Journal of Organometallic Chemistry 848 (2017) 89–94

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Communication

NHC-induced conversion of a W–Ge double bond into the triple bond through formation of W–Ge single and double bonded intermediates

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ARTICLE INFO

Article history:
Received 22 June 2017
Received in revised form
21 July 2017
Accepted 21 July 2017
Available online 23 July 2017

Keywords:
Germylene complex
Germylyne complex
NHC-carbene
Proton transfer
Hydride transfer
X-ray diffraction

ABSTRACT

Reaction of hydrido(hydrogermylene) complex $Cp^{*}(CO)_2(H)W{=}Ge(H)(Tsi)$ (**1**, Tsi = $C(SiMe_3)_3$) with 1 equiv of ^{Me}IMe (^{Me}IMe = 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene) immediately afforded NHC-stabilized germylene complex $Cp^{*}(CO)_2(H)WGe(H)(^{Me}IMe)(Tsi)$ (**2**) that has a zwitterionic, W–Ge single-bonded structure. Complex **2** was thermally unstable and intramolecular proton-transfer followed by hydride-transfer to the NHC-unit occurred slowly at room temperature to give anionic germylene complex $[Cp^{*}(CO)_2W{=}Ge(H)(Tsi)][H^{Me}IMe]$ ([**3**][$H^{Me}IMe$]) first and subsequently germylyne complex $Cp^{*}(CO)_2W{\equiv}Ge(Tsi)$ (**4**) and H_2 ^{Me}IMe. Although [**3**][$H^{Me}IMe$] was too unstable to be isolated, the salt of bulkier $[H^{Me}I^{i}Pr]^{+}$, $[Cp^{*}(CO)_2W{=}Ge(H)(Tsi)][H^{Me}I^{i}Pr]$ ([**3**][$H^{Me}I^{i}Pr$]), was thermally more stable and was isolated and fully characterized.

1. Introduction

Complexes having a triple bond between M (= transition metal) and E (= Group 14 elements) are attracting considerable attention in the fields of fundamental organometallic and coordination chemistry. Thanks to recent outstanding advances in the synthesis of suitable divalent precursors, the M≡E triple-bonded complexes are now available for all Group 14 elements E [1–4]. However, the number of their examples is still small, and study on their reactivity at the M≡E bond is even rarer [1c,5]. To elucidate the detailed chemical and physical properties of these M≡E triple-bonded complexes, development of convenient synthetic methods for them with a variety of substituents and metal fragments is indispensable.

Some typical synthetic routes reported for these M≡E triple bonded complexes are illustrated in Scheme 1. One is the direct reaction of a stable divalent Group 14 element halide with an anionic metal complex (Scheme 1, Type-I). Most of M≡E complexes have been synthesized by this type of reaction. For example, Power et al. synthesized the first example of germylyne complex $Cp(CO)_2Mo{\equiv}Ge\{2,6\text{-}Mes_2\text{-}C_6H_3\}$ by the reaction of anionic complex $Na[CpMo(CO)_3]$ with chlorogermylene $2,6\text{-}Mes_2\text{-}C_6H_3GeCl$ [2a]. Abstraction of a substituent on a Group 14 element ligand in M=E double-bonded complexes can also afford M≡E complexes (Scheme 1, Type-II). According to this procedure, some silylyne complexes [1a-d] have been synthesized. In all these reactions, stable divalent Group 14 element halides, their-base-stabilized ones, or their transition metal complexes were usually required as precursors.

We have previously reported a novel reaction of a hydrido(hydrogermylene) complex $Cp^{*}(CO)_2(H)W{=}Ge(H)(Tsi)$ (**1**, Tsi = $C(SiMe_3)_3$), which was easily prepared from a trihydrogermane and $Cp^{*}W(CO)_2L(Me)$ (L = CO, MeCN) [6], with ArNCO (Ar = Ph, Mes) giving a germylyne complex $Cp^{*}(CO)_2W{\equiv}Ge(Tsi)$ (**4**) in high yield via dehydrogenation [2h]. This type of reaction can be categorized into the Type-III reaction (Scheme 1), in which an organic substrate (Sub.) works as a hydrogen acceptor to convert an (H)M = E(H) double bond into an M≡E triple bond. We report here another Type-III reaction in which germylene complex **1** is converted to germylyne complex **4** by treatment with *N*-heterocyclic carbenes (NHCs). This reaction was proved to proceed through stepwise proton and hydride abstraction. Two types of intermediates were successfully isolated and structurally characterized. One of them, $[Cp^{*}(OC)_2W{=}Ge(H)(Tsi)][H^{Me}IMe]$ ([**3**][$H^{Me}IMe$]) (^{Me}IMe = 1,3-dimethyl-4,5-dimethylimidazol-2-ylidene), is the first example of anionic germylene complexes [7]. It should be mentioned that a

