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Synthesis of Bisgermavinylidene and Its Reaction with Chalcogens

Wing-Por Leung,* Cheuk-Wai So, Zhong-Xia Wang, Jin-Zhi Wang, and
Thomas C. W. Mak

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

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The lithium complex $[HC(PPh_2{=}NSiMe_3)_2Li(THF)]$ (**2**) prepared by the reaction of Bu^nLi with bis(iminophosphorano)methane reacts with $GeCl_2{\cdot}$dioxane in different stoichiometric ratios to afford $[HC(PPh_2{=}NSiMe_3)_2GeCl]$ (**3**) and $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (**4**), respectively. Bisgermavinylidene **4** can also be obtained by the reaction of **3** with $[Ge\{N(SiMe_3)_2\}_2]$ or **2**. Further reaction of **4** with Me_3NO afforded $[(\mu\text{-}N{=}Ph_2P)(Me_3SiN{=}Ph_2P)C{=}Ge(OSiMe_3)]_2$ (**5**), and direct reaction of elemental chalcogens (sulfur, selenium, and tellurium) with **4** afforded $[(Me_3SiN{=}PPh_2)_2C{=}Ge(\mu\text{-}E)]_2$ [E = S (**6**), Se (**7**), and Te (**8**)]. X-ray structures of compounds **2**−**8** have been determined.

Introduction

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 it can undergo oligomerization readily.[2] Nevertheless, stable germenes $R_2Ge{=}CR'_2$ can be synthesized by incorporating sterically bulky substituents at both germanium and carbon.[3] The low-valent germanium analogues such as germavinylidenes ($>C{=}Ge{:}$) are rare.

We have communicated the synthesis of bisgermavinylidene $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (**4**).[4] We have also reported the synthesis of some group 14 ketone analogues $R_2M{=}E$ from the direct reaction of group 14 carbene analogues MR_2 ($R = CH(SiMe_3)C_9H_6N\text{-}8$ or $CPh(SiMe_3)C_5H_4N\text{-}2$; M = Ge or Sn) with corresponding elemental chalcogens.[5] Recently, we were interested in the synthesis of compounds containing a $>C{=}Ge{=}E$ moiety, as they may be considered as germaketene analogues, which are also scarcely found. Their unusual structures and possibly the unknown reactivity have attracted our interest. We anticipated that the bisgermavinylidene **4** is potentially a source for the reactive monomeric intermediate germavinylidene "$:Ge{=}C(PPh_2{=}NSiMe_3)_2$", which may serve as a synthon for the direct synthesis of germaketene analogues through the active lone pair at the germanium center.

In this paper, we report the full details of the preparation and characterization of $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (**4**) and its reactivity with chalcogens in order to prepare the germaketene analogues.

Results and Discussion

Synthesis of Bisgermavinylidene $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (4). Treatment of bis(iminophosphorano)methane $[(Me_3SiN{=}PPh_2)_2CH_2]$ (**1**)[6] with Bu^nLi in THF afforded the monomeric $[HC(PPh_2{=}NSiMe_3)_2Li{\cdot}THF]$ (**2**), which has been reported earlier, but it has not been structurally characterized.[7] We have now determined the X-ray structure of **2**. The similar lithium complex $[Li\{HC(Cy_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa N,\kappa N'\}(OEt_2)]$ (Cy = cyclohexyl) prepared from the reaction of $[(Me_3SiN{=}PCy_2)_2CH_2]$ with excess MeLi has been reported.[8]

The reaction of 2 equiv of **2** with $GeCl_2{\cdot}$dioxane for 2 days afforded bisgermavinylidene $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (**4**) (Scheme 1). When the reaction was quenched after 1 day, $[HC(PPh_2{=}NSiMe_3)_2GeCl]$ (**3**) can be isolated as the intermediate compound. Compound **3** can be further dehydrochlorinated by **2** to form bisgermavinylidene **4**, if the reaction mixture was kept for a further 24 h. It is suggested that compound **2** acts both as a ligand transfer reagent and as a base for dehydrochlorination.

Bisgermavinylidene **4** can also be synthesized stepwisely by the reaction of $[Ge\{N(SiMe_3)_2\}_2]$ with $[HC(PPh_2{=}NSiMe_3)_2GeCl]$ (**3**), which was prepared sepa-

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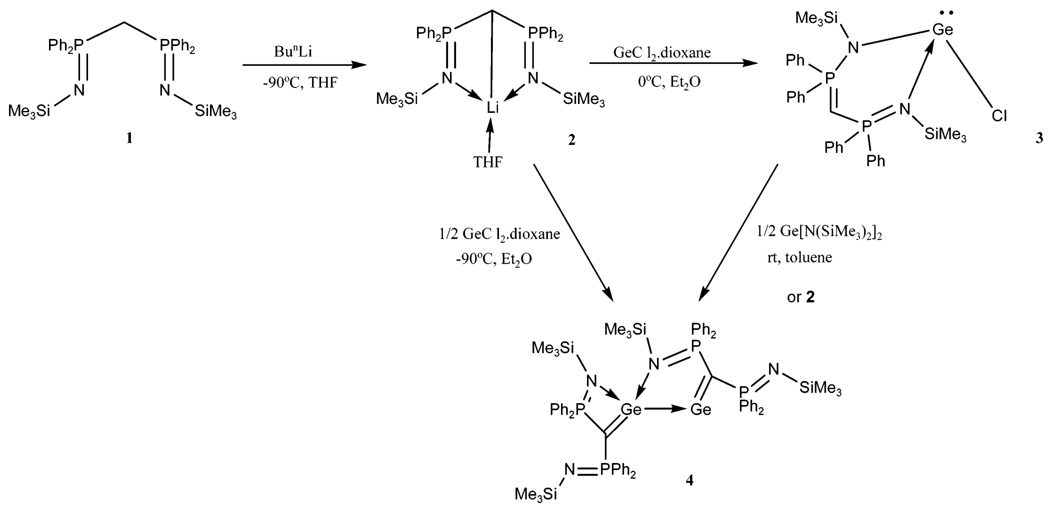
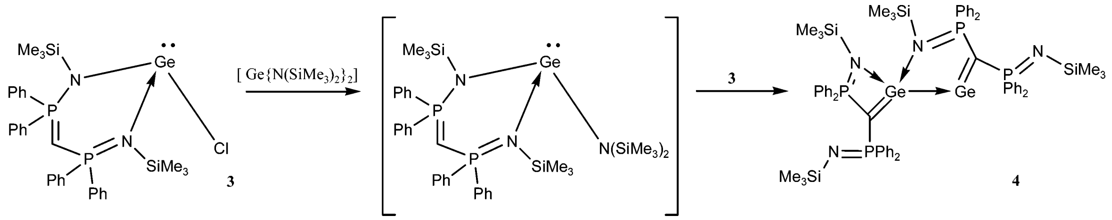
10.1021/om034071t CCC: $25.00

