Organometallics **2005,** *24,* 5033−5037

Synthesis of Novel Metal−Germavinylidene Complexes from Bisgermavinylidene

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

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

Received April 19, 2005

The bisgermavinylidene $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (**1**) has been used as the source of unstable germavinylidene for the synthesis of a series of metal−germavinylidene complexes. Treatment of **1** with $M(PPh_3)_4$ (M = Ni, Pd) afforded the metal−germavinylidene complexes $[\{(Me_3SiN{=}PPh_2)_2C{=}Ge\}_2Ni(PPh_3)_2]$ (**2**) and $[\{(Me_3SiN{=}PPh_2)_2C{=}Ge\text{-}\mu_2\}Pd(PPh_3)]_2$ (**3**), respectively. The germavinylidene moiety from **1** acts as a two-electron terminal and bridging ligand, respectively. Similar reaction of **1** with AgCl or AuI gave $[(Me_3SiN{=}PPh_2)_2C{=}Ge(Ag)(Cl)]_2$ (**5**) and $[(Me_3SiN{=}PPh_2)_2C{=}Ge(Au)(I)]_2$ (**6**), respectively. The result has shown that the germavinylidene moiety from **1** behaves as a Lewis base and undergoes an insertion reaction into the metal−halogen bond. X-ray structures of **2**, **3**, **5**, and **6** have been determined.

Introduction

The chemistry of transition metals bonded to heavy group 14 element carbene analogues, $:MR_2$ (M = Ge, Sn, Pb), has attracted much attention in the past few decades and has been the focus of several reviews.[1] Carbene analogues can behave as a Lewis base toward the transition metal or they can undergo insertion into transition-metal−halogen or metal−alkyl bonds.

We have recently reported the synthesis of the bisgermavinylidene $[(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2]$ (**1**), and its role as a carbene ligand $\{(Me_3SiN{=}PPh_2)_2C:\}$ transfer reagent has been demonstrated in the reaction of **1** with $Mo(CO)_5THF$ to form the molybdenum carbene complex *mer-/fac-*$(Me_3SiN{=}PPh_2)_2C{=}Mo(CO)_5$.[2] We also reported the synthesis of chalcogen-bridged dimers of the germaketene analogues $[(Me_3SiN{=}PPh_2)_2C{=}Ge(\mu\text{-}E)]_2$ (E = S, Se, Te) from the direct reaction of elemental chalcogens with **1**.[3] By the dissociation of Ge−Ge interaction in **1**, we anticipated that the reactive intermediate germavinylidene "$:Ge{=}C(PPh_2{=}NSiMe_3)_2$" can be generated in situ for subsequent formation of metal−germavinylidene complexes. Herein, we report the synthesis and structures of unprecedented group 10 metal−germavinylidene complexes and germavinylidyl group 11 metal complexes.

Results and Disscussion

Synthesis of Nickel(0) and Palladium(0) Germavinylidene Complexes. The reaction of bisgermavinylidene **1** with $Ni(PPh_3)_4$ in THF afforded $[\{(Me_3SiN{=}PPh_2)_2C{=}Ge\}_2Ni(PPh_3)_2]$ (**2**) as dark red crystalline solids (Scheme 1). The X-ray structure analysis of **2** showed that it contains two germavinylidene moieties bonded to the nickel(0) center. It is suggested that the intermediate germavinylidene generated from **1** in solution acted as a two-electron ligand and displaced two PPh_3 molecules from $Ni(PPh_3)_4$ to form the 18-electron nickel(0) complex **2**. Similar reaction of **1** with stoichiometric amounts of $Pd(PPh_3)_4$ gave the binuclear 14-electron Pd(0) complex $[\{(Me_3SiN{=}PPh_2)_2C{=}Ge\text{-}\mu_2\}Pd(PPh_3)]_2$ (**3**) with two bridging germavinylidene ligands (Scheme 2). Compound **3** reacts readily with CH_2Cl_2 to give $Cl_2Pd(PPh_3)_2$. Similar Lewis base type behavior of germylene has been demonstrated in the reaction of $M(PR_3)_4$ (M = Ni, Pd) with $[Ge\{N(SiMe_3)_2\}_2]$ to form $[(R_3P)_2MGe\{N(SiMe_3)_2\}_2]$.[4] Moreover, the reaction of **1** with $Cl_2Pd(PPh_3)_2$ in THF afforded $Pd(PPh_3)_4$ (**4**), showing that germavinylidene acts as a reducing agent. Germanium(II) compounds behave as a reducing agent, as reported in the synthesis of $Pd[Ge\{N(SiMe_3)_2\}_2]_3$.[5]

