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Synthesis of a Manganese Germavinylidene Complex from Bis(germavinylidene)

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The reaction of bis(germavinylidene) $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (**1**) with $CpMn(CO)_2(THF)$ ($Cp = \eta^5\text{-}C_5H_5$) in THF afforded $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Mn(CO)_2Cp]$ (**2**). Similar reaction of **1** with (cod)RhCl (cod = 1,5-cyclooctadiene) in THF gave $[(Me_3SiN{=}NPPh_2)_2\{(cod)Rh\}C{-}GeCl]$ (**3**). The results suggested that reactive germavinylidene may exist in solution. The X-ray structures of **2** and **3** have been determined.

Compounds containing a double bond between germanium and carbon ($>Ge{=}C<$) have attracted much attention in the past 15 years, and they have been the focus of several reviews.[1] It was found that the thermal stability of the Ge=C bond is intrinsically low and they can undergo oligomerization readily.[2] Nevertheless, stable germenes $R_2Ge{=}CR'_2$ have been synthesized by incorporating sterically bulky substituents at both germanium and carbon.[3] These germenes are highly reactive and can undergo 1,2-addition and $[2 + n]$ cycloaddition.[4] In contrast, the related germavinylidenes ($>C{=}Ge:$) are scarcely known. Because they lack any bulky substitutents at the germanium(II) center, germavinylidenes are expected to oligomerize more readily.

The unusual structure and the unknown reactivity of germavinylidenes have attracted our interest. Recently, we have communicated the synthesis and structure of bis(germavinylidene) $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (**1**).[5] Its role as a carbene ligand transfer reagent has been demonstrated in the reaction of **1** with $Mo(CO)_5(THF)$ to form *mer*/*fac*-$(Me_3SiN{=}PPh_2)_2C{=}Mo(CO)_5$.[6] We have also reported the synthesis of chalcogen-bridged dimers of germaketene analogues $[(Me_3SiN{=}PPh_2)_2C{=}Ge(\mu\text{-}E)]_2$ (E = S, Se, and Te) from the direct reaction of elemental chalcogens with **1**.[7] However, monomeric germavinylidene or its metal complex has not been structurally authenticated.

Because of the weak Ge−Ge interaction of **1** in solution, we anticipated that it could be a potential source of the reactive germavinylidene intermediate "$:Ge{=}C(PPh_2{=}NSiMe_3)_2$". In this paper, we report the synthesis of a manganese germavinylidene complex showing that germavinylidene is stabilized by the $CpMn(CO)_2$ moiety. The 1,2-addition of germavinylidene with (cod)RhCl (cod = 1,5-cyclooctadiene) is also reported.

The reaction of **1** with 2 equiv of $CpMn(CO)_2(THF)$ ($Cp = \eta^5\text{-}C_5H_5$) in THF afforded $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Mn(CO)_2Cp]$ (**2**; Scheme 1).[8] The structure of **2** has been confirmed by X-ray structure analysis. It showed that compound **2** contains a germavinylidene as a neutral ligand bonded to the Mn(I) center. The result suggested that a solution of **1** may contain the monomeric germavinylidene $[(Me_3SiN{=}PPh_2)_2C{=}Ge:]$ by dissociation of the donor−acceptor interaction between the germanium centers. The germavinylidene thus acts as a two-electron ligand and displaces THF in $CpMn(CO)_2(THF)$ to form compound **2**. Similar Lewis base type behavior of germanium(II) complexes toward transition metals has been demonstrated.[9] For

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(8) A solution of $CpMn(CO)_3$ (0.21 g, 1.03 mmol) in 80 mL of THF with stirring was irradiated by a 125-W medium-pressure mercury lamp for ca. 6 h, and then **1** (0.65 g, 0.52 mmol) in 80 mL of THF was added. The mixture was stirred at room temperature for ca. 2 days. THF was removed under reduced pressure, and the residue was extracted with ether. After filtration and concentration of the filtrate, **2** was obtained as yellow crystals. Yield: 0.52 g (63%).

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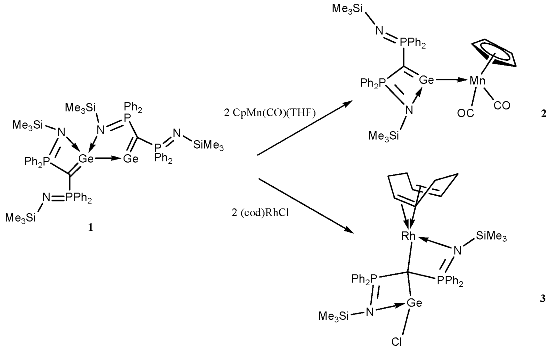
10.1021/ic050969u CCC: $30.25

