Intermediates in the Catalytic Dehydrogenative Coupling of Arylgermanes

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Abstract: The use of a new electron-withdrawing germane, $H_2Ge[3,5\text{-}(CF_3)_2C_6H_3]_2$ (**3**), has facilitated the isolation and characterization of three new complexes implicated in the dehydrogenative coupling of bisarylgermanes by Pt^0–phosphane complexes. The intermediates include a digermyl species, *trans*-$[(Et_3P)_2Pt\{GeH(Ar)_2\}_2]$ (**7**), a bound digermane showing the first stage of Ge–Ge catenation, *cis*-$[(Et_3P)_2Pt(H)\{Ge(Ar)_2\text{-}GeH(Ar)_2\}]$ (**8**), and the Ge–H activated form of this product, $[(Et_3P)_2HPtGe(Ar)_2\text{-}Ge(Ar)_2PtH(PEt_3)_2]$ (**6**). Complexes such as **6** and **8** have not previously been isolated as intermediates in dehydrogenative coupling reactions. An X-ray crystal structure was determined for complex **6**, confirming the *cis* geometry of the hydrogen and germanium ligands; this provides yet another example of the stability of germyl hydrides towards reductive elimination. A similar *cis* geometry was observed for complex **8**. Performing the dehydrogenative coupling reaction under a CO_2 atmosphere failed to yield any products containing trapped germylene species.

Keywords
dehydrogenative coupling · germanium · platinum · reaction mechanisms · structure elucidation

Introduction

Dehydrocoupling reactions of silanes and germanes have attracted considerable attention in recent years owing to an increased interest in silicon and germanium backbone polymers.[1–3] Interesting conduction, photoconduction, and thermochromic properties have spurred further investigations of the materials and encouraged efforts to control macromolecular properties, such as molecular weight and polydispersity. Significant progress has been achieved in the areas of new catalyst development and understanding of the mechanisms involved. Key breakthroughs include the development of Cp_2M (M = Ti, Zr)-derived catalysts that greatly enhance the degree of polymerization possible,[4, 5] and the recent discovery of a Ru-based demethanative coupling catalyst.[6] Progress has also been made towards understanding the mechanism of the platinum- and palladium-based oligomerization catalysts. However, important aspects of the reaction have remained elusive, including the role of silylene or germylene complexes in the formation of the E–E bond (E = Si, Ge).[7]

Recently, we observed the reversible reaction of the dihydrogermane $H_2Ge[N(SiMe_3)_2]_2$ with $(Et_3P)_2Pt(CO)_2$ to give *cis*-$[(Et_3P)_2Pt(H)Ge(H)\{N(SiMe_3)_2\}_2]$ (**1**) and then $[(Et_3P)_2PtGe\{N(SiMe_3)_2\}_2]$ (**2**) in a stepwise conversion with loss of CO and H_2.[8] The observation of a stable η^1-germylene complex in the dehydrogenative reaction of a germane demonstrates that germylene formation accompanied by loss of H_2 is a feasible step in the dehydrogenative coupling of germanes. In this case, the steric bulk of the germane prevented oligomerization. In order to probe the role of germylenes in the dehydrocoupling reaction, we decided to utilize the stable germylene complex **2** as a precatalyst, and to add a less sterically bulky bisarylgermane as the substrate.

The electronic character of the ligands on the germanium were expected to play a major role in determining the stability of the metal–germylene species and should have interesting effects on the physical properties of the germane oligomer as well. It was hoped that the presence of electron-withdrawing groups would strengthen the π-interaction between the filled Pt d orbitals and the empty germanium p orbitals. In addition, the Si and Ge polymers tend to have relatively low oxidation potentials,[9] and the introduction of electron-withdrawing groups could help to stabilize the polymers. Trifluoromethyl groups were chosen to functionalize the phenyl rings because they were expected to yield hydrocarbon-soluble complexes and polymers. Halogenated functional groups, although very desirable as part of a polymer, are problematic in the monomer because they can be sensitive to the Wurtz coupling conditions[10] as well as to the dehydrogenative coupling catalysts based on Group 4 transition metals.[11]

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Experimental Section

All procedures utilized air-free techniques and dry, de-oxygenated solvents.[12] $GeBr_4$ was prepared by the method of Curtis and Wolber.[13] 3,5-bis(trifluoromethyl)bromobenzene was used as received from Aldrich. Complex **2** was synthesized according to the literature procedure.[8a] ^{1}H (360 MHz) and ^{13}C NMR (90.6 MHz) spectra were recorded in C_6D_6 and shifts referenced to the residual protons of C_6D_6 at $\delta = 7.15$ and the natural abundance ^{13}C in C_6D_6 at $\delta = 128.0$, respectively. ^{31}P shifts are reported against 85% H_3PO_4 in D_2O. IR spectra were recorded on a Nicolet 5DXB spectrometer.