Insertion Reaction of Ag(I) and Au(I) Halides with Germavinylidene. The reaction of **1** with 2 equiv

---

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

(1) Selected recent reviews and examples: (a) Petz, W. *Chem. Rev.* **1986**, *86*, 1019. (b) Lappert, M. F.; Rowe, R. S. *Coord. Chem. Rev.* **1990**, *100*, 267. (c) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F.-R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1485. (d) Lappert, M. F.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1985**, 51. (e) Lappert, M. F.; Miles, S. J.; Power, P. P.; Carty, A. J.; Taylor, N. J. *J. Chem. Soc., Chem. Commun.* **1977**, 458. (f) Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J.-M. *Organometallics* **1998**, *17*, 2686. (g) Ayers, A. E.; Dias, H. V. R. *Inorg. Chem.* **2002**, *41*, 3259. (h) Tokitoh, N.; Manmaru, K.; Okazaki, R. *Organometallics* **1994**, *13*, 167. (i) Barrau, J.; Rima, G.; El Amraoui, T. E. *J. Organomet. Chem.* **1998**, *570*, 163. (j) Kuhl, O.; Lönnecke, P.; Heinicke, J. *Inorg. Chem.* **2003**, *42*, 2836. (k) Litz, K. E.; Bender, J. E.; Kampf, J. W.; Banaszak Holl, M. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 496. (l) Litz, K. E.; Henderson, K.; Gourley, R. W.; Banaszak Holl, M. M. *Organometallics* **1995**, *14*, 5008.

(2) (a) Leung, W.-P.; Wang, Z.-X.; Li, H.-W.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 2501. (b) Leung, W.-P.; So, C.-W.; Wang, J.-Z.; Mak, T. C. W. *Chem. Commun.* **2003**, 248.

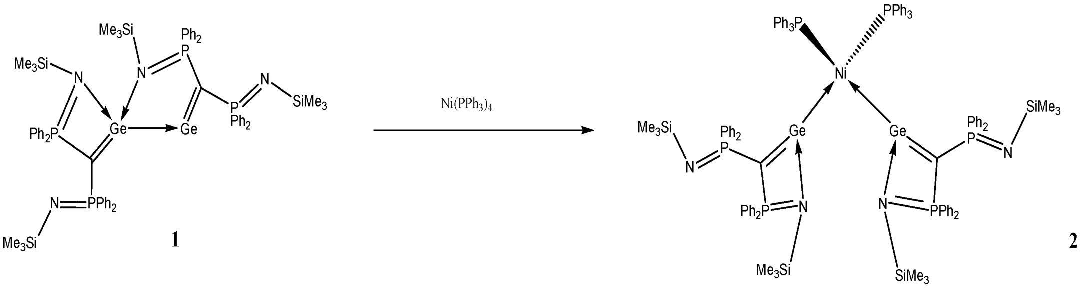
(3) Leung, W.-P.; So, C.-W.; Wang, Z.-X.; Wang, J.-Z.; Mak, T. C. W. *Organometallics* **2003**, *22*, 4305.

(4) (a) Bender, J. E.; Shusterman, A. J.; Banaszak Holl, M. M.; Kampf, J. W. *Organometallics* **1999**, *18*, 1547. (b) Cygan, Z. T.; Bender, J. E., IV; Litz, K. E.; Kampf, J. W.; Banaszak Holl, M. M. *Organometallics* **2002**, *21*, 5373.

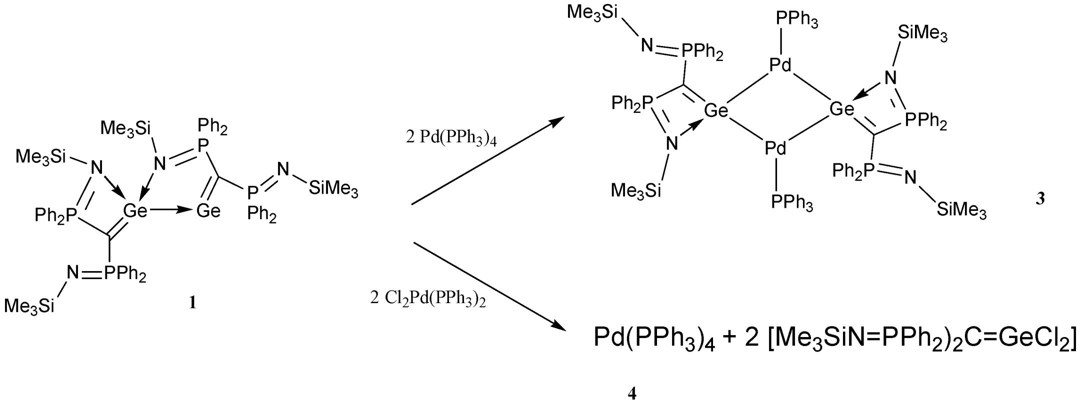
(5) Hitchcock, P. B.; Lappert, M. F.; Misra, M. C. *J. Chem. Soc., Chem. Commun.* **1985**, 863.