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http://dx.doi.org/10.1016/j.jorganchem.2017.07.027
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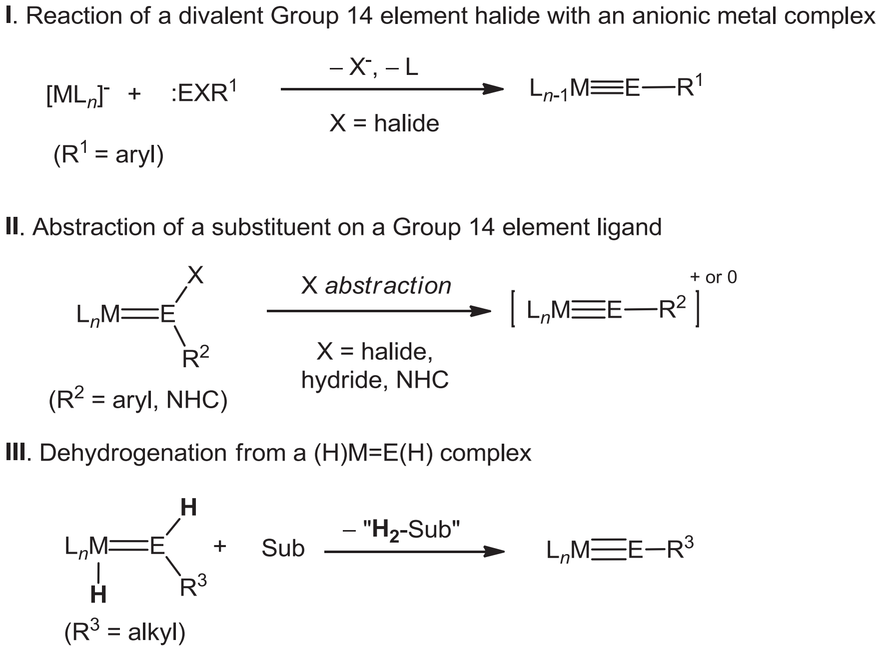


Scheme 1. Synthetic approaches to base-free M≡E triple-bonded complexes.

similar treatment of silylene complexes Cp*(CO)$_2$(H)W=Si(H)R [R = Tsi [8], Eind (1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl) [9]] with NHC gave analogous anionic silylene complexes [Cp*(OC)$_2$W=Si(H)R][H-NHC], but the reaction did not proceed further and their conversion into silylyne complexes Cp*(CO)$_2$W≡SiR (**A**: R = Tsi [1e], **B**: Eind [1f]) required the addition of a strong Lewis acid B(C$_6$F$_5$)$_3$ to the anionic silylene complexes.

2. Experimental

Reaction of 1 with ^{Me}IMe: To a solution of **1** (42 mg, 0.062 mmol) in toluene (4 mL) was added ^{Me}IMe (9 mg, 0.07 mmol) at room temperature. After 10 min, all volatiles were removed and the residue was washed with cold hexane and ether to give Cp*(CO)$_2$(H)WGe(H)(^{Me}IMe)(Tsi) (**2**) in 71% yield (35 mg, 0.043 mmol) as a light yellow powder. **2**: ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 300 K): $\delta = -5.44$ (s, 1H, $^1J_{WH} = 48.6$ Hz, WH), 0.47 (s, 27H, SiMe), 1.25, 1.27 (s, 3H × 2, MeC=CMe of ^{Me}IMe), 2.02 (s, 15H, Cp*), 3.27, 3.56 (s, 3H × 2, NMe), 5.45 (s, 1H, GeH); (400.1 MHz, THF-d_8, 270 K): $\delta = -6.16$ (s, 1H, $^1J_{WH} = 49.5$ Hz, WH), 0.21 (s, 27H, SiMe), 1.91 (s, 15H, Cp*), 2.19, 2.22 (s, 3H × 2, MeC=CMe of ^{Me}IMe), 3.84, 3.91 (s, 3H × 2, NMe), 5.41 (d, 1H, $^3J_{HH} = 1.3$ Hz, GeH); ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8, 270 K): $\delta = 1.5$ (*C*(SiMe)$_3$), 5.8 (SiMe), 8.3, 8.7 (*Me*C=C*Me* of ^{Me}IMe), 11.5 (C$_5$*Me*$_5$), 35.3, 38.4 (NMe), 98.9 (*C*$_5$Me$_5$), 126.7, 127.0 (Me*C*=*C*Me of ^{Me}IMe), 165.1 (NCN), 237.5, 247.2 (CO); ^{29}Si{^{1}H} NMR (79.5 MHz, THF-d_8, 270 K): $\delta = -0.2$ (SiMe); IR (KBr pellet, cm^{-1}): 1971 (w, ν_{GeH}), 1880 (s, ν_{CO}), 1784 (s, ν_{CO}); Elemental analysis: calcd. for C$_{29}$H$_{56}$GeN$_2$O$_2$Si$_3$W; C: 43.24, H: 7.01, N: 3.48; found C: 43.64, H: 6.89, N: 3.47.

