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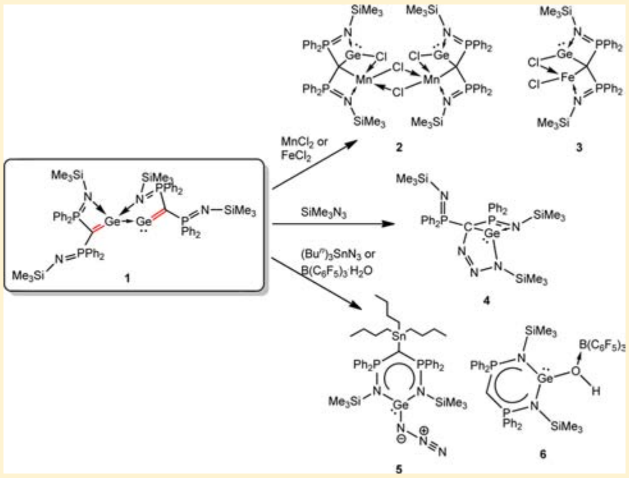
Synthesis of Hetero-Binuclear Complexes from Bisgermavinylidene

Wing-Por Leung,* Kwok-Wai Kan, Yuk-Chi Chan, and Thomas C. W. Mak

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

Supporting Information

ABSTRACT: Bisgermavinylidene $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (**1**) has been used as a source of unstable germavinylidene for the synthesis of a series of heterobinuclear complexes. The reaction of **1** with stoichiometric amounts of transition metal chlorides MCl_2 (M = Mn, Fe) yielded $[(Me_3SiN{=}PPh_2)_2(GeCl)CMn(\mu\text{-}Cl)]_2$ (**2**) and $[(Me_3SiN{=}PPh_2)_2(GeCl)CFeCl]$ (**3**), respectively. Treatment of **1** with Me_3SiN_3 gave the [2 + 3] cycloaddition product $[(Me_3SiN{=}PPh_2)_2\overline{CGeN(SiMe_3)N{=}N}]$ (**4**). While similar reaction of **1** with $(^nBu)_3SnN_3$ (^{n}Bu = *n*-butyl) and water-borane adduct $H_2O \rightarrow B(C_6F_5)_3$ afforded the 1,2-addition products $[(Me_3SiN{=}PPh_2)\{(^nBu)_3Sn\}CPPh_2NSiMe_3GeN_3]$ (**5**) and $[HC(PPh_2{=}NSiMe_3)_2Ge(OH)B(C_6F_5)_3]$ (**6**), respectively. The results suggested that the germanium−carbon bond in germavinylidene is capable of forming addition reaction products. The X-ray structures of **2**−**6** have been determined.



■ INTRODUCTION

Germenes are compounds containing a double bond between germanium and carbon (>C=Ge<). They have been the focus of several reviews.[1] Synthetic methods and structures of stable germenes $R_2Ge{=}CR'_2$ have been reported.[2] The most common routes for the synthesis of germene are the addition-elmination reaction of *tert*-butyllithium with halovinylgermane and the germylene−carbene coupling reaction. The 1,2-addition or [2 + *n*] cycloaddition reactions of germene have been studied extensively.[3] In contrast, the reactivity of germavinylidenes (>C=Ge:) is not known. It is due to the low stability of intermediate germavinylidene can only be detected by laser-induced fluorescence spectroscopy.[4]

The unusual structure and the reactivity of germavinylidenes have attracted our interest. We have communicated the synthesis and structure of bisgermavinylidene $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (**1**).[5] The Ge−Ge interaction is considered to be weak. It is proposed that bisgermavinylidene is a potential source to generate the reactive monomeric germavinylidene. It can serve as a synthon to synthesize heterobinuclear metal−germavinylidene complexes. In the solution state, it is proposed that it may exist as bisgermavinylidene (**A**), monomeric germavinylidene (**B** or **C**, where **C** is a possible resonance structure of **B** (Scheme 1)).

It is anticipated that germavinylidene can react (i) as a Lewis acid, (ii) as a Lewis base, (iii) undergoing addition reaction, (iv) undergoing oxidative addition reaction, or (v) as a ligand transfer reagent. The different reactive centers of germavinylidene are shown in Scheme 2. The addition reaction,[6,9−11] oxidative addition reaction,[7,10] ligand transfer reaction,[6] and the Lewis base properties[8,9] of germavinylidene have been reported. The existence of monomeric germavinylidene intermediate in solution was shown by the synthesis of manganese−germavinylidene complex $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Mn(CO)_2Cp]$ (Cp = η^5-C_5H_5).[9] Germavinylidene can also act as a starting compound for the preparation of various germenes by cycloaddition reaction with the germanium(II) center.[10] The reactivity of the germanium−carbon bond in germavinylidene has been demonstrated by the synthesis of $(Me_3SiN{=}PPh_2)_2\{(cod)RhCl\}CGeCl]$ (cod =1,5-cyclooctadiene)[9] and [2 + 2] cycloaddition reaction of germavinylidene with AdNCO (Ad = adamantyl).[11] Herein, the reactive center ii of bisgermavinylidene is demonstrated. We here report the synthesis and structures of novel heterobinuclear complexes from bisgermavinylidene. The [2 + 3] cycloaddition and 1,2-addition reaction of germavinylidene with Me_3SiN_3, $(Bu^n)_3SnN_3$, and $B(C_6F_5)_3{\cdot}H_2O$ are also reported.

■ RESULTS AND DISCUSSION

Treatment of bisgermavinylidene **1** with stoichiometric amounts of transition metal chlorides MCl_2 (M = Mn, Fe) yielded $[(Me_3SiN{=}PPh_2)_2(GeCl)CMn(\mu\text{-}Cl)]_2$ (**2**) and $[(Me_3SiN{=}PPh_2)_2(GeCl)CFeCl]$ (**3**) (Scheme 3). The X-ray structural determination of the products obtained have shown that the M—Cl bond (M = Mn, Fe) adds to the Ge=C bond of germavinylidene to form compounds **2** and **3**.

