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Formation of a Germylyne Complex: Dehydrogenation of a Hydrido(hydrogermylene)tungsten Complex with Mesityl Isocyanate**

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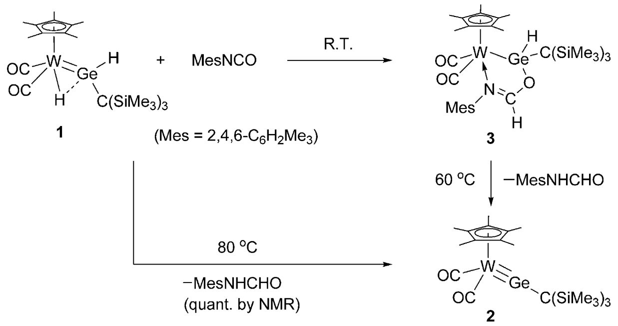
The heavier analogues of transition-metal carbyne complexes are attractive synthetic targets for research in fundamental organometallic and main-group chemistry. Over the last 15 years, the syntheses of a series of complexes with $M\equiv E$ bonds ($E=Si$,[1] Ge,[2] Sn,[3] Pb[4]) have been achieved, but examples are few. These complexes were synthesized by employing a base-stabilized halosilylene and stable divalent Group 14 element halides for $E=Ge$, Sn, or Pb as precursors. For example, Power and Simons reported the first example of this type of complex, $[Cp(CO)_2Mo\equiv Ge(C_6H_3\text{-}2,6\text{-}Mes_2)]$ (Mes = mesityl = 2,4,6-trimethylphenyl), which was obtained by salt elimination from a germanium(II) chloride $GeCl(C_6H_3\text{-}2,6\text{-}Mes_2)$ and an anionic complex $Na[MoCp(CO)_3]$.[2a]

Recently, we have synthesized a neutral hydrido (hydrogermylene) complex $[Cp^*(CO)_2(H)W{=}Ge(H)\{C(SiMe_3)_3\}]$ (**1**)[5] and found that **1** reacted with mesitylisocyanate MesNCO upon heating to produce a germylyne complex $[Cp^*(CO)_2W\equiv Ge\{C(SiMe_3)_3\}]$ (**2**) with release of MesNHCHO. In this reaction, **1** is formally dehydrogenated with MesNCO to give **2**. This type of synthesis of a germylyne complex from a germylene complex has not been previously reported. We also succeeded in the isolation of an intermediate $[Cp^*(CO)_2W(GeH(OCH{=}NMes)\{C(SiMe_3)_3\})]$ (**3**). Herein, we report the details of this novel transformation and our mechanistic investigations, including kinetic studies with **3** and DFT calculations.

We previously reported that **1** underwent hydrogermylation of PhNCO at the C=O bond at room temperature in 24 h to give a five-membered ring complex $[Cp^*(CO)_2W(GeH(OCH{=}NPh)\{C(SiMe_3)_3\})]$ (**4**) in 61% yield (85% NMR yield).[6] A similar reaction of **1** with sterically hindered MesNCO (3 equiv) proceeded very slowly at room temperature to give the analogous complex **3** in 76% yield after 10 days, together with germylyne complex **2** (24%) as determined from the ^1H NMR spectrum (Scheme 1). Complex **3** was isolated in 61% yield from a similar reaction using one equivalent of MesNCO for 22 days. The isolated compound **3** was heated at 60 °C for 10 days to give **2** and MesNHCHO in 95% and 90% NMR yields, respectively. This result clearly shows that **3** is an intermediate in the formation of **2**. Germylyne complex **2** was formed almost quantitatively by heating **1** and MesNCO at 80 °C for 3 days, and was isolated in 83% yield after recrystallization. The MesNHCHO was obtained as a mixture of *cis* and *trans* isomers and was identified spectroscopically.[7] In contrast, **4**, the phenyl derivative of **3**, gave only a trace amount of **2** after heating at 80 °C for 1 week.[8]



Scheme 1. Reaction of **1** with MesNCO.