10.1021/om0503085 CCC: $30.25

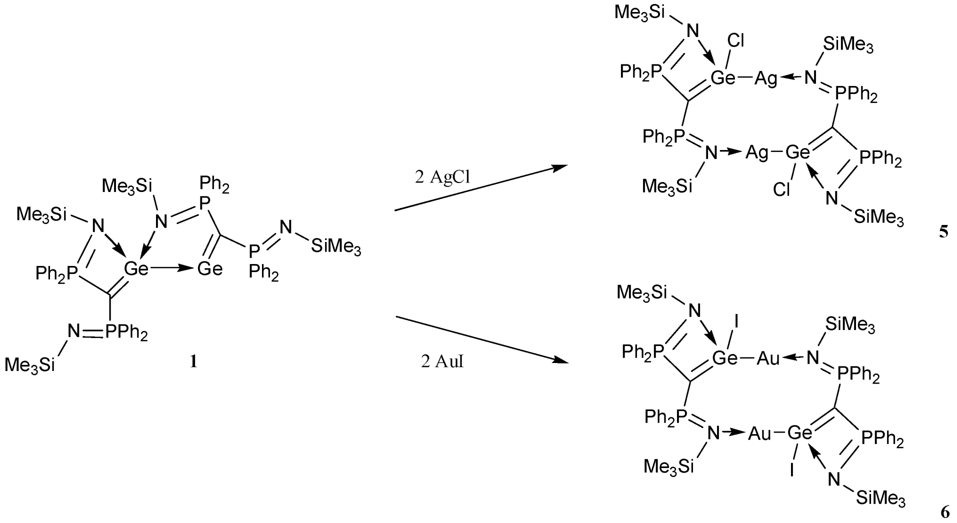
Scheme 1



Scheme 2



Scheme 3



of AgCl or AuI in THF afforded $[(Me_3SiN{=}PPh_2)_2C{=}GeAgCl]_2$ (**5**) and $[(Me_3SiN{=}PPh_2)_2C{=}GeAuI]_2$ (**6**), respectively (Scheme 3). The X-ray structures of **5** and **6** showed that the germanium atom of germavinylidene moieties inserted into the M−X bond to form **5** and **6**. This result is consistent with the theoretical calculation reported by Frenking and co-workers in which the germylene donor−acceptor complexes with group 11 metal chlorides.[6] To our knowledge, the (phosphine)-gold−trichlorogermyl complex $[\{R_3PAuGeCl_3\}_2]$ (R = Ph, *o*-Tol) is the only example demonstrating the insertion of a Ge(II) compound into a gold−chlorine bond.[7]

Spectroscopic Properties. Compounds **2** and **3** and compounds **5** and **6** were isolated as dark red and pale yellow crystalline solids, respectively. They are air-sensitive, soluble in THF, and sparingly soluble in Et_2O. The ^{31}P NMR spectrum of **2** displayed four singlets at δ 9.18, 35.96, 43.57, and 45.78 ppm, corresponding to four different phosphorus environments, as shown in the noncentrosymmetric molecular structure of **2**. It also indicates that **2** is fluxional in solution. The ^{31}P NMR spectrum of **3** displayed three signals at δ 33.45, 38.44, and 40.12 ppm due to three different phosphorus environments as in the solid-state structure. The ^{1}H and ^{13}C NMR spectra of **3** displayed one set of signals corresponding to the ligand backbone. The ^{31}P NMR spectra of **5** and **6** displayed one singlet (δ 46.17 (**5**); δ 43.42 (**6**)) due to fluxional motion in solution.

X-ray Structures. The molecular structures of **2**, **3**, **5**, and **6** are shown in Figures 1−4, respectively.

---

(6) Boehme, C.; Frenking, G. *Organometallics* **1998**, *17*, 5801.
(7) Bauer, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1996**, *118*, 5324.

