ORGANOMETALLICS

Synthesis and Structural Characterization of Metallogermylenes, Cp-Substituted Germylene, and a Germanium(II)-Borane Adduct from Pyridyl-1-azaallyl Germanium(II) Chloride

Wing-Por Leung,* Wang-Kin Chiu, and Thomas C. W. Mak

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

Supporting Information

ABSTRACT: The reaction of [{N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)}GeCl] (1) with Na[M(η^{5} -C₅H₅)(CO)₃]·2DME (M = Mo, W) afforded the metallogermylenes [{N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)}Ge-M(η^{5} -C₅H₅)(CO)₃] (M = Mo (2), W (3)). Compounds 2 and 3 have been characterized by X-ray crystallography and NMR and IR spectroscopy. Structural analyses of compounds 2 and 3 are consistent with the presence of lone-pair electrons at the germanium(II) center. The Ge–Mo and Ge–W bond distances of 2.875(1) and 2.852(1) Å are consistent with Ge–metal single bonds. The chlorogermylene 1 was also used in the synthesis of a substituted germylene, [{N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)}Ge(η^{1} -C₅H₅)] (4), by reaction with sodium cyclopentadienylide. The reaction of compound 1 with tris(pentafluorophenyl)borane led to the formation of a Lewis acid–base adduct, [{N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)}Ge(Cl)→B(C₆F₅)₃] (5).

■ INTRODUCTION

In the last three decades, the synthesis of compounds with group 14 elements in unusual or low oxidation states has received much attention¹ since the first isolation of a germylene complex by Lappert and co-workers in 1974.² In particular, organohalogermylenes (RGeX, R = monoanionic ligand; X = halogen atom), which constitute an interesting class of compounds in group 14 metal chemistry, have drawn much attention, as they are important precursors for the synthesis of new low-valent germanium compounds.³ For example, Power⁴ and Tokitoh⁵ respectively reported the synthesis of 1,2diaryldigermynes by the reduction of the chlorogermylenes supported by terphenyl ligands or the 1,2-diaryl-1,2-dibromodigermenes. Recently, Jones reported the synthesis of a digermyne with a Ge-Ge single bond by reduction of amido germanium(II) chloride,⁶ while the facile syntheses of Ge(I) dimers from the reduction of different chlorogermylenes have been reported by several research groups.⁷ In 2006, Driess and co-workers documented the synthesis and isolation of a ylidelike germylene by dehydrohalogenation of a chlorogermylene.⁸ By addition of AlH₃·NMe₃ or $[K{B(Bu^i)_3}H]$ to a β diketiminato germanium(II) chloride,⁹ a stable monomeric terminal germanium(II) monohydride was synthesized by Roesky, and the germanium(II) hydride has played an important role in synthetic chemistry and the activation of small molecules.¹⁰ In addition, the versatile chlorogermylenes were also employed in the formation of unusual heterobimetallic metal-metal bonded systems, which provide valuable structural information on the metal complexes supported by monodentate or bidentate ligands.¹¹ The aforementioned reports are only some highlights of the

importance of heteroleptic germanium(II) chlorides in lowvalent germanium chemistry, and it is not surprising that there is still intensive research activity focused on developing new ligands for stabilization of the low-valent germnaium(II) center in RGeCl or the continuation of the reactivity study of chlorogermylenes.¹²

Our group has recently reported the synthesis of a pyridyl-1azaallyl germanium(II) chloride, LGeCl (1) (L = $N(SiMe_3)$ - $C(Ph)C(SiMe_3)(C_5H_4N-2))$,^{13a} and its reaction with chalcogens.^{13b} We have also carried out reactivity studies of compound 1, which gave novel lithium germinate [{(PhC= $C_{3}Ge_{3}GeLi(Et_{2}O_{3}]$ and Ge(II)-M(I) (M = Cu and Au) adducts.^{13c} In a recent communication, we reported the synthesis of a pyridyl-1-azaallyl germanium(I) dimer and its reaction with sulfur to afford a germadithiocarboxylic acid anhydride.7d Further to these studies, herein we report the reactivity studies of compound 1. This includes the reaction with Na[M(η^5 -C₅H₅)(CO)₃]·2DME (M = Mo, W; DME = 1,2dimethoxyethane), which afforded novel intramolecularly donor-stabilized metallogermylenes. The salt elimination reaction of 1 with sodium cyclopentadienylide (NaCp) and the Lewis acid-base reaction of 1 with $B(C_6F_5)_3$ will also be described.

RESULTS AND DISCUSSION

Synthesis of Metallogermylenes. The pyridyl-1-azaallyl germanium(II) chloride LGeCl (1) was prepared according to the literature procedure.^{13a} Treatment of 1 with 1 equiv of

```
Received: August 10, 2012
Published: September 14, 2012
```



Na[M(η^{5} -C₅H₅)(CO)₃]·2DME¹⁴ (M = Mo or W; DME = 1,2dimethoxyethane) in THF afforded compounds **2** and **3** (Scheme 1). The metallogermylenes **2** and **3** [{N(SiMe₃)C-(Ph)C(SiMe₃)(C₅H₄N-2)}Ge-M(η^{5} -C₅H₅)(CO)₃] (M = Mo or W) were isolated as dark red crystals.

