Organometallics **2007,** *26,* 3802−3806

Formation of Germenes from Bis(germavinylidene)

Wing-Por Leung,* Kwok-Wai Kan, Cheuk-Wai So, and Thomas C. W. Mak

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, People's Republic of China

Received March 22, 2007

A series of germenes have been synthesized from the bis(germavinylidene) $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (**1**). The reaction of **1** with 2,2,6,6-tetramethylpiperidine *N*-oxide afforded $[(Me_3SiN{=}PPh_2)_2C{=}Ge(ONCMe_2C_3H_6CMe_2)_2]$ (**2**). Germavinylidene, the dissociation derivative of **1**, underwent [1 + 4] cycloaddition with azobenzene, followed by a 1,3-H shift to give $[(Me_3SiN{=}PPh_2)_2C{=}Ge(o\text{-}C_6H_4NHNPh)]$ (**3**). Treatment of **1** with benzil afforded the [1 + 4] cycloaddition compound $[(Me_3SiN{=}PPh_2)_2C{=}Ge\{O(Ph)C{=}C(Ph)O\}]$ (**4**). The results showed that the germavinylidene moiety dissociated from **1** acts as a synthon for the preparation of various germenes by addition to the germanium(II) center. The molecular structures of **2**−**4** have been determined.

Introduction

The chemistry of germenes ($>Ge{=}C<$) has attracted much attention over the past few decades.[1] It has been found that the thermal stability of the Ge=C bond is intrinsically low. A germene is usually treated as a reactive intermediate, and transient germenes can be trapped in situ with simple compounds such as alcohols, dienes, aldehydes, nitrones, and nitrosobenzene.[2] Nevertheless, the germenes $R_2Ge{=}CR'_2$ can be stabilized by incorporating sterically bulky substituents at both germanium and carbon.[3] For example, $Mes_2Ge{=}CR_2$ (Mes = 2,4,6-trimethylphenyl, CR_2 = fluorenylidene)[4] and $[\{(Me_3Si)_2N\}_2Ge{=}C(BBu^t)_2C(SiMe_3)_2]$[5] have been reported and structurally characterized. The most common routes for the synthesis of a germene are the dehydrohalogenation of a halogermane by a organolithium compound and the germylene−carbene coupling reaction. Novel methods such as the Peterson reaction[6] and germylene−CS_2 coupling reactions have also been employed in the synthesis of stable germenes.[7] The reactivities of germene such as 1,2-addition and [2 + *n*] cycloaddtion have been extensively studied.[8]

Recently, we reported the synthesis of the bis(germavinylidene) $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (**1**).[9] The existence of a monomeric germavinylidene intermediate in solution was demonstrated in the reaction of **1** with $CpMn(CO)_2THF$ to form $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Mn(CO)_2Cp]$.[10] The Lewis base property of germavinylidene toward transition metals has been shown in the synthesis of $[\{(Me_3SiN{=}PPh_2)_2C{=}Ge\}_2Ni(PPh_3)_2]$ and $[(Me_3SiN{=}PPh_2)_2C{=}Ge(MX)]_2$ (MX = AgCl and AuI).[11] We anticipated that the bis(germavinylidene) **1** could be a potential source for the reactive monomeric germavinylidene intermediate "$:Ge{=}C(PPh_2{=}NSiMe_3)_2$", which may serve as a synthon for the synthesis of germenes through its lone pair at the germanium(II) center.

Results and Discussion

Synthesis of Germenes. The reaction of **1** with 4 equiv of 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) in THF afforded $[(Me_3SiN{=}PPh_2)_2C{=}Ge(ONCMe_2C_3H_6CMe_2)_2]$ (**2**) (Scheme 1). The X-ray structure of **2** showed that it contains a germene moiety with iminophosphorano and alkoxy substituents bonded to carbon and germanium atoms, respectively. The result suggested that the bis(germavinylidene) **1** dissociated in solution to give the germavinylidene $[(Me_3SiN{=}PPh_2)_2C{=}Ge:]$ and reacted with TEMPO via a radical intermediate (Scheme 2). The lone-pair electron and the vacant orbital at the germanium center play roles in this reaction. Similar radical reactions of a germanium(II) complex toward TEMPO have also been reported by Kira and co-workers.[12]

Treatment of **1** with 2 equiv of azobenzene in THF gave compound **3**. The structure of **3** has been confirmed by X-ray structure analysis. The first step of the reaction was probably the formation of the five-membered-ring intermediate **A** via

---

* To whom correspondence should be addressed. E-mail: kevinleung@cuhk.edu.hk.