$H_2Ge[3,5\text{-}(CF_3)_2C_6H_3]_2$ (3): A $LiAlH_4$ pellet (0.361 g, 9.48 mmol) was dissolved in ether (30 mL) by stirring at RT for 2 h; a slight gray residue remained. The $LiAlH_4$ solution was cooled to −78 °C and a solution of $[3,5\text{-}(CF_3)_2C_6H_3]_2GeBr_2$ (7.50 g, 11.4 mmol) in ether (15 mL) was added slowly by syringe. The mixture was allowed to warm to ambient temperature and stirred for an additional 30 minutes. Ether was removed in vacuo leaving a gray-white solid which was extracted with warm hexane (2 × 40 mL). The extracts were combined and the solvent was removed to give a white solid. Vacuum sublimation at 65–70 °C gave 4.81 g (84%) of fur-like, air-stable, white crystals. ^{1}H NMR (C_6D_6): $\delta = 4.59$ (s, 2H, GeH), 7.55 (s, 4H, *o-CH*), 7.70 (s, 2H, *p-CH*); ^{13}C NMR (C_6D_6): $\delta = 135.90$ (s, *i*-C), 134.88 (m, *m-CH*), 131.79 [q, *C*-CF_3, ^2J(F,C) = 33.2 Hz], 123.67 [heptet, *p-CH*, ^3J(F,C) = 3.6 Hz], 123.76 [q, *C*F_3, ^1J(F,C) = 273.1 Hz]; ^{19}F NMR (C_6D_6): $\delta = -62.81$ (s, CF_3); IR (Nujol/NaCl): $\tilde{\nu} = 2086$ cm^{-1} (Ge–H).

$Br_3Ge[3,5\text{-}(CF_3)_2C_6H_3]$ (4): 3,5-Bis(trifluoromethyl)bromobenzene (22.8 mL, 0.132 mol) was added in 3 portions to Mg turnings (3.35 g, 0.138 mol) suspended in ether (100 mL) at 0 °C. The resulting dark brown-red mixture was added slowly by cannula over a period of 1 h to a solution of $GeBr_4$ (49.24 g, 0.1255 mol) in ether (150 mL) at 0 °C. The reaction mixture was then allowed to warm to 20 °C and stirred for 12 h. Ether was removed in vacuo and the solid residue was extracted with hexane (2 × 100 mL). The solids were allowed to settle and the extract removed with a syringe. Removal of hexane in vacuo left a crude liquid product. Vacuum distillation (65 °C, 10^{-3} Torr) gave a colorless liquid. Yield: 48.37 g (73%); ^{1}H NMR (C_6D_6): $\delta = 7.61$ (s, 2H, *o*-CH), 7.87 (s, 1H, *para*-CH); ^{13}C NMR (C_6D_6): $\delta = 123.0$ [q, *C*F_3, ^1J(F,C) = 273.5 Hz], 126.4 [heptet, *p-CH*, ^3J(F,C) = 3.7 Hz], 131.02 (m, *m-CH*), 132.65 [q, *C*–CF_3, ^2J(F,C) = 34.0 Hz], 139.54 (s, *i*-C); ^{19}F NMR (C_6D_6): $\delta = -63.062$ (s, CF_3).

