Cationic Metallogermylene and Dicationic Dimetallodigermenes: Synthesis by Chloride Abstraction from *N*-Heterocyclic Carbene-Stabilized Chlorometallogermylenes

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S *Supporting Information*

ABSTRACT: Reaction of NHC-stabilized dichlorogermylenes (NHC = *N*-heterocyclic carbene) with an anionic tungsten complex produced NHC-stabilized chlorometallogermylenes. Subsequent chloride abstraction from the products with NaBAr$_4$ (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$) gave a cationic metallogermylene or dicationic dimetallodigermenes.

Digermene, R$_2$Ge=GeR$_2$, has attracted great interest because of its peculiar *trans*-bent structure and high reactivity.[1] Since the isolable digermene was first reported by Lappert et al. in 1976,[2] digermenes with a variety of substituents have been prepared. Thus, Lappert et al. synthesized tetraalkyldigermene Dsi$_2$Ge=GeDsi$_2$ (Dsi = CH-(SiMe$_3$)$_2$) by the reaction of a stable germylene [N-(SiMe$_3$)$_2$]$_2$Ge: with LiDsi.[2] Masamune et al. reported the synthesis of tetraaryldigermene Ar$'_2$Ge=GeAr$'_2$ (Ar$'$ = 2,6-Me$_2$C$_6$H$_3$) by photochemical redistribution of cyclotrigermane *cyclo*-(Ar$'_6$Ge$_3$).[3] They also reported the direct formation of tetraaryldigermene Dipp$_2$Ge=GeDipp$_2$ (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$) by reductive coupling of extremely congested dichlorogermane Dipp$_2$GeCl$_2$.[4] This reaction was also used by Kira et al. for the synthesis of silyl-substituted digermenes (R$_3$Si)$_2$Ge=Ge(SiR$_3$)$_2$ (R$_3$ = ^{i}Pr$_2$Me, ^{t}BuMe$_2$, ^{i}Pr$_3$).[5] Although various types of digermene have ever been reported, transition metal-substituted digermenes have never been synthesized.

NHC-stabilized chlorogermylenes have recently been recognized as useful precursors for a variety of unique low-valent germanium species.[6] Inspired by these researches, we began to apply NHC-stabilized chlorogermylenes as precursors for the synthesis of transition metal-substituted low-valent germanium species. As a result, we have succeeded in the synthesis of a metallogermylene Cp(CO)$_3$WGe[GeCl(Mes)$_2$](^{Me}I^{i}Pr) (^{Me}I^{i}Pr = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene), by introduction of a metal fragment to an NHC-stabilized chlorogermylene GeCl[GeCl(Mes)$_2$](^{Me}I^{i}Pr), as a potential precursor for elusive digermavinylidene complexes M=Ge=GeR$_2$.[7] Here we report the synthesis of NHC-stabilized chlorometallogermylenes and their conversion to the first examples of a cationic metallogermylene or dicationic dimetallodigermenes by chloride abstraction.

Reactions of GeCl$_2$(NHC) (NHC = IPr,[6d,e] ^{Me}I^{i}Pr,[6a] ^{Me}I-Me[6g,h]) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene, ^{Me}IMe = 1,3,4,5-tetramethylimidazol-2-ylidene) with [Li(thf)$_2$][Cp*W(CO)$_3$] in toluene at room temperature for

2 h gave NHC-stabilized chlorometallogermylenes Cp*-(CO)$_3$WGeCl(NHC) (**1a**, NHC = IPr 95%; **1b**, NHC = ^{Me}I^{i}Pr 71%; **1c**, ^{Me}IMe 46%) (Scheme 1). These complexes