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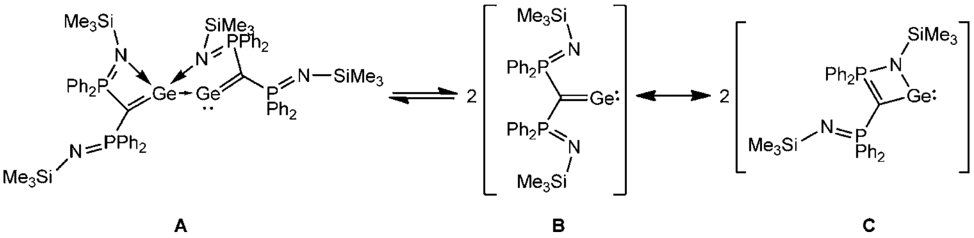
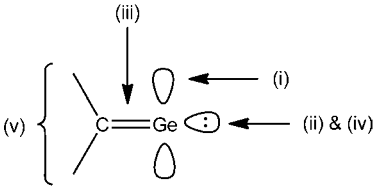
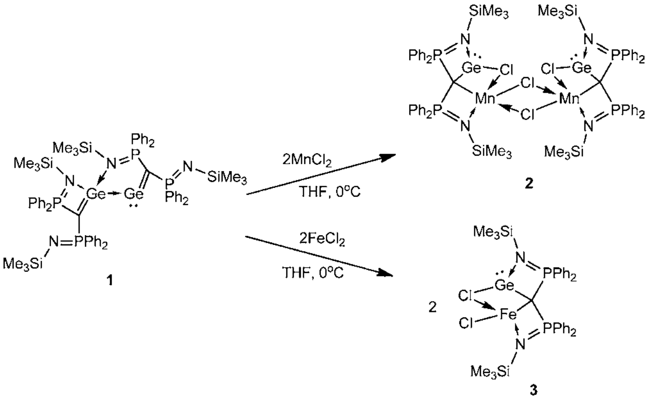
Scheme 1



Scheme 2. Different Reactive Centers in Germavinylidene: (i) Lewis Acid, (ii) Lewis Base, (iii) Addition Reaction, (iv) Oxidative Addition Reaction, or (v) as a Ligand Transfer Reagent



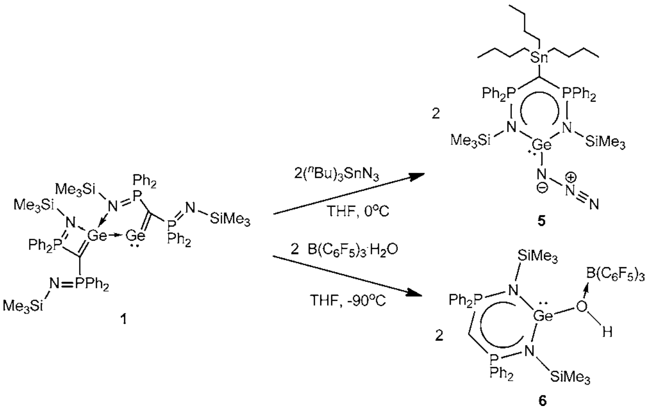
Scheme 3



Treatment of bisgermavinylidene **1** with stoichiometric amounts of Me_3SiN_3 in THF gave a cycloaddition product $[(Me_3SiN{=}PPh_2)_2\overline{CGeN(SiMe_3)N{=}N}]$ (**4**) (Scheme 4). It is proposed that the Ge═C bond in **1** underwent a [2 + 3] cycloaddition reaction with the N═N═N moiety of azidotrimethylsilane to yield **4**. The X-ray structure determination of **4** has shown that the Ge—C bond lengthened as the bond order decreased from two to one via the cycloaddition reactions. This further supports that the germanium−carbon bond in germavinylidene is a Ge═C bond. Similar results have been observed in the [2 + 2] cycloaddition reactions of $[MCl_2\{C(PPh_2{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2 N,N'\}]$ (M = Zr, Hf) with heteroallenes.[12]

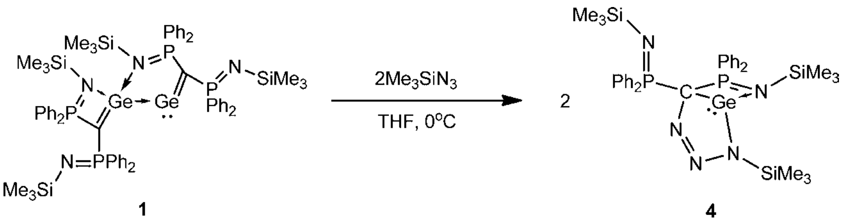
The reaction of bisgermavinylidene **1** with 2 equiv of $(Bu^n)_3SnN_3$ in THF afforded $[(Me_3SiN{=}PPh_2)\{(Bu^n)_3Sn\}\text{-}CPPh_2NSiMe_3GeN_3]$ (**5**). The X-ray structure determination of **5** has shown that $(Bu^n)_3SnN_3$ underwent a 1,2-addition reaction with germavinylidene in solution, followed by a rearrangement process in which the Ge—C bond was cleaved with the subsequent formation of Ge—N bond to give heterobinuclear compound **5** (Scheme 5). This contrasts with the result found in the reaction of **1** with Me_3SiN_3 in which the azide bond underwent a [2 + 3] cycloaddition reaction with germavinylidene to yield **5**. The different results may be due to the fact that the weaker metal-azide bond in $(Bu^n)_3SnN_3$ favors a 1,2-addition reaction. Similar examples with bis(iminophosphorano)methanediide ligand such as $[(AlMe)_2\{\mu^2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4 C,C',N,N'\}]$[13] and $[Cr\{\mu^2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\ \kappa^4 C,C',N,N'\}]_2$[14] have been reported.