(1) (a) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (b) Escudié, J.; Ranaivonjatovo, H. *Adv. Organomet. Chem.* **1999**, *44*, 113.

(2) (a) Riviere, P.; Castel, A.; Satgé, J. *J. Am. Chem. Soc.* **1980**, *102*, 5413. (b) Toltl, N. P.; Leigh, W. J. *J. Am. Chem. Soc.* **1998**, *120*, 1172. (c) Toltl, N. P.; Stradiotto, M.; Morkin, T. L.; Leigh, W. J. *Organometallics* **1999**, *18*, 5643. (d) Chaubon, M.-A.; Escudié, J.; Ranaivonjatovo, H.; Satgé, J. *J. Chem. Soc., Dalton Trans.* **1996**, 893.

(3) (a) Lazraq, M.; Couret, C.; Escudié, J.; Satgé, J. *Polyhedron* **1991**, *10*, 1153. (b) Couret, C.; Escudié, J.; Delpon-Lacaze, G.; Satgé, J. *Organometallics* **1992**, *11*, 3176.

(4) Couret, C.; Escudié, J.; Satgé, J.; Lazraq, M. *J. Am. Chem. Soc.* **1987**, *109*, 4411.

(5) Meyer, H.; Baum, G.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 798.

(6) Apeloig, Y.; Bendikov, M.; Yuzefovich, M.; Nakash, M.; Bravo-Zhivotovskii, D.; Bläser, D.; Boese, R. *J. Am. Chem. Soc.* **1996**, *118*, 12228.

(7) Tokitoh, N.; Kishikawa, K.; Okazaki, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1425.

(8) (a) Escudié, J.; Couret, C.; Ranaivonjatovo, H. *Coord. Chem. Rev.* **1998**, *178*, 565. (b) Lazraq, M.; Escudié, J.; Couret, C.; Satgé, J. *Organometallics* **1992**, *11*, 555. (c) Ech-Cherif El Kettani, S.; Escudié, J.; Couret, C.; Ranaivonjatovo, H.; Lazraq, M.; Soufiaoui, M.; Gornitzka, H.; Cretiu Nemes, G. *Chem. Commun.* **2003**, 1662. (d) Ech-Cherif El Kettani, S.; Lazraq, M.; Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Gornitzka, H.; Merceron, N. *Organometallics* **2004**, *23*, 5602. (e) Ech-Cherif El Kettani, S.; Lazraq, M.; Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Gornitzka, H.; Atmani, A. *Organometallics* **2005**, *24*, 5364.

(9) Leung, W.-P.; Wang, Z.-X.; Li, H.-W.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 2501.

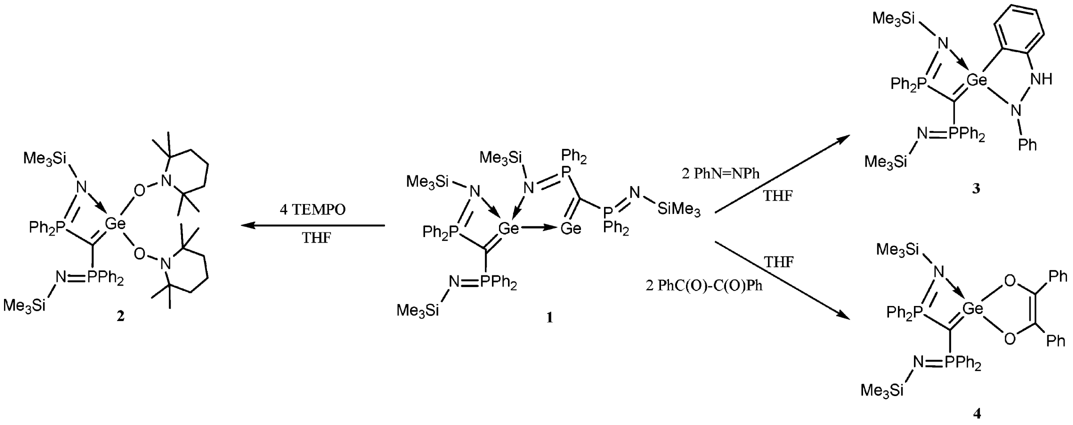
(10) Leung, W.-P.; So, C.-W.; Kan, K.-W.; Chan, H.-S.; Mak, T. C. W. *Inorg. Chem.* **2005**, *44*, 7286.