The molecular structures of **2** and **3** were unambiguously determined by X-ray crystallography.[9] The ORTEP of **2** (major component of two disordered geometries) and of **3** are depicted in Figures 1 and 2, respectively. Complex **2** adopts a three-legged piano-stool geometry. The W−Ge bond (2.2830(6) Å) is very short and comparable to reported W≡Ge triple bonds (2.28–2.32 Å).[2] The W1-Ge1-C13 angle is almost linear (173.39(16)°). The DFT-optimized structure of the model compound $[Cp(CO)_2W\equiv Ge\{C(SiH_3)_3\}]$ (**2′**) agrees well with the X-ray crystal structure.[10] The presence of the W≡Ge triple bond is clearly indicated by NBO analysis and Kohn–Sham MOs (see Table S9, Figure S6 in the Supporting Information). All of these results confirm that **2** is a tungsten germylyne complex.

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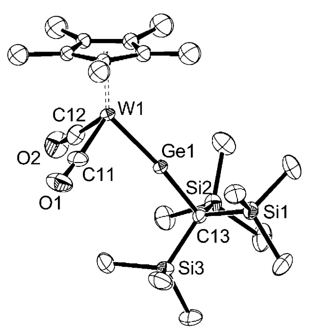

Figure 1. ORTEP of **2** with ellipsoids set at 50% probability (the form with the occupancy factor 51% was used). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: W1–Ge1 2.2830(6), W1–C11 1.945(7), W1–C12 1.961(7), Ge1–C13 1.940(5); W1-Ge1-C13 173.39(16), C11-W1-C12 91.6(3), Ge1-W1-C11 88.1(2), Ge1-W1-C12 86.8(2).

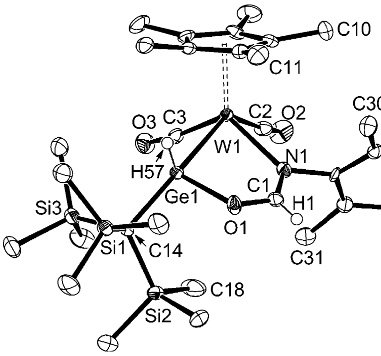

Figure 2. ORTEP of **3** with ellipsoids set at 50% probability. Hydrogen atoms except H1 and H57 are omitted for clarity. Selected bond lengths [Å] and angles [°]: W1–Ge1 2.6368(5), Ge1–O1 1.926(4), O1–C1 1.278(6), C1–N1 1.308(6), W1–N1 2.270(5), W1–C2 1.977(5), W1–C3 1.931(5); Ge1-W1-N1 74.63(12), W1-Ge1-O1 96.74(11), Ge1-O1-C1 116.2(3), O1-C1-N1 126.5(5), C1-N1-W1 123.9(4), Ge1-W1-C3 83.89(15), N1-W1-C2 82.0(2), C2-W1-C3 75.0(2).

Figure 2 shows that **3** is a five-membered ring complex having a W-Ge-O-C-N linkage. The overall structure of **3** is essentially the same as that of previously reported phenyl derivative **4**[6] except for the slightly elongated distances of the W1–Ge1 bond (2.6368(5) Å), W1–N1 bond (2.270(5) Å), and W1–C2 bond (1.977(5) Å) compared with the corresponding distances (2.6080(5), 2.250(4), and 1.944(6) Å, respectively) of **4**. This elongation would be caused by steric repulsion between the *o*-Me of Mes and the Cp*, $SiMe_3$, or CO ligands. Indeed, some of the distances are shorter than the sum of their van der Waals radii (C30···C10 3.41, C30···C11 3.58, C31···C18 3.54, C31···C2 3.13, C31···O2 3.09 Å). Steric repulsion is believed to be the driving force for facile elimination of MesNHCHO from **3**.

Spectroscopic data of **2** and **3** are consistent with their solid-state structures. The ^1H NMR spectrum of **2** shows only two singlet signals for Cp* and $SiMe_3$. In the $^{13}C\{^1H\}$ NMR spectrum of **2**, one signal for the CO ligands appears, reflecting the C_s symmetry. The germanium-bonded carbon shows a signal at 66.2 ppm, which is significantly downfield shifted compared to the corresponding signal (32.6 ppm) of germylene complex **1**. A similar tendency is observed in other germylyne complexes.[2] For **3**, all data closely resemble those of **4**[6] except for the signals of the Mes group.

The conversion of isolated **3** into **2** was monitored by ^1H NMR spectroscopy, and the rate constant *k* was determined at six temperatures between 45 and 70 °C.[10] The activation parameters determined by the Eyring plot were: $\Delta H^{\neq} = 125(3)\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\neq} = 23(8)\ \mathrm{J\,K^{-1}mol^{-1}}$, and $\Delta G_{298}{}^{\neq} = 118(5)\ \mathrm{kJ\,mol^{-1}}$. The positive $\Delta S^{\neq}$ value suggests that the transition state is sterically less-hindered than **3**.

