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Synthesis, characterization, and electronic structures of a methyl germyliumylidene ion and germylone-group VI metal complexes†

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The reaction of germylone (L)Ge (1) [L = 3-Ad-1-{C(^{t}Bu) = N(Mes)}$C_3H_4N_2$] with 1 equivalent of MeOTf afforded a germyliumylidene ion [(L)GeMe]$^+$OTf$^-$ (2), while reactions with $M(CO)_5$(thf) (M = Cr, Mo, W) gave the corresponding germylone-metal complexes [(L)Ge]$M(CO)_5$ (3–5). The former possesses a pyramidal Ge center, whereas the latter display a planar geometry around the Ge atom. Computational studies showed a unique bonding interaction between 1 and the $M(CO)_5$ unit, which involves a σ-donation as well as a weak π-back-donation.

Over the last two decades, the chemistry of stable singlet carbenes has rapidly developed since their isolation.[1] This class of molecules, particularly, N-heterocyclic carbenes (NHCs), have great synthetic utility, for instance, as organic catalysts or as versatile ligands for transition metal catalysts.[2] The corresponding germanium analogues, germylenes bearing a Ge atom in the +2 oxidation state, have also been widely studied for a long time.[3] Analogous to singlet carbenes, germylenes exhibit various chemical behaviours including activation of strong σ-bonds in inorganic and organic compounds,[4,5] coordination to metals[6–8] and cycloaddition reactions.[9] The unique chemical properties of germylenes are attributed to the electronic environment at the Ge center, which features a lone pair and an accessible vacant p-orbital (Fig. 1, left).

In recent years, several groups reported a novel class of germanium species, namely, ylidones.[10,11] Ylidones retain their valence electrons at the germanium center, and involve a germanium atom in the zero oxidation state.[12] Thus, the germanium center in ylidones formally possesses two lone pairs, which is in contrast to the electronic situation of germylenes (Fig. 1, right). Although various types of Ge(0) species have been developed thus far, their reactivities have rarely been studied. To the best of our knowledge, their ligand behaviours towards transition metals have never been explored.

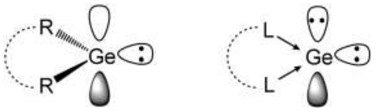
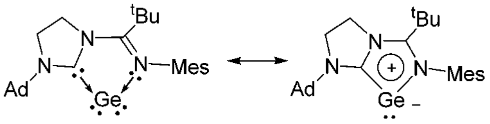


Fig. 1 Schematic representation of the electronic states of germylene (left) and germylone (right).

Recently, we have reported the synthesis of a Ge(0) species **1** supported by a bidentate imino-N-heterocyclic carbene (Fig. 2), which readily reacted with 2 equivalents of methyl trifluoromethanesulfonate (MeOTf) to afford a dicationic species.[13] Compound **1** may also be deemed a mesoionic germylene **1′**, a heavier analogue of imidazol-5-ylidene.[14] It has been reported that the ligand nature of imidazol-5-ylidene is different from that of NHCs.[14,15] Hence, it is reasonable to envisage that compound **1** would show peculiar chemical properties. Indeed, our preliminary study has shown the unique nucleophilic properties of **1** as a donor of two lone pairs, which prompted us to investigate further its behaviour as a lone pair donor to electrophiles such as MeOTf and group VI transition metals (Cr, Mo, and W). Herein, we reported the synthesis, single-crystal X-ray diffraction and the computational studies of a cationic germanium species **2** and germylone-group VI complexes **3–5**.

One equivalent of MeOTf was added dropwise to a toluene solution of compound **1** at room temperature. Instantaneously,



1 **1'**

Fig. 2 Canonical forms of compound **1** (Ad = 1-admantyl, Mes = 2,4,6-trimethylphenyl).

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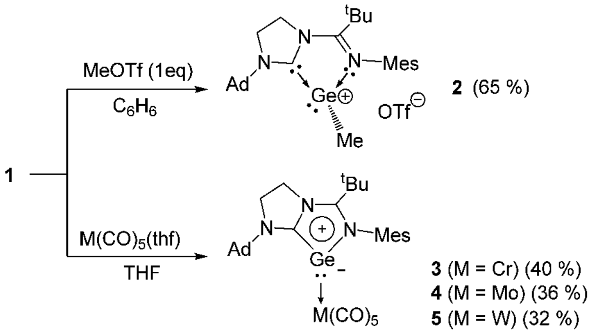
† Electronic supplementary information (ESI) available: Experimental and calculation details, and crystallographic information for **2**, **3**, **4** and **5**. CCDC 1429594–1429597. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc08665e



Scheme 1 Synthesis of compounds **2–5**.