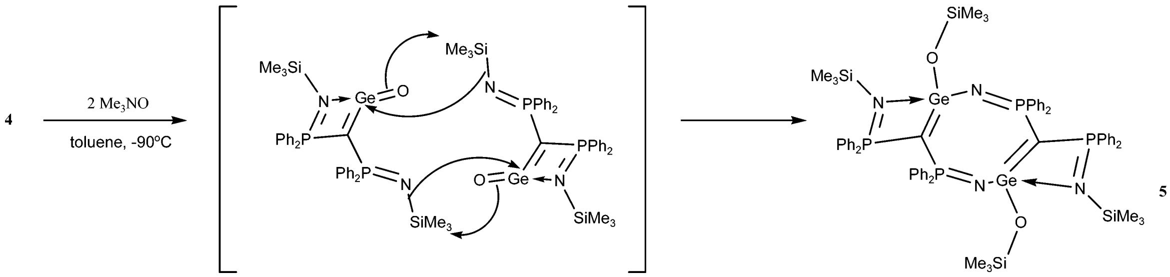
Scheme 1



Scheme 2



Scheme 3



rately by the reaction of 1 equiv of **2** with $GeCl_2$·dioxane in Et_2O. It is proposed that the ligand transfer intermediate $[Ge\{CH(PPh_2{=}NSiMe_3)_2\}\{N(SiMe_3)_2\}]$ formed underwent dehydrochlorination and deamination with **3** to form bisgermavinylidene **4** (Scheme 2). In contrast, the reaction of **3** with $MgBu^n_2$ and $AlMe_3$ in toluene at room temperature gave the known bis(iminophosphorano)methanide complexes $[HC(PPh_2{=}NSiMe_3)_2Mg(\mu\text{-}Cl)]_2$ and $[HC(PPh_2{=}NSiMe_3)_2AlMe_2]$, respectively.[9,10]

Reaction of Bisgermavinylidene with Chalcogens. We have attempted to prepare the germaketene analogue containing a terminal >C=Ge=O moiety by the reaction of bisgermavinylidene **4** with 2 equiv of Me_3NO in toluene. However, the product obtained was $[(\mu\text{-}N{=}Ph_2P)(Me_3SiN{=}Ph_2P)C{=}Ge(OSiMe_3)]_2$ (**5**) isolated as a pale yellow crystalline solid (Scheme 3). It is proposed that the intermediate compound bearing a >C=Ge=O moiety underwent an insertion of the GeO unit into the N−$SiMe_3$ bond of the imino group. The unsuccessful isolation of the compound with a terminal >C=Ge=O moiety is probably due to the reactive Ge=O bond. Some previous attempts to generate >Ge=O species from germylenes, which led to the formation of germaindanol,[11] oxo-bridged dimer $[\{(Me_3Si)_2N\}_2Ge(\mu\text{-}O)]_2$,[12] or *gem*-dihydroxy compound $[(2,6\text{-}Mes_2H_3C_6)_2Ge(OH)_2]$,[13] have been reported in the literature.

The reaction of **4** with stoichiometric amounts of elemental chalcogens in THF afforded chalcogen-bridged dimers of germaketene analogues $[(Me_3SiN{=}PPh_2)_2C{=}Ge(\mu\text{-}E)]_2$ [E = S (**6**), Se (**7**), and Te (**8**)], respectively (Scheme 4). Compounds **6**−**8** were isolated as colorless, yellow, and red crystalline solids, respectively. The unsuccessful isolation of compounds with terminal germaketene moieties >C=Ge=E could be due to the prolonged and more polar >C=Ge=E skeleton as compared to >C=Ge=O, which is more susceptible to dimerize at the chalcogen end and cannot be stabilized kinetically by the ligand. Similar results have been found for the synthesis of germaketone analogues in the

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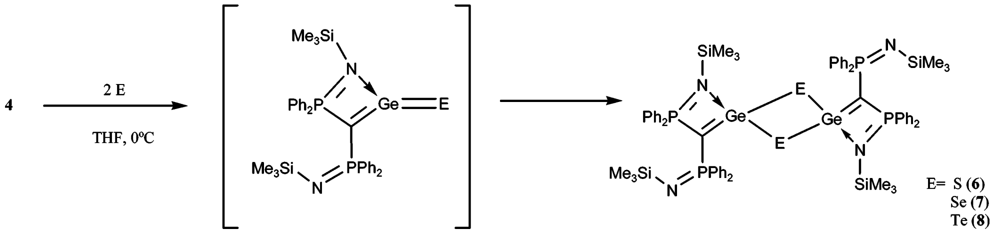
Scheme 4



reaction of germylenes with chalcogens, where chalcogen-bridged dimers were formed.[14] Compounds **7** and **8** are light sensitive, as they turned black when exposed to light. Therefore, the preparations of **7** and **8** were carried out with the exclusion of light.