Scheme 5



Treatment of bisgermavinylidene **1** with 2 equiv of borane−water adduct $H_2O{\rightarrow}B(C_6F_5)_3$ in THF afforded the borane-stabilized germanium(II) hydroxide complex $[HC(PPh_2{=}NSiMe_3)_2Ge(OH)B(C_6F_5)_3]$ (**6**). It is proposed that the C═Ge bond in germavinylidene underwent a 1,2-addition with H_2O from $H_2O{\rightarrow}B(C_6F_5)_3$, followed by a rearrangement process in which the Ge—C bond was cleaved with the subsequent formation of Ge—N bond to yield **6**. Attempts to

Scheme 4



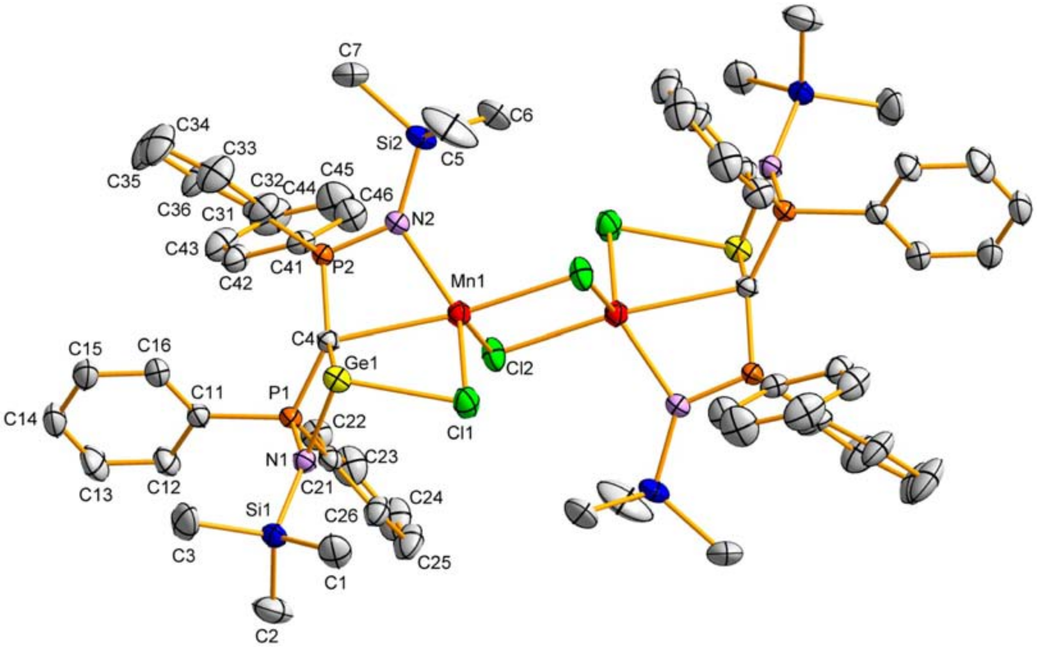


Figure 1. Molecular structure of $[(Me_3SiN{=}PPh_2)_2(GeCl)CMn(\mu\text{-}Cl)]_2$ (**2**) (30% ellipsoids probability). Hydrogen atoms and CH_2Cl_2 molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Ge1—N1 1.985(2), Ge1—C4 2.024(3), Ge1—Cl1 2.549(9), Mn1—N2 2.128(2), Mn1—Cl1 2.457(9), Mn1—Cl2 2.418(9) Mn1—Cl2A 2.517(9), Mn1—C4 2.584(3), N1—Ge1—C4 77.3(1), N1—Ge1—Cl1 96.9(7), C4—Ge1—Cl1 93.5, N2—Mn1—Cl2 116.5(7), N2—Mn1—Cl1 125.7(7), Cl2—Mn1—Cl1 114.5(4), N2- Mn1—Cl2A 88.8(3), Cl2—Mn1—Cl2A 92.7(3), N2—Mn1—C4 67.5(8), Cl2—Mn1—C4 104.6(6), Cl2A—Mn1-C4 166.6(6), Mn1—Cl1—Ge1 83.5(3), Ge1—C4—Mn1 91.9(1).

prepare compound **6** with 2 equiv of H_2O was not successful; only $H_2C(PPh_2{=}NSiMe_3)_2$ was obtained. To the best of our knowledge, it is the first reported synthetic method for the synthesis of germanium(II) hydroxide via the addition reaction of H_2O with germavinylidene. Similar germanium(II) hydroxide was prepared from the substitution reaction of heteroleptic germanium(II) chloride with H_2O in the presence of *N*-heterocyclic carbene.[15]

Spectroscopic Properties. Compounds **3**–**5** were isolated as yellow crystalline solids whereas compound **2** and **6** were isolated as colorless crystalline solids. They are air and moisture-sensitive, soluble in THF and CH_2Cl_2 and sparingly soluble in Et_2O. Compounds **2** and **3** have been characterized by FAB mass spectroscopy and elemental analysis. Compounds **4**–**6** have been characterized by NMR spectroscopy and elemental analysis. Compounds **2** and **3** are paramagnetic, no satisfactory NMR spectra have been obtained. The FAB mass spectrum of compound **2** displayed a $[M/2]^+$ peak, suggesting it exists as a monomer in vapor phase. The fragment due to the $[M - SiMe_3]^+$ peak was observed in the FAB mass spectrum of **3**. The ^1H NMR spectrum of **4** displayed two singlets at δ −0.09 ppm and δ 0.26 ppm which correspond to two different $SiMe_3$ groups. The ^{31}P NMR spectrum (25 °C) of **4** showed one singlet at δ 7.1 ppm, which is not agreed with the X-ray structure. At −80 °C, the ^{31}P NMR spectrum of **4** displayed two signals at δ 7.1 and δ −3.2 ppm. This is due to the fluxional coordination of imino nitrogen atoms at the germanium center in solution. The ^1H and ^{13}C NMR spectra of compound **5** displayed two set of signals due to bis(iminophosphorano)-methanediide ligand and the *n*-butyl groups. The ^{31}P NMR spectrum of **5** showed two singlets at δ 10.6 and 45.5 ppm due to two different phosphorus environments as found in the solid-state structure. The ^{119}Sn NMR spectrum of **5** displayed one upfield signal of δ −44.6 ppm as compared with the signal of δ −249.5 ppm in $[Sn\{CH(SiMe_3)C_9H_6N\text{-}8\}_2Cl_2]$.[16] The ^1H NMR spectrum of compound **6** displayed two sets of singlet at δ −0.19 ppm and δ 0.15 ppm which correspond to two different $SiMe_3$ groups. The methanide proton displayed a signal at δ 3.91 ppm. The multiplet signal at δ 4.96 ppm is due to the hydroxyl proton coupled to boron from $B(C_6F_5)_3$. The ^{31}P NMR spectrum of **6** showed two signals at δ −7.2 and δ 20.9 ppm. The ^{11}B NMR spectrum of **6** showed one signal at δ −2.9 ppm. Both spectra are consistent with the X-ray structure. From the IR spectrum of compound **6**, an absorption around 3400 cm^{-1} can be assigned to the O−H stretching frequency, which is comparable to the absorption band at 3571 cm^{-1} in $[HC\{(CMe)(2,6\text{-}^iPr_2C_6H_3N)\}_2\ GeOH]$.[41]