Scheme 1. Synthesis of NHC-Stabilized Chlorometallogermylenes 1a–c

1a: R^1 = Dipp, R^2 = H, 95%
1b: R^1 = ^{i}Pr, R^2 = Me, 71%
**1c**: R^1 = Me, R^2 = Me, 46%
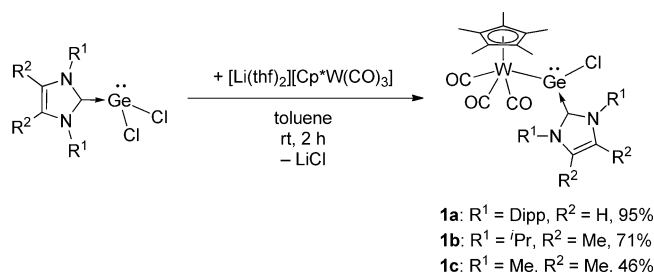
were fully characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, elemental analysis, and X-ray crystal structure analysis. In the ^{13}C NMR of **1a–c**, three signals assigned to the CO ligands were observed. This implies that the germanium center of **1a–c** is chiral and this causes two CO ligands cis to the germanium ligand mutually inequivalent.

The molecular structure of **1c** is shown in Figure 1. The W center adopts a four-legged piano-stool geometry and the Ge center is pyramidalized (the sum of bond angles around Ge: 315.1°). This is attributable to the existence of a lone pair on the Ge atom. The W–Ge bond length (2.7413(11) Å) is slightly shorter than those of other base-stabilized metallogermylenes Cp(CO)$_3$WGe(^{Me}I^{i}Pr)GeCl(Mes)$_2$ (2.8127(8) Å)[7] and Cp(CO)$_3$WGe[N(SiMe$_3$)C(Ph)C(SiMe$_3$)(2-C$_5$H$_4$N)] (2.852(1) Å).[8] The Ge–C bond length (2.083(10) Å) undergoes very little change from that of the starting dichlorogermylene GeCl$_2$(^{Me}IMe) (2.082(3)).[6g] The Ge–Cl bond length (2.330(3) Å) is comparable to that of GeCl$_2$(^{Me}IMe) (2.3363(1) and 2.3019(1) Å).[6g]

Treatment of Cp*(CO)$_3$WGeCl(IPr) (**1a**) with NaBAr$_4$ (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$) in fluorobenzene at room temperature immediately gave a cationic metallogermylene [Cp*-(CO)$_3$WGe(IPr)](BAr$_4$) (**2**) as blue crystals in 59% yield (Scheme 2).[9] Although the NMR and UV/vis spectra of **2** in solution were unable to be measured due to its instability and poor solubility of the crystals in fluorobenzene, *o*-dichlor-
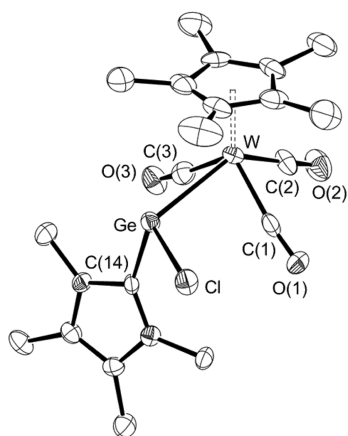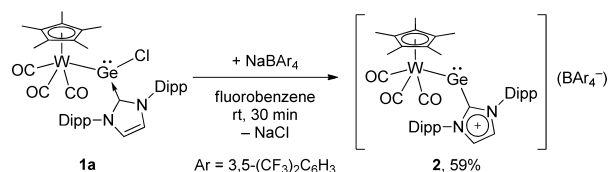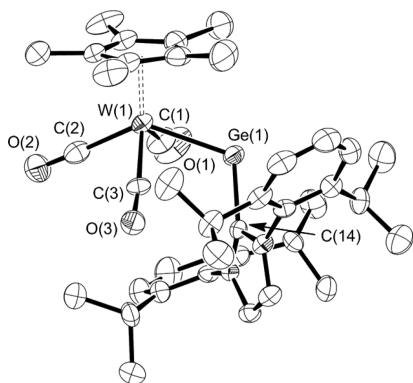
Figure 1. ORTEP drawing of **1c** with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): W–Ge 2.7413(11), W–C(1) 1.973(12), W–C(2) 1.950(11), W–C(3) 1.969(12), Ge–Cl 2.330(3), Ge–C(14) 2.083(10), C(1)–O(1) 1.143(14), C(2)–O(2) 1.168(14), C(3)–O(3) 1.159(14), W–Ge–Cl 109.51(8), W–Ge–C(14) 110.8(2), Cl–Ge–C(14) 94.8(3).