Spectroscopic Properties of Compounds. The ^{1}H and ^{13}C NMR spectra of **2** displayed one set of signals due to the bis(iminophosphorano)methanide ligand and THF, which is different from the unsolvated compound reported by Stephan and co-workers.[7]

The ^{1}H NMR spectrum of **3** displayed one singlet signal for the $SiMe_3$ group and a triplet at δ 3.50 ppm (J_{P-H} = 12 Hz) for the methine proton on the P−C−P backbone with coupling to two equivalent phosphorus nuclei. The data indicate considerable delocalization throughout the N−P−C−P−N backbone of the ligand, consistent with the solid-state structure of **3**. This is also consistent with a singlet at δ 13.97 ppm in the ^{31}P NMR spectrum. The ^{13}C NMR spectrum of **3** is normal and consistent with the ^{1}H NMR spectrum.

The ^{1}H and ^{13}C NMR spectra of **5** are normal. The ^{31}P NMR spectrum of **5** displayed two signals at δ 18.66 and 44.61 ppm due to two different phosphorus environments, consistent with the solid-state structure.

The ^{1}H and ^{13}C NMR spectra of **6**−**8** showed a similar pattern and displayed one set of signals due to the bis(iminophosphorano)methandiide ligand. The ^{31}P NMR spectra of **6**−**8** displayed two sharp singlets [δ 10.69, 57.52 (**6**); δ 13.97, 60.80 (**7**); δ 11.78, 58.97 ppm (**8**)] due to two different phosphorus environments, consistent with the solid-state structures. It is suggested that the coordination of the imino groups to the germanium centers in **6**−**8** is nonfluxional in solution. The ^{77}Se NMR spectrum of **7** displayed a singlet at δ 860.88 ppm, which showed a downfield shift as compared with the signal at δ −476.0 ppm for $[Ge\{(NSiMe_3)_2\}_2(\mu\text{-}Se)]_2$,[14d] but similar to that of δ 940 ppm in [(Tbt)(Mes)Ge=Se].[15] It is suggested that **7** may exist as a monomer in solution. The ^{125}Te NMR spectrum of **8** displayed a singlet at δ 1025.53, which is comparable to the signal of δ 1184 ppm in $[Ge\{(NSiMe_3)_2\}_2(\mu\text{-}Te)]_2$.[14d] The FAB-mass spectrum of compound **5** did not show the parent peak. The FAB-mass spectra of compounds **6**−**8** displayed the peak due to $[M/2 + H]^+$, suggesting that **6**−**8** may exist as monomeric species in the vapor phase.

X-ray Structures. The solid-state structure of **2** is shown in Figure 1. Selected bond distances (Å) and angles (deg) of **2** are listed in Table 2. The four-coordinated Li(1) is bonded to the methanide carbon atom C(55), two imino nitrogen atoms from the ligand, and O(1) from the THF to form two strained four-membered metallacycles sharing the Li(1)−C(55) edge. The Li(1)−C(55) bond distance of 2.622(9) Å in **2** is similar to that of 2.633(7) Å in $[Li\{HC(Cy_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa N,\kappa N'\}(OEt_2)]$.[8] The Li(1)−N distances of 1.980(9) and 2.017(9) Å in **2** are comparable to those of 2.033(6) and 2.012(7) Å in $[Li\{HC(Cy_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa N,\kappa N'\}(OEt_2)]$.[8] The P−N distances of 1.572(4) and 1.575(3) Å and the C−P bonds of 1.717(4) and 1.722(4) Å are different from those of $[(Me_3SiN{=}PPh_2)_2CH_2]$ (**1**) (P−N = 1.536(2) Å; C−P = 1.825(1) Å).[6] These suggest considerable delocalization throughout the N−P−C−P−N ligand backbone.

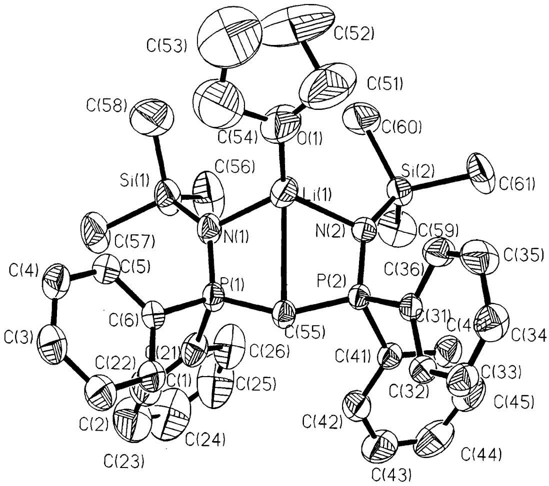


Figure 1. Crystal structure of **2** with atomic numbering scheme.

Compound **3** is a monomeric heteroleptic germylene. The solid-state structure of **3** is shown in Figure 2. Selected bond distances (Å) and angles (deg) of **3** are listed in Table 2. The bis(iminophosphorano)methanide ligand is bonded in a N,N′-chelate fashion to the germanium center and adopts a trigonal pyramidal geometry. The sum of bond angles at the metal center is 299.97°, which deviates significantly from the tetracoordinated germylene.[16] This is consistent with a stereoactive lone pair at the germanium center. The distance between the methanide carbon and germanium of 3.339 Å is significantly longer than the Li−C bond distance of 2.622(9) Å in **2** and the Mg−C bond distance of 2.460(8) Å in $[HC(PPh_2{=}NSiMe_3)_2Mg(\mu\text{-}Cl)]_2$,[10] suggesting no interaction between germanium and methanide carbon. The bond distances of Ge−N, P−N, and

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Table 1. Crystallographic Data for Compounds 2, 3, and 5 and 6−8