X-ray Structures. Molecular structures with atom numbering schemes and selected bond distances and angles for compounds **2**–**6** are shown in Figure 1–5, respectively. Compound **2** crystallizes in the monoclinic space group *C*2/*c* with two solvated CH_2Cl_2 molecules in the solid state. It is a chloro-bridged dimer with "GeCl" and "MnCl" moieties bonded to the methanediide carbon. The germanium center is bound to one of imino group in a trigonal pyramidal geometry, while the other is bound to the manganese center and adopts a distorted trigonal bipyramidal geometry. The sum of angles at the germanium is 267.7°, consistent with a stereoactive lone-pair of electrons at the germanium center. There is no interaction between germanium and manganese as indicated by a long distance of 3.335 Å. The C—Ge—Mn—Cl and Mn_2Cl_2 rings are almost planar and the dihedral angle between the two planes is 59.4°. Similar to compound **2**, the Ge—C bond distance of 2.024(3) Å in **2** is lengthened as compared to the Ge=C distances in **1**. It is also similar to the Ge—C single bond distances in $[Ge\{CH(SiMe_3)_2\}_2]_2$ (2.016 Å)[17] and $[Ge\{CPh(SiMe_3)C_5H_4N\text{-}2\}_2]$ (2.116 Å).[18] The Ge—Cl bond distance of 2.549(9)Å in **2** is longer than those

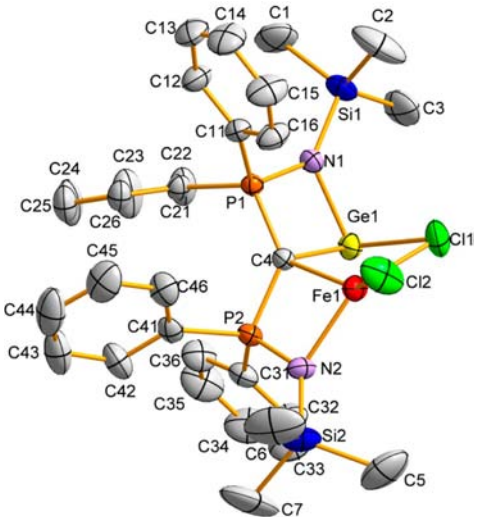


Figure 2. Molecular structure of $[(Me_3SiN{=}PPh_2)_2(GeCl)CFeCl]$ (**3**) (30% ellipsoids probability). Hydrogen atoms, THF, and CH_2Cl_2 molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Ge1—N1 1.962(4), Ge1—C4 2.059(4), Ge1—Cl1 2.581(2), Fe1—N2 2.042(4), Fe1—Cl2 2.227(2), Fe1—C4 2.241(5), Fe1—Cl1 2.365(2), N1—Ge1—C4 76.7(2), N1—Ge1—Cl1 99.3(1), C4—Ge1—Cl1 88.6(1), N2—Fe1—Cl2 113.9(1), N2—Fe1—C4 74.6(2), Cl2—Fe1—C4 143.6(1), N2—Fe1—Cl1 131.9(1), Cl2—Fe1—Cl1 105.4(8), C4—Fe1—Cl1 90.1(1), Fe1—Cl1—Ge1 79.9(5).

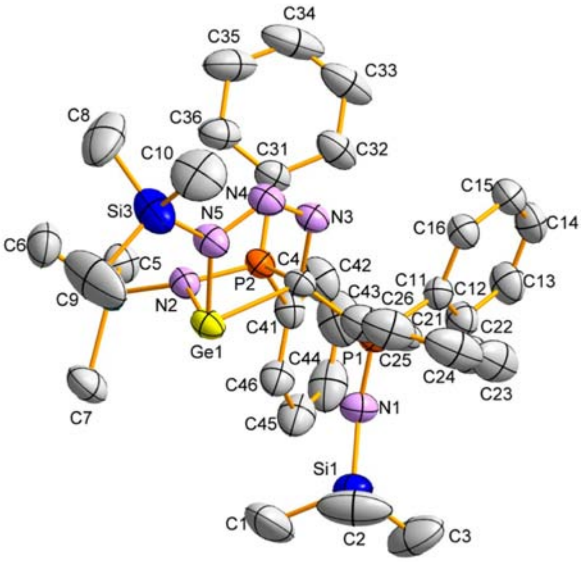


Figure 3. Molecular structure of $[(Me_3SiN{=}PPh_2)_2CGeN(SiMe_3)\text{-}N{=}N]$ (**4**) (30% ellipsoids probability) Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ge1—N5 1.948(3), Ge1–C4 2.125(3), Ge1—N2 2.070(3), P1—N1 1.537(3), P1—C4 1.814(3), P2—N2 1.606(3), P2—C4 1.808(3), N3—N4 1.262(4), N3—C4 1.503(4), N4—N5 1.387(4), N5—Ge1—N1 97.9(1), N5—Ge1—C4 78.9(1), N2—Ge1—C4 76.3(1), N4—N3—C4 115.5(3), N3—N4—N5 119.2(3), N4—N5—Ge1 117.6(2).