Scheme 1



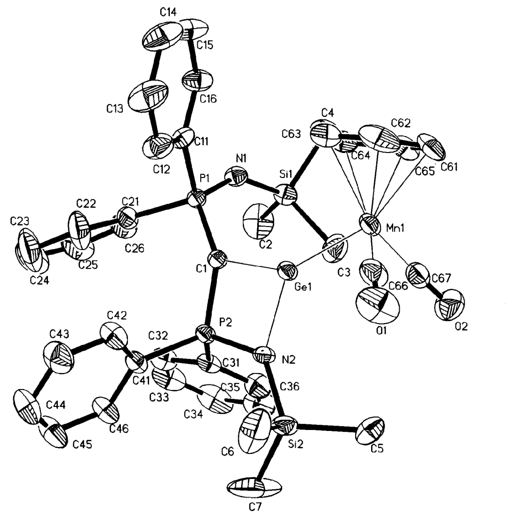


Figure 1. Molecular structure of **2** (30% probability ellipsoids). Selected bond distances [Å] and angles [deg]: Ge1−Mn1, 2.236(1); Ge1−C1, 1.885(3); Ge1−N2, 1.939(2); C1−P1, 1.748(3); C1−P2, 1.713(3); P1−N1, 1.549(3); P2−N2, 1.653(3); C66−O1, 1.160(5); C67−O2, 1.159(4); Mn1−C66, 1.770(4); Mn1−C67, 1.774(4); C1−Ge1−Mn1, 145.4(8); N2−Ge1−Mn1, 133.1(7); C1−Ge1−N2, 81.4(1); P1−C1−Ge1, 128.6(2); P2−C1−Ge1, 91.5(1); P1−C1−P2, 136.5(2); Ge1−N2−P2, 91.5(1); Ge1−Mn1−C66, 93.9(1); Ge1−Mn1−C67, 91.2(1).

example, $[M(CO)_5Ge\{N(SiMe_3)_2\}_2]$ (M = Cr, Mo, or W),[10] $[M(PR_3)_2Ge\{N(SiMe_3)_2\}_2]$ (M = Ni or Pd),[11] and $[Fe(CO)_4Ge(OAr)_2]$ {Ar = 2,4,6-tris[(dimethylamino)methyl]phenyl}[12] have been reported. Recently, Barrau and co-workers have reported the synthesis of $[(Salen)Ge{\rightarrow}Mn(CO)_2(Cp)]$ from the reaction of [(Salen)Ge] with $CpMn(CO)_2(THF)$.[13]

A similar reaction of **1** with 2 equiv of (cod)RhCl in THF gave $[(Me_3SiN{=}NPPh_2)_2\{(cod)Rh\}C{-}GeCl]$ (**3**).[14] The X-ray structure of **3** showed that (cod)RhCl underwent a 1,2-addition with germavinylidene in solution. The Ge═C bond inserted into the Rh−Cl bond underlining the nucleophilic character at the carbene center. This contrasts with the results found in the reaction of $[MCl_2\{C(PPh_2{=}NSiMe_3)_2\text{-}\kappa C,\kappa^2 N,N'\}]$, in which the electrophilic moiety was added to the carbene center.[15] The result is different from that of $[RhCl\{Ge(NBu^t)_2SiMe_2\}_4]$[16] or *cis*-$[RhCl\{Ge(NR_2)_2\}(PPh_3)]$ (R = $SiMe_3$),[9b] in which the germanium(II) center acted as a Lewis base toward RhCl. The X-ray structure also showed that the Ge−C bond distance is lengthened (by 0.191 Å) significantly in **3**, as compared with the Ge−C double bond distance in **2**. Therefore, the germavinylidene exists as a vinylidene structure instead of an ylide−amide structure in the solution.[17] Compound **3** is a bimetallic bis(iminophosphorano)methanide complex. Other bimetallic examples such as $[(AlMe)_2\{\mu^2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4 C,C',N,N'\}]$[18] and $[Cr\{\mu^2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4 C,C',N,N'\}]_2$[19] have been reported. A rhodium bis(iminophosphorano)methanide complex $[Rh\{CH(PPh_2{=}N{-}C_6H_4\text{-}4\text{-}CH_3)_2\}(cod)]$ has also been synthesized.[20]

Compounds **2** and **3** were isolated as yellow crystalline solids. They are air-sensitive, soluble in THF, and sparingly soluble in Et_2O. They have been characterized by NMR spectroscopy and X-ray structure analysis.[21] The ^{31}P NMR spectrum of **2** at 298 K showed one singlet at δ 32.37 ppm, which does not correspond to the X-ray structure. This may be due to the fluxional coordination of the imino nitrogen atoms at the germanium center in solution. At 238 K, the fluxional coordination slowed and the ^{31}P NMR of **2** displayed two singlets at δ 5.06 and 62.42 ppm, consistent with the X-ray structure. The ^{31}P NMR spectrum of **3** showed two signals at δ 45.53 and 58.43 ppm due to two different phosphorus environments as in the solid-state structure.