	2	**3**	**5**
formula	$C_{35}H_{47}LiN_2OP_2Si_2$	$C_{31}H_{39}ClGeN_2P_2Si_2$	$C_{62}H_{76}N_4P_4O_2Si_4Ge_2$
fw	636.81	665.80	1290.69
color	colorless	pale yellow	pale yellow
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	11.028(2)	12.021(4)	26.24(3)
b (Å)	11.311(2)	15.050(4)	13.746(7)
c (Å)	16.174(3)	20.647(6)	20.021(8)
α (deg)	72.96(3)	90.000(6)	90
β (deg)	88.60(3)	90.000(6)	107.08(9)
γ (deg)	82.62(3)	66.460(4)	90
V (Å^3)	1912.7(7)	3424.6(17)	6903(9)
Z	2	4	4
d_{calcd} (g cm^{-3})	1.106	1.291	1.242
μ (mm^{-1})	0.203	1.158	1.075
F(000)	680	1384	2688
cryst size (mm)	0.60 × 0.50 × 0.40	1.30 × 0.79 × 0.78	0.32 × 0.15 × 0.15
2θ range (deg)	2.27−25.00	0.99−28.28	1.62−28.11
index range	$-13 \le h \le 13$, $-13 \le k \le 0$, $-19 \le l \le 18$	$-10 \le h \le 15$, $-18 \le k \le 19$, $-27 \le l \le 27$	$-25 \le h \le 34$, $-18 \le k \le 18$, $-26 \le l \le 19$
no. of reflns collected	7100	23 036	23 200
no. of indep reflns	6728	16 172	8352
R1, wR2 ($I > 2(\sigma)I$)	0.0647, 0.1762	0.1010, 0.2552	0.0649, 0.1198
R1, wR2 (all data)	0.1467, 0.2126	0.1189, 0.2723	0.2073, 0.1625
goodness of fit, F^2	1.056	1.005	0.782
no. of data/restraints/params	6728/1/388	16172/0/703	8352/0/353
largest diff peaks, e Å^{-3}	0.402 to −0.340	3.046 to −0.808	0.876 to −0.523

	6	**7**	**8**
formula	$C_{62}H_{76}N_4Ge_2P_4S_2Si_2$	$C_{62}H_{76}N_4Ge_2P_4Se_2Si_2$	$C_{62}H_{76}N_4Ge_2P_4Si_2Te_2$
fw	1322.81	1418.62	1513.89
color	white	yellow	red
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	10.1970(6)	11.8491(14)	10.4130(5)
b (Å)	11.5672(7)	16.902(2)	11.6373(6)
c (Å)	15.9241(9)	17.737(2)	15.0654(7)
α (deg)	79.1130(10)	90	103.7030(10)
β (deg)	88.5170(10)	105.057(3)	90.9820(10)
γ (deg)	69.3700(10)	90	101.5030(10)
V (Å^3)	1724.49(18)	3430.3(7)	1734.05(15)
Z	1	2	1
d_{calcd} (g cm^{-3})	1.274	1.373	1.450
μ (mm^{-1})	1.133	2.140	1.891
F(000)	688	1452	760
cryst size (mm)	0.50 × 0.17 × 0.17	1.00 × 0.18 × 0.16	0.45 × 0.26 × 0.24
2θ range (deg)	1.30−28.02	1.69−28.07	1.84−28.00
index range	$-13 \le h \le 13$, $-15 \le k \le 11$, $-20 \le l \le 21$	$-15 \le h \le 15$, $-17 \le k \le 22$, $-23 \le l \le 20$	$-13 \le h \le 13$, $-9 \le k \le 15$, $-19 \le l \le 15$
no. of reflns collected	11 921	22 966	11 765
no. of indep reflns	8215	8299	8186
R1, wR2 ($I > 2(\sigma)I$)	0.0616, 0.1336	0.0667, 0.1555	0.0364, 0.0789
R1, wR2 (all data)	0.1510, 0.1682	0.1357, 0.1787	0.0594, 0.0859
goodness of fit, F^2	0.879	0.901	0.904
no. of data/restraints/params	8215/0/352	8299/7/397	8186/0/352
largest diff peaks, e Å^{-3}	0.643 to −0.570	1.444 to −1.077	0.837 to −0.504

C−P are similar. This shows considerable delocalization throughout the N−P−C−P−N backbone of the ligand. The Ge−N distances of 1.983(4) and 2.002(4) Å in **3** are similar to those distances reported for typical Ge−N single bond distances ranging from 1.910 to 2.042 Å.[17] The Ge−Cl bond distance of 2.334(2) Å in **3** is longer than that of 2.203(10) Å in [Ge(C_6H_3-2,6-Trip$_2$)Cl][18] and 2.295(12) Å in [{HC(CMeNAr)$_2$}GeCl].[19]

The molecular structure of **5** is shown in Figure 3. Selected bond distances (Å) and angles (deg) of **5** are listed in Table 2. Compound **5** is comprised of two germenes joined by the "Ph$_2$P═N" bridges to form an eight-membered heterocyclic ring. The geometry around the germanium atom is tetrahedral. The Ge−C distance of 1.915(5) Å is slightly longer than those of 1.905(8) and 1.908(7) Å in **4**. The Ge−O distance of 1.759(4) Å is relatively shorter when compared with the Ge−O bond distance of 1.792 Å in [(2,6-Mes$_2$H$_3$C$_6$)$_2$Ge(OH)$_2$],[13] 1.805 Å in [{(Me$_3$Si)$_2$N}$_2$Ge(μ-O)]$_2$,[12] and the sum of the covalent radii of germanium (1.22 Å) and oxygen (0.66 Å).

