH} = 6.0 Hz, OCH), 4.26 (s, 1H, GeCH), 2.54 (s, 6H, Mes *o*-CH_3), 2.2[28] (m, 1H, cyclopropyl), 2.16 (s, 3H, Mes *p*-CH_3), 1.80 (s, 9H, Mes *p*- and *o*-CH_3), 1.67 (dddd, 1H, cyclopropyl, J_{HH} = 5.7, 5.7, 5.7, 9.0 Hz), 1.28 (ddd, 1H, cyclopropyl, J_{HH} = 4.8, 4.8, 9.0 Hz), 1.03 (ddd, 1H, cyclopropyl, J_{HH} = 4.8, 4.8, 9.0 Hz); ^{13}C NMR (C_6D_6) δ 144.07 (fluorenyl C), 143.36 (phenyl), 142.22 (fluorenyl C), 142.19 (Mes *o*-C), 141.89 (Mes *o*-C), 141.07 (fluorenyl C), 140.00 (fluorenyl C), 139.86 (fluorenyl C), 138.86 (Mes *p*-C), 138.49 (Mes *p*-C), 136.97 (Mes *i*-C), 135.63 (Mes *i*-C), 129.50 (Mes CH), 128.55 (Mes CH), 126.44 (fluorenyl CH), 126.41 (fluorenyl CH), 126.15, 126.13 (fluorenyl CH, phenyl), 125.28 (phenyl), 124.34 (fluorenyl CH), 123.17 (fluorenyl CH), 120.51 (fluorenyl CH), 118.71 (fluorenyl CH), 74.57 (OCH), 42.62 (GeCH), 27.51 (cyclopropyl), 23.71 (Mes *o*-CH_3), 22.52 (Mes *o*-CH_3),

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20.71 (Mes *p*-CH_3), 20.35, 20.32 (cyclopropyl, Mes *p*-CH_3), 13.12 (cyclopropyl CH_2); high-resolution EI-MS for $C_{41}H_{40}{}^{74}GeO$ (M^+) *m*/*z* calcd 622.2300, found 622.2299.

9: yellow solid; mp 107−113 °C; ^{1}H NMR (C_6D_6) δ 7.90 (d, 1H fluorenyl, J_{HH} = 8 Hz), 7.58−7.57 (m, 2H, fluorenyl), 7.53−7.52 (m, 1H, fluorenyl), 7.23−7.18 (m, 2H, fluorenyl), 7.14−7.12 (m, 3H, fluorenyl, Ph *m*-CH), 7.06−7.00 (m, 2H, fluorenyl, Ph *p*-CH), 6.98−6.96 (m, 2H, Ph *o*-CH), 6.11 (d, 1H, vinyl, J_{HH} = 9.6 Hz), 2.54 (dddd, 1H, cyclopropyl CHR, J_{HH} = 4.2, 5.4, 9.0, 9.0 Hz), 1.97 (ddd, 1H, cyclopropyl CHPh, J_{HH} = 4.2, 6.0, 10 Hz), 1.29 (ddd, 1H, cyclopropyl CH_2, J_{HH} = 4.8, 6.0, 8.4 Hz), 0.97 (ddd, 1H, cyclopropyl CH_2, J_{HH} = 4.2, 4.2, 10 Hz); ^{13}C NMR (C_6D_6) δ 141.74 (*i*-Ph), 141.07 (fluorenyl C), 139.77 (fluorenyl C), 138.84 (fluorenyl C), 137.93 (fluorenyl C), 135.89 (*C*═CH), 132.81 (C═CH), 128.79 (Ph *m*-CH), 127.92 (fluorenyl CH), 127.66 (fluorenyl CH), 127.21 (fluorenyl CH), 127.02 (fluorenyl CH), 126.31 (Ph *p*-CH), 126.29 (Ph *o*-CH), 124.78 (fluorenyl CH), 120.13 (fluorenyl CH), 119.93 (fluorenyl CH), 119.89 (fluorenyl CH), 27.65 (cyclopropyl), 25.08 (cyclopropyl), 18.90 (cyclopropyl); IR (cm^{-1}) 3060 (w), 3028 (w), 2922 (w), 2851 (w), 1644 (m), 1603 (m), 1495 (w), 1447 (m), 1183 (w), 1030 (w), 935 (w), 773 (m), 728 (s), 696 (m); high-resolution EI-MS for $C_{23}H_{18}$ (M^+) *m*/*z* calcd 294.1409, found 294.1411.

$[Mes_2Ge(fluorenyl)]_2O$:[24a] ^{1}H NMR (C_6D_6) δ 7.91−8.44 (br s, 2H), 7.77 (br d, 2H), 7.24 (br s, 2H), 6.97 (br s, 2H), 5.48−6.43 (br s, 4H), 5.38 (s, 1H), 3.02−3.69 (br s, 3H), 1.03−2.62 (br s, 16H); low-resolution ESI-MS *m*/*z* 991 ($M + Na^+$), 661 ($M - 2$ fluorenyl $+ Na^+$).

■ ASSOCIATED CONTENT

Supporting Information. CIF files giving crystallographic data for **6** and figures giving a thermal ellipsoid plot of **6**, the stereoisomers of **7**, and ^{1}H NMR spectra of **7a**−**d** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: kbaines2@uwo.ca.

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