The molecular structure of **2** is shown in Figure 1.[22] Compound **2** is comprised of a monomeric germavinylidene

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(14) A solution of **1** (0.47 g, 0.37 mmol) in THF (30 mL) was added dropwise to (cod)RhCl (0.18 g, 0.75 mmol) in THF (30 mL) at 0 °C. The reaction mixture was stirred at room temperature for 40 h. Volatiles in the mixture were removed under reduced pressure, and the residue was extracted with Et_2O. After filtration and concentration of the filtrate, **2** was obtained as yellow crystals. Yield: 0.54 g (78%).

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(21) **2**. Mp: 149.6 °C (dec). Anal. Calcd for $C_{38}H_{43}GeMnN_2O_2P_2Si_2$: C, 56.66; H, 5.38; N, 3.48. Found: C, 56.38; H, 5.13; N, 3.25. ^1H NMR (THF-d_8): δ −0.11 (s, 18H, $SiMe_3$), 4.33 (s, 5H, η^5-C_5H_5), 7.30−7.32 (m, 8H, Ph), 7.39−7.41 (m, 4H, Ph), 7.60−7.72 (m, 8H, Ph). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 3.79 ($SiMe_3$), 81.13 (η^5-C_5H_5), 129.06, 129.22, 131.52, 131.92, 132.68, 133.10, 133.24, 137.29 (Ph), 231.22 (CO). $^{31}P\{^1H\}$ NMR (298 K, THF-d_8): δ 32.37. $^{31}P\{^1H\}$ NMR (238 K, THF-d_8): δ 5.06, 62.42. IR (cm^{-1}): ν_{CO} = 1855 (w), 1897 (s), 2018 (s). **3**. Mp: 144.5 °C (dec). Anal. Calcd for $C_{39}H_{50}ClGeN_2P_2RhSi_4{\cdot}THF$: C, 54.48; H, 6.17; N, 2.95. Found: C, 54.13; H, 6.17; N, 2.55. ^1H NMR (THF-d_8): δ −0.31 (s, 9H, $SiMe_3$), 0.05 (s, 9H, $SiMe_3$), 1.85−2.27 (m, 8H, cod-CH_2), 3.95 (br, 2H, cod-CH), 5.14 (br, 2H, cod-CH), 6.90 (m, 2H, Ph), 7.11−7.14 (m, 3H, Ph), 7.28−7.46 (m, 9H, Ph), 7.67−7.70 (m, 2H, Ph), 7.84−7.87 (m, 2H, Ph), 7.84−7.87 (m, 2H, Ph) 8.13−8.14 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 3.39 ($SiMe_3$), 4.74 ($SiMe_3$), 29.59, 30.31, 31.03, 31.74, 34.18, 34.72 (cod-H_2C_{allyl}), 75, 77, 77.92, 83.22, 85.43 (cod-HC_{vinyl}), 128.65, 128.81, 128.99, 129.14, 131.75, 132.08, 132.28, 132.44, 133.58, 135.67, 133.73, 133.81, 134.62, 134.77, 135.34, 135.43, 140.01 (Ph). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 45.53, 58.43.

bonded to the Mn center. One of the imino groups of the ligand coordinates to the germanium center, while the others remain uncoordinated. Thus, the geometry around the germanium center is trigonal planar. The differences in the P−N bond distances of 1.549(3) and 1.653(2) Å suggest that the delocalization of π electrons resulted from the conjugation of P═N and C═Ge double bonds in germavinylidene. Therefore, the Ge1−C1 distance of 1.885(3) Å in **2** is longer than the calculated value of 1.784−1.815 Å in H_2C═Ge:.[23] The Ge1−C1 distance is comparable with those of 1.905(8) and 1.908(7) Å in **1**.[5] The Ge1−Mn1 distance of 2.236(1) Å is similar to that of 2.250(1) Å in $[\{(\eta^5\text{-}C_5H_5)Mn(CO)_2\}_3\text{-}Ge]$[24] and that of 2.180(2) Å in $[\mu\text{-}Ge\{(\eta^5\text{-}C_5Me_5)Mn(CO)_2\}_2]$.[25]