$Br_2Ge[3,5\text{-}(CF_3)_2C_6H_3]_2$ (5): 3,5-Bis(trifluoromethyl)bromobenzene (6.90 mL, 0.040 mol) was added in 2 portions to Mg turnings (0.971 g) suspended in ether (60 mL) at 0 °C. The resulting Grignard reagent was added slowly to a solution of $3,5\text{-}(CF_3)_2C_6H_3GeBr_3$ (20.04 g, 0.038 mol) in ether (50 mL) at 0 °C. Within 30 minutes, a precipitate appeared; the dark red-brown mixture was stirred for 12 h at 20 °C. The ether was removed in vacuo and the resulting mixture of liquid and solid extracted with warm hexane (2 × 50 mL). The extracts were combined and evaporated to give a viscous brown oil. Vacuum distillation (88–90 °C, 10^{-3} Torr) gave 9.57 g of a colorless oil (38%). ^{1}H NMR (C_6D_6): $\delta = 7.53$ (s, 2H, *p*-CH), 7.82 (s, 4H, *o*-CH); ^{13}C NMR (C_6D_6): $\delta = 123.18$ [q, *C*F_3, ^1J(F,C) = 273.5 Hz], 126.11 [heptet, *p-CH*, ^3J(F,C) = 3.6 Hz], 132.58 (m, *m-CH*), 132.92 [q, *C*-CF_3, ^2J(F,C), 33.9 Hz], 137.04 (s, *i*-C). A small amount (< 5%) of an unidentified impurity was also present, probably $[3,5\text{-}(CF_3)_2C_6H_3]_3GeBr$. It does not yield a volatile hydrogenation product which makes separation convenient following hydrogenation.

$[(Et_3P)_2HPtGe(Ar)_2Ge(Ar)_2PtH(PEt_3)_2]$ (6): $[(Et_3P)_2PtGe\{N(SiMe_3)_2\}_2]$ (**2**) (203 mg, 0.25 mmol) was heated to 40 °C in benzene (15 mL) in the presence of $H_2Ge(Ar)_2$ (123 mg, 0.25 mmol). An initially formed white precipitate redissolved over a 4 h period at which time all volatiles were removed in vacuo. The resulting white solid was recrystallized from ether to afford **6** (52 mg, 23%). ^{1}H NMR ([D$_8$]THF): $\delta = -4.67$ [dd w/Pt satellites, 2H, ^2J(P,H) = 159 Hz, ^2J(P,H) = 16.5 Hz, ^1J(Pt,H) = 767 Hz], 0.74 (m, 18H, CH_2CH_3), 0.95 (m, 18H, CH_2CH_3), 1.34 (m, 12H, CH_2CH_3), 1.79 (m, 12H, CH_2CH_3), 7.75 (s, 4H, *p*-CH), 8.01 (s, 8H, *o*-CH); ^{13}C NMR ([D$_8$]THF): $\delta = 137.0$ (m), 130.40 [q, *C*-CF_3, ^2J(F,C) = 32.2 Hz], 125.12 [q, *C*F_3, ^1J(F,C) = 272.7 Hz], 121.0 (m), 22.53 (m, CH_2CH_3), 19.14 (m, CH_2CH_3), 8.78 (m, CH_2CH_3); ^{31}P NMR (C_6D_6): $\delta = 18.54$ [dd with Pt satellites, ^1J(Pt,P) = 2270 Hz, ^2J(P,P) = 13 Hz] 13.88 [dd with Pt satellites, ^1J(Pt,P) = 2220 Hz, ^2J(P,P) = 16 Hz]; IR (Nujol/NaCl): $\tilde{\nu} = 2052$ cm^{-1} (Pt–H); MS (CH_4, CI): *m/z* = 931 with an isotope pattern consistent with the molecular formula $C_{56}H_{74}Ge_2P_4Pt_2$. We were unable to detect the *ipso*-carbon in either [D$_6$]benzene or [D$_8$]THF.

Crystal structure analysis of 6:[15] Space group $P2_1/c$, $a = 1186.3(2)$, $b = 1575.2(2)$, $c = 2001.3(2)$ pm, $\beta = 102.12(1)°$, $V = 3.6564(9)$ nm^3, $Z = 2$, $\mu(Mo_{K\alpha}) = 1.147$ mm^{-1}. 9186 reflections measured, $2\theta_{max} = 52°$, $T = 178$ K, empirical absorption correction (XABS2), 7176 unique reflections, refined in full-matrix on F^2. All non-hydrogen atoms anisotropic, H atoms in idealized positions. $R1 = 0.028$, $wR^2 = 0.056$ ($I > 2\sigma I$); $R1 = 0.046$, $wR^2 = 0.058$ (all data).