(11) Leung, W.-P.; So, C.-W.; Kan, K.-W.; Chan, H.-S.; Mak, T. C. W. *Organometallics* **2005**, *24*, 5033.

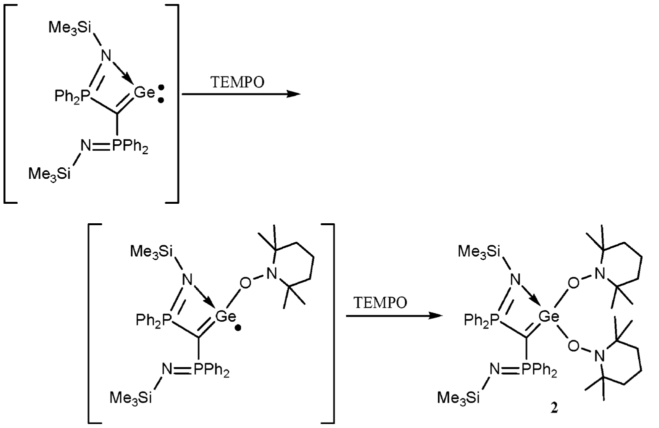
(12) Iwamoto, T.; Masuda, H.; Ishida, S.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2003**, *125*, 9300.

10.1021/om7002706 CCC: $37.00

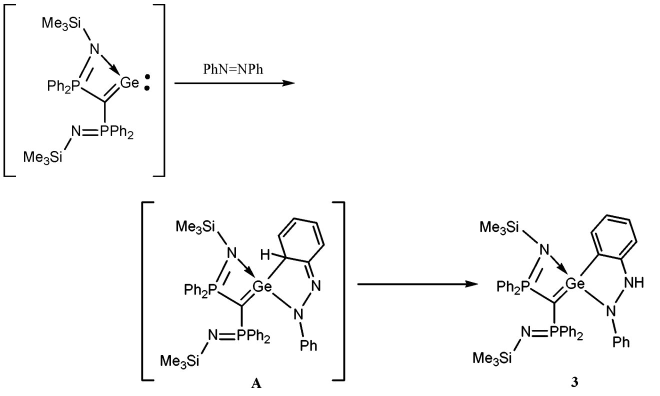
Scheme 1



Scheme 2



Scheme 3



[1 + 4] cycloaddition between the Ge(II) center and N=NC=C moiety of azobenzene, followed by rearomatization via a 1,3-H shift (Scheme 3). Unlike a germene, the >C=Ge: bond of the germavinylidene was not involved in the cycloaddition. This may be due to the delocalization between P=N and C=Ge bonds, which reduces the reactivity of the >C=Ge: bond.[13] Steric hindrance at the gemanium center may also contribute to the lesser reactivity of the >C=Ge: bond. To our knowledge, compound **3** is the first example resulting from the cycloaddition of a germanium(II) compound with azobenzene.

The bis(germavinylidene) **1** also underwent [1 + 4] cycloaddition with 2 equiv of benzil in THF to form [$(Me_3SiN=PPh_2)_2C=Ge\{O(Ph)C=C(Ph)O\}$] (**4**), as confirmed by X-ray structure analysis. Similar 1,4-addition reactions of germanium(II) complexes with benzil have been documented. For example, [(Tb)(Tip)Ge{O(Ph)C=C(Ph)O}] (Tb = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Tip = 2,4,6-triisopropylphenyl),[14] [$\{(Me_3Si)_2N\}_2Ge\{O(Ph)C=C(Ph)O\}$],[15] [$(ArO)_2Ge\{O(Ph)C=C(Ph)O\}$] (Ar = 2,4,6-tris[(dimethylamino)methyl]phenyl),[16] [$Me_2Si\{N(Bu^t)\}_2Ge\{O(Ph)C=C(Ph)O\}$],[17]and [$Ge(OC_6HPh_4\text{-}2,3,5,6)_2\{O(Ph)C=C(Ph)O\}$][18] have been reported.