Thermal reaction of 2: Formation of germylyne complex 4 and H$_2$ ^{Me}IMe (5a): A solution of **2** (4 mg, 0.005 mmol) in C$_6$D$_6$ (0.5 mL) containing a small amount of C$_6$Me$_6$ as an internal standard was kept at room temperature. After 6 days, formation of Cp*(CO)$_2$W≡GeTsi (**4**) and H$_2$ ^{Me}IMe (**5a**) was observed in 73% and 58% conversion yields, respectively, at the conversion of 93% of **2**. During this reaction, formation of an intermediate [Cp*(CO)$_2$W=Ge(H)(Tsi)][H^{Me}IMe] ([**3**][H^{Me}IMe]) (in 20% NMR yield after 4 h) was observed by ^{1}H NMR. After 6 days, all volatiles were transferred into an NMR tube by bulb-to-bulb distillation under vacuum to measure a ^{1}H NMR spectrum of **5a**. **5a**: ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 300 K) $\delta = 1.53$ (s, CMe, 6H), 2.22 (s, NMe, 6H), 3.62 (s, NCH$_2$N, 2H); ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$, 300 K): $\delta = 9.9$ (C*Me*), 37.9 (NMe), 81.3 (NCN), 123.8 (*C*Me). [**3**][H^{Me}IMe]: ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 300 K) $\delta = 0.70$ (s, 27H, SiMe), 0.93 (s, 6H, C=CMe), 2.46 (s, 15H, Cp*), 2.98 (s, 6H, NMe), 8.93 (s, 1H, NCHN), 13.28 (s, $^2J_{WH} = 31.8$ Hz, 1H, GeH).

Germylyne complex **4** was isolated in 52% yield (14 mg, 0.020 mmol) by a larger scale reaction using **2** (31 mg, 0.039 mmol) in toluene (5 mL) and heating at 40 °C for 5 days, followed by recrystallization from hexane at −30 °C. The NMR data of **4** obtained from this experiment agreed well with the literature data [2h]. **4**: ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 300 K): $\delta = 0.33$ (s, 27H, SiMe), 2.08 (s, 15H, Cp*); ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$, 300 K): $\delta = 4.4$ (SiMe), 12.2 (C$_5$Me$_5$), 66.2 (*C*(SiMe)$_3$), 100.8 (*C*$_5$Me$_5$), 224.8 (CO).

Reaction of 1 with ^{Me}I^{i}Pr: Isolation of anionic silylene complex [3][H^{Me}I^{i}Pr]: A solution of **1** (5 mg, 0.008 mmol) and a small amount of C$_6$Me$_6$ in C$_6$D$_6$ (0.5 mL) was treated with ^{Me}I^{i}Pr (3 mg, 0.02 mmol) at room temperature to give [Cp*(CO)$_2$W=Ge(H)(Tsi)][H^{Me}I^{i}Pr] ([**3**][H^{Me}I^{i}Pr]) instantaneously in 91% NMR yield. Complex [**3**][H^{Me}I^{i}Pr] was isolated in 74% yield (20 mg, 0.023 mmol) as red crystals in a larger scale reaction using **1** (21 mg, 0.031 mmol) and ^{Me}I^{i}Pr (5.5 mg, 0.31 mmol) in C$_6$D$_6$ (0.5 mL) followed by recrystallization from a THF solution layered with toluene at room temperature. [**3**][H^{Me}I^{i}Pr]: ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 300 K): $\delta = 0.66$ (s, 27H, SiMe), 1.26 (d, $^3J_{HH} = 6.4$ Hz, 12H, CH*Me*$_2$), 1.44 (s, 6H, C=CMe), 2.47 (s, 15H, Cp*), 3.84 (sept, $^3J_{HH} = 6.4$ Hz, 2H, C*H*Me$_2$), 8.84 (s, 1H, NCHN), 13.18 (s, $^2J_{WH} = 32.7$ Hz, 1H, GeH); (400.1 MHz, THF-d_8, 300 K): $\delta = 0.19$ (s, 27H, SiMe), 1.58 (d, $^3J_{HH} = 6.4$ Hz, 12H, CH*Me*$_2$), 2.13 (s, 15H, Cp*), 2.35 (s, 6H, C=CMe), 4.64 (sept, $^3J_{HH} = 6.4$ Hz, 2H, C*H*Me$_2$), 8.89 (s, 1H, NCHN), 12.54 (s, $^2J_{WH} = 33.5$ Hz, 1H, GeH); ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8, 300 K): $\delta = 4.5$ (SiMe), 8.3 (C=C*Me*), 12.4 (C$_5$Me$_5$), 22.8 (CH*Me*$_2$), 24.2 (*C*(SiMe)$_3$), 51.5 (*C*HMe$_2$), 98.2 (*C*$_5$Me$_5$), 127.6 (Me*C*=*C*Me of H^{Me}I^{i}Pr), 130.9 (N*C*HN), 242.4 (CO); ^{29}Si{^{1}H} NMR (79.5 MHz, C$_6$D$_6$, 300 K): $\delta = -5.1$ (SiMe); IR (KBr pellet, cm^{-1}): 3178 (w, ν_{NCHN}), 1847 (w, ν_{GeH}), 1801 (s, ν_{CO}), 1720 (s, ν_{CO}); Elemental analysis: calcd. for C$_{33}$H$_{64}$GeN$_2$O$_2$Si$_3$W; C: 46.00, H: 7.49, N: 3.25; found C: 46.23, H: 7.35, N: 3.26.