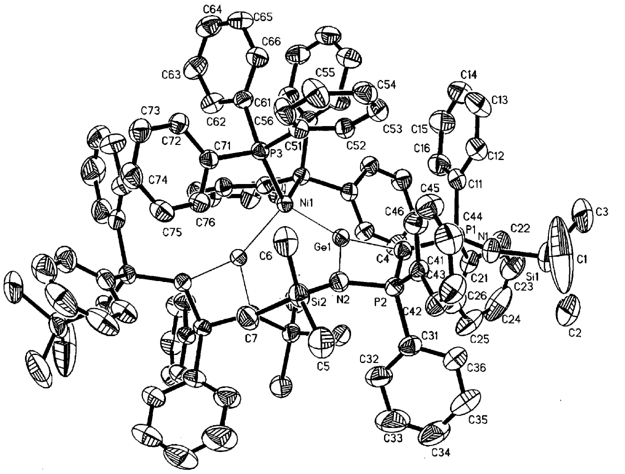


Figure 1. Molecular structure of $[\{(Me_3SiN{=}PPh_2)_2C{=}Ge\}_2{\rightarrow}Ni(PPh_3)_2]$ (**2**).

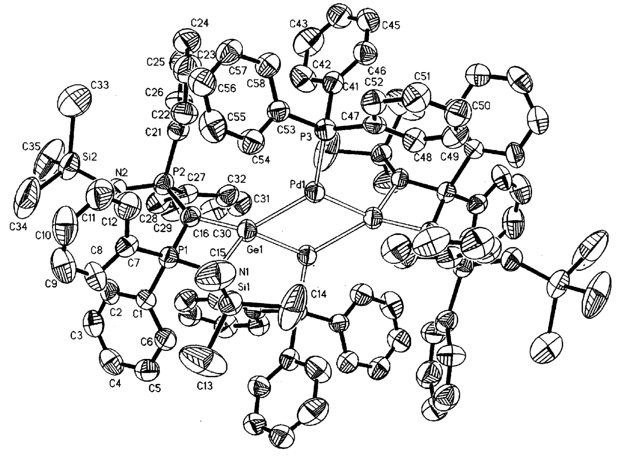


Figure 2. Molecular structure of $[\{(Me_3SiN{=}PPh_2)_2C{=}Ge\text{-}\mu_2\}Pd(PPh_3)]_2$ (**3**).

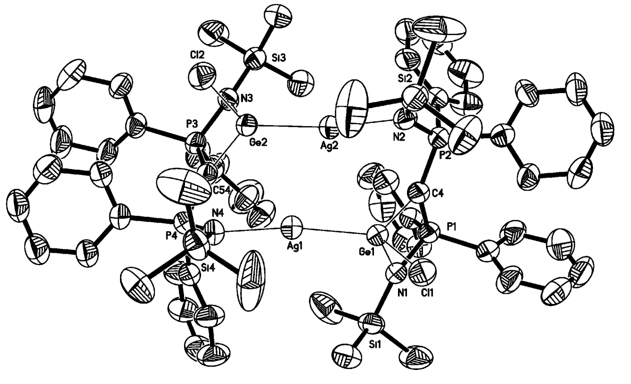


Figure 3. Molecular structure of $[(Me_3SiN{=}PPh_2)_2C{=}Ge(Ag)(Cl)]_2$ (**5**).

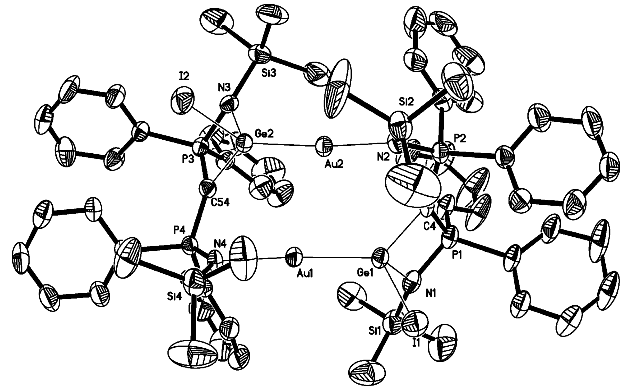


Figure 4. Molecular structure of $[(Me_3SiN{=}PPh_2)_2C{=}Ge(Au)(I)]_2$ (**6**).

Selected bond distances (Å) and angles (deg) are listed in Tables 2 and 3. Compound **2** is comprised of two germavinylidenes $[(Me_3SiN{=}PPh_2)_2C{=}Ge{:}]$ and two PPh_3 groups bonded to the nickel center in a distorted-tetrahedral geometry. The Ni(1)−Ge(1) bond distance of 2.273(7) Å is similar to that of 2.240 Å in $Ni[Ge\{1,8\text{-}(Pr^iN)_2C_{10}H_6\}]_4$[8] and 2.206 Å in $[(Ph_3P)_2NiGe\{N(SiMe_3)_2\}_2]$.[4a] The Ge(1)−C(4) bond distance of 1.933(4) Å in **2** is slightly longer than those of 1.905(8) and 1.908(7) Å in **1**. One of the imino nitrogens coordinates to Ge(1) at a distance of 2.032(4) Å, and Ge(1) is subtended at an angle of 153.5(1)° with Ni(1) and C(4), instead of a linear $Ni{\leftarrow}Ge{=}C{<}$ moiety. The difference in the P−N bond distances of 1.557(4) and 1.641(4) Å suggests the delocalization of π electrons resulting from the conjugation of P=N and C=Ge double bonds. The Ni(1)−P(3) bond distance of 2.224(1) Å is similar to that of 2.181(1) Å in $[(Ph_3P)_2NiGe\{2,4,6\text{-}(CF_3)_3C_6H_2\}_2]$.[4a]