To obtain more information on the reaction mechanism, theoretical calculations (DFT with B3PW91) were performed[10] on model compounds in which the Cp* and $SiMe_3$ groups were replaced by Cp and SiH_3 groups. The optimized structures of the model complexes[10] agreed well with the X-ray crystal structures of **1**–**4**.[9] The Gibbs energy ($\Delta G°$) for the reaction of model compound $[Cp(CO)_2(H)W{=}Ge(H)\{C(SiH_3)_3\}]$ (**1′**) with ArNCO (Ar = Mes, Ph) at 298 K is illustrated in Figure 3.[11,12] In the course of the reaction, five intermediates (**Int1**–**Int5**) and four transition states (**TS1**–**TS4**) were found. The third intermediate **Int3** corresponds to $[Cp(CO)_2W(GeH(OCH{=}NAr)\{C(SiH_3)_3\})]$ (**3′**: Ar = Mes; **4′**: Ar = Ph) at the lowest energy at 298 K. The rate-determining

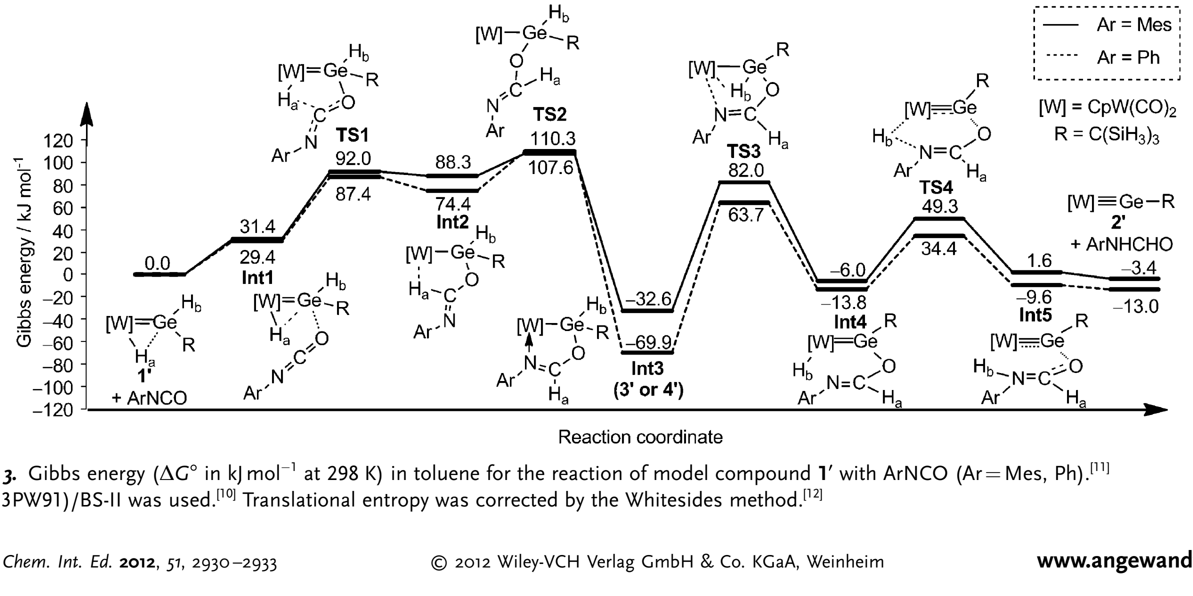

Figure 3. Gibbs energy ($\Delta G°$ in kJ mol^{-1} at 298 K) in toluene for the reaction of model compound **1′** with ArNCO (Ar = Mes, Ph).[11] DFT(B3PW91)/BS-II was used.[10] Translational entropy was corrected by the Whitesides method.[12]

step for the formation of **2′** is the conversion process of **Int3** to **Int4**. Gibbs activation energy for this step is calculated to be 115 kJ mol^{-1} for Ar = Mes and 134 kJ mol^{-1} for Ar = Ph. The former value is fairly close to the experimental value. The latter is 19 kJ mol^{-1} higher than the former, which explains the lack of conversion of **4** to **2** at room temperature.