Thermal reaction of [3][H·^{Me}I^{i}Pr]: A solution of [**3**][H^{Me}I^{i}Pr] (4 mg, 0.005 mmol) containing a small amount of C_6Me_6 in C_6D_6 (0.5 mL) was heated at 60 °C. After 9 days, formation of **4** and H_2 ^{Me}I^{i}Pr (**5b**) was observed in 71% and 43% NMR conversion yields, respectively, at the conversion of 92% of [**3**][H^{Me}I^{i}Pr]. Obtained **5b** was identified by comparing its chemical shifts δ_H and δ_C with those of previously reported H_2 ^{Me}I^{i}Pr [10]. H_2 ^{Me}I^{i}Pr (**5b**): ^{1}H NMR (400.1 MHz, C_6D_6, 300 K) $\delta = 0.97$ (d, $^3J_{HH} = 6.4$ Hz, 12H, CH*Me*$_2$), 1.59 (s, 6H, C=CMe), 3.30 (sept, $^3J_{HH} = 6.4$ Hz, 2H, C*H*Me$_2$), 4.20 (s, 2H, NCHN); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): $\delta = 10.4$ (C*Me*), 18.4 (CH*Me*$_2$), 47.1 (CHMe$_2$), 61.6 (NCN), 121.2 (CMe).

Spectral data and X-ray crystal structure analysis data are available as a Supplementary Material.

3. Results and discussion

Treatment of Cp*(CO)$_2$(H)W=Ge(H)(Tsi) (**1**) with 1 equiv. of ^{Me}IMe at room temperature gave a base-stabilized germylene complex Cp*(CO)$_2$(H)WGe(H)(^{Me}IMe)(Tsi) (**2**) via coordination of ^{Me}IMe to the germanium atom (Scheme 2). Complex **2** was isolated in 71% yield and characterized by various spectroscopic data and elemental analysis. In the ^{1}H NMR spectrum of **2**, a singlet signal of GeH is observed at $\delta = 5.45$ ppm. A resonance for WH appears at −5.44 ppm with $^1J_{WH} = 48.6$ Hz. This chemical shift is slightly shifted downfield compared with that of a base-free complex **1** (−8.15 ppm, $^1J_{WH} = 60.0$ Hz) [6]. Two strong ν_{CO} absorption bands appear at 1880 and 1784 cm^{-1} in the IR spectrum, which are considerably lower in wavenumber compared with those of base-free complex **1** (1927 and 1853 cm^{-1}). This tendency is the same as that for their silicon analogues Cp*(CO)$_2$(H)WSi(H)(^{Me}IMe)(Tsi) (**6**) (1871 and 1780 cm^{-1}) [11] and Cp*(CO)$_2$(H)W=Si(H)(Tsi) (**7**) (1928 and 1853 cm^{-1}) [8]. These results indicate that the electronic structure of **2** is well described as a zwitterionic single-bonded structure, Cp*(CO)$_2$(H)W$^-$–Ge(H)(^{Me}IMe$^+$)(Tsi) in Scheme 2. The structure of **2** was further confirmed by X-ray crystallography (Fig. 1). The W–Ge bond length (2.5711(4) Å) is longer than that of a base-free germylene complex Cp*(CO)$_2$(D)W=Ge(D)(Tsi) (**1-*D***) (2.4288(7) Å) [6] and is within the range of W–Ge single bond lengths (2.51–2.68 Å) [12]. The sum of the three bond angles around Ge(1) except for those with the C(13)–Ge(1) bond is 335(2)°, indicating that the Ge atom is nearly *sp*^{3}-hybridized. In addition, the interatomic distance between the Ge1 and the hydrido ligand H1 is ca. 2.4 Å, which is much longer than that of germylene complex **1-D** having a Ge···D interligand interaction (2.07(6) Å) [6,13]. This Ge···H distance indicates that there is no Ge···H interligand interaction in **2**.