Scheme 2. Cl⁻ Abstraction from Chlorometallogermylene 1a

obenzene, and acetonitrile, the solid-state structure of **2** was determined by X-ray crystal structure analysis (Figure 2). There
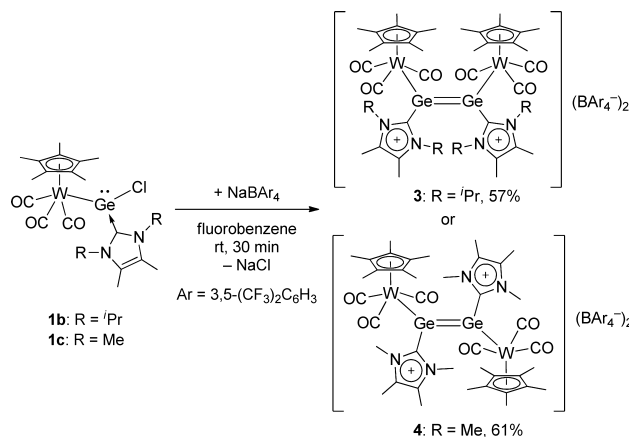

Figure 2. ORTEP drawing of one of the two independent cationic parts of **2** with thermal ellipsoids at 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): W(1)–Ge(1) 2.5780(10), W(1)–C(1) 1.979(11), W(1)–C(2) 1.981(11), W(1)–C(3) 1.978(9), Ge(1)–C(14) 2.032(8), C(1)–O(1) 1.155(13), C(2)–O(2) 1.161(13), C(3)–O(3) 1.173(11), W–Ge–C(14) 112.6(2).

are two independent molecules with nearly identical structures in an asymmetric unit cell. The Ge center of **2** is two-coordinate and the W–Ge–C bond is greatly bent (112.4(2)°).[10] The W–Ge bond length (2.5787(10) Å)[10] is significantly shorter than that of the chlorometallogermylenes **1a–c** (2.7413(11)–2.7894(8) Å).[11] This shortening is attributable to the increase of π back-donation from a filled d orbital of the W to the empty p orbital of the Ge, in other

words, delocalization of a positive charge over the W–Ge–C bond, which is reflected in the high-wavenumber shift of the ν_{CO} bands from **1a** (1950, 1876, 1839 cm⁻¹) to **2** (1996, 1932, 1907 cm⁻¹).

Cl⁻ abstraction from chlorometallogermylenes with sterically less hindered NHCs, **1b** and **1c**, led to different results. Thus, reaction of **1b** with NaBAr₄ in fluorobenzene afforded a dicationic dimetallodigermene **3**, a dimer of a cationic metallogermylene, as orange/green dichroic crystals in 57% yield (Scheme 3). In the case of the reaction of **1c** with NaBAr₄

**Scheme 3. Cl⁻ Abstraction from Chlorometallogermylenes 1b and 1c**

under the same reaction conditions, a dicationic complex **4** was obtained as red crystals in 61% yield. These crystals were almost insoluble in organic solvents, but were characterized by IR spectroscopy, elemental analysis, and X-ray crystallography.