The formation of intermediate **Int1** suggests that the reaction is initiated by nucleophilic attack of the oxygen atom of MesNCO on the germanium atom of the germylene ligand in **1′**. At the same time, the Ge–H$_a$ bond of **1** begins to break. In **TS1**, the W–Ge and W–H$_a$ bonds become weaker and the H$_a$ atom moves toward the carbon atom of the MesNCO, and then **Int2** is produced through formation of the Ge–O and C–H$_a$ bonds. Subsequent rotation of the C–O bond followed by the coordination of the nitrogen atom of the ArN=CH–O moiety to the W center affords **Int3** through **TS2**. These results strongly support our previously proposed mechanism for the formation of **4**.[6] From **Int3**, movements of the ArNCHO moiety and the H$_b$ atom through a rotation around the W–Ge bond lead to **TS3**. 1,2-H migration then occurs from Ge to W to form a hydrido(germylene) intermediate **Int4**. From **Int4**, the W–H$_b$ interaction becomes weaker and the H$_b$ atom starts to interact with the N atom to form the six-membered ring structure of **TS4**. Finally, ArNHCHO is eliminated through **Int5** to produce **2′**. Reverse reaction from the **2** + MesNHCHO to **3** was not observed experimentally. Though calculations of the model system indicate that **2′** + MesNHCHO is less stable than **Int3**, calculations with the real system show that **2** + MesNHCHO is much more stable than **3**, which is consistent with the experimental results.[13] Free energy calculations at 80 °C reveal that **Int3** becomes less stable and **2′** + MesNHCHO becomes more stable relative to those at 25 °C.[10]

In summary, the synthesis of germylyne complex **2** from germylene complex **1** through dehydrogenation with MesNCO demonstrates a new synthetic route for germylyne complexes. Further investigation of other substrates that dehydrogenate **1** to **2** and on the reactivity of both **1** and **2** are in progress.

Experimental Section

All manipulations were conducted in an atmosphere of dry argon or nitrogen by employing either standard Schlenk techniques or a glovebox. **2**: A thick-walled NMR tube was charged with **1** (47 mg, 0.069 mmol), MesNCO (19 mg, 0.064 mmol), and C_6D_6 (0.6 mL). The NMR tube was degassed and flame-sealed, and the sealed tube was heated at 80 °C for 3 days. After removal of volatiles, the residue was recrystallized from hexane at −30 °C to give **2** as orange crystals in 83 % yield (36 mg, 0.053 mmol). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 0.33$ (s, 27 H, $SiMe_3$), 2.08 ppm (s, 15 H, Cp*); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): $\delta = 4.5$ ($SiMe_3$), 12.2 ($C_5\mathit{Me}_5$), 66.2 ($\mathit{C}(SiMe_3)_3$), 100.9 (C_5Me_5), 224.9 ppm (CO); $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6, DEPT, 25 °C): $\delta = -5.6$ ppm; IR (C_6D_6): 1911 (vs, ν_{CO}), 1845 cm^{-1} (vs, ν_{CO}); MS (EI, 70 eV): *m*/*z* (%) 680 (70) [M^+], 665 (28) [M^+-Me], 635 (12) [M^+-3Me], 607 (8) [$M^+-3Me-CO$], 73 (100) [$SiMe_3$]; Anal. calcd (%) for $C_{22}H_{42}GeO_2Si_3W$: C 38.90, H 6.23; found: C 38.46, H 6.04; **3**: An NMR sample tube containing **1** (52 mg, 0.076 mmol), MesNCO (12 mg, 0.074 mmol), and C_6D_6 (0.8 mL) was kept at room temperature. The sample was monitored periodically by ^{1}H NMR. After 22 days, volatiles were removed under vacuum, and the residue was washed with hexane to give **3** as yellow crystals in 61 % yield (38 mg, 0.045 mmol). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 0.52$ (s, 27 H, $SiMe_3$), 1.60 (s, 15 H, Cp*), 1.69 (s, 3 H, $C_6H_2\mathit{Me}_3$), 2.12 (s, 3 H, $C_6H_2\mathit{Me}_3$), 2.27 (s, 3 H, $C_6H_2\mathit{Me}_3$), 6.41 (s, 1 H, GeH), 6.65 (s, 1 H, $C_6\mathit{H}_2Me_3$), 6.79 (s, 1 H, $C_6\mathit{H}_2Me_3$), 7.69 ppm (s, 1 H, O=C-H); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): $\delta = 5.2$ (SiMe), 10.8 ($C_5\mathit{Me}_5$), 12.2 ($\mathit{C}(SiMe_3)_3$), 19.7, 20.6, 21.7 ($C_6H_2\mathit{Me}_3$), 101.9 (C_5Me_5), 128.8, 130.4, 130.5, 134.9, 135.4, 147.8 ($\mathit{C}_6H_2Me_3$), 170.7 (N-*C*H=O), 243.0, 246.7 ppm (CO); $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6, DEPT, 25 °C): $\delta = -1.3$ ppm; IR (C_6D_6) 1922 (vs, ν_{CO}), 1830 (vs, ν_{CO}), 1560 cm^{-1} (m, $\nu_{N=C}$); MS (EI, 70 eV): *m*/*z* (%) 843 (1) [M^+], 815 (3) [M^+-CO], 680 (100) [M^+−MesNHCHO], 665 (19) [M^+−MesNHCHO−Me], 635 (11) [M^+−MesNHCHO−3 Me], 607 (8) [M^+−MesNHCHO−3 Me −CO], 163 (65) [MesNHCHO], 73 (38) [$SiMe_3$]; Anal. calcd (%) for $C_{32}H_{55}GeNO_3Si_3W$: C 45.62, H 6.58, N 1.66; found: C 45.92, H 6.29, N 1.75.