distances in $[(^iPr_2ATI)GeCl]$ [2.364(2)Å][19] (ATI = aminotroponimato) and $[HC(CMeNPh)_2GeCl]$ [2.340(6)Å],[20] which is probably owing to the chelation with manganese. The Mn—C bond distance of 2.584(3)Å in **2** is significantly longer than some reported Mn—C bond distances ranging from 2.010 to 2.108 Å.[21] It is suggested that the Mn—C bond is lengthened in order to release the steric crowding at the methanediide carbon. The average Mn—Cl bond distance of 2.467 Å in **2** is similar to those (μ-Cl)$_2$-bridges in $[Mn(\mu\text{-}Cl)\{C(SiMe_3)_2(SiMe_2\text{-}NMe_2)\}]_2$ (2.428 Å),[22] $[Mn(THF)(\mu\text{-}Cl)\{C(SiMe_3)_2\ (SiMe_2OMe_2)\}]_2$ (2.488 Å),[22] and [LMn(μ-

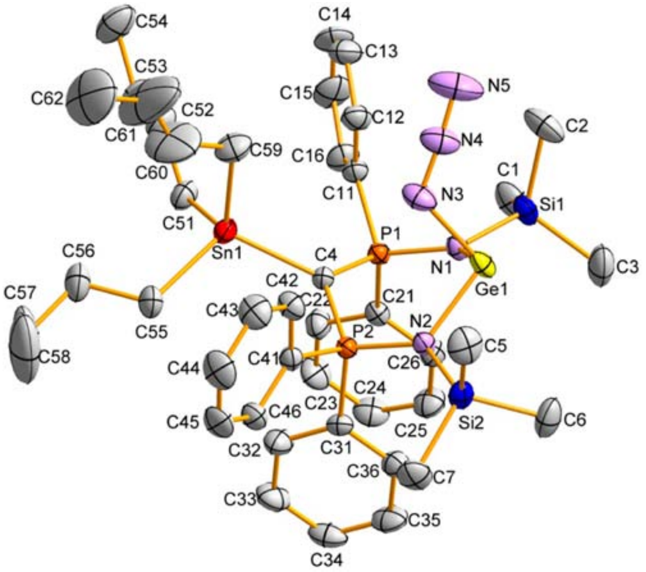


Figure 4. Molecular structure of $[(Me_3SiN{=}PPh_2)\{(Bu^n)_3Sn\}\text{-}CPPh_2NSiMe_3GeN_3]$ (**5**) (30% ellipsoids probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ge1—N1 1.979(2), Ge1—N2 1.974(2), Ge1—N3 2.027(3), Sn1—C4 2.157(4), N3—N4 1.197(4), N4—N5 1.134(5), N2—Ge1—N1 97.8(1), N2—Ge1—N3 94.8(1), N1—Ge1—N3 98.9(1), N5—N4—N3 175.9(5), C4—Sn1—C55 111.4(1), C4—Sn1—C59 109.2(1), C4—Sn1—C51 112.9(1), C59—Sn1—C55 108.7(2).

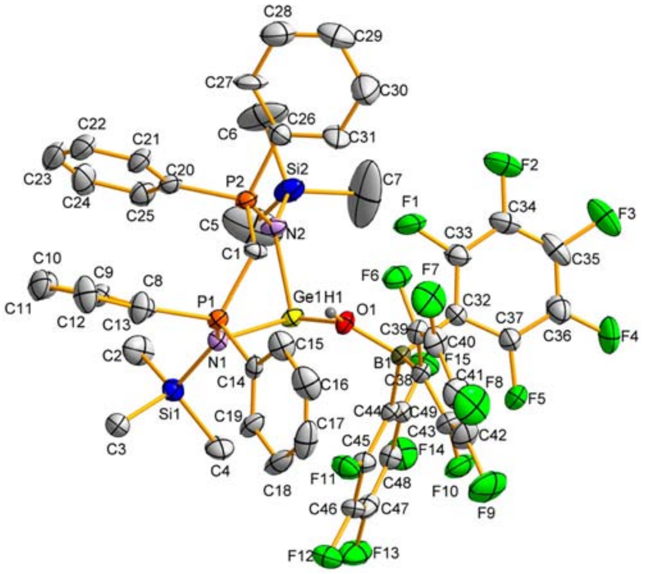


Figure 5. Molecular structure of $[HC(PPh_2{=}NSiMe_3)_2Ge(OH)B\text{-}(C_6F_5)_3]$ (**6**) (30% ellipsoids probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ge1—O1 1.785(4), Ge1—N1 2.153(4), Ge1—N2 2.119(4), P1—N1 1.592(4), P2—N2 1.598(4), C1—P1 1.805(6), C1—P2 1.805(6), O1—H 0.820 O1—B1 1.496(7), N1—Ge1—O1 97.1(2), N2—Ge1—O1 98.5(2), N1—Ge1—N2 92.4(2), Ge1—O1—B1 125.9(3), O1—B1—C38 109.9(5), O1—B1—C44 107.3(5), C32—B1—C44 110.2(5), C32—B1—C38 102.4(5).

