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Bis(germavinylidene) [$(Me_3SiN=PPh_2)_2C=Ge \rightarrow Ge=C-$ ($Ph_2P=NSiMe_3$)] and 1,3-Dimetallacyclobutanes [$M\{\mu^2-C(Ph_2P=NSiMe_3)_2\}$]₂ (M = Sn, Pb)**

Wing-Por Leung,* Zhong-Xia Wang, Hung-Wing Li, and Thomas C. W. Mak

Compounds containing a double bond between a Group 14 element and carbon (>M=C <; M = Si, Ge, Sn) have attracted much attention in the past 15 years, and have been the focus of several reviews.^[11] By contrast, the low-valent, analogous metallavinylidenes (:M=C <) are scarce. Nevertheless, spectroscopic and theoretical studies of the transient silavinylidene [:Si=CH₂] and germavinylidene [:Ge=CH₂] have been carried out.^[2-5] The low stability of these metallavinylidenes could be due to the reduced steric crowding at the low-coordinate metal center, which more readily leads to oligomerization. We report here the synthesis and structures of the first example of a stable bis(germavinylidene) as well as two novel, low-valent 1,3-dimetalla-

cyclobutanes; the latter are believed to form by dimerization of the intermediate metallavinylidenes

The monolithium salt $[CH(Ph_2P=NSiMe_3)_2Li(thf)]$ (1) was used as the ligand transfer reagent. It was prepared by the metalation reaction of bis(iminophosphorano)methane, $CH_2(Ph_2P=NSiMe_3)_2$, with *n*BuLi in THF. This lithium salt had been reported by Stephan and Ong,^[6] but its structure was not well-established as X-ray quality crystals were not obtained. We have now determined the X-ray structure of 1. The NMR spectral data of 1 are slightly different from that of the unsolvated compound reported previously.^[6]

The reaction of $\text{GeCl}_2 \cdot \text{dioxane}$ with two equivalents of **1** afforded bis(germavinylidene) **2** (Scheme 1). Unexpectedly **2**

 $[(Me_3SiN=PPh_2)_2C=Ge \rightarrow Ge=C(Ph_2P=NSiMe_3)_2] \qquad 2$

was formed upon further deprotonation of **1**. Compound **1** acts both as a ligand transfer reagent and as a base for dehydrochlorination. The by-product in the reaction is presumably the neutral bis(iminophosphorano)methane. The analogous reaction of **1** with PbCl₂ afforded the 1,3-plumbacyclobutane [Pb{ μ^2 -C(Ph₂P=NSiMe₃)₂]]₂ (**3**). Metal compounds derived from monolithium salts by double deprotonation of the ligands have been reported. For example, [Pd(μ -Cl)₂Pt{C(PPh₂)₂]_n],^[7] [Pt₂{C(PH₂P=S)₂}-(MeOcod)₂] (MeOcod = 8-methoxycyclooct-4-ene-1-yl),^[8]



Scheme 1.

and $[(AlMe_2)_2[\mu^2-C(Ph_2P=NSiMe_3)_2-\kappa^4C,C'N,N']]^{[9]}$ result from double deprotonation of the P-CH₂-P backbone.

The dimetallacyclobutanes $[M{\mu^2-C(Ph_2P=NSiMe_3)_2}]_2$ (M=Pb (3), Sn (4)) can also be prepared from the reaction of $M{N(SiMe_3)_2}_2$ with $CH_2(Ph_2P=NSiMe_3)_2$. Similar reactions have been reported by Cavell and co-workers in the synthesis of hafnium and samarium complexes containing M=Cbonds.^[10, 11] It is suggested that **3** and **4** result from the headto-tail cyclodimerization of metallavinylidene intermediates $[:M=C(Ph_2P=NSiMe_3)_2]$ (M=Pb, Sn).

Compounds 1-4 have been characterized by elemental analysis, NMR spectroscopy, and X-ray crystallography. The X-ray structure data for 1 and 4 will be reported elsewhere.