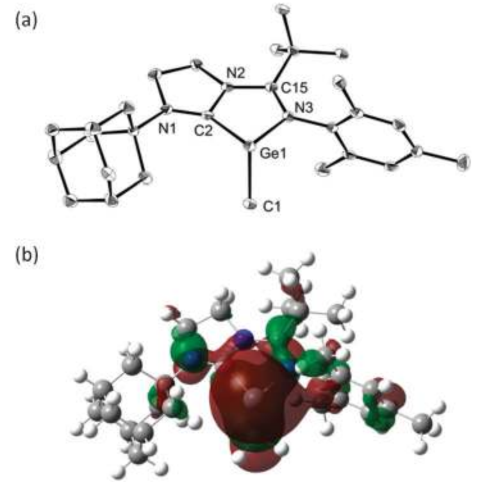


Fig. 3 (a) Solid-state structure of **2** (hydrogen atoms, solvent molecules, and OTf^- are omitted for clarity). Thermal ellipsoids are set at the 50% probability. (b) The HOMO of **2** calculated at the B3LYP/6-311G(d,p) level of theory.

the colour of the solution darkened and changed from yellow to red. After work-up, compound **2** was obtained as a red solid in 65% yield (Scheme 1). The molecular structure of **2** was determined by X-ray diffraction analysis, which revealed the formation of a germyliumylidene ion (Fig. 3a). The five C_2N_2Ge atoms form a nearly planar five-membered ring (the sum of internal pentagon angles = 538.05°). The tri-coordinate Ge center displays a pyramidal geometry (the sum of bond angles = 278.22°), and the Me group on the Ge atom is located nearly perpendicularly to the outside of the five-membered ring (C1–Ge1–N3: 98.28(9)°. C1–Ge1–C2: 101.71(10)°). The smaller C2–Ge1–N3 angle (78.23(9)°) and the longer Ge1–C2 (2.024(2) Å) and Ge1–N3 (2.040(2) Å) bond distances in **2** in comparison to those of **1** (C–Ge–N: 80.59(6)°, Ge–C: 1.8870(15) Å, Ge–N: 1.9680(13) Å) are confirmed, and these metric parameters are similar to those of $[(L)GeCl]^+GeCl_3^-$ (C–Ge–N: 76.88(7)°, Ge–C: 2.0588(19) Å, Ge–N: 2.0560(16) Å),[13] indicating the loss of the electron delocalization over the five-membered C_2N_2Ge ring.

To gain an insight into the electronic feature of **2**, quantum chemical density functional theory (DFT) calculation was performed for the cationic part of **2**.[16] The HOMO displays a lone-pair orbital which is mainly localized on the Ge atom (Fig. 3b). Natural bond orbital (NBO) analysis showed Wiberg bond index (WBI) values of the $Ge–C_{carbene}$ bond (0.76) and the Ge–N bond (0.42) that are smaller than those in **11** ($Ge–C_{carbene}$: 1.21, Ge–N: 0.56) and comparable to those of $[(L)GeCl]^+GeCl_3^-$ ($Ge–C_{carbene}$: 0.61, Ge–N: 0.39), thus confirming the lack of electron delocalization over the five-membered C_2N_2Ge ring.