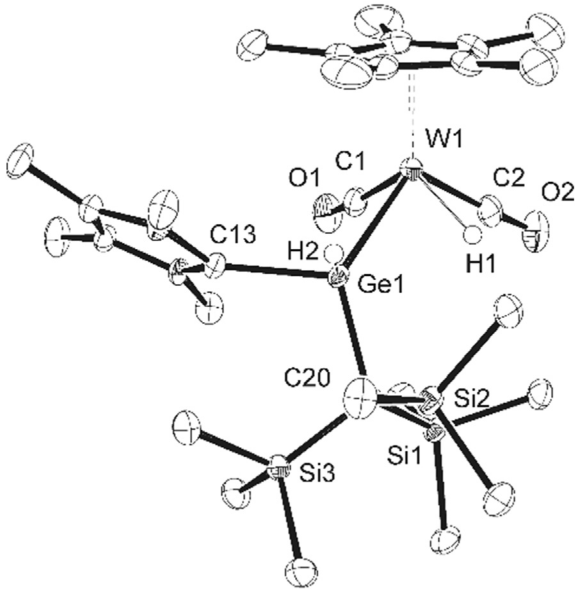
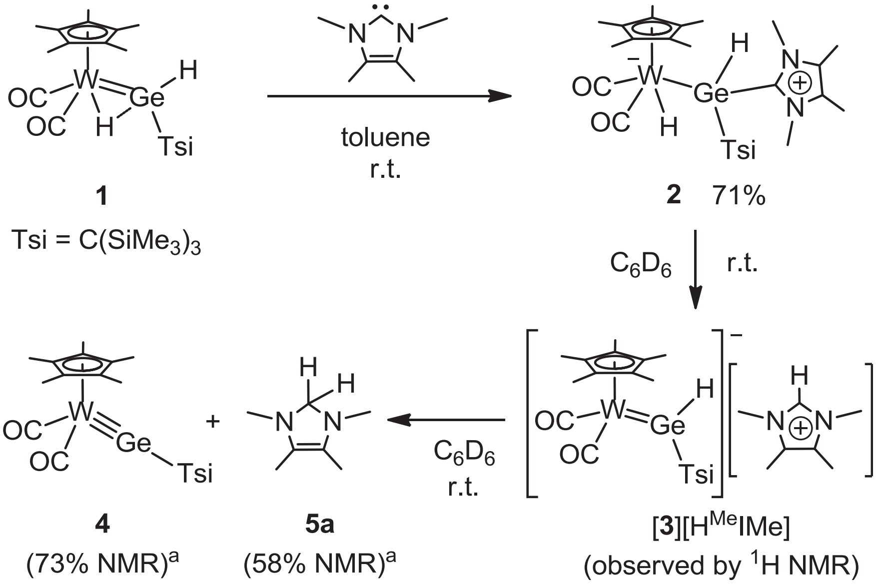


Fig. 1. ORTEP drawing of **2**. The thermal ellipsoids are plotted with 50% probability. Hydrogen atoms except H1 and H2 are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: W1–Ge1 = 2.5711(4), W1–C1 = 1.947(4), C1–O1 = 1.166(5), W1–C2 = 1.947(4), C2–O2 = 1.162(5), W1–H1 = 1.70(4), Ge1–H2 = 1.49(5), Ge1–C13 = 2.091(4), Ge1–C20 = 2.071(3), C1–W1–C2 = 77.0(2), C1–W1–Ge1 = 89.34(11), Ge1–W1–H1 = 65.4(15), H1–W1–C2 = 66.4(14), W1–Ge1–H2 = 110(2), H2–Ge1–C20 = 96(2), C20–Ge1–W1 = 129.29(10).

Interestingly, isolated base-coordinated complex **2** was thermally unstable at room temperature, and was observed by ^{1}H NMR in a C_6D_6 solution to convert gradually to a germylyne complex Cp*(CO)$_2$W≡Ge(Tsi) (**4**) in 73% conversion yield with release of H_2 ^{Me}IMe (**5a**) in 58% conversion yield at the conversion of 93% of **2** in 6



1

Tsi = C(SiMe$_3$)$_3$

2 71%

4
(73% NMR)^a

5a
(58% NMR)^a

[**3**][H^{Me}IMe]
(observed by ^{1}H NMR)

Scheme 2. Reaction of germylene complex **1** with ^{Me}IMe. ^{a}The yields are conversion yields at the conversion of 93% of **2**.

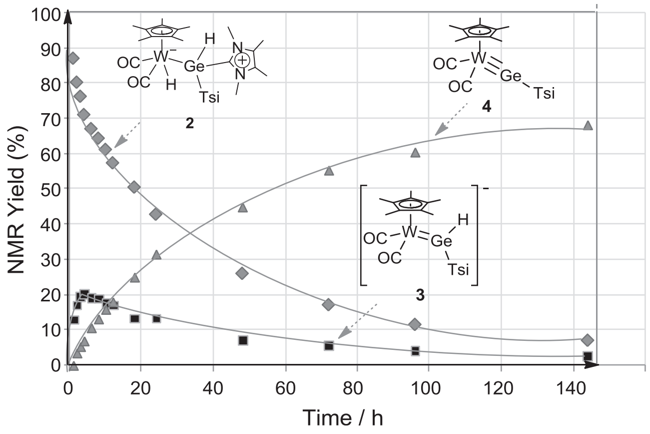


Fig. 2. Time course of the thermal conversion of isolated **2** to **3** and **4** in C_6D_6 at 300 K.