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[8] As suggested by one of referees, we heated **4** at a higher temperature (140 °C) in [D$_{20}$]-nonane for 1 day, which raised the yield of **2** up to 98 % (based on consumed **4**; 92% conversion). This result is consistent with the computational result of Figure 3.

[9] **2**: triclinic; $P\bar{1}$; $a = 9.2585(3)$, $b = 12.8608(6)$, $c = 13.3699(5)$ Å, $\alpha = 67.992(2)$, $\beta = 89.596(2)$, $\gamma = 79.946(3)°$, $V = 1450.33(10)$ Å^3, $Z = 2$; $C_{22}H_{42}GeO_2Si_3W$, $T = 150(2)$ K, 13716 reflections, 6568 independent reflections ($R_{int} = 0.0356$), $R1 = 0.0353$ ($I > 2\sigma(I)$), $wR2 = 0.0974$; $\mu = 5.137$ mm^{-1}; **3**: monoclinic; $P2_1/n$; $a = 20.3156(5)$, $b = 8.7258(3)$, $c = 21.7626(6)$ Å, $\beta = 105.2805(8)°$, $Z = 4$; $C_{32}H_{55}GeNO_3Si_3W$, $T = 150(2)$ K, 32256 reflections, 8486 independent reflections ($R_{int} = 0.1266$), $R1 = 0.0487$ ($I > 2\sigma(I)$), $wR2 = 0.1274$; $\mu = 4.023$ mm^{-1}; refinement by full-matrix least-squares methods on F^2. All carbon atoms of the Cp* ligand of **2** were disordered in two positions with occupancy factors of 51 % and 49 %. The positions of the hydrogen atoms of the Ge−H and W−H groups of **3** were located in the Fourier difference electron-density map and were refined with isotropic thermal parameters. CCDC 788617 (**2**) and 788616 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] For more details, see the Supporting Information.

[11] We also calculated the energy of the final stage postulated as **2′** + 1/2(ArNHCHO)$_2$, where formamide generated a dimer through formation of two hydrogen bonds, because the NH proton appeared as a broad peak in the ^{1}H NMR spectrum. This assumption stabilized the final stage much more ($\Delta G° = -14.1$ kJ mol^{-1} (Ar = Mes), -30.8 kJ mol^{-1} (Ar = Ph) relative to **1′** + ArNCO in Figure 3).

[12] Translational entropy was evaluated according to: M. Mammen, E. I. Shakhnovich, J. M. Deutch, G. M. Whitesides, *J. Org. Chem.* **1998**, *63*, 3821–3830.

[13] We calculated the free energy of important species for the real system **1′** + MesNCO (0), **Int3** (−4.7), and **2′** + MesNHCHO (−35.4 kJ mol^{-1}). These data demonstrate that the steric effects of Cp* and SiMe$_3$ actually raise the relative energy of **Int3** greatly. Accordingly, it is reasonably expected that this steric effects would also destabilize some other states such as **TS3**.