Scheme 1. Synthesis of Compounds 2-5



Synthesis of Heteroleptic Germylene and Germanium(II)–Borane Adduct. The salt elimination reaction with NaCp was performed, which afforded a monomeric heteroleptic germylene, $[{N(SiMe_3)C(Ph)C-(SiMe_3)(C_5H_4N-2)}Ge(\eta^1-C_5H_5)]$ (4). We have previously shown that the reaction of 1 with group 11 metal iodides afforded the corresponding Ge(II)–Cu(I) or –Au(I) Lewis acid–base adducts.^{13c} To investigate the Lewis base behavior of 1, compound 1 was treated with tris(pentafluorophenyl)borane, B(C₆F₅)₃. This reaction afforded the adduct [{N(SiMe_3)C-(Ph)C(SiMe_3)(C_5H_4N-2)}Ge(Cl)→B(C_6F_5)_3] (5) (Scheme 1).

Spectroscopic Properties. Compounds 2-5 were isolated as dark red or yellow crystalline solids that decompose readily upon contact with air or moisture. They show good solubility in THF, ether, and toluene but are sparingly soluble in hexane. The ¹H NMR spectra of compounds 2 and 3 show a similar pattern. The singlets due to the two SiMe₃ groups in 2 are observed at δ 0.12 and 0.15 ppm, and those for 3 are observed at δ 0.19 and 0.25 ppm, respectively. Two singlets are found respectively at δ 5.23 and 5.12 ppm in the ¹H NMR spectra of compounds 2 and 3, which are due to the protons from the Cp rings coordinated to the molybdenum and tungsten centers. The ¹³C NMR spectra of compounds 2 and 3 are similar. The singlets due to the carbons of the two SiMe₃ groups in 2 are observed at δ 2.10 and 2.88 ppm, while those for **2** are observed at δ 2.68 and 3.55 ppm, respectively. Signals due to the carbons from the Cp rings are observed at δ 81.65 and 82.38 ppm, respectively. Signals due to the pyridyl and phenyl carbons in 2 are observed at δ 126.32–154.08 ppm, while those for 3 are

observed at δ 122.12–156.08 ppm. The ¹H and ¹³C NMR signals are consistent with the solid-state structures of 2 and 3.

Two sharp singlets due to the SiMe₃ groups are observed at δ -0.20 and -0.14 ppm in the ¹H NMR spectrum of compound 4. In addition, a sharp singlet is found at δ 6.07 ppm, which is the signal for the protons from the Cp ring. Signals due to the phenyl and pyridyl protons are observed at δ 7.28–8.47 ppm. The ¹³C spectrum of 4 displays two singlets at δ 2.17 and 3.16 ppm, which are due to the carbons from the two SiMe₃ groups. Also, in the ¹³C spectrum, a sharp singlet is observed at δ 113.54 ppm, which corresponds to the carbons from the Cp ring. The NMR signals suggest that the Cp ring in 4 is fluxional, with the point of attachment of the Ge atom to the Cp ring migrating rapidly from one carbon to another via a series of 1,2or 1,3-shifts of the Ge atom around the η^1 -C₅H₅ ring.^{15a,b} Therefore, only one signal is observed for the Cp ring in either the ¹H or ¹³C NMR spectra even at temperatures as low as -80 °C due to the low-energy barrier to the interconversion. The fluxional behavior of the η^1 -C₅H₅ group has also been observed for $[Fe(\eta^1-C_5H_5)(\eta^5-C_5H_5)(CO)_2]^{15b^1}$ and $[fac-(\eta^1-C_5H_5)Re (CO)_{3}(P(CH_{3})_{3})]^{.15c}$

The ¹H NMR spectrum of 5 displays two sharp singlets at δ -0.15 and -0.10 ppm due to the two SiMe₃ groups in compound 5. Signals due to the phenyl and pyridyl protons are observed at δ 7.38–8.72 ppm. The ¹³C spectrum of 5 displays two sharp singlets at δ 1.74 and 2.83 ppm, which are due to the carbons from the two SiMe₃ groups. Signals due to the phenyl and pyridyl carbons in the ligand backbone and the carbons from B(C₆F₅)₃ are observed at δ 120.44–149.80 ppm. The ¹¹B NMR spectrum of 5 shows a broad signal at δ 2.80 ppm, which shows a downfield shift in comparison to that of the germanium(II) hydride–borane adduct supported by the pyridyl-1-azaallyl ligand (δ –38.88 ppm).^{13c} The signal also shows a downfield shift when compared to those observed for related complexes containing a Ge(II)-B bond. ¹¹B NMR chemical shifts for $[\{2,6-(NMe_2),2C_6H_3\},Ge\rightarrow BH_3]$ (δ -35 ppm),¹⁶ [{HC(CMeNAr)₂}GeH(BH₃)] (δ -42 ppm; Ar = 2,6- $Pr_{2}^{i}C_{6}H_{3}$,¹⁷ and NHC \rightarrow (Mes)₂Ge \rightarrow BH₃ (δ -28.49 ppm; NHC = $[C{N(Pr^{i})C(CH_{3})}_{2}]$, Mes = 2,4,6-Me₃C₆H₂)¹⁸ have been reported.