$Cl)_2Mn(THF)(\mu\text{-}Cl)_2MnL]$ (L = $HC\{CMeN\text{-}(2,6\text{-}{}^iPr_2C_6H_3)\}_2$) (2.402 Å).[23] The Mn−N bond distance of 2.128(2) Å in **2** is similar to that of some β-diketiminato manganese(II) complexes.[24]

Compound **3** is a monomer solvated with 1/4 CH_2Cl_2 and 1/2 THF molecules in the solid state structure. It is comprised of "GeCl" and "FeCl" moieties bonded to the methanediide carbon. The geometry at the germanium and iron center are trigonal pyramidal and distorted tetrahedral respectively. The C−Fe−Cl−Ge ring is almost planar as shown by the sum of angles of 353.8°. The Ge−Fe distance of 3.179 Å shows that no interaction between the two metal centers. The Ge−C bond distance of 2.059(4) Å in **3** is within the range of some reported Ge−C single bond distances [1.98−2.14 Å].[25] The Ge−Cl bond distance of 2.581(1) Å in **3** is longer than those in $[Ge(C_6H_3\text{-}2,6\text{-}Trip_2)Cl]$ [2.203(1) Å][26] and $[HC(CMeNPh)_2GeCl]$ [2.340(6) Å].[20] The Fe−C bond distance of 2.241(5) Å in **3** is longer than that of 2.051(1) Å in $Fe[C(SiMe_3)_3]_2$[27] and that of 2.045(4) Å in $Fe(Tsi)_2$ (Tsi = tris(trimethylsilyl)-methyl),[28] which may be due the steric crowding at the methanediide carbon. The $Fe{-}Cl_{terminal}$ bond distance of 2.227(2) Å is similar to those found in LFeCl (L = 2,4-bis(2,6-diisopropylphenylimido) pentyl) [2.172(1) Å].[29] The $Fe{-}Cl_{bridging}$ bond distance of 2.345(2) Å is similar to that of 2.324(1) and 2.338(1) Å in $LFe(\mu\text{-}Cl)_2\text{-}Li(THF)_2$.[29] The Fe−N bond distance of 2.042(2) Å in **3** is similar to those distances found in some bis(iminophosphorano)methanide iron(II) complexes.[30]

Compound **4** is comprised of a five-membered C—N═N—N—Ge ring. The germanium center of **4** displays a trigonal pyramidal geometry as indicated by the sum of angles of 253.17 at Ge1, which is consistent with a stereoactive lone pair at the germanium center. The Ge1—C4 bond distance of 2.125(3) Å in **4** is similar to that of 2.135(4) Å in $Ge[CPh(SiMe_3)(C_5H_4N\text{-}2)]_2$[18] and that of 2.067(1) Å in $[Ge\{CH(SiMe_3)_2\}\{C(SiMe_3)_3\}]$,[31] but longer than the Ge—C distances of 1.905(8) and 1.908(7) Å in **1**, showing that the bond order of Ge—C bond changed from two to one. The Ge1—N5 bond distance of 1.948(3) Å in **4** is similar to those found in $ArGeN(SiMe_3)_2$ [Ar = 2,6-bis((diethylamino)methyl)phenyl] [1.956(1) Å][32] and $[Ge\{C(C_5H_4N\text{-}2)C(Ph)N(SiMe_3)_2\}\{N(SiMe_3)C(Ph)(SiMe_3)\text{-}(C_5H_4N\text{-}2)\}]$ [1.940(2) Å].[33] The N3—N4 bond distance in **4** is assignable to a N═N bond. The C4—N3 and N4—N5 bond distances in **4** are normal. The Ge1—N2 bond distance of 2.070(3) Å in **4** is similar to those reported N → Ge bond distances.

Compound **5** is a heterobinuclear complex containing a germanium(II) azide and a tin(IV) tetraalkyl. The ligand is bonded in a *N,N′*-chelate fashion to the germanium center which displays a trigonal pyramidal geometry. The tin center is bonded to the methanediide carbon and adopts a tetrahedral geometry. The Ge—N—P—C—P—N metallacycle in **5** displays a distorted boat conformation. There is no interaction between germanium and the methanediide carbon. The P—N bond distances of 1.636(3) and 1.633(3) Å and the C—P bond distances of 1.720(3) and 1.711(3) Å in **5** are different from those of $[(Me_3SiN{=}PPh_2)_2CH_2]$ [P—N = 1.536(2)Å; C—P = 1.825(1)Å],[34] suggesting that considerable charge delocalization is present in the NPCPN backbone of the ligand. The Ge—N distances of 1.974(2) and 1.979(2) Å in **5** are similar to those of 1.983(4) and 2.002(4) Å found in $[(Me_3SiN{=}PPh_2)_2CHGeCl]$[35] and those of 1.971(4) and 1.959(4) Å found in $[HC(CMeNAr)_2GeCl]$ (Ar = $2,6\text{-}Pr^i_2C_6H_3$).[36] The average Sn—C bond distance of 2.162 Å in **5** is similar to those distances for a Sn(IV)—C single bond of 2.134 Å in $[\{Ph_2P(CH_2)_3\}_2SnCl_2]$[37] and 2.136 Å in $[{}^nBuSnCl_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$.[38] The azide moiety in **5** are almost linear as indicate from the N—N—N bond angle of 175.9(5)°. The bonding in the Ge—N_3 may be described by two canonical forms: Ge—N═N═N and Ge—N—N≡N. It was found that the dominant canonical form of the Ge—N_3 moieties in $[({}^nPr_2ATI)GeN_3]$ (ATI = aminotroponimato)[39] and $[(Mes_2DAP)GeN_3]$ (Mes_2DAP = 2,4-dimethyl-*N,N′*-bis-(2,4,6-trimethylphenyl)-1,5-diazapentadienyl)[40] is Ge—N—N≡N. The $Ge{-}N_{azide}$ bond distance of 2.027(3) Å in **5** is close to that of 2.047(2) Å in $[({}^nPr_2ATI)GeN_3]$[39] and that of 1.979(5) Å in $[(Mes_2DAP)GeN_3]$.[40] The N—N bond distances in **5** [1.197(4), 1.134(5) Å] are also similar to those found in $[({}^nPr_2ATI)GeN_3]$[37] [1.197(3), 1.144(4) Å] and $[(Mes_2DAP)GeN_3]$[40] [1.199(7), 1.152(8) Å]. Thus, the N—N bond lengths in **5** suggest that the dominant canonical form of the Ge—N_3 moiety is Ge—N—N≡N. This is also consistent with the results from theoretical calculations.[39]