Next, reactions of **1** with group VI metals were examined. The treatment of a THF solution of **1** with a stoichiometric amount of $M(CO)_5(thf)$ (M = Cr, Mo, W)[17] at room temperature proceeded immediately as indicated by the fast coloration of the reaction mixture to red. Red single crystals were obtained by recrystallization from a concentrated solution of THF at −26 °C [**3** (M = Cr): 40%, **4** (M = Mo): 36%, **5** (M = W): 32% yields, respectively] (Scheme 1). Under an inert atmosphere, compounds **3–5** are thermally stable both in the solid state and in solution, and even under heating conditions at 80 °C for several hours in toluene, no decomposition was detected. However, they rapidly decompose upon exposure to air. Note that compounds **3–5** represent the first examples of germylone–transition metal complexes. Compounds **3–5** have been fully characterized by NMR spectroscopy and a single-crystal X-ray diffraction analysis (Fig. 4). The crystallographic study revealed that complexes **3–5** exhibit a similar molecular geometry involving η^1-coordination of the Ge center to the $\{M(CO)_5\}$ (M = Cr, Mo, W) unit. The C_2N_2Ge five-membered rings still persist their original coplanar geometries (the sum of internal pentagon angles = 539.90° (**3**), 539.9° (**4**), 539.90° (**5**), respectively). Notably, the Ge atoms in complexes **3–5** display a trigonal planar geometry (the sum of the bond angles around the Ge atom = 358.93° (**3**), 359.07° (**4**), 358.95° (**5**)), which is in marked contrast to the case of **2** featuring a pyramidal Ge center (Fig. 3a). The C–Ge–N bond angles in **3** (83.60(7)°), **4** (83.7(2)°) and **5** (83.70(16)°) are about 3° larger than that of **1** (80.59(6)°). Both of the Ge–C and Ge–N bond distances in **3** (1.8587(17) Å, 1.9303(14) Å), **4** (1.858(6) Å, 1.934(4) Å) and **5** (1.847(4) Å, 1.932(3) Å) are slightly shorter than those of **1** (1.8870(15) Å, 1.9680(13) Å). The Ge–Cr bond distance of 2.4883(3) Å is significantly shorter than

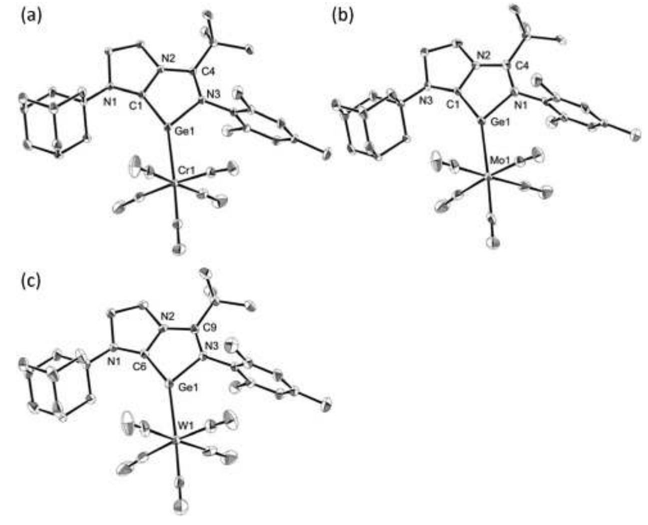


Fig. 4 Solid-state structures of **3** (a), **4** (b) and **5** (c) (hydrogen atoms and solvent molecules are omitted for clarity). Thermal ellipsoids are set at the 50% probability.

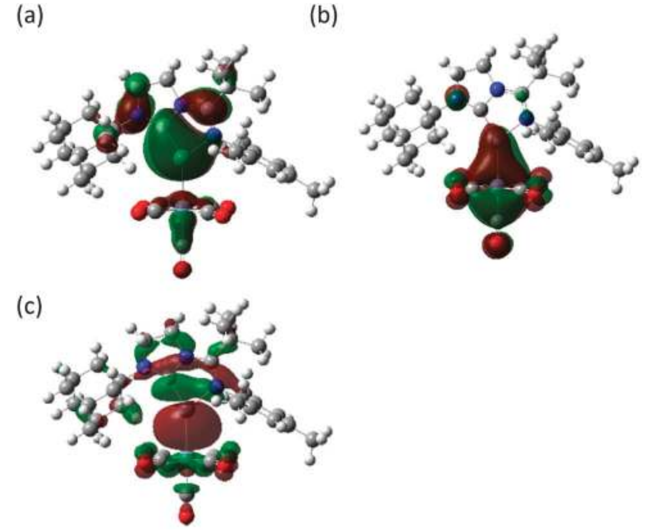


Fig. 5 Plots of the HOMO (a), HOMO−2 (b) and HOMO−7 (c) of **3** calculated at the B3LYP/6-311G(d,p) level of theory, with the LANL2TZ(f) pseudo-potential applied for the Cr atoms.

the Ge–Mo bond (2.6176(8) Å) in **4** and the Ge–W bond (2.6085(5) Å) in **5**, suggesting a strong back-donation from the metal center to ligand **1** in complexes **3**. However, these Ge–M bonds are longer than those of the relevant germylene-metal complexes such as $(ArS)_2GeCr(CO)_5$ (Ge–Cr: 2.367(2) Å),[7k] $(NHGe)_3Mo(CO)_3$ (Ge–Mo: 2.5452(3) Å),[7d] and ArAr*GeW$(CO)_5$ (Ge–W: 2.5934(8) Å).[7i]