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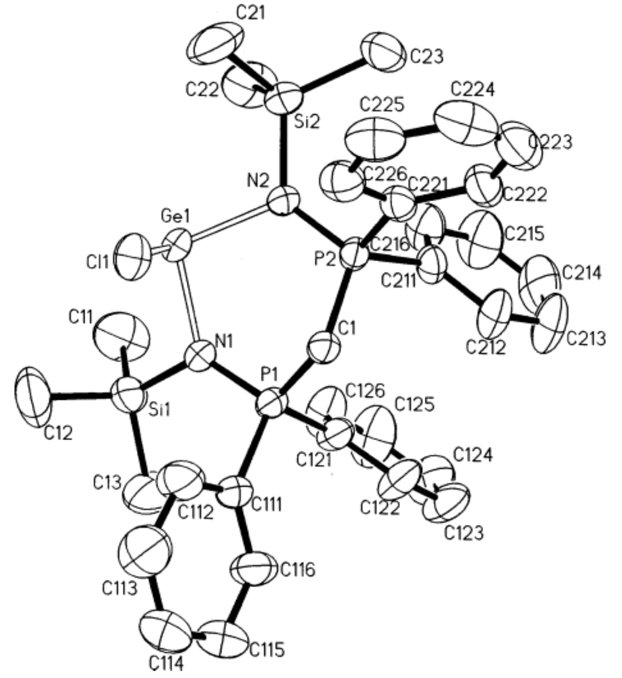

Figure 2. Crystal structure of **3** with atomic numbering scheme.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 2, 3, and 5

	$[HC(PPh_2{=}NSiMe_3)_2Li.THF]$ (**2**)		
Li(1)−O(1)	1.892(10)	P(1)−N(1)	1.572(4)
Li(1)−C(55)	2.622(9)	P(2)−N(2)	1.575(3)
Li(1)−N(1)	1.980(9)	P(1)−C(55)	1.722(4)
Li(1)−N(2)	2.017(9)	P(2)−C(55)	1.717(4)
O(1)−Li(1)−N(1)	122.2(5)	N(1)−P(1)−C(55)	113.51(19)
O(1)−Li(1)−N(2)	122.8(5)	N(2)−P(2)−C(55)	113.19(18)
N(1)−Li(1)−C(55)	72.1(3)	P(1)−C(55)−Li(1)	74.3(2)
N(2)−Li(1)−C(55)	71.3(3)	P(2)−C(55)−Li(1)	74.8(2)
Li(1)−N(1)−P(1)	99.2(3)	P(1)−C(55)−P(2)	130.3(2)
Li(1)−N(2)−P(2)	98.3(3)		
	$[HC(PPh_2{=}NSiMe_3)_2GeCl]$ (**3**)		
Ge(1)−Cl(1)	2.334(2)	P(1)−N(1)	1.640(4)
Ge(1)−N(1)	1.983(4)	P(2)−N(2)	1.637(4)
Ge(1)−N(2)	2.002(4)	C(1)−P(1)	1.719(4)
		C(1)−P(2)	1.700(4)
N(1)−Ge(1)−N(2)	102.52(15)	Ge(1)−N(1)−P(1)	120.0(2)
Cl(1)−Ge(1)−N(1)	99.41(12)	N(2)−P(2)−C(1)	113.58(19)
Cl(1)−Ge(1)−N(2)	98.04(11)	N(1)−P(1)−C(1)	114.2(2)
Ge(1)−N(2)−P(2)	120.54(19)	P(1)−C(1)−P(2)	119.2(2)
	$[(\mu\text{-}N{=}Ph_2P)(Me_3SiN{=}Ph_2P)C{=}Ge(OSiMe_3)]_2$ (**5**)		
C(1A)−Ge	1.915(5)	P(2)−N(2)	1.574(5)
Ge(1)−O(1)	1.759(4)	Ge(1)−N(2)	1.745(5)
O(1)−Si(1)	1.633(4)	P(1)−N(1)	1.642(4)
C(1A)−P(1)	1.720(6)	N(1)−Ge(1)	1.956(5)
C(1)−P(2)	1.716(6)		
O(1)−Ge(1)−C(1A)	112.0(2)	P(2)−C(1)−P(1A)	133.4(3)
O(1)−Ge(1)−N(2)	108.3(2)	N(1)−P(1)−C(1A)	97.4(2)
P(2)−N(2)−Ge(1)	131.0(3)		

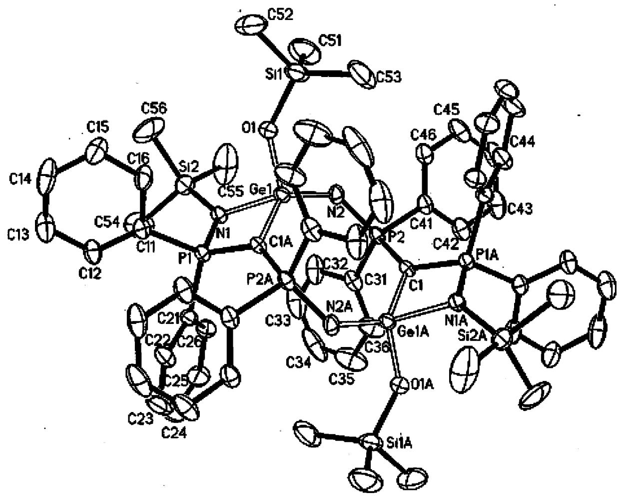

Figure 3. Crystal structure of **5** with atomic numbering scheme.

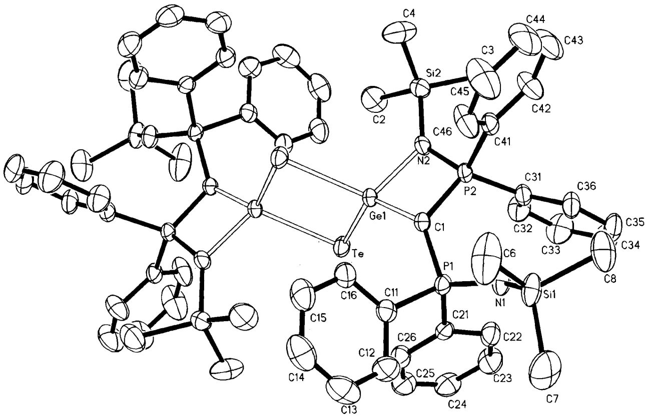

Figure 4. Crystal structure of **8** with atomic numbering scheme.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compounds 6−8