Compound **6** is comprised of a germanium(II) hydroxide coordinated to the imino group of bis(iminophosphorano)-methane and the oxygen atom in OH group is coordinated to the tris(pentafluorophenyl)borane. The angle sum of 289.5° at the germanium center deviates from a normal sp^3 tetrahedral geometry. Therefore, the germanium center adopts a trigonal pyramidal geometry and is consistent with a stereoactive lone pair at the germanium center. The angle sum of 429.8° at the boron atom is comparable to a normal sp^3 tetrahedral geometry, so the boron atom adopts a tetrahedral geometry. The P—N bond distances of 1.592(4) and 1.598(4) Å and the C—P bond distances of 1.805(6) Å in **6** are different from those of $[(Me_3SiN{=}PPh_2)_2CH_2]$ [P—N = 1.536(2) Å; C—P = 1.825(1) Å],[34] suggesting that considerable delocalization throughout the NPCPN backbone of the ligand. The Ge—O bond distance of 1.785 Å is in good agreement with $[HC\{(CMe)(2,6\text{-}{}^iPr_2C_6H_3N)\}_2GeOH]$ [1.828 Å][15] and the theoretical value of 1.804 Å in $Ge(OH)_2$.[41] The O—H bond distance of 0.820 Å in compound **6** is comparable to $[HC\{(CMe)(2,6\text{-}{}^iPr_2C_6H_3N)\}_2GeOH]$ [0.795(7) Å][15] but significantly shorter than the theoretical value of 0.972 Å in $Ge(OH)_2$.[41]

CONCLUSIONS

Heterobinuclear complex consisting of main-group metalloid chloride and transition metal chloride, $[(Me_3SiN{=}PPh_2)_2(GeCl)CMn(\mu\text{-}Cl)]_2$ (**2**) and $[(Me_3SiN{=}PPh_2)_2(GeCl)CFeCl]$ (**3**) have been prepared from bisgermavinylidene. Bisgermavinylidene underwent a [2 + 3] cycloaddition reaction to yield $[(Me_3SiN{=}PPh_2)_2CGeN(SiMe_3)N{=}N]$ (**4**). While the reaction of bisgermavinylidene with $({}^nBu)_3SnN_3$ (${}^nBu$ = *n*-butyl) and water−borane adduct $H_2O{\to}B(C_6F_5)_3$ afforded 1,2-addition product $[(Me_3SiN{=}PPh_2)\{({}^nBu)_3Sn\}\text{-}CPPh_2NSiMe_3GeN_3]$ (**5**) and $[HC(PPh_2{=}NSiMe_3)_2Ge(OH)\text{-}B(C_6F_5)_3]$ (**6**), respectively. The results demonstrated that germanium−carbon bond in germavinylidene is capable of forming addition reaction products.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under an inert atmosphere of dinitrogen gas by standard Schlenk techniques. Solvents were dried over and distilled from CaH_2(hexane) and/or Na (Et_2O, toluene, and THF). The bis(germavinylidene) [(Me_3SiN═

$PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$[5] and borane−water adduct $H_2O{\rightarrow}B(C_6F_5)_3$[42] were prepared by literature procedures. $MnCl_2$, $FeCl_2$, Me_3SiN_3, and $^nBu_3SnN_3$ were purchased from Aldrich Chemicals and used without further purification. The ^1H, ^{13}C, ^{31}P, ^{11}B, and ^{119}Sn NMR spectra were recorded on Bruker WM-300 and Varian 400 spectrometers. The NMR spectra were recorded in THF-d_8, and the chemical shifts are relative to $SiMe_4$ and 85% H_3PO_4 for ^1H, ^{13}C, and ^{31}P, respectively.

Reaction of 1 with $MnCl_2$. A solution of **1** (0.64g, 0.51 mmol) in THF (20 mL) was added slowly to $MnCl_2$ (0.13g, 1.02 mmol) suspension in THF (20 mL) at 0 °C. The reaction mixture was stirred at room temperature for 46 h. Volatiles in the mixture were removed under reduced pressure, and the residue was extracted with CH_2Cl_2. After filtration and concentration of the filtrate, **2** was obtained as colorless crystals. Yield: 0.27g (35%). Mp: 210.2 °C (dec). Anal found: C, 49.57; H, 5.27; N, 3.86. Calcd for $C_{62}H_{76}Cl_4Ge_2Mn_2N_4P_4Si_4$: C, 49.30; H, 5.07; N, 3.71. MS (FAB): *m/z* 756 (60, $[M/2]^+$).

Reaction of 1 with $FeCl_2$. A solution of **1** (0.68g, 0.54 mmol) in THF (20 mL) was added slowly to $FeCl_2$ (0.14g, 1.08 mmol) suspension in THF (20 mL) at 0 °C. The reaction mixture was stirred at room temperature for 39 h. Volatiles in the mixture were removed under reduced pressure, and the residue was extracted with 1:1 mixture of Et_2O/CH_2Cl_2. After filtration and concentration of the filtrate, **3** was obtained as pale yellow crystals. Yield: 0.38g (47%). Mp: 152.3−154.2 °C. Anal found: C, 48.92; H, 5.24; N, 3.67. Calcd for $C_{31}H_{38}Cl_2GeFeN_2P_2Si_2$: C, 49.24; H, 5.07; N, 3.70. MS (FAB): *m/z* 684 (17, $[M - SiMe_3]^+$).