Spectroscopic Properties. Compounds **2**−**4** have been isolated as colorless (**2**) or yellow (**3**, **4**) 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. The ^{31}P NMR spectra of **2** and **3** displayed two signals (δ 10.57, 49.94 ppm (**2**); δ 12.60, 30.04 ppm (**3**)) due to two different phosphorus environments, as found in the solid-state structures. In contrast, the ^{31}P NMR spectrum of **4** showed one singlet at δ 26.72 ppm. This does not correspond to the X-ray structure. It may be due to the fluxional behavior of the imino nitrogen atoms at the germanium center in solution. At 238 K, as the fluxional coordination process slowed down, the ^{31}P NMR of **4** displayed two singlets at δ 5.56 and 53.77 ppm, consistent with the X-ray structure. It is suggested that the sterically bulky substituents at the germanium centers in **2** and **3** prohibit their fluxional behavior.

The ^1H and ^{13}C NMR spectra of **2** displayed signals due to the bis(iminophosphorano)methanediide ligand and 2,2,6,6-tetramethylpiperidyl groups. The ^1H NMR spectrum of **3** exhibited one broad signal at δ 7.83 ppm, which is assigned to the −PhN*H*NPh moiety. It also showed multiplet signals due to the phenyl group in the normal range (δ 7−8 ppm). The ^1H and ^{13}C spectra of **4** are normal. No ^{13}C NMR signal could be recorded for the methanediide carbons in **2**−**4**. A similar phenomenon has been reported by Cavell and co-workers for some metal bis(iminophosphorano)methanediide complexes.[19]

X-ray Structures. Molecular structures with the atom-numbering schemes for compounds **2**−**4** are shown in Figures 1−3, respectively. Selected bond distances (Å) and angles (deg) of **2**−**4** are given in Tables 2−4, respectively.

---

[13] Lazraq, M.; Escudié, J.; Couret, C.; Satgé, J.; Soufiaoui, M. *Organometallics* **1991**, *10*, 1140.

[14] Tokitoh, N.; Manmaru, K.; Okazaki, R. *Organometallics* **1994**, *13*, 167.

[15] Litz, K. E.; Bender, J. E.; Sweeder, R. D.; Banaszak Holl, M. M.; Kampf, J. W. *Organometallics* **2000**, *19*, 1186.

[16] Barrau, J.; Rima, G.; El Amraoui, T. *Organometallics* **1998**, *17*, 607.

[17] Billeb, G.; Bootz, K.; Neumann, W. P.; Steinhoff, G. *J. Organomet. Chem.* **1991**, *406*, 303.

[18] Weinert, C. S.; Fenwick, A. E.; Fanwick, P. E.; Rothwell, I. P. *Dalton Trans.* **2003**, 532.

[19] (a) Jones, N. D.; Lin, G.; Gossage, R. A.; McDonald, R.; Cavell, R. G. *Organometallics* **2003**, *22*, 2832. (b) Lin, G.; Jones, N. D.; Gossage, R. A.; McDonald, R.; Cavell, R. G. *Angew. Chem., Int. Ed.* **2003**, *42*, 4054.

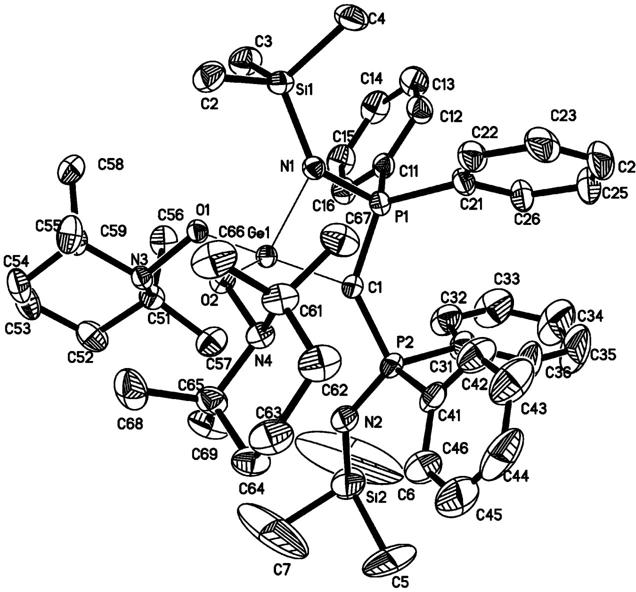


Figure 1. Molecular structure of **2**.