The molecular structure of compound **3** is comprised of two germavinylidenes bridged to two Pd(0) centers. The C(16)P(1)N(1)Ge(1) plane is perpendicular to the Pd(1)Ge(1)Pd(1A)Ge(1A) plane. Therefore, the geometry around the germanium center is tetrahedral. The Ge(1)−C(16) distance of 1.906(13) Å is similar to those of 1.905(8) and 1.908(7) Å in **1**. The Ge−Pd bond distances of 2.476(2) and 2.465(2) Å are significantly longer than that of 2.328(1) Å in $[(Ph_3P)_2PdGe\{N(SiMe_3)_2\}_2]$ and 2.337(2) Å in $[(dppe)PdGe\{N(SiMe_3)_2\}_2]_2$.[4b] The distance between the Pd atoms (2.684(2) Å) is shorter than that of Pd(0) in the bulk metal (2.751 Å) but is slightly longer than the Pd(I)−Pd(I) distance of $[Pd(\mu\text{-}Br)(PBu^t_3)]_2$ (2.628(2) Å)[9] in Pd(I) complexes with a linear $R_3P{-}Pd{-}Pd{-}PR_3$ moiety. The geometry of the Pd atom is trigonal planar, as the sum of Pd bond angles is 359.6°. The Pd−P bond distance of 2.274(4) Å is similar to that of 2.301(9) Å in $[(Ph_3P)_2PdGe\{N(SiMe_3)_2\}_2]$.[4b]

The molecular structures of **5** and **6** are isostructural and are comprised of two halogermenes forming the Ge−N chelating bridges with the Ag(I) and Au(I) metal centers. The metal−halogen distances of 3.88 Å in **5** and 3.95 Å in **6** are longer than the group 11 metal−halogen single bond. These structures have shown that the germavinylidene underwent insertion into a M−X bond instead of forming a donor−acceptor interaction. The Ag···Ag distance of 2.979(2) Å in **5** is longer than that of 2.654(1) Å in $[\{2\text{-}(Me_3Si)_2C(Ag)C_5H_4N\}]_2$[10] and 2.733(3) Å in $[\{Ag(C_6H_2Me_3\text{-}2,4,6)\}_4]$[11] but is still shorter than the sum of van der Waals radii of two Ag atoms (∼3.4 Å), suggesting that a weak silver−silver interaction is possible. The Au···Au distance of 3.092(7) Å in **6** is within the range of 2.5−3.2 Å for similar interactions

---

(8) Bazinet, P.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2001**, *123*, 11162.

(9) Vilar, R.; Mingos, D. M. P.; Cardin, C. J. *J. Chem. Soc., Dalton Trans.* **1996**, 4313.

(10) Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1984**, 612.

(11) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1087.