X-ray Structure. The molecular structures of compounds 2 and 3 are shown in Figures 1 and 2. Selected bond distances (Å) and angles (deg) are listed in Table 1. The Ge-Mo bond distance of 2.875(1) Å in 2 is longer than that of 2.271-2.319Å in the molybdenum-germylyne complexes reported by groups of Power and Filippou.¹⁹ Theoretical calculations and bonding analysis by Pandey's research group revealed that the π -bonding contributions in metallogermylenes are weaker than those in metallogermylynes and that the σ -bonding contributions in the former compounds are stronger than those in the latter.²⁰ The Ge–Mo bond distance of 2.875(1) Å in 2 is also longer than those reported for molybdenum-germylidene complexes (2.402-2.537 Å)²¹ and the calculated Ge-Mo bond distance of 2.695 Å for [MeGe-Mo(η^5 -C₅H₅)(CO)₃].^{20a} To the best of our knowledge, there are no structurally characterized molybdenum-germylene σ -complexes possessing a Ge(II)-Mo single bond, although there are recent reports of irongermylenes of general formula RGe-Fe $(\eta^5$ -C₅H₅)(CO)₂ by Driess^{11h} and Jones,^{11g} respectively. Compound 2 is the first structurally characterized hetero-bimetallic complex featuring a Ge(II)–Mo σ -bond with the presence of a stereoactive lonepair at the germanium(II) center.

Organometallics



Figure 1. Molecular structure of $[{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}Ge-Mo(\eta^5-C_5H_5)(CO)_3]$ (2). Hydrogen atoms are omitted for clarity; 30% thermal ellipsoids are shown.



Figure 2. Molecular structure of $[{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}Ge-W(\eta^5-C_5H_5)(CO)_3]$ (3). Hydrogen atoms are omitted for clarity; 30% thermal ellipsoids are shown.

There is only one reported example of a structurally characterized tungsten–germylene σ -complex that has a Ge–W single bond of 2.681(3) Å.^{11c} The Ge–W bond distance of 2.852(1) Å in **3** is significantly longer than those reported for tungsten–germylidene complexes (2.402–2.632 Å)²² and tungsten–germylyne complexes (2.277–2.338 Å).^{11c,d,f,19a,b}

The Mo-C_{CO} and Mo-C_{η 5-C_{SH5}} distances (av 1.952(6), 2.358(6) Å) in compound **2** are similar to those observed in the structure of the dimer {Mo(η ⁵-C₅H₅)(CO)₃}₂ (av 1.977(3), 2.338(3) Å). The W-C_{CO} and W-C_{η 5-C₅H5} distances (av 1.955(6), 2.351(6) Å) in compound **3** are also very similar to the corresponding ones in the dimer {W(η ⁵-C₅H₅)(CO)₃}₂ (av 1.976(6), 2.342(6) Å).²³ In compound **2**, the germanium(II) center Ge(1) is bonded to one molybdenum atom Mo(1) and two nitrogen atoms N(1) and N(2). The sum of the bond

Table 1. Selected Bond Distances	(A)) and	Angles	(deg)) for
Compounds 2 and 3					

$[\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)\}Ge-M(\eta^5-C_5H_5)(CO)_3]$						
	M = Mo (2)	M = W(3)				
Ge(1) - M(1)	2.875(1)	2.852(1)				
Ge(1) - N(1)	2.057(4)	2.011(4)				
Ge(1)-N(2)	1.940(3)	1.978(3)				
N(1)-C(5)	1.346(6)	1.353(6)				
N(1)-Ge(1)-M(1)	107.3(1)	106.6(1)				
N(2)-Ge(1)-M(1)	113.2(1)	115.9(1)				
N(2)-Ge(1)-N(1)	88.7(1)	88.0(2)				
C(25)-M(1)-Ge(1)	73.6(2)	72.7(1)				

angles at the Ge(1) atom is 309.2°, which is consistent with a stereoactive lone-pair at the germanium(II) center. Similarly, in the tungsten–germylene 3, the sum of the bond angles at the Ge(1) atom being 310.5° is also consistent with the presence of a lone-pair at the germanium(II) center. The distorted structures of compounds 2 and 3 are obviously different from those observed in the metallogermylyne complexes, which show almost linear structures (bent angles at Ge range from 170.9(3)° to 178.9(2)°).^{11c,d,f,19} On the other hand, the N–Ge–M angles in 2 and 3 are similar to those observed in the nitrogen-stabilized iron–germylenes.^{11g,h}

The molecular structure of 4 is depicted in Figure 3, and selected bond distances and angles are shown in Table 2.



Figure 3. Molecular structure of $[{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}Ge(\eta^1-C_5H_5)]$ (4). Hydrogen atoms are omitted for clarity; 30% thermal ellipsoids are shown.