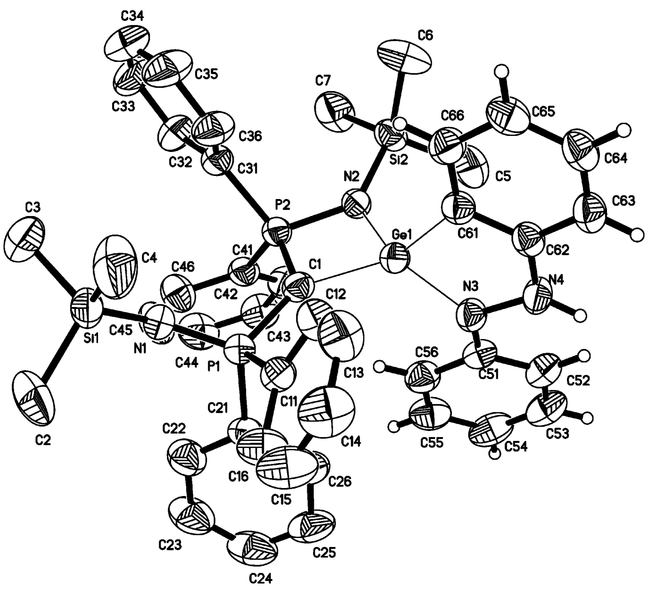


Figure 2. Molecular structure of **3**.

The structures of compounds **2**−**4** are consistent with a germene compound. The C−Ge bond distances of 1.859(1) Å in **2**, 1.852(1) Å in **3**, and 1.850(4) Å in **4** are slightly longer than that of 1.827(4) Å in $[\{(Me_3Si)_2N\}_2Ge{=}C(BBu^t)_2C(SiMe_3)_2]$[5] and 1.803(4) Å in $[Mes_2Ge{=}CR_2]$.[20] This is probably due to the delocalization of π electrons resulting from the conjugation of P═N and C═Ge bonds, which lengthens the $>C{=}Ge<$ bond distance. However, the C−Ge distances of **2**−**4** are shorter than those of **1** (1.908(7), 1.905(8) Å),[9] owing to the higher oxidation state of germanium in **2**−**4**. One imino group of the ligand coordinates to the germanium(IV) center; the other one remains uncoordinated. Thus, the geometry around the germanium atom in **2**−**4** is tetrahedral. Compounds **2**−**4** are the first examples of germenes containing a four-coordinate germanium center to be characterized by X-ray diffraction methods. Other germenes reported display trigonal-planar geometry at both germanium and carbon.

The Ge−O bond distances in **2** and **4** (1.782(2), 1.772(2) Å (**2**); 1.781(3), 1.794(3) Å (**4**)) are comparable to those of compounds containing Ge−O single bonds (1.75−1.85 Å).[21]

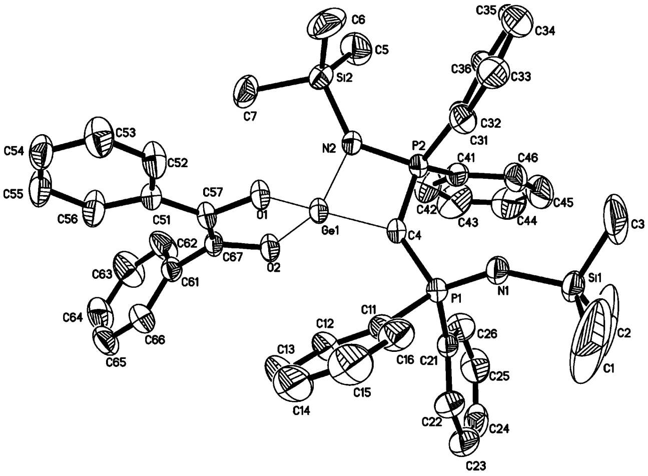


Figure 3. Molecular structure of **4**.

The C(57)−C(67) bond distance of 1.336 Å in **4** is consistent with a normal C═C double bond.