The molecular structure of **3** is shown in Figure 2.[26] It showed that (cod)RhCl was added to the C═Ge bond in the anti position. The imino groups of the ligand coordinate to the germanium and rhodium centers, respectively. The Ge1−C4 distance of 2.076(3) Å in **3** is elongated in comparison to the C−Ge distances in **1**. The Ge1−C4 distance is similar to the Ge−C single-bond distances of 2.067 and 2.012 Å in $[Ge\{CH(SiMe_3)_2\}\{C(SiMe_3)_3\}]$[27] and 2.116 Å in $[Ge\{CPh(SiMe_3)C_5H_4N\text{-}2\}_2]$.[28] The Ge1−Cl1 bond distance of 2.350(1) Å in **3** is slightly longer than that of 2.203(10) Å in $[Ge(C_6H_3\text{-}2,6\text{-}Trip_2)Cl]$[29] and that of 2.295(12) Å in $[\{HC(CMeNAr)_2\}GeCl]$.[30] The bond distances of Rh1−C4 [2.204(3) Å] and Rh1−N2 [2.181(3) Å] in **3** are similar to those in $[Rh(CH_2PPh_2$═$N-C_6H_4-CH_3\text{-}4)(cod)]$ [Rh−C, 2.128(3) Å; Rh−N, 2.132(3) Å].[31] The Rh1−C58 and Rh1−C51 bond distances of 2.102(4) and 2.116(4) Å are longer than those of Rh1−C54 [2.146(4) Å] and Rh1−C55 [2.157(4) Å]. This can be ascribed to the higher trans influence of the carbon atom compared to the nitrogen atom of the bis(iminophosphorano)methanide ligand.[31,32] Similar structural features can also be found in $[Rh(CH_2PPh_2$═$N-C_6H_4-CH_3\text{-}4)(cod)]$[31] and $[Rh(p\text{-}tol\text{-}N$═$PPh_2CHPPh_2NH\text{-}p\text{-}tol)(cod)]$.[32]

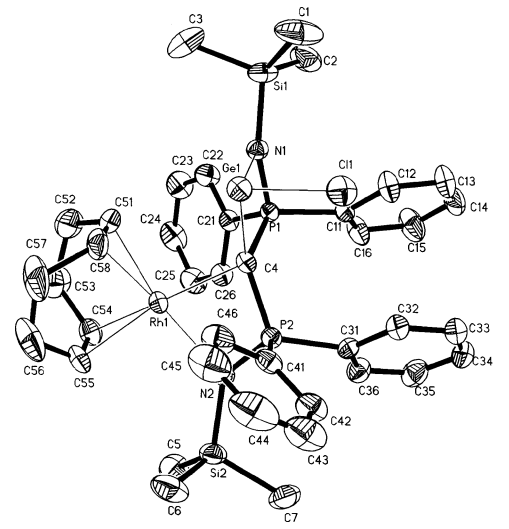

Figure 2. Molecular structure of **3** (30% probability ellipsoids). Selected bond distances [Å] and angles [deg]: C4−Ge1, 2.076(3); Ge1−Cl1, 2.350(1); Ge1−N1, 2.037(3); P1−N1, 1.612(3); P1−C4, 1.755(3); C4−Rh1, 2.204(3); Rh1−N2, 2.181(3); P2−N2, 1.607(3); P2−C4, 1.737(3); Rh1−C51, 2.116(4); Rh1−C58, 2.102(4); Rh1−C54, 2.146(4); Rh1−C55, 2.157(4); C4−Ge1−Cl1, 101.1(9); N1−Ge1−Cl1, 101.9(1); Ge1−N1−P1, 95.4(1); N1−P1−C4, 97.6(1); P1−C4−P2, 127.3(2); Ge1−C4−Rh1, 112.7(1); Ge1−C4−P1, 89.8(1); Rh1−C4−P2, 86.0(1); C4−P2−N2, 103.7(2); P2−N2−Rh1, 90.1(1).

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Supporting Information Available: Details in CIF format about the X-ray crystal structures, including ORTEP diagrams and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Crystal data for **2** ($C_{38}H_{43}GeMnN_2O_2P_2Si_2$): formula weight 805.39; a = 19.929(9) Å, b = 10.072(5) Å, c = 22.510(10) Å; α = 90°, β = 116.226(7)°, γ = 90°; V = 4053(3) Å^3; Z = 4; space group Cc (monoclinic); T = 293(2) K; λ = 0.710 73 Å; μ = 1.225 mm^{-1}; D_{calc} = 1.320 g cm^{-3}; R1 = 0.0291, wR2 = 0.0650.

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(26) Crystal data for **3** ($C_{39}H_{50}ClGeN_2P_2RhSi_4$·THF): formula weight 947.98; a = 9.728(2) Å, b = 10.947(2) Å, c = 23.382(4) Å; α = 83.703(4)°, β = 78.379(4)°, γ = 69.488(4)°; V = 2282.3(7) Å^3; Z = 2; space group $P\bar{1}$ (triclinic); T = 293(2) K; λ = 0.710 73 Å; μ = 1.235 mm^{-1}; D_{calc} = 1.379 g cm^{-3}; R1 = 0.0403, wR2 = 0.0936.

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