Compound 4 is a monomeric heteroleptic germylene. The germanium(II) center in compound 4 adopts a trigonalpyramidal geometry with the germanium atom Ge(1) bonding with one carbon atom, C(20), and two nitrogen atoms, N(1) and N(2). The Ge(1)–C(20) bond distance of 2.115(3) Å in 4 is comparable to those of 2.040(3) and 2.004(4) Å in $[{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}Ge(Bu^t)]$ and $[{N-(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}Ge(C=CPh)]$.^{13c} The Ge(1)–C(20) distance is also comparable to those observed in the monomeric germanium(II) alkynyl compounds RGeTable 2. Selected Bond Distances (\AA) and Angles (deg) for Compounds 4 and 5

$[{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}Ge(\eta^1-C_5H_5)] (4)$						
Ge(1) - N(1)	2.052(2)	Ge(1) - N(2)	1.963(2)			
Ge(1) - C(20)	2.115(3)	N(1)-C(1)	1.351(3)			
N(2)-Ge(1)-N(1)	86.2(1)	N(2)-Ge(1)-C(20)	98.2(1)			
N(1)-Ge(1)-C(20)	93.5(1)	C(21)-C(20)-Ge(1)	96.4(2)			
C(24) - C(20) - Ge(1)	96.1(2)	C(21)-C(20)-C(24)	105.5(3)			
$[\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)\}Ge(Cl) \rightarrow B(C_6F_5)_3] $ (5)						
Ge(1) - B(1)	2.186(3)	Ge(1)-Cl(1)	2.171(1)			
Ge(1) - N(1)	1.981(3)	Ge(1) - N(2)	1.860(2)			
N(1)-Ge(1)-B(1)	110.3(1)	N(2)-Ge(1)-B(1)	139.4(1)			
Cl(1)-Ge(1)-B(1)	104.3(1)	N(2)-Ge(1)-N(1)	90.4(1)			
N(1)-Ge(1)-Cl(1)	98.7(1)	N(2)-Ge(1)-Cl(1)	106.6(1)			

 $(C \equiv C)R'$ (1.976(4)−2.017(2) Å; R = $(Bu^{t})_{2}ATI$ (ATI = aminotroponiminate), methylaminomethyl-*m*-xylyl, HC{C-(Me)N(2,6-Prⁱ₂C₆H₃)}₂; R' = H, Ph, (C₅H₄)Fe(C₅H₅)),^{12g,24} but significantly longer than that of the germanium(II) alkynyl complexes (1.911(2), 1.907(2) Å) supported by terphenyl ligands due to the possible long-range conjugation of the alkynyl groups through the Ge–Ge linkage.^{12e} The C(21)–C(22) and C(23)–C(24) distances (1.353(5), 1.346(5) Å) in 4 are typical for a carbon–carbon double bond. Other bond distances within the ligand backbones are comparable to those in compound 1.^{13a}

The molecular structure of 5 is depicted in Figure 4, and selected bond distances and angles are listed in Table 2. The



Figure 4. Molecular structure of $[{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}Ge(Cl)\rightarrow B(C_6F_5)_3]$ (5). Hydrogen atoms are omitted for clarity; 30% thermal ellipsoids are shown.

Ge–B distance of 2.186(3) Å in **5** is similar to that of 2.156(4) Å in [{Me₂ATI}GePh(BPh₃)] (ATI = aminotroponiminate).²⁵ However, it is longer than that of 2.064(6) Å in the pyridyl-1azaallyl germanium(II) hydride–borane adduct [{N(SiMe₃)C-(Ph)C(SiMe₃)(C₅H₄N-2)}GeH(BH₃)] due to the increased bulkiness of the substituent at the B(1) center.^{13c} Similary, the Ge(1)–B(1) bond is also longer than that in the β -diketiminato germanium(II) hydride–borane adduct [{HC(CMeNAr)₂}- GeH(BH₃)] (2.015(7) Å).¹⁷ It is noteworthy that the abovementioned Ge(II)-borane adducts were formed by using the corresponding chlorogermylenes as the starting material. Homoleptic germylenes acting as a Lewis base toward boranes have also been demonstrated in [{2,6-(NMe₂)₂C₆H₃}₂Ge→ BH₃]¹⁶ and a NHC-stabilized dimesitylgermylene-borane adduct.¹⁸

The Ge(1) of compound **5** adopts a tetrahedral geometry with a Ge–N_{amide} bond distance of 1.860(2) Å. The distance is shorter when compared to the corresponding bond distance of compound **1** (1.920(2) Å). The shortening of the Ge–N_{amide} bond is probably due to the fact that the germanium(II) center in **5** forms a donor–acceptor interaction with the borane, and so the electron density at the germanium center is diminished as compared to compound **1**. Similar shortening of the Ge–N_{amide} bonds is also observed in the Ge(II)–Cu(I) or –Au(I) Lewis acid–base adduct with **1** (1.888(8), 1.884(2) Å).^{13c}

CONCLUSIONS

In this paper, we have reported the synthesis and structural characterization of novel nitrogen-stabilized molybdenum- and tungsten-germylenes **2** and **3** from the facile reaction of pyridyl-1-azaallyl germanium(II) chloride (1) with Na[M(η^{5} -C₅H₅)-(CO)₃]·2DME (M = Mo, W). The salt elimination reaction of **1** with NaCp afforded the monomeric heteroleptic germylene [{N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)}Ge(η^{1} -C₅H₅)] (4). Furthermore, the reaction of **1** with B(C₆F₅)₃ led to the formation of the Lewis acid-base pair [{N(SiMe₃)C(Ph)C-(SiMe₃)(C₅H₄N-2)}Ge(Cl) \rightarrow B(C₆F₅)₃] (**5**).