Reaction of 1 with $SiMe_3N_3$. A solution of **1** (0.72g, 0.57 mmol) in THF (20 mL) was added slowly to Me_3SiN_3 (0.20 mL, 1.52 mmol) in THF (20 mL) at 0 °C. The resultant pale yellow solution was raised to room temperature and stirred for 31 h. The volatiles were removed under reduced pressure. The residue was extracted with Et_2O. After filtration and concentration of the filtrate, compound **4** was obtained as pale yellow crystals. Yield: 0.15g (42%). Mp: 111.7−112.5 °C. Anal found: C, 54.74; H, 6.37; N, 9.12. Calcd for $C_{34}H_{47}GeN_5P_2Si_3$: C, 54.84; H, 6.36; N, 9.41. ^1H NMR (THF-d_8, 25 °C): $\delta = -0.09$, (s, 18H, $SiMe_3$), −0.26, (s, 9H, $SiMe_3$), 7.23−7.26 (m, 3H, Ph), 7.27−7.30 (m, 5H, Ph), 7.31−7.33 (m, 4H, Ph), 7.38−7.45 (m, 2H, Ph), 7.46−7.49 (m, 2H, Ph), 7.74−7.81 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (THF-d_8, 25 °C): $\delta = -0.04$ ($SiMe_3$), 3.6 ($SiMe_3$), 125.9, 126.1, 126.2, 126.5, 128.9, 129.8, 129.8, 130.0, 130.2, 130.4, 130.7, 131.6, 131.9, 132.1, 132.2 (Ph). $^{31}P\{^1H\}$ NMR (THF-d_8, 25 °C): $\delta = 7.1$, (THF-d_8, −80 °C): $\delta = 7.1, -3.2$.

Reaction of 1 with $(Bu^n)_3SnN_3$. A solution of **1** (0.73g, 0.58 mmol) in THF (20 mL) was added slowly to the $(Bu^n)_3SnN_3$ (0.35 mL, 1.27 mmol) in THF (20 mL) at 0 °C. The resultant yellow solution was raised to room temperature and stirred for 18 h. The volatiles were removed under reduced pressure. The residue was extracted with Et_2O. After filtration and concentration of the filtrate, compound **5** was obtained as yellow crystals. Yield: 0.31g (28%). Mp: 80.6 °C (dec). Anal found: C, 53.77; H, 7.07; N, 6.65. Calcd for $C_{43}H_{64}GeN_5P_2Si_2Sn$: C, 53.72; H, 6.81; N, 7.28. ^1H NMR (THF-d_8, 25 °C): $\delta = -0.16$, (s, 9H, $SiMe_3$), −0.08, (s, 9H, $SiMe_3$), 0.30 (m, 6H, CH_2-^{n}Bu), 0.80 (t, 9H, CH_3-^{n}Bu, $J_{H-H} = 6$ Hz), 0.30 (m, 12H, C_2H_4-^{n}Bu), 7.10−7.14 (m, 4H, Ph), 7.20−7.25 (m, 2H, Ph), 7.29−7.48 (m, 10H, Ph), 7.87−7.91 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (THF-d_8, 25 °C): $\delta = 3.5$ ($SiMe_3$), 4.7 ($SiMe_3$), 14.1, 17.5, 28.2, 30.0 (^{n}Bu), 38.1 (PCP), 130.2, 130.8, 131.0, 131.2, 131.8, 132.0, 132.1, 132.2, 132.8, 132.9, 134.0, 136.4, 144.4, 144.8 (Ph). $^{31}P\{^1H\}$ NMR (THF-d_8, 25 °C): $\delta = 10.6, 45.5$. $^{119}Sn\{^1H\}$ NMR (THF-d_8): $\delta = -44.6$.

Reaction of 1 with $H_2O{\rightarrow}B(C_6F_5)_3$. A solution of **1** (1.34g, 1.06 mmol) in THF (20 mL) was added to a solution of $B(C_6F_5)_3{\cdot}H_2O$ (1.13g, 2.13 mmol) in THF (10 mL) at −90 °C. The reaction mixture turned colorless, and it was stirred at room temperature for 1 h. A colorless solution was formed. All the volatiles in the reaction mixture were removed under reduced pressure and the residue was extracted with Et_2O (20 mL). After filtration and concentration of the filtrate, compound **6** was isolated as colorless crystals. Yield: 1.43g (57.7%). Mp: 128.5 °C. Anal found: C, 51.22; H, 3.96; N, 2.54. Calcd For $C_{49}H_{40}BF_{15}GeN_2OP_2Si_2$: C, 50.76; H, 3.48; N, 2.42. ^1H NMR (THF-d_8, 25 °C): $\delta = -0.15$ (s, 9H, $SiMe_3$), 0.19 (s, 9H, $SiMe_3$), 3.91 (m, 1H, CH), 4.96 (m, 1H, OH), 7.28−7.32 (m, 4H, Ph), 7.34−7.39 (m, 6H, Ph), 7.59−7.64 (m, 2H, Ph), 7.67−7.72 (m, 5H, Ph), 7.76−7.87 (m, 3H). $^{13}C\{^1H\}$ NMR (THF-d_8, 25 °C): $\delta = 3.7, 4.5$ ($SiMe_3$), 129.3, 129.8, 130.3, 131.2, 131.8, 132.4, 133.0, 133.2, 133.8, 135.5 (Ph), 136.7, 139.1, 148.1, 150.5 (C_6F_5). $^{31}P\{^1H\}$ NMR (THF-d_8, 25 °C): $\delta = 20.9, -7.2$. ^{11}B NMR (THF-d_8, 25 °C): $\delta = -2.9$. IR (KBr): $\tilde{\nu}$ = 3401, 3068, 2957, 2888, 2588, 2346, 1971, 1921, 1828, 1641, 1591, 1512, 1460, 1440, 1391, 1382, 1357, 1323, 1271, 1255, 1182, 1121, 1084, 1028, 1000, 962, 841, 798, 774, 767, 759, 747, 705, 694, 683, 658, 598, 528, 509, 488, 470.

X-ray Crystallography. Single crystals were sealed in Lindemann glass capillaries under nitrogen. X-ray data of **2**−**6** were collected on a Rigaku R-AXIS II imaging plate using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) from a rotating-anode generator operating at 50 kV and 90 mA. Crystal data are summarized in Tables 6 and 7 (Supporting Information). The structures were solved by direct phase determination using the computer program SHELXTL-PC on a PC 486 and refined by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms.[43] Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factor calculations. Full details of the crystallographic analysis of **2**−**6** are given in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details about the X-ray crystal structures in CIF format, including tables of selected bond distances and angles, and tables of crystal data for **2**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kevinleung@cuhk.edu.hk. Fax: +852 2609 5057.

Notes

The authors declare no competing financial interest.

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