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

	2	**3**	**5**	**6**
formula	$C_{98}H_{106}Ge_2N_4NiP_6Si_4$	$C_{98}H_{106}Ge_2N_4P_6Pd_2Si_4$	$C_{62}H_{76}Ag_2Cl_2Ge_2N_4P_4Si_4$	$C_{62}H_{76}Au_2Ge_2I_2N_4P_4Si_4$
fw	1841.94	1996.03	1545.33	1906.42
color	dark red	dark red	pale yellow	pale yellow
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	C_2	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	23.502(5)	13.317(3)	16.056(3)	16.229(9)
b (Å)	19.525(4)	14.373(3)	22.997(5)	23.225(1)
c (Å)	13.015(3)	17.117(3)	24.380(5)	24.210(1)
α (deg)	90.00	68.11(3)	90.70(3)	90.00(0)
β (deg)	115.10(3)	68.23(3)	105.85(3)	102.36(10)
γ (deg)	90.00	72.63(3)	91.27(3)	90.00(0)
V (Å^3)	5408.4(19)	2774.0(10)	8656.0(3)	8913.5(9)
Z	2	1	4	4
d_{calcd} (g cm^{-3})	1.131	1.195	1.186	1.421
μ (mm^{-1})	0.899	1.026	1.357	4.799
F(000)	1920	1024	3136	3680
cryst size (mm)	0.45 × 0.40 × 0.30	0.50 × 0.40 × 0.25	0.40 × 0.30 × 0.20	0.50 × 0.40 × 0.20
2θ range (deg)	1.91−25.52	1.73−25.73	1.32−25.00	1.23−25.00
index range	$0 \le h \le 28$ $-23 \le k \le 23$ $-14 \le l \le 13$	$-16 \le h \le 15$ $-15 \le k \le 0$ $-20 \le l \le 18$	$-19 \le h \le 19$ $0 \le k \le 27$ $-28 \le l \le 28$	$-19 \le h \le 19$ $-27 \le k \le 21$ $-28 \le l \le 28$
no. of rflns collected	8855	5254	23 010	47662
no. of indep rflns	8754	5254	23010	15677
R1, wR2 ($I > 2\sigma(I)$)	0.0456, 0.1377	0.0985, 0.2613	0.0944, 0.2923	0.0566, 0.1944
R1, wR2 (all data)	0.0462, 0.1388	0.1226, 0.2845	0.1071, 0.3074	0.0985, 0.2176
goodness of fit, F^2	1.135	1.136	1.119	1.066
no. of data/restraints/params	8754/1/520	5254/0/523	23 010/4/1441	15 677/2/721
largest diff peaks, e Å^{-3}	+0.736 to −0.608	+0.966 to −0.914	+1.249 to −0.923	+1.900 to −0.910

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

[{$(Me_3SiN{=}PPh_2)_2C{=}Ge$}$_2 \rightarrow Ni(PPh_3)_2$] (**2**)			
Ge(1)−Ni(1)	2.273(7)	C(4)−P(1)	1.751(4)
Ni(1)−P(3)	2.224(1)	C(4)−P(2)	1.726(4)
C(4)−Ge(1)	1.933(4)	P(1)−N(1)	1.557(4)
Ge(1)−N(2)	2.032(4)	P(2)−N(2)	1.641(4)
P(3)−Ni(1)−P(3A)	108.6(6)	C(4)−P(2)−N(2)	96.9(2)
Ge(1)−Ni(1)−Ge(1A)	103.9(4)	P(2)−C(4)−P(1)	119.5(2)
P(3)−Ni(1)−Ge(1)	107.3(3)	P(2)−N(2)−Ge(1)	91.6(2)
[{$(Me_3SiN{=}PPh_2)_2C{=}Ge$-$\mu_2$}$Pd(PPh_3)$]$_2$ (**3**)			
Pd(1)−Pd(1A)	2.684(2)	C(16)−P(1)	1.737(14)
Ge(1)−Pd(1)	2.476(2)	C(16)−P(2)	1.745(13)
C(16)−Ge(1)	1.906(13)	P(1)−N(1)	1.650(10)
Ge(1)−N(1)	1.954(10)	P(2)−N(2)	1.545(13)
Pd(1)−P(3)	2.274(4)		
Pd(1)−Ge(1)−Pd(1A)	65.8(6)	C(16)−Ge(1)−N(1)	80.5(5)
Ge(1)−Pd(1)−Ge(1A)	114.2(6)	Ge(1)−N(1)−P(1)	92.7(5)
P(3)−Pd(1)−Ge(1)	127.4(1)	N(1)−P(1)−C(16)	94.8(6)
P(3)−Pd(1)−Ge(1A)	118.1(1)	P(1)−C(16)−P(2)	126.0(8)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compounds 5 and 6