The structures of the dicationic parts of **3** and **4** and the Newman projections along the Ge–Ge bond are shown in Figures 3 and 4, respectively. The selected bond lengths and
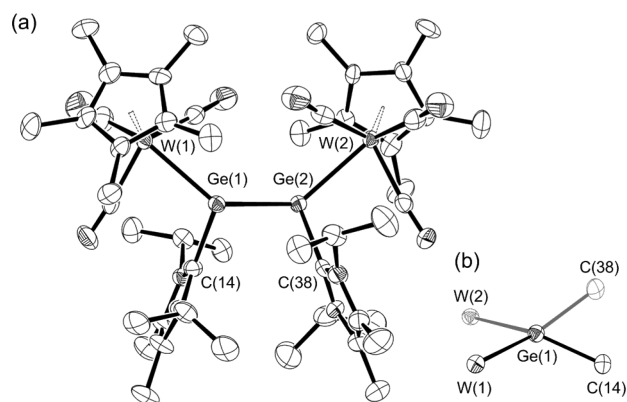
Figure 3. (a) ORTEP drawing of the dicationic part of **3** with thermal ellipsoids at 50% probability level. All hydrogen atoms are omitted for clarity. (b) A Newman projection along the Ge(1)–Ge(2) bond of **3**.

angles of **3** and **4** are shown in Table 1. Complex **3** takes a twisted Z-configuration accompanied by a *trans*-bent geometry (*trans*-bent angle = 34.6 and 35.3°; twist angle = 50.0°).[12] The Ge–Ge bond length of **3** (2.4286(11) Å) is in the range of previously reported Ge–Ge double bond lengths of digermenes (2.21–2.51 Å).[1e] On the other hand, complex **4** adopts an untwisted E-configuration with a *trans*-bent geometry (*trans*-
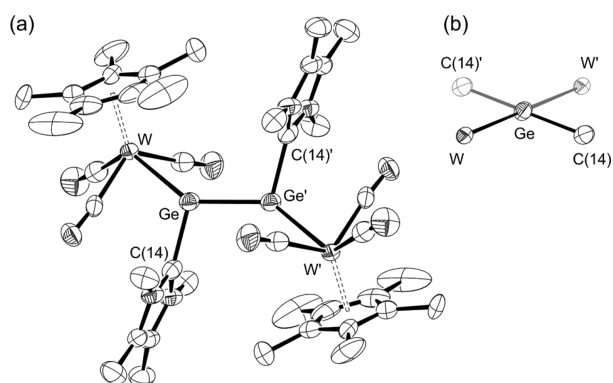
Figure 4. (a) ORTEP drawing of the dicationic part of **4** with thermal ellipsoids at 50% probability level. All hydrogen atoms are omitted for clarity. (b) A Newman projection along the Ge–Ge′ bond of **4**.
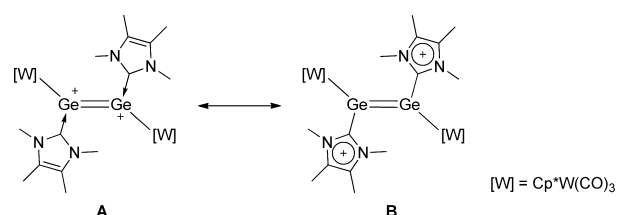

Figure 5. Two possible resonance structures for **4**.

bent angle = 30.5°; twist angle = 0°)[12] and the molecule has an inversion center at the midpoint of the Ge–Ge bond. The Ge–Ge bond length of **4** (2.345(2) Å) is distinctly shorter than that of **3**. These differences are attributable to the steric repulsion between the substituents on the N atoms of NHCs and/or the metal fragments. Namely, more sterically hindered **3** has a more distorted and elongated Ge–Ge bond in comparison with that of **4**. Interestingly, the structure of the gemylene moiety $Cp^*(CO)_3WGe(NHC)$ in **3** closely resembles that in **4** (Table 1). The W–Ge bond length of **3** and **4** are much longer than that of **2** (2.5780(10) Å). These bond elongations suggest that the π back-donation from W to Ge in **3** and **4** is significantly weaker than that in **2**. The Ge–C bond lengths of **3** (2.033(8) and 2.053(8) Å) and **4** (2.029(11) Å) are shorter than those of **1b** (2.087(7) Å)[11] and **1c** (2.083(10) Å), respectively. This implies that the positive charge of **3** and **4** is partially distributed at the NHC rings.[13]