The C(61)−C(62) and N(4)−N(3) bond lengths of 1.399(7) and 1.457(5) Å in **3** correspond to the C═C bond and N−N bond, respectively. The Ge(1)−C(61) bond distance of 1.919(5) Å is similar to that of 1.989(5) Å in $[GeCl\{C_6H_3\text{-}2,6\text{-}Trip\}]$ (Trip = $C_6H_2\text{-}2,4,6\text{-}Pr^i{}_3$).[22] The Ge(1)−N(3) bond distance of 1.878(4) Å in **3** is comparable with that of 1.920(2) Å in $[Ge\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}Cl]$[23] and 1.988(2) Å in $[\{HC(CMeNAr)_2\}GeCl]$.[24] The Ge−N dative bond distance of 1.926(2) Å in **2**, 1.941(4) Å in **3**, and 1.892(3) Å in **4** are comparable with those of 1.971(6) and 1.974(6) Å in **1**.[9]

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) $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ was prepared by literature procedures.[9] TEMPO, azobenzene, and benzil were purchased from Aldrich Chemicals and used without further purification. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Brüker WM-300 and Varian 400 spectrometers. The NMR spectra were recorded in THF-d_8, and the chemical shifts δ are relative to $SiMe_4$ and 85% H_3PO_4 for ^1H, ^{13}C, and ^{31}P, respectively.

Reaction of 1 with TEMPO. A solution of **1** (0.57 g, 0.45 mmol) in THF (20 mL) was added slowly to TEMPO (0.28 g, 1.80 mmol) in THF (20 mL) at 0 °C. The resultant yellow solution was raised to room temperature and stirred for 30 h. The volatiles were removed under reduced pressure. The residue was extracted with Et_2O. After filtration and concentration of the filtrate, **2** was obtained as colorless crystals. Yield: 0.53 g (63%). Mp: 157.2 °C dec. Anal. Found: C, 62.19; H, 7.73; N, 5.64. Calcd for $C_{49}H_{74}GeN_4O_2P_2Si_2$: C, 62.48; H, 7.92; N, 5.92. ^1H NMR (THF-d_8): δ −0.33 (s, 9H, $SiMe_3$), −0.13 (s, 9H, $SiMe_3$), 1.12 (s, 12H, CH_3, tetramethylpiperidyl), 1.17 (s, 12H, CH_3, tetramethylpiperidyl), 1.22−1.35 (m, 6H, CH_2, tetramethylpiperidyl), 1.41−1.55 (m, 6H, CH_2, tetramethylpiperidyl), 7.21−7.27 (m, 6H, Ph), 7.29−7.37 (m, 6H, Ph), 7.55−7.68 (m, 8H, Ph). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 3.91, 4.54

---

[20] Lazraq, M.; Escudié, J.; Couret, C.; Satgé, J.; Dräger, M.; Dammel, R. *Angew. Chem., Int. Ed.* **1998**, *27*, 828.

[21] Baines, K. M.; Stibbs, W. G. *Coord. Chem. Rev.* **1995**, *145*, 157.

[22] Pu, L.; Olmstead, M. M.; Power, P. P.; Schiemenz, B. *Organometallics* **1998**, *17*, 5602.

[23] Leung, W.-P.; So, C.-W.; Wu, Y.-S.; Li, H.-W.; Mak, T. C. W. *Eur. J. Inorg. Chem.* **2005**, 513.

[24] Ding, Y.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-S.; Power, P. P. *Organometallics* **2001**, *20*, 1190.

Table 1. Crystallographic Data for Compounds 2−4

	2	3	4
formula	$C_{49}H_{74}GeN_4O_2P_2Si_2$	$C_{43}H_{48}GeN_4P_2Si_2$	$C_{45}H_{48}GeN_2O_2P_2Si_2$
fw	941.83	811.56	839.56
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	13.2520(16)	12.022(2)	11.492(2)
b (Å)	12.4869(16)	19.184(4)	14.430(3)
c (Å)	32.041(4)	19.438(4)	15.903(3)
α (deg)	90	90	65.49(3)
β (deg)	94.022(2)	90.00(3)	74.47(3)
γ (deg)	90	90	72.29(3)
V (Å^3)	5289.0(11)	4482.9(15)	2252.2(8)
Z	4	4	2
d_{calcd} (g cm^{-3})	1.183	1.202	1.236
μ (mm^{-1})	0.724	0.841	0.840
$F(000)$	2008	1696	876
cryst size (mm)	0.50 × 0.40 × 0.40	0.50 × 0.40 × 0.20	0.50 × 0.40 × 0.20
2θ range (deg)	1.27−28.33	2.00−25.00	2.07−25.00
index ranges	$-14 \le h \le 17$ $-16 \le k \le 16$ $-42 \le l \le 40$	$-13 \le h \le 13$ $-22 \le k \le 0$ $-22 \le l \le 23$	$-13 \le \mathrm{h} \le 13$ $-17 \le \mathrm{k} \le 0$ $-18 \le \mathrm{l} \le 17$
no. of rflns collected	36 307	10 841	8288
no. of indep rflns	13 126	6453	7944
R1, wR2 ($I > 2(\sigma)I$)	0.0434, 0.1090	0.0639, 0.1505	0.0504, 0.1347
R1, wR2 (all data)	0.0762, 0.1295	0.0782, 0.1610	0.0952, 0.1534
goodness of fit, F^2	1.012	1.144	1.032
no. of data/restraints/params	13 126/11/550	6453/1/469	7944/0/488
largest diff peaks, e Å^{-3}	0.693/−0.672	0.446/−0.670	0.546/−0.489