$trans\text{-}[(Et_3P)_2Pt\{GeH(Ar)_2\}_2]$ (7): A benzene solution (3 mL) of $[(Et_3P)_2PtGe\{N(SiMe_3)_2\}_2]$ (**2**) (150 mg, 0.182 mmol) and $H_2Ge(Ar)_2$ (182 mg, 0.364 mmol) was stirred at 20 °C for 2.5 h. Dissolution of the starting materials was followed by evolution of gas and rapid formation of a white precipitate. The volume of the solution was reduced by half and filtered to give **7** as a white powder (163 mg, 63%). ^{1}H NMR ([D$_8$]THF): $\delta = 8.14$ (s, 8H, *o*-CH), 8.02 (s, 4H, *p*-CH), 5.25 [t with Pt satellites, 2H, Ge–H, ^3J(P,H) = 10.3 Hz, ^2J(Pt,H) = 74 Hz], 2.00 (m, 12H, CH_2CH_3), 0.88 (m, 18H, CH_2CH_3); IR: $\tilde{\nu} = 1961$ cm^{-1} (Ge–H); MS (FAB, Xe) *m/z* = 1432 [*M* − 1]; $C_{44}H_{44}F_{24}Ge_2P_2Pt$: calcd C 36.9, H 3.1; found C 35.1, H 3.03.

$cis\text{-}[(Et_3P)_2Pt(H)\{Ge(Ar)_2GeH(Ar)_2\}]$ (8): $trans\text{-}[(Et_3P)_2Pt\{GeH(Ar)_2\}_2]$ (**7**) (150 mg, 0.121 mmol) was heated to 75 °C in benzene (90 mL) in a 100 mL round-bottom flask in under Ar for 2 h to yield a colorless solution. All volatiles were removed in vacuo. The resulting white solids were dissolved in hexane, filtered, and recrystallized to give a white powdery solid (35mg, 23%). ^{1}H NMR (C_6D_6) $\delta = 8.11$ (s, 4H, *o*-CH), 7.89 (s, 4H, *o*-CH), 7.75 (s, 2H, *p*-CH), 7.73 (s, 2H, *p*-CH), 5.54 (m with Pt satellites, 1H, Ge–H, ^2J(Pt,H) = 55 Hz], 1.38 (m, 6H, CH_2CH_3), 0.99 (m, 6H, CH_2CH_3), 0.75 (m, 9H, CH_2CH_3), 0.49 (m, 9H, CH_2CH_3), −4.74 [dd with Pt satellites, Pt–H, ^1J(Pt,H) = 760 Hz, ^2J(P,H) = 17.3 and 157.5 Hz]; ^{13}C NMR (C_6D_6): $\delta = 150.35$ (s, *i-C*), 142.02 (s, *i-C*), 135.92 (m, *m-CH*), 135.19 (m, *m-CH*), 131.50 [q, *C*-CF_3, ^2J(F,C) = 32.8 Hz], 131.20 [q, *C*-CF_3, ^2J(F,C) = 32.6 Hz], 124.10 [q, *C*F_3, ^1J(F,C) = 273.0 Hz], 123.90 [q, *C*F_3, ^1J(F,C) = 272.9 Hz], 122.63 (m, *p-CH*), 121.91 (m, *p-CH*), 21.76 (m, CH_2CH_3), 18.66 (m, CH_2CH_3), 8.31 (m, CH_2CH_3); ^{31}P NMR (C_6D_6): $\delta = 18.45$ [^1J(Pt,P) = 2462 Hz], 13.14 [^1J(Pt,P) = 2189 Hz]; $C_{44}H_{44}F_{24}Ge_2P_2Pt$: calcd C 36.9, H 3.1; found C 37.0, H 3.04.