days [14]. Complex **4** was isolated in 52% yield by a larger scale reaction and was identified by comparison of its ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data with the literature data [2h]. Furthermore, formation of an intermediate that can be characterized as a salt of anionic germylene complex $[\mathrm{Cp^*(CO)_2W{=}Ge(H)(Tsi)}]^-$ (**3**) and imidazolium cation $[\mathrm{H}^{\mathrm{Me}}\mathrm{IMe}]^+$, [**3**]$[\mathrm{H}^{\mathrm{Me}}\mathrm{IMe}]$, was observed spectroscopically at the early stage of this reaction (vide infra) [15]. In the ^{1}H NMR spectrum, a characteristic signal was observed at 13.28 ppm, which can be assigned to the hydrogen on the germylene ligand of **3**. The other signals assigned to **3** were observed at 0.70 ppm for SiMe and 2.46 ppm for Cp*, which are shifted downfield compared with those of neutral complex **1** (SiMe, 0.36 ppm; Cp*, 1.88 ppm). The chemical shifts for these signals of **3** agree well with those of isolated [**3**]$[\mathrm{H}^{\mathrm{Me}}\mathrm{I}^{i}\mathrm{Pr}]$ that will be discussed later. The signal assignable to the imidazoliumC(2) proton of the counter cation was observed at 8.93 ppm. The time course of the conversion of **2** to **3** and **4** at 300 K is shown in Fig. 2. In the early stage of this reaction (0–4 h), along the decrease of complex **2**, the anionic germylene complex **3** rapidly increased, while the germylyne complex **4** slowly increased. The amount of **3** reached a maximum after 4 h, and then started to decrease and nearly became zero after 6 days. On the other hand, the amount of **4** constantly increased and reached to 68% (= 73% conversion yield at the 93% conversion of **2**) after 6 days. Since the pattern of the change of the ratio of these three complexes is typical of that of the A→B→C consecutive first-order reaction [16], complex **3** is considered to be an intermediate for formation of **4**.

Though isolation of the intermediate [**3**]$[\mathrm{H}^{\mathrm{Me}}\mathrm{IMe}]$ was unsuccessful because of its thermal instability, we succeeded in isolation of $[\mathrm{Cp^*(CO)_2W{=}Ge(H)(Tsi)}][\mathrm{H}^{\mathrm{Me}}\mathrm{I}^{i}\mathrm{Pr}]$ ([**3**]$[\mathrm{H}^{\mathrm{Me}}\mathrm{I}^{i}\mathrm{Pr}]$), a salt of **3** having a bulkier counter cation, which is the first example of an anionic germylene complex. This complex was formed instantaneously by the reaction of complex **1** and $^{\mathrm{Me}}\mathrm{I}^{i}\mathrm{Pr}$ at room temperature, and was isolated as very air-sensitive red crystals in 74% yield after recrystallization (Scheme 3). Formation of base-stabilized germylene complex analogous to **2** was not observed in this reaction, probably