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 Na (Et₂O, toluene, and THF). Compound 1 [{N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)}-GeCl]^{13a} and Na[M(η^5 -C₅H₃)(CO)₃]·2DME¹⁴ (M = Mo or W; DME = 1,2-dimethoxyethane) were prepared according to the literature procedures. Sodium cyclopentadienylide and tris-(pentafluorophenyl)borane were purchased from Aldrich Chemical Co. and used without further purification. The NMR spectra were recorded on Brüker 400 spectrometers and recorded in THF-*d*₈. The chemical shifts δ are relative to SiMe₄ for ¹H and ¹³C{¹H} and BF₃·OEt₂ for ¹¹B{¹H} NMR. Elemental (C, H, N) analyses were performed by MEDAC Ltd., United Kingdom. IR spectra were recorded with a Nicolet Impact 420 FT-IR spectrometer.

Synthesis of $[{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}Ge-Mo(\eta^5 C_5H_5$)(CO)₃] (2). A solution of 1 (0.81 g, 1.81 mmol) in THF (25 mL) was added slowly to a stirring solution of Na[Mo(η^5 - $C_5H_5)(\text{CO})_3]\mbox{-}2DME$ (0.82 g, 1.83 mmol) in THF (30 mL) at -90°C. The resultant dark red mixture was warmed to ambient temperature and stirred for 12 h. The solution was filtered, and the volatiles were removed under reduced pressure. The dark red residue was extracted with Et₂O. After filtration, concentration of the filtrate afforded dark red crystals. Yield: 0.72 g (61%). Mp: 162 °C. Anal. Found: C 49.38, H 5.01, N 4.76. Calcd for C₂₇H₃₂GeMoN₂O₃Si₂: C 49.34, H 4.91, N 4.26. ¹H NMR (THF-*d*₈): δ 0.12 (s, 9H, SiMe₃), 0.15 (s, 9H, SiMe₃), 5.23 (s, 5H, C₅H₅), 6.67 (d, 1H, Py, ${}^{2}J_{H-H'} = 6.2$ Hz), 7.04 (t, 1H, Py, ${}^{2}J_{H-H'} = 6.2$ Hz), 7.20 (d, 1H, Py, ${}^{2}J_{H-H'} = 6.2$ Hz), 7.31–7.38 (m, 5H, Ph), 8.03 (t, 1H, Py, ${}^{2}J_{H-H'} = 6.2$ Hz). ${}^{13}C{}^{1}H{}$ NMR (THF- d_8): δ 2.10, 2.88 (SiMe₃), 81.65 (C_5H_5), 119.19 (CSiMe₃), 126.32, 128.17, 129.89, 132.44, 134.12, 136.58, 138.82, 139.12, 141.35, 146.71, 154.08 (Ph and Py), 166.31 (NCPh), 211.33 (CO). IR (KBr, cm⁻¹): ν (CO) 2005.95 (s), 1927.33 (s), 1889.19 (s). Synthesis of $[{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}Ge-W(\eta^5-$

 C_5H_5)(CO)₃] (3). A solution of 1 (0.65 g, 1.45 mmol) in THF (20 mL) was added slowly to a stirring suspension of Na[W(η^5 -

 $C_5H_5)(CO)_3]$ ·2DME (0.81 g, 1.51 mmol) in THF at -90 °C. The resultant dark red mixture was warmed to ambient temperature and stirred for 12 h. The solution was filtered, and the volatiles were removed under reduced pressure. The dark red residue was extracted with toluene. After filtration, addition of 5 mL of THF and concentration of the filtrate afforded dark red crystals. Yield: 0.61 g (56%). Mp: 198 °C. Anal. Found: C 43.72, H 4.67, N 4.03. Calcd for C₂₇H₃₂GeWN₂O₃Si₂: C 43.52, H 4.33, N 3.76. ¹H NMR (THF-d₈): δ 0.19 (s, 9H, SiMe₃), 0.25 (s, 9H, SiMe₃), 5.12 (s, 5H, C₅H₅), 6.95 (d, 1H, Py, ${}^{2}J_{H-H'}$ = 6.8 Hz), 7.09 (t, 1H, Py, ${}^{2}J_{H-H'}$ = 6.8 Hz), 7.27 (d, 1H, Py, ${}^{2}J_{H-H'} = 6.8$ Hz), 7.38–7.45 (m, 5H, Ph), 8.13 (t, 1H, Py, ${}^{2}J_{H-H'} = 6.8$ Hz). ${}^{13}C{}^{1}H$ NMR (THF- d_{8}): δ 2.68, 3.55 (SiMe₃), 82.38 (C₅H₅), 114.91 (CSiMe₃), 122.12, 124.36, 127.16, 131.44, 132.98, 135.57, 137.14, 138.93, 143.93, 146.62, 156.08 (Ph and Py), 168.35 (NCPh), 218.90 (CO). IR (KBr, cm⁻¹): ν (CO) 2001.78 (s), 1943.86 (s), 1876.65 (s).