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 2

C(1)−Ge(1)	1.859(1)	P(1)−N(1)	1.649(2)
Ge(1)−O(1)	1.787(2)	P(2)−N(2)	1.544(3)
Ge(1)−O(2)	1.772(2)	C(1)−P(1)	1.722(3)
Ge(1)−N(1)	1.926(2)	C(1)−P(2)	1.786(2)
O(1)−Ge(1)−O(2)	102.9(8)	O(2)−Ge(1)−N(1)	115.3(9)
O(1)−Ge(1)−N(1)	115.3(9)	Ge(1)−N(1)−P(1)	91.1(9)
N(1)−Ge(1)−C(1)	82.1(1)	N(1)−P(1)−C(1)	95.0(9)
C(1)−Ge(1)−O(2)	129.6(1)	P(1)−C(1)−P(2)	131.7(9)
O(1)−Ge(1)−C(1)	122.6(9)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 3

C(1)−Ge(1)	1.852(1)	Ge(1)−C(61)	1.919(5)
Ge(1)−N(2)	1.941(4)	C(61)−C(62)	1.399(7)
C(1)−P(1)	1.790(3)	C(62)−N(4)	1.421(6)
C(1)−P(2)	1.722(4)	N(4)−N(3)	1.457(5)
P(1)−N(1)	1.564(4)	N(3)−Ge(1)	1.878(4)
P(2)−N(2)	1.664(4)		
N(2)−Ge(1)−C(61)	116.5(2)	N(2)−P(2)−C(1)	93.3(1)
C(61)−Ge(1)−N(3)	87.9(2)	P(2)−C(1)−Ge(1)	93.5(2)
N(3)−Ge(1)−C(1)	126.4(2)	P(2)−C(1)−P(1)	122.9(1)
C(1)−Ge(1)−N(2)	81.0(2)	Ge(1)−C(61)−C(62)	109.9(4)
N(2)−Ge(1)−N(3)	116.1(2)	C(61)−C(62)−N(4)	117.8(4)
C(1)−Ge(1)−C(61)	131.7(2)	C(62)−N(4)−N(3)	112.5(4)
Ge(1)−N(2)−P(2)	92.2(2)	N(4)−N(3)−Ge(1)	111.8(3)

Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound 4

C(4)−Ge(1)	1.850(4)	Ge(1)−O(1)	1.781(3)
Ge(1)−N(2)	1.892(3)	Ge(1)−O(2)	1.794(3)
P(2)−N(2)	1.660(3)	O(1)−C(57)	1.401(4)
P(1)−N(1)	1.538(3)	O(2)−C(67)	1.398(4)
C(4)−P(2)	1.719(4)	C(57)−C(67)	1.336(5)
C(4)−P(1)	1.746(4)		
O(1)−Ge(1)−O(2)	91.4(1)	N(2)−P(2)−C(4)	94.9(2)
O(2)−Ge(1)−C(4)	126.6(2)	P(2)−C(4)−Ge(1)	90.6(2)
C(4)−Ge(1)−N(2)	83.5(2)	P(2)−C(4)−P(1)	131.9(2)
N(2)−Ge(1)−O(1)	112.2(1)	Ge(1)−O(1)−C(57)	108.7(2)
O(1)−Ge(1)−C(4)	128.5(2)	O(1)−C(57)−C(67)	115.3(3)
O(2)−Ge(1)−N(2)	116.2(1)	C(57)−C(67)−O(2)	116.5(3)
Ge(1)−N(2)−P(2)	91.0(2)	C(67)−O(2)−Ge(1)	107.9(2)