	$[(Me_3SiN{=}PPh_2)_2C{=}Ge(\mu\text{-}E)]_2$		
	E = S (**6**)	E = Se (**7**)	E = Te (**8**)
Ge(1)−E(1)	2.230(2)	2.357(4)	2.585(4)
Ge(1)−E(1A)	2.236(2)	2.370(4)	2.577(4)
Ge(1)−C(1)	1.875(5)	1.873(2)	1.912(3)
P(1)−N(1)	1.552(5)	1.531(2)	1.560(3)
P(2)−N(2)	1.645(4)	1.655(2)	1.664(3)
Ge(1)−N(2)	1.895(4)	1.911(2)	1.938(2)
P(1)−C(1)	1.748(5)	1.744(2)	1.735(3)
P(2)−C(1)	1.713(5)	1.701(2)	1.721(3)
Ge(1)−E(1)−Ge(1A)	84.67(5)	83.73(1)	81.42(1)
E(1)−Ge(1)−E(1A)	95.33(5)	96.28(1)	98.58(1)
N(2)−Ge(1)−C(1)	82.1(2)	81.53(8)	81.93(12)
Ge(1)−C(1)−P(2)	90.7(2)	91.74(10)	90.32(14)
C(1)−P(2)−N(2)	95.0(2)	94.81(10)	96.43(13)
P(2)−N(2)−Ge(1)	92.1(2)	91.89(8)	91.18(12)
P(1)−C(1)−P(2)	121.9(3)	126.95(13)	124.71(17)

Compounds **6**−**8** are isostructural and comprised of the chalcogen-bridged germaketene dimers. The molecular structure of **8** is shown in Figure 4. Selected bond distances (Å) and angles (deg) of **6**−**8** are listed in Table 3. The Ge−C(1) bond distances of 1.875(5) Å in **6** and 1.873(2) Å in **7** are shorter than those of 1.905(8) and 1.908(7) Å in **4**. The Ge−C(1) distance of 1.912(3) Å in **8** is slightly longer compared with those of 1.905(8) and 1.908(7) Å in **4**. The average germanium−chalcogen distances [2.233 Å (**6**), 2.364 Å (**7**), and 2.581 Å (**8**)] increase with the covalent radii of chalcogens. One of the imino groups of the ligand in **6**−**8** coordinates to the germanium center, the others remaining uncoordinated. The differences in the P−N bond distances [1.552(5), 1.645(4) Å (**6**); 1.531(2), 1.655(2) Å (**7**); and 1.560(3), 1.664(3) Å (**8**)] suggest the delocalization of π-electrons resulted from the conjugation of P=N and C=Ge double bonds in germavinylidene.

The Ge−S distances of 2.230(2) and 2.236(2) Å in **6** are longer than the Ge=S bond distance of 2.049(3) Å in [Tbt(Tip)Ge=S], but similar to those distances reported for typical Ge−S single bonds (2.17−2.25 Å).[20] The Ge−Se distances of 2.357(4) and 2.370(4) Å in **7** are in the range 2.337−2.421 Å for some Ge−Se single bonds reported, but slightly shorter than the Ge−Se distance of 2.426(2) Å in [{CPh(SiMe$_3$)$_2$C$_5$H$_4$N-2}$_2$Ge=Se].[5] The Ge−Te bond distances of 2.585(4) and 2.577(4) Å in **8** are slightly shorter than that in alkylidene−telluragermirane (2.591(3) Å)[21] and [Ge{N(SiMe$_3$)$_2$}(μ-Te)]$_2$ (2.595(2), 2.596(2) Å).[14d]

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$_2$O, toluene, and THF). Sulfur, selenium, and tellurium powders were purchased from Aldrich Chemicals and used without further purification. GeCl$_2$·dioxane[22] and [Ge{N(SiMe$_3$)$_2$}$_2$][23] were prepared by reported procedures. The ^{1}H, ^{13}C, ^{31}P, ^{77}Se, and ^{125}Te NMR spectra were recorded on Brüker WM-300 or Varian 400 spectrometers. The NMR spectra were recorded in benzene-d_6 or THF-d_8, and the chemical shifts δ are relative to SiMe$_4$, 85% H$_3$PO$_4$, Ph$_2$Se$_2$, and Me$_2$Te$_2$ for ^{1}H, ^{13}C, ^{31}P, ^{77}Se, and ^{125}Te NMR, respectively.

[HC(PPh$_2$=NSiMe$_3$)$_2$Li·THF] (2). Bu^{n}Li (6.3 mL, 10.11 mmol, 1.6 M solution in *n*-hexane) was added slowly to the solution of [(Me$_3$SiN=PPh$_2$)$_2$CH$_2$] (5.65 g, 10.11 mmol) in THF (60 mL) at −90 °C. The brown suspension was raised to ambient temperature and stirred overnight. Volatiles were removed under reduced pressure, and the residue was extracted by Et$_2$O. The precipitate was filtered. Hexane was added to the filtrate and concentrated under reduced pressure. Compound **2** was obtained as pale yellow crystals. Yield: 4.52 g (70%). Mp: 128−131 °C. Anal. Found: C, 65.68; H, 7.57; N, 4.49. Calcd for C$_{35}$H$_{47}$N$_2$LiOP$_2$Si$_2$: C, 66.01; H, 7.44; N, 4.40. ^{1}H NMR (C$_6$D$_6$): δ 0.22 (s, 18H, SiMe$_3$), 1.22−1.26 (m, 4H, THF), 1.67 (t, J_{P-H} = 2.7 Hz, 1H, PC(H)P), 3.61−3.65 (m, 4H, THF), 7.02−7.08 (m, 12H, Ph), 7.74−7.81 (m, 8H, Ph). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 4.35 (SiMe$_3$), 23.56 (t, $^1J_{P-C}$ = 128.8 Hz, PCP), 25.31, 68.66 (THF), 127.77 (s, *p*-Ph), 129.23 (s, *m*-Ph), 131.37 (t, $^2J_{P-C}$ = 5.2 Hz, *o*-Ph), 142.08 (d, $^1J_{P-C}$ = 95.5 Hz, *ipso*-Ph). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 29.42.