As shown in Figure 5, two resonance structures are possible for **4**. Structure **A** is regarded as a dimetallodigermene-1,2-diylium ion in which a vacant p orbital on the Ge is coordinated by ^{Me}IMe. Structure **B** is regarded as a dicationic dimetallodigermene. To shed light on the validity of two resonance structures, a theoretical calculation for a model dicationic complex $[\{Cp(CO)_3WGe(IMe)\}_2]^{2+}$ (**4′**) (IMe = 1,3-dimethylimidazol-2-ylidene) was carried out at the B3LYP level.[11] The lengths of W–Ge (2.611 Å), Ge–C (2.006 Å), and Ge–Ge (2.324 Å) bonds in the optimized structure agree well with those in the crystal structure of **4**. Wiberg bond index (WBI) analysis indicates that the Ge–Ge bond has a considerable double bond character (Ge–Ge: 1.432). The

natural population analysis (NPA) shows that both the Ge atom and the IMe moiety are highly positively charged (+0.65 and +0.44, respectively), while the tungsten moiety is slightly negatively charged (−0.09). These results corroborate that the contributions of resonance structures **A** and **B** are equally significant in **4**.

In summary, we synthesized NHC-stabilized chlorometallogermylenes **1a–c** as precursors. Chloride abstraction from the bulkiest NHC-stabilized chlorogermylene **1a** gave a cationic metallogermylene **2**. On the other hand, chloride abstraction from less hindered **1b** and **1c** led to dimerization accompanied by formation of a Ge═Ge bond to provide dicationic dimetallodigermenes **3** and **4** with *Z*- and *E*-configurations, respectively. The bulkiness of substituents on the N atoms of NHCs is an important factor to control not only the reaction routes but also the stereochemistry of the products.

■ ASSOCIATED CONTENT

S **Supporting Information**

Text, figures, tables, and CIF files giving synthetic procedures and characterization data for **1–4**, details of the crystal structure refinement for **1–4**, details of the calculation of a model dication complex of **4**, and X-ray crystallographic data for **1–4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Dicationic Parts of 3 and 4

	3		4
W(1)–Ge(1)	2.6386(9)	W–Ge	2.6368(11)
W(2)–Ge(2)	2.6511(8)		
Ge(1)–C(14)	2.033(8)	Ge–C(14)	2.029(11)
Ge(2)–C(38)	2.053(8)		
Ge(1)–Ge(2)	2.4274(11)	Ge–Ge′	2.345(2)
W(1)–Ge(1)–C(14)	110.4(2)	W–Ge–C(14)	109.4(3)
W(2)–Ge(2)–C(38)	110.3(2)		
W(1)–Ge(1)–Ge(2)	135.20(4)	W–Ge–Ge′	134.22(7)
W(2)–Ge(2)–Ge(1)	135.47(4)		
C(14)–Ge(1)–Ge(2)	97.5(2)	C(14)–Ge–Ge′	104.2(3)
C(38)–Ge(2)–Ge(1)	97.9(2)		

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(9) The closely related silicon analogue, $[Cp*(CO)_3CrSi(SIdipp)]$ (BAr_4) (SIdipp = 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene), has been synthesized by reaction of a cationic silylyne complex $[Cp*(CO)_2Cr{\equiv}Si(SIdipp)](BAr_4)$ with CO. Filippou, A. C.; Baars, B.; Chernov, O.; Lebedev, Y. N.; Schnakenburg, G. *Angew. Chem., Int. Ed.* **2014**, *53*, 565.

(10) An average of the values for two independent molecules in the asymmetric unit cell.

(11) See the Supporting Information.

(12) In a digermene $(R^1)_2Ge{=}Ge(R^2)_2$, the *trans*-bent angle is defined as the tilt angle of the R-Ge−R plane toward the Ge=Ge bond. The twist angle is defined as a dihedral angle between the R^1-Ge−R^1 and R^2-Ge−R^2 mean planes.

(13) In **1b** and **1c**, the Ge is saturated (sp^3 hybridized), while in **3** and **4**, the Ge is sp^2 hybridized. As suggested by a reviewer, this difference of hybridization could also account for the shortening of the Ge−C bond.