The frontier orbitals of **3** are depicted in Fig. 5. We also confirmed that complexes **4** and **5** show the similar MOs to **3** (see the ESI†). The HOMO of **3** is mainly a C–Ge π-bonding orbital exhibiting antibonding conjugation with the π-orbitals of the carbon-bearing ^{t}Bu group (Fig. 5a), thus, indicating the delocalization of π-electrons over the C_2N_2Ge five-membered ring. Interestingly, the HOMO−2 represents a d-orbital of the Cr atom that involves π-bonding interaction with the Ge atom through a back-donation (Fig. 5b). It is inferred that the delocalization of π-electrons over the C_2N_2Ge five-membered ring allows the Ge center to accept d-electrons partially from the Cr atom. The planarity of the Ge center in complex **3** may presumably originate from the effective overlap of a d-orbital of the Cr atom and the p-orbital of the Ge atom. Indeed, germyliumylidene ion **2** in which no such d–p interaction is involved displays a contrasting pyramidal geometry at the Ge center. A donation of a σ-type lone pair from the ligand to the Cr center is confirmed in HOMO−7 (Fig. 5c). The WBI value of the Ge–C1 bond is 1.11, indicating the partial Ge–C double bond character. WBI values larger than 1.0 for the C1–N2 (1.08), N2–C4 (1.23), and C4–N3 (1.33) bonds were also confirmed, which supports the delocalization of electrons in the C_2N_2Ge π-system. The WBI value of 0.77 for the Ge–Cr bond indicates the relatively strong interaction between them. The larger WBI value of the Cr–CO_{trans} bond (1.15) than those of the Cr–CO_{cis} bonds (1.03, 1.03, 1.04, and 1.05) is probably due to the greater σ-donating ability of **1** than CO. Natural Population Analysis (NPA) indicates an overall charge transfer of 0.70e (**3**), 0.71e (**4**), and 0.75e (**5**) from the ligand **1** to the $M(CO)_5$ fragment in complexes **3–5**.

To evaluate the ligand donating/accepting ability of **1**, infrared spectra of complexes **3–5** were recorded (see the ESI†). The ν(CO) frequencies were observed at 2048 (s), 1976 (m), 1917 (s), and 1899 (s) cm^{-1} for **3**, 2061 (s), 1985 (m), 1923 (s), and 1897 (s) cm^{-1} for **4**, and 2059 (s), 1978 (m), 1917 (s), and 1895 (s) cm^{-1} for **5**. The presence of four absorption bands ($A_1^{(2)}$, B_1, E, $A_1^{(1)}$) for ν(CO) frequencies indicates a distortion of the $M(CO)_5$ moiety.[18] Based on the $A_1^{(2)}$ bands of **4** and **5**, the Tolman Electronic Parameter (TEP) values for the ligand **1** were calculated.[19] The average of the TEP values estimated for **1** is 1868 cm^{-1}, which is significantly smaller than those for the reported N-heterocyclic germylenes (2073–2080 cm^{-1}),[7d] suggesting the strong σ-donating ability of **1**. The observed $A_1^{(1)}$ bands (**3**: 1899 cm^{-1}, **4**: 1895 cm^{-1}, and **5**: 1895 cm^{-1}) corresponding to the vibration of CO in the *trans* position to the donor ligand[20] are smaller than those of the reported germylene–$M(CO)_5$ complexes,[7,21] but comparable to those of pyridine–$M(CO)_5$ complexes (Cr: 1905 cm^{-1}, Mo: 1890 cm^{-1}, and W: 1895 cm^{-1}).[20c] These results indicate the poor π-acceptor ability of **1**, which might be due to the electron-richness of the 6π-system over the five-membered ring.

In summary, we studied the reactivity of compound **1** toward a stoichiometric amount of MeOTf and group VI metal–pentacarbonyl complexes. The former afforded a germyliumylidene ion **2** bearing a pyramidal Ge center, whereas the latter produced the corresponding metal complexes **3–5** containing a trigonal planar germanium center. Computational studies showed that a lone pair is mainly localized on the Ge atom in **2**, while one of the lone pairs on the Ge atom in **3–5** is involved in the π-system over the C_2N_2Ge five-membered ring. IR spectroscopic analysis suggests a strong σ-donating but weak π-accepting nature of **1**.

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