	[$(Me_3SiN{=}PPh_2)_2C{=}Ge(M)(X)$]$_2$	
	M = Ag, X = Cl (**5**)	M = Au, X = I (**6**)
Ge(1)−M(1)	2.438(2)	2.330(1)
Ge(1)−X(1)	2.277(4)	2.666(2)
Ge(1)−C(4)	1.910(8)	1.860(1)
Ge(1)−N(1)	1.944(10)	1.953(10)
P(1)−N(1)	1.641(10)	1.641(13)
C(4)−P(1)	1.699(11)	1.703(13)
C(4)−P(2)	1.724(10)	1.750(10)
P(2)−N(2)	1.603(10)	1.624(10)
N(2)−M(2)	2.158(9)	2.111(10)
M(2)−Ge(2)	2.409(2)	2.341(1)
Ge(2)−X(2)	2.273(4)	2.648(2)
Ge(2)−C(54)	1.906(8)	1.860(1)
Ge(2)−N(3)	1.961(9)	1.955(10)
P(3)−N(3)	1.636(9)	1.622(11)
C(54)−P(3)	1.690(12)	1.708(12)
C(54)−P(4)	1.733(11)	1.744(10)
M(1)−M(2)	2.979(2)	3.092(7)
M(1)−Ge(1)−C(4)	131.0(3)	132.0(4)
Ge(1)−M(1)−N(4)	171.5(3)	175.7(3)
X(1)−Ge(1)−M(1)	110.9(1)	103.4(6)
C(4)−Ge(1)−X(1)	108.0(4)	111.0(4)
M(1)−N(4)−P(4)	110.3(5)	109.8(5)
N(4)−P(4)−C(54)	109.8(5)	107.6(5)
P(4)−C(54)−Ge(2)	126.5(6)	126.9(6)
P(3)−C(54)−Ge(2)	92.1(5)	93.5(4)
C(54)−Ge(2)−M(2)	130.4(3)	133.1(4)
C(54)−Ge(2)−X(2)	108.8(4)	109.0(4)
X(2)−Ge(2)−M(2)	109.7(1)	105.4(6)
Ge(2)−M(2)−N(2)	171.6(2)	173.7(3)
N(2)−P(2)−C(4)	108.0(5)	108.0(5)
P(2)−C(4)−Ge(1)	126.1(6)	131.0(7)
P(1)−C(4)−Ge(1)	93.0(4)	93.7(4)

reported.[12] The Ge−Ag bond distances of 2.438(2) and 2.409(2) Å in **5** are longer than the theoretically calculated Ge−Ag donor−acceptor bond distance in [{N(H)CH=CHN(H)}Ge→AgCl] (2.349 Å).[6] The Ge−Au bond distances of 2.329(1) and 2.341(1) Å in **6** are comparable to that of 2.376(1) Å in [{(*o*-Tol$_3$P)AuGeCl$_3$}$_2$].[7] The average Ge−C bond distance of 1.908 Å in **5** and 1.860 Å in **6** are similar to those of 1.905(8) and 1.908(7) Å in **1**.

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). $Ni(PPh_3)_4$, $Pd(PPh_3)_4$, $Cl_2Pd(PPh_3)_2$, AgCl, and AuI were purchased from Aldrich Chemicals and used without further purification. The ^1H, ^{13}C, and ^{31}P spectra were recorded on Bruker WM-300 and Varian 400 spectrometers. The NMR spectra were

---

(12) Grohmann, A.; Schmidbaur, H. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 3.

recorded in THF-d_8, and the chemical shifts δ are relative to $SiMe_4$ and 85% H_3PO_4 for ^1H and ^{13}C and for ^{31}P, respectively.

[{$(Me_3SiN{=}PPh_2)_2C{=}Ge$}$_2$→$Ni(PPh_3)_2$] (2). A solution of **1** (0.81 g, 0.64 mmol) in THF (30 mL) was added dropwise to $Ni(PPh_3)_4$ (0.70 g, 0.64 mmol) in THF (30 mL) at −90 °C in the absence of light. The reaction mixture was stirred at room temperature for 18 h, and a dark red solution was formed. 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 dark red crystals. Yield: 0.84 g (75%). Mp: 87−88 °C. Anal. Found: C, 65.73; H, 5.82; N, 2.90. Calcd for $C_{98}H_{106}Ge_2N_4NiP_6Si_4$: C, 66.01; H, 5.99; N, 3.14. ^1H NMR (THF-d_8, 300 MHz): δ −0.57 (s, 18H, $SiMe_3$), −0.15 (s, 18H, $SiMe_3$), 6.88−7.70 (m, 70H, Ph). $^{13}C\{^1H\}$ NMR (THF-d_8, 75.5 MHz): δ 2.84 ($SiMe_3$), 4.15 ($SiMe_3$), 128.29, 128.50, 128.57, 128.66, 129.09, 129.18, 129.33, 131.14, 132.38, 132.87, 134.38, 134.63, 134.75, 138.65 (Ph). $^{31}P\{^1H\}$ NMR (THF-d_8, 121.5 MHz): δ 9.18, 35.96, 43.57, 45.78.