Synthesis of [{N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)}Ge(η^1 -C₅H₅)] (4). Sodium cyclopentadienylide (0.74 mL, 2 M in THF, 1.48 mmol) was added dropwise to a solution of 1 (0.65 g, 1.45 mmol) in THF (20 mL) at 0 °C. The resultant yellowish-orange solution was warmed to room temperature and stirred for another 12 h. The volatiles were then removed under reduced pressure and extracted with Et₂O (15 mL). Concentration of the extract afforded yellow crystals. Yield: 0.51 g (74%). Mp: 128 °C. Anal. Found: C 60.21, H 6.74, N 6.03. Calcd for C₂₄H₃₂GeN₂Si₂: C 60.39, H 6.76, N 5.87. ¹H NMR (THF-*d*₈, 28 °C): δ -0.20 (s, 9H, SiMe₃), -0.14 (s, 9H, SiMe₃), 6.07 (s, 5H, C₅H₅), 7.28 (t, 1H, Py, ${}^{2}J_{H-H'}$ = 6.5 Hz), 7.39–7.59 (m, 5H, Ph), 7.68 (s, 1H, Py), 7.87 (t, 1H, Py, ${}^{2}J_{H-H'}$ = 6.5 Hz), 8.47 (d, 1H, Py, ${}^{2}J_{H-H'}$ = 6.5 Hz). ¹³C{¹H} NMR (THF- d_8 , 28 °C): δ 2.17, 3.16 (SiMe₃), 112.48 (CSiMe₃), 113.54 (C₅H₅), 120.36, 125.17, 127.01, 127.93, 130.13, 131.05, 132.01, 139.31, 144.09, 146.11, 156.61 (Ph and Py), 169.53 (NCPh).

Synthesis of $[{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}Ge(Cl) \rightarrow B (C_6F_5)_3$] (5). A solution of 1 (0.35 g, 0.78 mmol) in Et₂O (25 mL) was added to a solution of $B(C_6F_5)_3$ (0.41 g, 0.80 mmol) in Et₂O (5 mL) at 0 °C. The resultant yellow solution was warmed to room temperature and stirred for another 24 h. The volatiles were then removed under reduced pressure and extracted with toluene (25 mL). Concentration of the extract afforded yellow crystals. Yield: 0.45 g (60%). Mp: 157 °C. Anal. Found: C 46.62, H 2.74, N 2.63. Calcd for C₂₇H₂₇BClF₁₅GeN₂Si₅: C 46.31, H 2.84, N 2.92. ¹H NMR (THF-d₈): $\delta - 0.15$ (s, 9H, SiMe₃), -0.10 (s, 9H, SiMe₃), 7.38 - 7.45 (m, 4H, Ph), 7.52–7.65 (m, 2H, Py), 7.70 (d, 1H, Ph, ${}^{2}J_{H-H'}$ = 6.5 Hz), 7.99 (t, 1H, Py, ${}^{2}J_{H-H'} = 6.5$ Hz), 8.72 (d, 1H, Py, ${}^{2}J_{H-H'} = 6.5$ Hz). ${}^{13}C{^{1}H}$ NMR (THF-d₈): δ 1.74, 2.83 (SiMe₃), 115.71 (CSiMe₃), 120.44, 126.10, 127.74, 129.29, 130.90, 133.11, 136.53, 139.10, 139.90, 140.21, 144.11 (Ph and Py), 145.38, 147.42, 148.80, 149.80 (C₆F₅), 164.71 (NCPh). ¹¹B{¹H} NMR (THF- d_{s}): δ 2.80.

X-ray Crystallography. Single crystals were sealed in Lindemann glass capillaries under nitrogen. X-ray data of compounds 2–5 were collected on a Rigaku R-AXIS II imaging plate using graphite-monochromatized Mo K α radiation (I = 0.71073 Å) from a rotating-anode generator operating at 50 kV and 90 mA. Crystal data are summarized in Table S1. The structures were solved by direct phase determination using the computer program SHELXTL-PC²⁶ 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.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic files in CIF format for the structure determinations of compounds 2-5 are available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kevinleung@cuhk.edu.hk.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Research Grants Council of The Hong Kong Special Administrative Region, China (Project No. CUHK 402210).

REFERENCES

(1) Selected recent reviews: (a) Nagendran, S.; Roesky, H. W. Organometallics 2008, 27, 457. (b) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. Chem. Rev. 2009, 109, 3479. (c) Power, P. P. Nature 2010, 463, 171. (d) Fischer, R. C.; Power, P. P. Chem. Rev. 2010, 110, 3877. (e) Asay, M.; Jones, C.; Driess, M. Chem. Rev. 2011, 111, 354. (f) Lee, V. Y.; Sekiguchi, A. Inorg. Chem. 2011, 50, 12303. (g) Yao, S.; Xiong, Y.; Driess, M. Organometallics 2011, 30, 1748. (h) Sen, S. S.; Khan, S.; Nagendran, S.; Roesky, H. W. Acc. Chem. Res. 2012, 45, 578.