The molecular structure of **2** is shown in Figure 1.^[12] It comprises two germavinylidenes [:Ge=C(Ph₂P=NSiMe₃)₂] bonded together in a head-to-head manner. The molecule is asymmetrical with two different germanium environments: Ge(1) is bonded to the methanediide carbon atom C(1') and Ge(2), and subtended at an angle of 89.3(3)°. The fourcoordinate Ge(2) is bonded to Ge(1), C(2'), and two imino nitrogen atoms from the germavinylidenes. Each germavinylidene has an additional uncoordinated imino group. The Ge-Ge bond distance of 2.483(1) Å is longer than those reported for compounds containing a Ge-Ge double bond (2.213-2.347 Å).^[13] Therefore, the Ge–Ge bonding in **2** is more appropriately described as a donor-acceptor interaction, similar to that in the tin(II)-tin(II) complexes $[R_2^N Sn \rightarrow SnCl_2]$ ($R^N = CH(SiMe_3)C_6H_6N-8$) and the asymmetric distannene 5.^[14, 15] In 2, the four-coordinate Ge(2) behaves as the donor and the two-coordinate Ge(1) behaves as a Lewis acid center. The Ge-C bond in 2 (1.905(8) and 1.908(7) Å) are much shorter than the Ge-C single bonds in some Ge^{II}-alkyl and Ge^{II}-aryl compounds (2.012-2.135 Å).^[16] The structure of 2 also shows trans linkage of the C=Ge-Ge=C skeleton $(C(1')-Ge(1)-Ge(2) 89.3(3)^\circ)$,

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Figure 1. ORTEP drawing of **2**; hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Ge(1)-Ge(2) 2.4827(13), Ge(1)-C(1') 1.908(7), Ge(2)-C(2') 1.905(8), Ge(2)-N(1) 1.971(6), Ge(2)-N(3) 1.974(6), P(1)-C(1') 1.755(8), P(2)-C(1') 1.754(8), P(3)-C(2') 1.702(9), P(4)-C(2') 1.746(8), P(1)-N(1) 1.623(7), P(2)-N(2) 1.535(8), P(3)-N(3) 1.655(7), P(4)-N(4) 1.552(8); C(1')-Ge(1)-Ge(2) 89.3(3), C(2')-Ge(2)-N(1) 120.1(3), C(2')-Ge(2)-N(3) 80.4(3), N(1)-Ge(2)-N(3) 108.4(3), C(2')-Ge(2)-Ge(1) 128.2(3), N(1)-Ge(2)-Ge(1) 100.5(2), N(3)-Ge(2)-Ge(1) 117.5(2), P(1)-C(1')-P(2) 121.0(4), P(3)-C(2')-P(4) 125.7(5).

C(2')-Ge(2)-Ge(1) 128.2(3)°). The bis(germavinylidene) skeleton is twisted along the Ge–Ge axis at an angle of 43.9°.

The ¹H and ¹³C NMR spectra of **2** showed only one set of SiMe₃ signals, which does not correspond to the X-ray structure. This may be due to fluxional coordination of the imino nitorogen atoms at the germanium centers in solution.

The molecular structure of 1,3-dimetallacyclobutane **3** is shown in Figure 2. It consists of two metal atoms bridged by two methanediide carbon atoms, forming a 1,3- M_2C_2 fourmembered ring. The two imino nitrogen atoms of the ligand coordinate to the tetrahedral metal center to form MCPN four-membered rings. These MCPN rings together with the M_2C_2 ring, as the base, form a structure framework similar to an "open box". The geometry around each of the metal centers is square pyramidal.

The average Sn–C distance of 2.376 Å in **4** is longer than that in the stannene [{ $(Me_3Si)_2CH$ }_Sn=C{ $(BtBu)_2C(SiMe_3)_2$ }] (2.025(4) Å).^[16] Similarly the Pb–C bond in **3** (2.477 Å) is longer than that in the lead(II) alkyl compound [Pb{CH(Si-Me_3)(C₉H₆N-8)}_2] (2.336(3) Å).^[17] The metal – metal distances in dimetallacyclobutanes **3** and **4** are too long to consider the presence of bonding interactions.

Experimental Section

2: A solution of **1** (1.16 g, 1.82 mmol) in Et₂O (25 mL) was added to a cooled (ca. -90° C) suspension of GeCl₂·dioxane (0.21 g, 0.91 mmol) in Et₂O with stirring. The mixture was stirred at room temperature for 18 h and then filtered. Hexane (20 mL) was added to the filtrate, and the solution concentrated to about 5 mL. After the mixture was allowed to

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stand for 5 d, compound **2** was obtained as redorange crystals (0.24 g, 42%), m.p. 110–111°C. Elemental analysis calcd (%) for $C_{62}H_{76}N_4Ge_2P_4$. Si₄: C 59.16, H 6.09, N 4.45; found: C 58.95, H 6.30, N 4.47; ¹H NMR (300 MHz, C₆D₆, 25°C, TMS): $\delta = 0.08$ (s, 36H, SiMe₃), 7.00–7.08 (m, 24H, Ph), 7.73–7.80 (m, 16H, Ph); ¹³C{¹H} NMR (75.47 MHz, C₆D₆, 25°C, TMS): $\delta = 3.53$ (SiMe₃), 128.10, 130.47, 131.95, 137.02 (Ph); ³¹P{¹H} NMR (161.92 MHz, C₆D₆, 25°C, 80% H₃PO₄): $\delta = 34.59$.