$[3,5\text{-}(CF_3)_2C_6H_3]_2(H)GeGe(H)[3,5\text{-}(CF_3)_2C_6H_3]_2$ (9): A mixture of **3** (500 mg) and **2** (50 mg, 6 mol%) dissolved in benzene was refluxed for 60 h. All volatiles were removed in vacuo and the solid washed with pentane (5 mL) to afford **9**. Yield: 65%. ^{1}H NMR (C_6D_6): $\delta = 7.66$ (s, 4H, *p*-CH), 7.52 (s, 8H, *o*-CH), 4.91 (s, 2H, Ge–H); ^{13}C NMR ([D$_8$]THF): $\delta = 138.27$ (s, i-*C*), 136.33 (s, o-*C*), 132.61 [q, ^2J(C,F) = 33 Hz, m-*C*), 124.51 [q, ^1J(C,F) = 273 Hz, *C*F_3), 124.83 (s, *p-C*); MS(FAB, Xe) *m/z* = 1000 [*M* + 1]; $C_{32}H_{14}F_{24}Ge_2$: calcd C 38.45, H 1.41; found C 37.69, H 1.72

Results and Discussion

$H_2Ge[3,5\text{-}(CF_3)_2C_6H_3]_2$ (**3**) was synthesized from $GeBr_4$ by the general method of Tabern et al.[14] An ethereal solution of the aryl Grignard was added to $GeBr_4$ to afford $Br_3Ge[3,5\text{-}(CF_3)_2C_6H_3]$ (**4**). Repeating this procedure on the isolated tribromide gave $Br_2Ge[3,5\text{-}(CF_3)_2C_6H_3]_2$ (**5**), which was isolated and then reduced by $LiAlH_4$ to give the desired bisarylgermane **3**.

The reaction of one equivalent of **3** with $[(Et_3P)_2PtGe\{N(SiMe_3)_2\}_2]$ (**2**) at 40 °C in benzene resulted in the initial formation of a white, crystalline precipitate. After 4 h at 40 °C, a new set of inequivalent PEt_3 multiplets appeared at $\delta = 1.43$, 1.00, 0.80, and 0.53. They are associated with two new aryl singlets at $\delta = 7.83$ and 8.28. The spectroscopic data suggest a *cis* square-planar geometry for the platinum complex; however, we were perplexed at the absence of Ge–H features in the IR or NMR spectra for a complex that otherwise appeared similar to **1**. Single crystals of the product were grown from diethyl ether at −10 °C and the X-ray structure of $[(Et_3P)_2HPtGe(Ar)_2Ge(Ar)_2PtH(PEt_3)_2]$ (**6**) was determined (Figure 1; Ar = 3,5-$(CF_3)_2C_6H_3$).[15] The most striking feature is the presence of two platinum centers in the *cis* geometry on each end of the nascent organogermane oligomer. Distortion of the square-planar geometry of the platinum center is observed, consistent with the steric requirements of the ligands. Bond lengths are as expected from consideration of the covalent radii, with the exception of the Pt–Ge bond length of 2.4363(5) Å.[16]

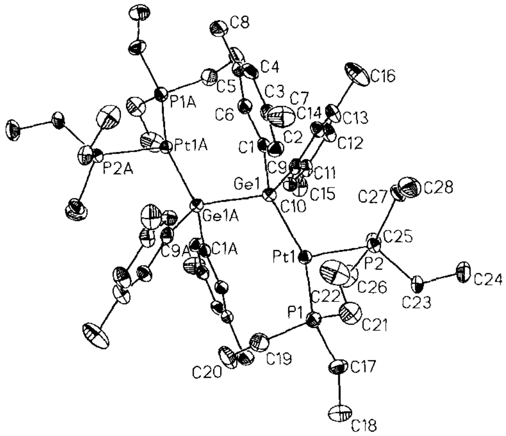
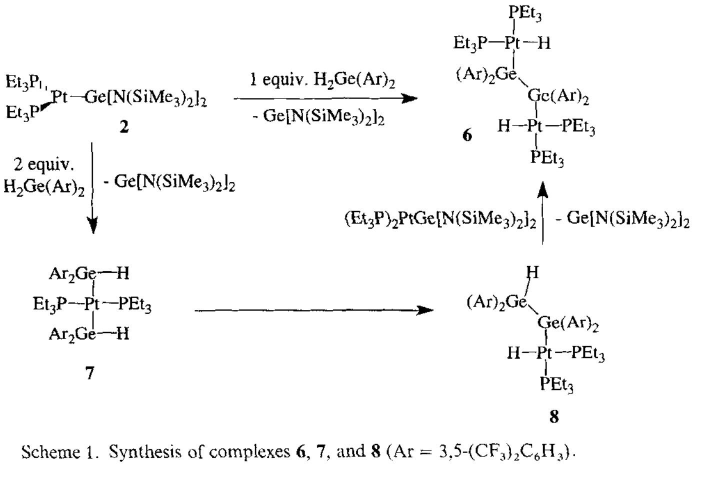