(2) (a) Harris, D. H.; Lappert, M. F.; Pedley, J. B.; Sharp, G. J. J. Chem. Soc., Dalton Trans. 1976, 945. (b) Davidson, P. J.; Harris, D. H.; Lappert, M. F. J. Chem. Soc., Dalton Trans. 1976, 2268.

(3) (a) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. Chem. Rev.
2002, 102, 3031. (b) Kühl, O. Coord. Chem. Rev. 2004, 248, 411.
(c) Leung, W.-P.; Kan, K.-W.; Chong, K.-H. Coord. Chem. Rev. 2007, 251, 2253. (d) Mandal, S. K.; Roesky, H. W. Chem. Commun. 2010, 46, 6016.

(4) (a) Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. Angew. Chem., Int. Ed. 2002, 41, 1785. (b) Pu, L.; Phillips, A. D.; Richards, A. F.; Stender, M.; Simons, R. S.; Olmstead, M. M.; Power, P. P. J. Am. Chem. Soc. 2003, 125, 11626.

(5) Sugiyama, Y.; Sasamori, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. J. Am. Chem. Soc. 2006, 128, 1023.

(6) Li, J.; Schenk, C.; Goedecke, C.; Frenking, G.; Jones, C. J. Am. Chem. Soc. 2011, 133, 18622.

(7) (a) Green, S. P.; Jones, C.; Junk, P. C.; Lippert, K.-A.; Stasch, A. Chem. Commun. 2006, 3978. (b) Nagendran, S.; Sen, S. S.; Roesky, H. W.; Koley, D.; Grubmüller, H.; Pal, A.; Herbst-Irmer, R. Organometallics 2008, 27, 5459. (c) Wang, W.; Inoue, S.; Yao, S.; Driess, M. Chem. Commun. 2009, 2661. (d) Leung, W.-P.; Chiu, W.-K.; Chong, K.-H.; Mak, T. C. W. Chem. Commun. 2009, 6822. (e) Jones, C.; Bonyhady, S. J.; Holzmann, N.; Frenking, G.; Stasch, A. Inorg. Chem. 2011, 50, 12315. (f) Chia, S.-P.; Yeong, H.-X.; So, C.-W. Inorg. Chem. 2012, 51, 1002.

(8) Driess, M; Yao, S.; Brym, M.; van Wüllen, C. Angew. Chem., Int. Ed. 2006, 45, 4349.

(9) (a) Pineda, L. W.; Jancik, V.; Starke, K.; Oswald, R. B.; Roesky, H. W. Angew. Chem., Int. Ed. 2006, 45, 2602. (b) Jana, A.; Ghoshal, D.; Roesky, H. W.; Objartel, I.; Schwab, G.; Stalke, D. J. Am. Chem. Soc. 2009, 131, 1288. See also other examples: (c) Choong, L. S.; Woodul, W. D.; Schenk, C.; Stasch, A.; Richards, A. F.; Jones, C. Organometallics 2011, 30, 5543. (d) Khan, S.; Samuel, P. P.; Michel, R.; Dieterich, J. M.; Mata, R. A.; Demers, J.-P.; Lange, A.; Roesky, H. W.; Stalke, D. Chem. Commun. 2012, 48, 4890.

(10) (a) Rivard, E.; Power, P. P. Dalton Trans. 2008, 4336.
(b) Mandal, S. K.; Roesky, H. W. Acc. Chem. Res. 2012, 45, 298.

(11) (a) Jutzi, P.; Leue, C. Organometallics 1994, 13, 2898.
(b) Simons, R. S.; Power, P. P. J. Am. Chem. Soc. 1996, 118, 11966.
(c) Pu, L.; Twamley, B.; Haubrich, S. T.; Olmstead, M. M.; Mork, B. V.; Simons, R. S.; Power, P. P. J. Am. Chem. Soc. 2000, 122, 650.
(d) Filippou, A. C.; Philippopoulos, A. I.; Portius, P.; Neumann, D. U. Angew. Chem., Int. Ed. 2000, 39, 2778. (e) Filippou, A. C.; Portius, P.; Philippopoulos, A. I. Organometallics 2002, 21, 653. (f) Filippou, A. C.; Weidemann, N.; Philippopoulos, A. I.; Schnakenburg, G. Angew. Chem., Int. Ed. 2006, 45, 5987. (g) Jones, C.; Rose, R. P.; Stasch, A. Dalton Trans. 2008, 2871. (h) Inoue, S.; Driess, M. Organometallics

2009, *28*, 5032. (i) Filippou, A. C.; Barandov, A.; Schnakenburg, G.; Lewall, B.; van Gastel, M.; Marchanka, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 789.