3 (method 1): A mixture of CH₂(Ph₂P=NSiMe₃)₂ (1.28 g, 2.29 mmol) and Pb{N(SiMe₃)₂}₂ (1.23 g, 2.33 mmol) in toluene (25 mL) was stirred at room temperature for 40 h. Solvent was removed in vacuo and the residue was dissolved in Et2O. After filtration, the filtrate was concentrated to about 5 mL. After the mixture was allowed to stand for 3 d, yellow crystals of 3 (1.40 g, 79.8%) were obtained, m.p. 234-237 °C. Elemental analysis calcd (%) for C62H76N4P4Pb2Si4: C 48.74, H 5.01, N 3.67; found: C 48.80, H 5.08, N 3.74; ¹H NMR (300 MHz, C_6D_6 , 25 °C, TMS): $\delta = -0.43$ (s, 36 H, SiMe₃), 6.90-7.70 (m, 40 H, Ph); ¹³C¹H} NMR (75.47 MHz, C_6D_6 , 25 °C, TMS): $\delta = 4.18$ (SiMe₃), 128.24, 128.50, 130.47, 131.14, 131.94, 133.15 (Ph); $^{31}P{^{1}H}$ NMR (161.92 MHz, C₆D₆, 25 °C, 80 % H₃PO₄): $\delta = 5.46$.

3 (method 2): A cooled solution of 1 (0.77 g, 1.21 mmol) in Et₂O (20 mL) was added to $PbCl_2$ (0.17 g, 0.61 mmol) with stirring. The mixture was warmed to RT and stirred for 18 h. After filtration

and concentration of the filtrate, **3** obtained as yellow crystals (0.39 g, 83.6 %).

4: A mixture of $CH_2(Ph_2P=NSiMe_3)_2$ (0.27 g, 0.49 mmol) and $Sn\{N(SiMe_3)_2\}_2$ (0.44 g, 1.00 mmol) in toluene (15 mL) was stirred at room temperature for 42 h. After removal of the solvent in vacuo, the residue was extracted with Et₂O and filtered. Hexane (20 mL) was added to the filtrate, and the solution concentrated to about 2 mL. After the mixture was allowed to stand for 3 d, yellow crystals of complex **4** (0.23 g, 70.2%) were obtained, m.p. 210–211°C. ¹H NMR (300 MHz, C₆D₆, 25°C, TMS):



Figure 2. ORTEP drawing of **3**; hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Pb(1)-C(2') 2.452(7), Pb(1)-C(1') 2.493(6), Pb(1)-N(2) 2.619(5), Pb(1)-N(3) 2.708(6), Pb(2)-C(1') 2.451(7), Pb(2)-C(2') 2.510(7), Pb(2)-N(4) 2.572(5), Pb(2)-N(1) 2.689(6), P(1)-N(1) 1.573(6), P(2)-N(2) 1.604(5), P(3)-N(3) 1.581(6), P(4)-N(4) 1.595(6); C(2')-Pb(1)-C(1') 91.6(2), C(1')-Pb(2)-C(2') 91.2(2), C(1')-Pb(1)-N(2) 63.2(2), C(2')-Pb(1)-N(2) 108.6(2), C(2')-Pb(1)-N(3) 61.3(2), C(1')-Pb(1)-N(3) 109.7(2), N(2)-Pb(1)-N(3) 168.45(18), C(1')-Pb(2)-N(4) 106.2(2), C(2')-Pb(2)-N(4) 64.21(19), C(1')-Pb(2)-N(1) 62.4(2), C(2')-Pb(2)-N(1) 113.1(2), N(4)-Pb(2)-N(1) 168.53(19).

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δ = 0.04 (s, 36 H, SiMe₃), 6.92 – 7.11 (m, 24 H, Ph), 7.40 – 7.74 (m, 16 H, Ph); ¹³C{¹H} NMR (75.47 MHz, C₆D₆, 25 °C, TMS): δ = 3.65 (SiMe₃), 130.09, 132.87, 139.25, 140.44 (Ph); ³¹P{¹H} NMR (161.92 MHz, C₆D₆, 25 °C, 80 % H₃PO₄): δ = 12.34.