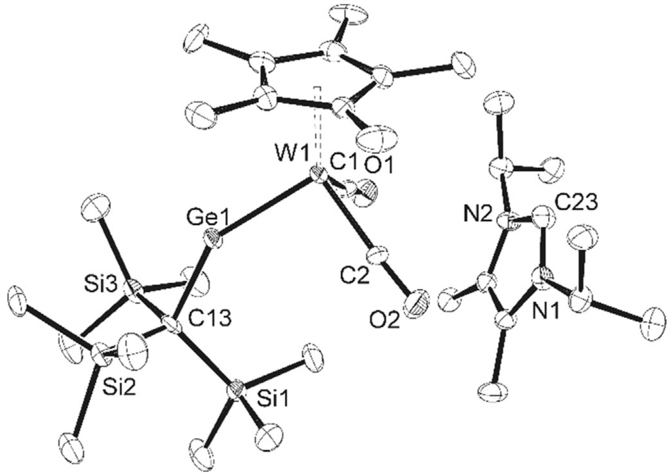
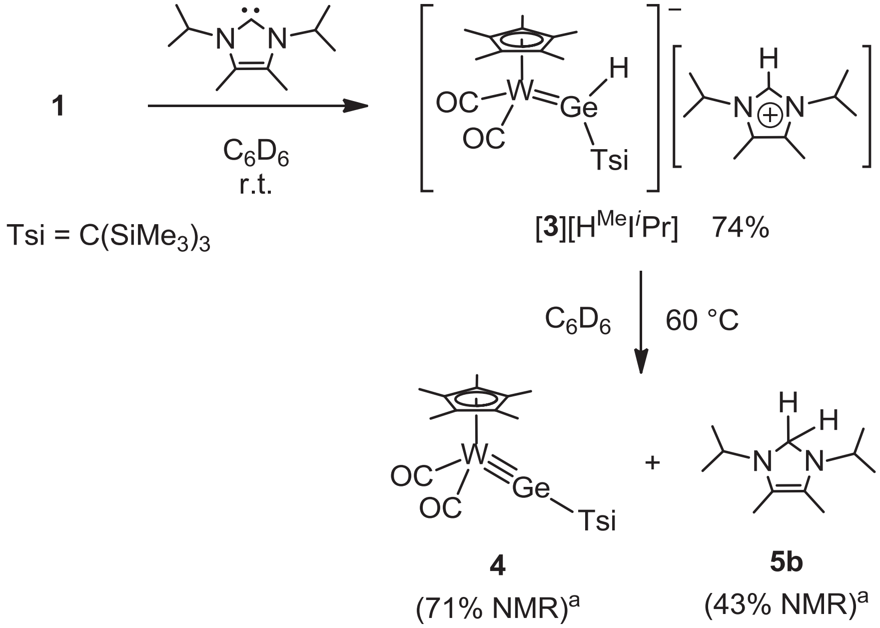
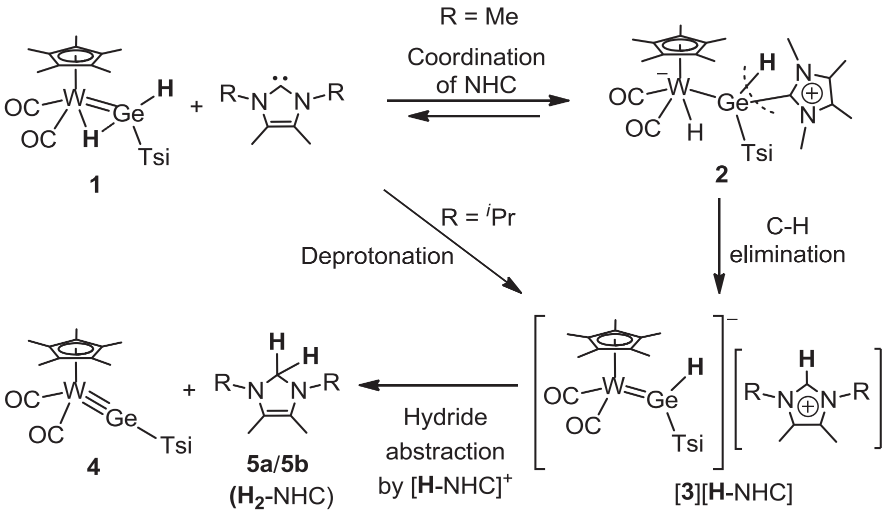


Fig. 3. ORTEP drawing of [**3**]$[\mathrm{H}^{\mathrm{Me}}\mathrm{I}^{i}\mathrm{Pr}]$. The thermal ellipsoids are plotted with 50% probability. The position of a hydrogen atom attached to Ge1 was not determined. The other hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): W1–Ge1 = 2.3886(8), W1–C1 = 1.925(8), W1–C2 = 1.921(8), Ge–C13 = 2.042(7), C1–W1–C2 = 83.0(3), C1–W1–Ge1 = 94.1(2), C2–W1–Ge1 = 95.4(2), W1–Ge1–C13 = 145.7(2).



Scheme 3. Reaction of germylene complex **1** with $^{\mathrm{Me}}\mathrm{I}^{i}\mathrm{Pr}$. ^{a}The yields are conversion yields at the conversion of 92% of [**3**]$[\mathrm{H}^{\mathrm{Me}}\mathrm{I}^{i}\mathrm{Pr}]$.



Scheme 4. A possible reaction mechanism.

because ^{Me}I^{i}Pr is too bulky to coordinate to the sterically congested germanium center of **1**. Complex [**3**][H^{Me}I^{i}Pr] was stable at room temperature, but was slowly converted into germylyne complex **4** at 60 °C accompanied by formation of hydrogenated NHC, i.e. H$_2$ ^{Me}I^{i}Pr (**5b**) [15]. The conversion yields of **4** and **5b** reached to 71% and 43%, respectively, at the conversion of 92% of [**3**][H^{Me}I^{i}Pr], after 9 days.