[{$(Me_3SiN{=}PPh_2)_2C{=}Ge$-$\mu_2$}$Pd(PPh_3)$]$_2$ (3). A solution of **1** (0.42 g, 0.33 mmol) in THF (30 mL) was added dropwise to $Pd(PPh_3)_4$ (0.75 g, 0.65 mmol) in THF (30 mL) at −90 °C in the absence of light. The reaction mixture was stirred at room temperature for 18 h, and a dark red solution was formed. Volatiles in the mixture were removed under reduced pressure, and the residue was extracted with Et_2O. After filtration and concentration of the filtrate, **3** was obtained as dark red crystals. Yield: 0.18 g (27%). Mp: 128−129 °C. Anal. Found: C, 58.67; H, 5.14; N, 2.46. Calcd for $C_{98}H_{106}Ge_2N_4P_6Pd_2Si_4$: C, 58.97; H, 5.35; N, 2.81. ^1H NMR (THF-d_8, 300 MHz): δ 0.03 (s, 18H, $SiMe_3$), 0.11 (s, 18H, $SiMe_3$), 7.38−7.47 (m, 40H, Ph), 7.64−7.68 (m, 10H, Ph), 7.71−7.79 (m, 10H, Ph), 7.85−7.94 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (THF-d_8, 75.5 MHz): δ 1.38, 1.63 ($SiMe_3$), 128.52, 128.77, 129.03, 129.19, 131.29, 131.56, 131.92, 133.27, 132.76, 132.88, 134.67 (Ph). $^{31}P\{^1H\}$ NMR (THF-d_8, 161 MHz): δ 33.45 (PdP), 39.44, 40.12 (PCP).

Reaction of 1 with $PdCl_2(PPh_3)_2$. A solution of **1** (0.54 g, 0.43 mmol) in THF (30 mL) was added dropwise to $Cl_2Pd(PPh_3)_2$ (0.63 g, 0.90 mmol) in THF (30 mL) at 0 °C. The reaction mixture was stirred at room temperature for 18 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, **4** was obtained as yellow crystals. Yield: 0.49 g (47%).

[$(Me_3SiN{=}PPh_2)_2C{=}Ge(Ag)(Cl)$]$_2$ (5). A solution of **1** (0.46 g, 0.37 mmol) in THF (30 mL) was added dropwise to a suspension of AgCl (0.11 g, 0.73 mmol) in THF (30 mL) at 0 °C in the absence of light. The reaction mixture was stirred at room temperature for 2 days, and a pale yellow solution was formed. After filtration and concentration, **5** was obtained as pale yellow crystals. Yield: 0.28 g (40%). Mp: 187.5 °C dec. Anal. Found: C, 47.92; H, 4.81; N, 3.39. Calcd for $C_{62}H_{76}Ag_2Cl_2Ge_2N_4P_4Si_4$: C, 48.19; H, 4.96; N, 3.63. ^1H NMR (THF-d_8, 300 MHz): δ −0.13 (s, 36H, $SiMe_3$), 6.90−7.72 (m, 40H, Ph). $^{13}C\{^1H\}$ NMR (THF-d_8, 75.5 MHz): 4.54 ($SiMe_3$), 129.05, 129.20, 131.54, 132.64, 132.71, 132.78 (Ph). $^{31}P\{^1H\}$ NMR (THF-d_8, 121.5 MHz): δ 46.17.

[$(Me_3SiN{=}PPh_2)_2C{=}Ge(Au)(I)$]$_2$ (6). A solution of **1** (0.61 g, 0.49 mmol) in THF (30 mL) was added dropwise to a suspension of AuI (0.42 g, 0.97 mmol) in THF (30 mL) at 0 °C in the absence of light. The reaction mixture was stirred at room temperature for 2 days, and a pale yellow solution was formed. After filtration and concentration, **6** was obtained as pale yellow crystals. Yield: 0.45 g (60%). Mp: 202.2 °C dec. Anal. Found: C, 39.40; H, 4.32; N, 2.90. Calcd for $C_{62}H_{76}Au_2Ge_2I_2N_4P_4Si_4\cdot{}^1/_2THF$: C, 39.57; H, 4.15; N, 2.88. ^1H NMR (THF-d_8, 300 MHz): δ −0.06 (s, 36H, $SiMe_3$), 6.98−7.52 (m, 40H, Ph). $^{13}C\{^1H\}$ NMR (THF-d_8, 75.5 MHz): 3.71 ($SiMe_3$), 128.98, 129.15, 129.31, 131.55, 132.01, 133.17, 134.94 (Ph). $^{31}P\{^1H\}$ NMR (THF-d_8, 121.5 MHz): δ 43.42.

X-ray Crystallography. Single crystals were sealed in Lindemann glass capillaries under nitrogen. X-ray data of **2**, **3**, **5**, and **6** were collected on a Rigaku R-AXIS II imaging plate using graphite-monochromatized Mo Kα radiation (I = 0.710 73 Å) from a rotating-anode generator operating at 50 kV and 90 mA. Crystal data are summarized in Table 1. The structures were solved by direct phase determination using the computer program SHELXTL-PC[13] 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**, **5**, and **6** 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: Details about the X-ray crystal structures, as CIF files, for **2**, **3**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0503085

---

[13] 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.