[HC(PPh$_2$=NSiMe$_3$)$_2$GeCl] (3). A solution of [HC(PPh$_2$=NSiMe$_3$)$_2$Li·THF] (**2**) (0.91 g, 1.43 mmol) in Et$_2$O (20 mL) was added slowly to the solution of GeCl$_2$·dioxane (0.33 g, 1.43 mmol) in Et$_2$O (20 mL) at 0 °C. The yellow suspension was raised to ambient temperature and stirred for 18 h. The precipitate was filtered. Hexane was added to the filtrate and concentrated under reduced pressure. Compound **3** was obtained as pale yellow crystals. Yield: 0.70 g (73%). Mp: 254 °C (dec). Anal. Found: C, 57.08; H, 6.15; N, 4.24. Calcd for C$_{31}$H$_{39}$ClGeN$_2$P$_2$Si$_2$·1/2 hexane: C, 57.68; H, 6.40; N, 3.96. ^{1}H NMR (THF-d_8): δ −0.15 (s, 18H, SiMe$_3$), 3.50 (t, J_{P-H} = 12 Hz, 1H, PC(H)P), 7.29−7.37 (m, 13H, Ph), 7.66−7.72 (m, 7H, Ph). ^{13}C{^{1}H} NMR (THF-d_8): δ 3.01 (SiMe$_3$), 37.14 (t, $^1J_{P-C}$ = 270.9 Hz, PCP), 128.58 (t, $^2J_{P-C}$ = 24.0 Hz, *m*-Ph and *p*-Ph), 131.14 (s, *o*-Ph), 132.31 (t, $^2J_{P-C}$ = 21.0 Hz, *ipso*-Ph). ^{31}P{^{1}H} NMR (THF-d_8): δ 13.97.

[(Me$_3$SiN=PPh$_2$)$_2$C=Ge→Ge=C(PPh$_2$=NSiMe$_3$)$_2$] (4).[4] Method A: A solution of **3** (1.30 g 1.95 mmol) in toluene (30 mL) was added to a stirred solution of [Ge{N(SiMe$_3$)$_2$}$_2$] (0.49 g, 1.25 mmol) in toluene (30 mL) at room temperature. The reaction was stirred for 2 days. The volatiles were removed under reduced pressure, and the residue was extracted with hexane/Et$_2$O, 1:1. After filtration and concentration of the filtrate, compound **4** was obtained as orange-red crystals. Yield: 0.63 g (79%).

Method B: A solution of **2** (1.16 g, 1.82 mmol) in Et$_2$O (30 mL) was added slowly to a stirred solution of GeCl$_2$·dioxane (0.21 g, 0.91 mmol) in Et$_2$O (30 mL) at −90 °C. The yellow suspension was raised to ambient temperature and stirred for 2 days. The precipitate was filtered. Hexane was added to the filtrate and concentrated under reduced pressure. **4** was obtained as orange-red crystals. Yield: 0.24 g (42%).

[(μ-N=Ph$_2$P)(Me$_3$SiN=Ph$_2$P)C=Ge(OSiMe$_3$)]$_2$ (5). A solution of **4** (0.70 g, 0.55 mmol) in toluene (30 mL) was added to Me$_3$NO (0.095 g, 1.27 mmol) in toluene (30 mL) at −90 °C with stirring. The reaction mixture faded gradually when raised to ambient temperature. The pale yellow solution was stirred at room temperature for 17 h. The volatiles were removed under reduced pressure, and the residue was extracted with Et$_2$O. It was filtered and concentrated, yielding pale yellow crystals of **5**. Yield: 0.33 g (46%). Mp: 196 °C (dec). Anal. Found: C, 57.27; H, 5.73; N, 4.03. Calcd for C$_{62}$H$_{76}$N$_4$P$_4$O$_2$Si$_4$Ge$_2$: C, 57.69; H, 5.93; N, 4.34. ^{1}H NMR (C$_6$D$_6$): δ −0.02 (s, 18H, SiMe$_3$), 0.71 (s, 18H, OSiMe$_3$), 6.51−8.73 (m, 40H, Ph). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 2.29 (SiMe$_3$), 3.76 (OSiMe$_3$), 127.03 (m, Ph), 129.36 (m, Ph), 130.95 (d, $^1J_{P-C}$ = 60.6 Hz, *p*-Ph′), 132.21 (d, $^1J_{P-C}$ = 45.6 Hz, *m*-Ph′), 133.18 (s, *o*-Ph′), 133.40 (d, $^1J_{P-C}$ = 42.9 Hz, *ipso*-Ph′). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 18.66, 44.61.

[(Me$_3$SiN=PPh$_2$)$_2$C=Ge(μ-S)]$_2$ (6). A solution of **4** (0.34 g, 0.27 mmol) in THF (30 mL) was added dropwise to the colorless solution of powdered sulfur (0.017 g, 0.53 mmol) in THF (30 mL) at 0 °C with stirring. The resultant yellow solution was raised to room temperature and stirred for 36 h. After filtration and concentration of the filtrate, compound **6** was obtained as white crystals. Yield: 0.11 g (30%). Mp: 175−176 °C. Anal. Found: C, 56.16; H, 5.80; N, 4.05. Calcd for C$_{62}$H$_{76}$N$_4$Ge$_2$P$_4$S$_2$Si$_2$: C, 56.29; H, 5.79; N, 4.24. ^{1}H NMR (THF-d_8): δ −0.46 (s, 18H, SiMe$_3$), −0.32 (s, 18H, SiMe$_3$), 7.17−7.40 (m, 24H, Ph), 7.41−7.44 (m, 4H, Ph), 7.61−7.72 (m, 8H, Ph), 7.80−7.88 (m, 4H, Ph). ^{13}C{^{1}H} NMR (THF-d_8): δ 2.16, 4.14 (SiMe$_3$), 128.20 (d,$^1J_{P-C}$ = 48.3 Hz, *m*-Ph), 128.58 (t, $^2J_{P-C}$ = 24.0 Hz, *o*-Ph), 128.87 (d, $^1J_{P-C}$ = 50.4 Hz, *ipso*-Ph), 130.08 (s, *p*-Ph), 131.15 (s, *p*-Ph′), 132.32 (s, *m*-Ph′), 132.59 (d, $^1J_{P-C}$ = 67.2 Hz, *o*-Ph′), 133.71 (d, $^1J_{P-C}$ = 46.2 Hz, *ipso*-Ph′). ^{31}P{^{1}H} NMR (THF-d_8): δ 10.69, 57.52. FAB-MS: *m/z* found 663.1040; calcd for C$_{31}$H$_{38}$N$_2$GeP$_2$SSi 663.1054 ([M/2 + H]$^+$).