In the ^{1}H NMR spectrum of [**3**][H^{Me}I^{i}Pr] in C_6D_6, the signal of the hydrogen on the germylene ligand appears at $\delta = 13.18$ ppm. The chemical shift is comparable to that of base-free neutral germylene complex **1** (13.33 ppm) [6]. The signals of the SiMe groups and Cp* ligand are observed at 0.66 and 2.47 pm, respectively. A resonance assigned to the ring proton of the imidazolium cation appears at 8.84 ppm with an intensity of one proton. The IR spectrum of [**3**][H^{Me}I^{i}Pr] displays two strong ν_{CO} absorption bands at 1801 and 1720 cm^{-1} that are much lower in wavenumber than those of base-stabilized neutral complex **2** (1880 and 1784 cm^{-1}). The decrease of wavenumber values in these bands indicates that the W center of anionic complex **3** is more electron-rich than that of neutral complex **2**, which causes stronger π-back donation to the CO ligands in [**3**][H^{Me}I^{i}Pr]. X-ray crystal structure analysis confirmed that [**3**][H^{Me}I^{i}Pr] was an anionic germylene complex accompanied by a counter cation [H^{Me}I^{i}Pr]$^+$, although the position of the H atom attached to the Ge1 atom was not determined (Fig. 3). The W–Ge bond length of **3** (2.3886(8) Å) is significantly shorter than that of neutral germylene complex Cp*(CO)$_2$(D)W=Ge(D)(Tsi) (**1-D**) (2.4288(7) Å) [6], indicating that the W=Ge double bond of **3** is stronger than that of **1-D**. The two bond angles of **3**, ∠Ge(1)–W(1)–C(1) (94.1(2)°) and ∠Ge(1)–W(1)–C(2) (95.4 (2)°), are nearly identical, which is different from those of **1-D** where one of Ge–W–C(CO) angles is much larger than the other (86.25(15)° and 110.4(2)°). This is consistent with the change of geometry around the W center, i.e. the four-legged piano-stool geometry of **1** changed to the three-legged piano-stool geometry of **3** by this deprotonation process. The two W–CO bond lengths of **3** (1.925(8) Å and 1.921(8) Å) are also shorter than those of **1-D** (1.933(6) Å and 1.930(7) Å). The shortening of these W–Ge and W–CO bonds is obviously caused by stronger π-back donation from the anionic W center to the germylene ligand and the CO ligands compared with that in neutral complex **1-D**.

A possible reaction mechanism for formation of germylyne complex **4** and **5a**/**5b** is illustrated in Scheme 4. In the reaction of **1** with 1 equiv. of ^{Me}IMe, coordination of ^{Me}IMe to the germylene ligand occurs to give ^{Me}IMe-coordinated germylene complex **2**. C–H elimination of imidazolium (H^{Me}IMe$^+$) from **2** then takes place to afford the salt of complex anion **3** and imidazolium cation (H-NHC), probably via 1,1-elimination from the Ge center followed by hydrogen migration from W center. Another possible mechanism, *i.e.* 1,2-elimination from the W–Ge moiety, appears unfavorable because the imidazolium group and the hydrido ligand are in the anti-conformation through the W–Ge bond in the crystal structure of **2**. This geometry makes the migration of the hydride to the C2 atom of the NHC difficult, which is considered to be a requirement for the 1,2-elimination. Subsequent hydride abstraction from the Ge–H moiety of **3** by the imidazolium counter cation (H-NHC) provides germylyne complex **4** and **5a**. In the reaction of **1** with ^{Me}I^{i}Pr, the salt of **3** and [H^{Me}I^{i}Pr]$^+$ was formed either through an intermediate analogous to **2** or by direct deprotonation of **1** with ^{Me}I^{i}Pr. The intermediate analogous to **2** having ^{Me}I^{i}Pr instead of ^{Me}IMe on the germylene ligand, even if it exists, must be significantly destabilized by the steric repulsion between bulky ^{Me}I^{i}Pr and Tsi groups. Hydride abstraction in [**3**][H^{Me}I^{i}Pr], on the other hand, is retarded by the larger steric hindrance of the substituents on the counter cation.

4. Conclusions

We discovered a new route for conversion of a (H)W=Ge(H) system to the W≡Ge system through stepwise proton and hydride transfer to NHC giving H$_2$NHC. Full characterization of intermediate complexes corresponding to (H)W$^-$=Ge(H)(NHC$^+$) (zwitterionic) and W$^-$=Ge(H) (anionic) systems strongly supports this novel reaction mechanism induced by the high and unique reactivity of the carbene center of NHC. The unprecedented anionic germylene complex is particularly interesting as a versatile precursor for various germylene and germyl complexes. Its reactivity is now under active research.

Acknowledgments

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan (Grants-in-aid for Scientific Research Nos. JP15H03782, JPK05444, and JP25•1537) and a Grant-in-Aid for Scientific Research on Innovative Areas, “Stimuli-responsive Chemical Species for the Creation of Functional Molecules” [#2408] (JSPS KAKENHI Grant Number No. JP24109011), and JSPS Research Fellowships for Young Scientists (T. F.).

Supplementary material

CCDC 1557586 and 1557587 contain the supplementary crystallographic data for **2** and [**3**][$\mathrm{H}^{\mathrm{Me}}\mathrm{I}^{i}\mathrm{Pr}$]. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif.

Appendix A. Supplementary data

Supplementary data related to this chapter can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.07.027.

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