Figure 1. X-ray crystal structure of $[(Et_3P)_2HPtGe(Ar)_2Ge(Ar)_2PtH(PEt_3)_2]$ (**6**). Selected bond lengths (Å) and angles (°): Pt–Ge, 2.4363(5); Pt–P1, 2.2904(12); Pt–P2, 2.3131(12); Ge–Ge, 2.4663(10); Ge–C1, 1.9994(4); Ge–C9, 2.003(4); P1-Pt-Ge, 158.97(3); P2-Pt-Ge, 97.41(3); P1-Pt-P2, 103.49(4); Pt-Ge-Ge, 116.86; C1-Ge-C9, 102.1(2); C1-Ge-Pt, 109.73(13); C9-Ge-Pt, 121.85(12); C1-Ge-Ge, 103.17(13); C9-Ge-Ge, 100.73(14).

Formation of **6**, as well as the continued growth of the oligomer, is possible by a Curtis–Epstein type[1, 17] or germylene-containing mechanisms.[1, 18] In order to gain clues to the mechanism of the dehydrogenation and oligomerization steps, the identity of intermediate species was pursued. The initially formed white precipitate was identified as **7** (Scheme 1) on the basis of IR, MS, NMR, and elemental analysis. This complex could be isolated in a 63% yield by adjusting the reaction conditions to the more appropriate 2:1 stoichiometry of germane:Pt complex. Compound **7** did not dissolve in benzene at ambient temperature; however, heating 150 mg in 90 mL of benzene at 75 °C for 2 h yielded **8** (Scheme 1). It is interesting to note that complex **8** does not undergo facile irreversible reductive elimination or β-elimination reactions, unlike the related alkyl complexes.[19] The reaction of **8** with one equivalent of **2** afforded **6**. These results confirm that **7** and **8** are intermediates in the formation of **6**.



Scheme 1. Synthesis of complexes **6**, **7**, and **8** (Ar = 3,5-$(CF_3)_2C_6H_3$).

The two complexes characterized on route to **6**, as well as the isolation of **6** itself, provide new evidence regarding the possible intermediate species involved in dehydrogenative catenation reactions with Group 10 metals. Direct heating of **6** yielded the germane dimer $[3,5\text{-}(CF_3)_2C_6H_3]_2(H)GeGe(H)[3,5\text{-}(CF_3)_2C_6H_3]_2$ (**9**). In addition, catalytic coupling of **3** to give the dimer **9** was achieved by refluxing 5 mol% precatalyst **2** with 500 mg of germane **3** in benzene for 60 h. The overall yield of **9** was 65% according to the ^1H NMR spectrum; the remainder was a distribution of higher oligomers. We note that silicon complexes related to **7** and **8** had been previously observed by Michalczyk et al.,[20] but not as intermediates in dehydrocoupling reactions.[21] Complex **8** is thermally stable to at least 75 °C, unlike the spectroscopically characterized Si analogue, which decomposes when warmed above −25 °C. Silicon complexes related to **6** have also been observed during the dehydrogenative coupling of organosilanes by Tilley et al.[22] and Tessier–Youngs et al.[23]

In principle, platinum germylenes could be present during the dehydrogenation and/or the oligomerization steps. Experiments designed to detect the presence of intermediate germylene species in these reactions by trapping with CO_2 failed to detect the presence of any platinum germylenes. Based on the observed formation of a square-planar Pt^{II} complex upon the reaction of **2** with CO_2[8a] and the irreversible binding of CO_2 by $[(Et_3P)_2PtGe\{CH(SiMe_3)_2\}_2]$,[8b] we believe that a species such as $[(Et_3P)_2PtGe\{3,5\text{-}(CF_3)_2C_6H_3\}_2]$ should bind CO_2 to form a stable complex. Although our conclusion is clearly speculative, this evidence suggests that germylene species are *not* formed during the course of this dehydrogenative oligomerization, requiring a series of oxidative additions and the formation of a formal Pt^{IV} intermediate prior to the formation of digermyl **7**.[7e, 17, 23a] Studies designed to elucidate the mechanistic pathways and to differentiate between Curtis–Epstein and germylene-based mechanisms in a more definitive fashion are in progress.

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