($SiMe_3$), 18.37, 18.59, 21.26 (CH_3, tetramethylpiperidyl), 35.59, 40.98, 41.38, 41.99, 43.45, 44.90 (CH_2, tetramethylpiperidyl), 61.40 (quaternary C, tetramethylpiperidyl), 128.39, 128.53, 129.05, 129.57, 130.12, 130.89, 131.54, 132.71, 133.02, 133.64, 134.34 (Ph). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 10.57, 49.94.

Reaction of 1 with Azobenzene. A solution of **1** (0.62 g, 0.49 mmol) in THF (20 mL) was added slowly to azobenzene (0.18 g, 0.98 mmol) in THF (20 mL) at 0 °C. The resultant orange solution was raised to room temperature and stirred for 36 h. The volatiles were removed under reduced pressure. The residue was extracted with Et_2O. After filtration and concentration of the filtrate, **3** was obtained as yellow crystals. Yield: 0.37 g (46%). Mp: 133.5 °C dec. Anal. Found: C, 63.37; H, 5.62; N, 6.78. Calcd for $C_{43}H_{48}GeN_4P_2Si_2$: C, 63.63; H, 5.96; N, 6.90. ^1H NMR (THF-d_8): δ −0.43 (s, 9H, $SiMe_3$), −0.33 (s, 9H, $SiMe_3$), 6.66−6.74 (m, 2H, Ph), 6.76−6.85 (m, 2H, Ph), 6.98−7.15 (m, 4H, Ph), 7.20−7.37 (m, 4H, Ph), 7.39−7.52 (m, 8H, Ph), 7.64−7.77 (m, 9H, Ph), 7.83 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 3.16, 5.14 ($SiMe_3$), 115.99, 117.38, 119.46, 120.82, 122.92, 123.37, 125.03, 127.55, 128.75, 129.71, 131.39, 132.01, 133.37 (Ph). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 12.60, 30.04.

Reaction of 1 with Benzil. A solution of **1** (0.54 g, 0.43 mmol) in THF (20 mL) was added slowly to benzil (0.18 g, 0.86 mmol) in THF (20 mL) at 0 °C. The resultant yellow solution was raised to room temperature and stirred for 42 h. The volatiles were removed under reduced pressure. The residue was extracted with Et_2O. After filtration and concentration of the filtrate, **4** was obtained as yellow crystals. Yield: 0.38 g (52%). Mp: 143−144 °C. Anal. Found: C, 63.93; H, 5.48; N, 3.06. Calcd for $C_{45}H_{48}GeN_2O_2P_2Si_2$: C, 64.37; H, 5.76; N, 3.34. ^1H NMR (THF-d_8): δ −0.19 (s, 18H, $SiMe_3$), 7.04−7.21 (m, 6H, Ph), 7.28−7.38 (m, 10H, Ph), 7.38−7.43 (m, 6H, Ph), 7.73−7.79 (m, 8H, Ph). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 3.28 ($SiMe_3$), 126.55, 127.97, 128.22, 128.97, 129.02, 129.11, 129.28, 132.05, 132.71, 132.78, 133.04, 133.19, 133.91,

---

(25) Sheldrick, G. M. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and Databases*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: New York, 1985; p 175.

135.91, 135.74, 136.04, 137.37, 138.69 (Ph and Ph*C*═*C*Ph). ^{31}P{^{1}H} NMR (298 K, THF-d_8): δ 26.72. ^{31}P{^{1}H} NMR (238 K, THF-d_8): δ 5.56, 53.77.

X-ray Crystallography. Single crystals were sealed in Lindemann glass capillaries under nitrogen. X-ray data of **2**−**4** were collected on a Rigaku R-AXIS II imaging plate using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) from a rotating-anode generator operating at 50 kV and 90 mA. Crystal data for **2**−**4** are summarized in Table 1. The structures were solved by direct phase determination using SHELXTL-PC[25] 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**−**4** are given in the Supporting Information.

Acknowledgment. This work was supported by the Hong Kong Research Grants Council (Project No. CUHK 401404).

Supporting Information Available: Tables of crystal data and structure refinement details, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM7002706