(12) See for recent examples: (a) Arii, H.; Nakadate, F.; Mochida, K. Organometallics 2009, 28, 4909. (b) Jana, A.; Roesky, H. W.; Schulzke, C.; Samuel, P. P.; Döring, A. Inorg. Chem. 2010, 49, 5554. (c) Matioszek, D.; Katir, N.; Saffon, N.; Castel, A. Organometallics 2010, 29, 3039. (d) Woodul, W. D.; Richards, A. F.; Stasch, A.; Driess, M.; Jones, C. Organometallics 2010, 29, 3655. (e) Lei, H.; Fettinger, J. C.; Power, P. P. Organometallics 2010, 29, 5585. (f) Sen, S. S.; Ghadwal, R. S.; Kratzert, D.; Stern, D.; Roesky, H. W.; Stalke, D. Organometallics 2011, 30, 1030. (g) Siwatch, R. K.; Kundu, S.; Kumar, D.; Nagendran, S. Organometallics 2011, 30, 1998. (h) Matioszek, D.; Katir, N.; Ladeira, S.; Castel, A. Organometallics 2011, 30, 2230. (i) Arii, H.; Nakadate, F.; Mochida, K.; Kawashima, T. Organometallics 2011, 30, 4471. (j) Wang, W.; Inoue, S.; Yao, S.; Driess, M. Organometallics 2011, 30, 6490. (k) Yang, Y.; Zhao, N.; Zhu, H.; Roesky, H. W. Organometallics 2012, 31, 1958. (1) Siwatch, R. K.; Nagendran, S. Organometallics 2012, 31, 3389. (m) Yang, Y.; Zhao, N.; Wu, Y.; Zhu, H.; Roesky, H. W. Inorg. Chem. 2012, 51, 2425.

(13) (a) Leung, W.-P.; So, C.-W.; Wu, Y.-S.; Li, H.-W.; Mak, T. C. W. *Eur. J. Inorg. Chem.* **2005**, *3*, 513. (b) Leung, W.-P.; Chong, K.-H.; Wu, Y.-S.; So, C.-W.; Chan, H.-S.; Mak, T. C. W. *Eur. J. Inorg. Chem.* **2006**, 808. (c) Leung, W.-P.; So, C.-W.; Chong, K.-H.; Kan, K.-W.; Chan, H.-S.; Mak, T. C. W. *Organometallics* **2006**, *25*, 2851.

(14) Hayter, R. G. Inorg. Chem. 1963, 2, 1031.

(15) (a) Romão, C. C.; Veiros, L. F. Organometallics **2007**, *26*, 1777. (b) Bennett, M. J.; Cotton, F. A.; Davison, A.; Faller, J. W.; Lippard, S.

J.; Morehouse, S. M. J. Am. Chem. Soc. 1966, 88, 4371. (c) Casey, C.
 P.; O'Connor, J. M.; Jones, W. D.; Haller, K. J. Organometallics 1983, 2, 535.

(16) Drost, C.; Hitchcock, P. B.; Lappert, M. F. Organometallics 1998, 17, 3838.

(17) Ding, Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 4806.

(18) Rupar, P. A.; Jennings, M. C.; Ragogna, P. J.; Baines, K. M. Organometallics 2007, 26, 4109.

(19) (a) Filippou, A. C.; Philippopoulos, A. I.; Portius, P.; Schnakenburg, G. Organometallics 2004, 23, 4503. (b) Filippou, A. C.; Schnakenburg, G.; Philippopoulos, A. I.; Weidemann, N. Angew. Chem., Int. Ed. 2005, 44, 5979. (c) See, also, refs 11b-f, i.

(20) (a) Pandey, K. K.; Lein, M.; Frenking, G. J. Am. Chem. Soc. **2003**, 125, 1660. (b) Pandey, K. K.; Lledós, A. Inorg. Chem. **2009**, 48, 2748.

(21) (a) Kühl, O.; Lönnecke, P.; Heinicke, J. *Inorg. Chem.* 2003, 42, 2836. (b) Shinohara, A.; McBee, J.; Tilley, T. D. *Inorg. Chem.* 2009, 48, 8081. (c) Filippou, A. C.; Stumpf, K. W.; Chernov, O.; Schnakenburg, G. *Organometallics* 2012, 31, 748.

(22) (a) Huttner, G.; Weber, U.; Sigwarth, B.; Scheidsteger, O.; Lang, H.; Zsolnai, L. J. Organomet. Chem. **1985**, 282, 331. (b) Jutzi, P.; Hampel, B.; Stroppel, K.; Krüger, C.; Angermund, K.; Hofmann, P. Chem. Ber. **1985**, 118, 2789. (c) Jutzi, P.; Hampel, B.; Hursthouse, M. B.; Howes, A. J. J. Organomet. Chem. **1986**, 299, 19. (d) Du Mont, W.-W.; Lange, L.; Pohl, S.; Saak, W. Organometallics **1990**, 9, 1395. (e) Tokitoh, N.; Manmaru, K.; Okazaki, R. Organometallics **1994**, 13, 167. (f) Ueno, K.; Yamaguchi, K.; Ogino, H. Organometallics **1999**, 18, 4468. (g) Hashimoto, H.; Tsubota, T.; Fukuda, T.; Tobita, H. Chem. Lett. **2009**, 38, 1196.

(23) Adams, R. D.; Collins, D. M.; Cotton, F. A. Inorg. Chem. 1974, 13, 1086.

(24) (a) Jutzi, P.; Keitemeyer, S.; Neumann, B.; Stammler, H.-G. Organometallics 1999, 18, 4778. (b) Yao, S.; van Wüllen, C.; Driess, M. Chem.Commun. 2008, 5393.

(25) Dias, H. V. R.; Wang, Z. J. Am. Chem. Soc. 1997, 119, 4650.

(26) 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.