[(Me$_3$SiN=PPh$_2$)$_2$C=Ge(μ-Se)]$_2$ (7). A solution of **4** (0.68 g, 0.54 mmol) in THF (30 mL) was added dropwise to the colorless solution of powdered selenium (0.089 g, 1.13 mmol) in THF (30 mL) at 0 °C with stirring in the absence of light. The resultant orange solution was raised to room temperature and stirred for 2 days. It was filtered and concentrated, obtaining yellow crystals of **7**. Yield: 0.17 g (23%). Mp: 328 °C (dec). Anal. Found: C, 51.87; H, 5.58; N, 3.95. Calcd for C$_{62}$H$_{76}$N$_4$Ge$_2$P$_4$Se$_2$Si$_2$: C, 52.49; H, 5.54; N, 3.95. ^{1}H NMR (THF-d_8): δ −0.48 (s, 18H, SiMe$_3$), −0.25 (s, 18H, SiMe$_3$), 7.18−7.42 (m, 24H, Ph), 7.49−7.58 (m, 4H, Ph), 7.61−7.68 (m, 8H, Ph), 7.78−7.85 (m, 4H, Ph). ^{13}C{^{1}H} NMR (THF-d_8): δ 2.50, 4.39 (SiMe$_3$), 128.49 (d, $^1J_{P-C}$ = 47.7 Hz, *m*-Ph), 128.81 (s, *o*-Ph), 129.18 (d, $^1J_{P-C}$ = 50.7 Hz, *ipso*-Ph), 130.37 (s, *p*-Ph), 131.46 (s, *p*-Ph′), 132.68 (s, *m*-Ph′), 132.90 (d, $^1J_{P-C}$ = 43.8 Hz, *o*-Ph′), 133.91 (d, $^1J_{P-C}$ = 46.8 Hz, *ipso*-Ph′). ^{31}P{^{1}H} NMR (THF-d_8): δ 13.97, 60.80. ^{77}Se NMR (THF-d_8): δ 860.88. FAB-MS: *m/z* found 711.0510; calcd for C$_{31}$H$_{38}$N$_2$GeP$_2$SeSi$_2$ 711.0499 ([M/2 + H]$^+$).

[(Me$_3$SiN=PPh$_2$)$_2$C=Ge(μ-Te)]$_2$ (8). A solution of **4** (0.72 g, 0.57 mmol) in THF (30 mL) was added slowly to the colorless solution of powdered tellurium (0.15 g, 1.18 mmol) in THF (30 mL) at 0 °C with stirring in the absence of light. The resultant red solution was raised to room temperature and stirred for 2

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days. The unreacted tellurium power was filtered off; the filtrate was concentrated, yielding red crystals of **8**. Yield: 0.31 g (36%). Mp: 258 °C (dec). Anal. Found: C, 48.48; H, 4.85; N, 3.90. Calcd for $C_{62}H_{76}N_4Ge_2P_4Si_2Te_2$: C, 49.19; H, 5.06; N, 3.70. ^{1}H NMR (THF-d_8): δ −0.48 (s, 18H, SiMe$_3$), −0.15 (s, 18H, SiMe$_3$), 7.21−7.42 (m, 22H, Ph), 7.45−7.53 (m, 4H, Ph), 7.67−7.78 (m, 14H, Ph). ^{13}C{^{1}H} NMR (THF-d_8): δ 2.38, 4.12 (SiMe$_3$), 128.21 (d, $^1J_{P-C} = 46.5$ Hz, *m*-Ph), 128.58 (t, $^2J_{P-C} = 24.0$ Hz, *o*-Ph), 128.85 (d, $^1J_{P-C} = 49.8$ Hz, *ipso*-Ph), 130.00 (s, *p*-Ph), 131.14 (s, *p*-Ph′), 132.46 (m, *m*-Ph′ and *o*-Ph′), 133.36 (d, $^1J_{P-C} = 46.2$ Hz, *ipso*-Ph′). ^{31}P{^{1}H} NMR (THF-d_8): δ 11.78, 58.97. ^{125}Te NMR (THF-d_8): δ 1025.53. FAB-MS: *m*/*z* found 761.0409; calcd for $C_{31}H_{38}N_2GeP_2Si_2Te$ 761.0396 ([M/2 + H]$^+$).

X-ray Crystallography. Single crystals were sealed in 0.3 or 0.5 mm Lindemann glass capillaries under nitrogen. X-ray data of **2**, **3**, and **5**−**8** were collected on a Rigaku R-AXIS II imaging plate using graphite-monochromatized Mo Kα radiation ($I = 0.71073$ Å) from a rotating-anode generator operating at 50 kV and 90 mA. Crystal data for **2**, **3**, and **5**−**8** are summarized in Table 1. The structures were solved by direct phase determination using the computer program SHELXTL-PC[24] on a PC 486 and refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms. 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**, **3**, and **5**−**8** are given in the Supporting Information.

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Supporting Information Available: Details of 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**, **3**, and **5**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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