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- [12] Crystal data for 2 ($C_{64}H_{81}Ge_2N_4O_{0.5}P_4Si_4$): M = 1295.75, crystal size $0.60 \times 0.45 \times 0.25$ mm, a = 21.030(4), b = 16.453(3), c = 19.919(4) Å, $\alpha = 90, \beta = 91.62(3), \gamma = 90^{\circ}, V = 6890(2) \text{ Å}^3, \rho_{\text{calcd}} = 1.249 \text{ g cm}^{-3}, \mu =$ 1.075 mm⁻¹, Z = 4, monoclinic, space group $P2_1/c$, $\lambda = 0.71073$ Å, T =293(2) K, $2\theta_{\text{max}} = 48^{\circ}$, 11179 measured reflections, 10823 independent and 5511 observed reflections $(I > 2\sigma(I))$, 697 refined parameters, R1 = 0.0725, wR2 = 0.1843, largest diff. peak and hole 0.3833 and $-0.696 \text{ e} \text{ Å}^{-3}$. Crystal data for **3** (C₆₂H₇₆N₄P₄Pb₂Si₄): M = 152.89, crystal size $0.78 \times 0.19 \times 0.17$ mm, a = 10.4752(14), b = 44.827(6), c =14.068(2) Å, $\alpha = 90, \beta = 100.796(3), \gamma = 90^{\circ}, V = 6489.0(15) Å^3, \rho_{calcd} =$ 1.564 g cm⁻³, $\mu = 5.395$ mm⁻¹, Z = 4, monoclinic, space group $P2_1/n$, $\lambda = 0.71073$ Å, T = 293(2) K, ϕ/ω scans, $2\theta_{\text{max}} = 56.22^{\circ}$, 45654 measured reflections, 15684 independent and 8598 observed reflections $(I > 2\sigma(I))$, 686 refined parameters, R1 = 0.0468, wR2 = 0.0804, largest diff. peak and hole 1.356 and $-1.686 \text{ e} \text{ Å}^{-3}$. The crystal data were measured on an IP Rigaku diffractometer (for 2) or a Brüker SMART CCD area detector (for 3). The structures were solved by direct methods using SHELXS-97 and refined using SHELXL-97. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-160423 and 160424. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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A Synthetic Pore-Mediated Transmembrane Transport of Glutamic Acid**

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Synthetic constructs that are specifically designed to allow transport of hydrophilic substances across cell membranes are important research tools with possible applications in gene and antisense therapy, metabolite regulation, and drug delivery.^[1] However, surprisingly the design of synthetic transmembrane pores from first principles has remained largely unexplored.^[2, 3] Here we describe the design and functional characterization of a self-assembling transmembrane portion functional that is capable of highly efficient transport of L-glutamic acid.

Appropriately designed cyclic peptides with an even number of hydrophobic α -amino acids with alternating D and L configurations have been previously shown to selfassemble through directed hydrogen-bonding networks into antiparallel β -sheet tubular structures in lipid bilayers forming active ion channels.^[4] One attractive feature of the selfassembling peptide nanotube class of transmembrane supramolecular structures is that pore size can be tuned by the choice^[5] and the number of α -amino acids employed in the cyclic peptide subunit design. In this context we have shown previously that cyclic octapeptides size-selectively transport small ions,^[4, 6] whereas decapeptides can also transport small molecules such as glucose.^[3]

The present system is based on eight- and ten-residue cyclic peptides $1^{[4]}$ and 2,^[3] respectively, which form transmembrane channels (Scheme 1). Inspection of space-filling models derived from X-ray structural analogues of peptide nanotubes suggests that a completely dehydrated glutamate ion in an extended conformation would barely fit inside a channel formed by the cyclic octapeptide 1 (7 Å van der Waals internal diameter) but could be easily accommodated in a transmembrane pore derived from cyclic decapeptide 2 (10 Å van der Waals internal diameter).^[3] We therefore sought to examine the utility of self-assembling peptide nanotubes for size-selective transmembrane transport of glutamate ions.

Previous attenuated total reflection/Fourier transform infrared (ATR-FTIR) spectroscopic studies of the peptide **1** in lipid multibilayers indicated that the self-assembled transmembrane channel adopts an orientation of $7 \pm 1^{\circ}$ relative to the average plane of membrane.^[7] In analogous studies for decapeptide **2**, the peptide assembly in the lipid bilayer displayed backbone amide bands indicative of the expected

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- Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

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