ORGANOMETALLICS

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Experimental and Computational Study of Auxiliary Molecular Effects on the Mechanism of the Addition of Hydrazines to a Low-Valent Germanium Complex

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Supporting Information

ABSTRACT: Reaction of the diarylgermylene $Ge(Ar^{Me_6})_2$ (Ar^{Me_6} = $C_6H_3-2,6-(C_6H_2-2,4,6-(CH_3)_3)_2$) with hydrazine and methylhydrazine gave the first structurally characterized Ge(IV) hydrazide complexes, Ge: $(Ar^{Me_6})_2Ge(H)NHNHR$ (R = H, Me). A detailed computational study of the mechanism of this N-H bond activation showed that the reaction proceeds via an intermolecular proton transfer, which is mediated by a second equivalent of hydrazine that interacts with the hydrazine- $Ge(Ar^{Me_6})_2$ adduct intermediate through N---H hydrogen bonding. This auxiliary effect is blocked when the substituted derivative N,Ndimethylhydrazine is used, and a Lewis adduct complex of Ge(Ar^{Me6})₂ is the only product obtained.

 ${\displaystyle S}$ ince 2005, the activation of small molecules by main-group complexes under ambient conditions has been attracting increasing interest.¹ The first example involved the cleavage of dihydrogen by a germanium analogue of an alkyne.² In addition, Stephan and Bertrand also demonstrated the roomtemperature activation of dihydrogen and ammonia by frustrated Lewis pairs³ and singlet carbenes.⁴ Since these initial discoveries, the reactivity of certain open-shell main-group complexes has been shown to often mimic that of transition metals⁵ through the activation of several small molecules such as olefins, 6 P₄, 7 and CO₂. ⁸ Investigations of the activation of N–H bonds by main-group-metal complexes^{4,9,10} have been prominent because of their importance as potential precursors to main-group-metal nitrides,¹¹ and because the transitionmetal-mediated activation of N-H bonds in processes such as hydroamination is rare since they tend to favor the formation of Lewis base (Werner) complexes.¹² Hydrazine and its substituted congeners have proven to be an interesting class of compounds for reactivity studies because of their extensive use in industry as fuels,¹³ in organic synthesis,¹⁴ and as intermediates in the biological reduction of dinitrogen to ammonia.¹⁵ Although numerous examples of main-group hydrazides have been reported in the literature, mechanistic insights into their formation and reactivity are rare, and direct comparisons with related amido complex formation have been limited.¹⁶ To date, the reactivity of main-group-metal complexes toward hydrazine and related substrates has largely focused on reactions of substituted hydrazines with metal alkyls or hydrides which, via alkane or H₂ elimination, yield numerous interesting cage structures.^{17,18} Fox example, Uhl and coworkers have isolated several unusual group 13 metal hydrazide cage species and their thermolysis products, including the notable gallium "hydrazinetetraide", which contains a $[N-N]^{4-}$



H₂NNHR

R = H, Me

fragment coordinated by six gallium atoms.¹⁹ Roesky and coworkers have reported that silvlenes, LSi^{II} (L= β -diketiminate), undergo N-H bond insertion to yield a Si(IV) hydrazide complex,²⁰ as well as the isolation of a Ge(II) hydrazide which undergoes proton insertion from the hydrazine molecule onto the unsaturated backbone of the diketiminate.²

Herein we describe the process by which hydrazines react with the heavier element carbene analogue $Ge(Ar^{Me_6})_2 (Ar^{Me_6})_2$ $C_6H_3-2,6-(C_6H_2-2,4,6-(CH_3)_3)_2)^{22}$ to yield the first germanium(IV) hydrazides, $(Ar^{Me_6})_2Ge(H)NHNHR$ (R = H (1), Me (2)). Density functional theory (DFT) calculations on the formation of 1 show that there is a transition state in which a second molecule of hydrazine is also involved in N-H bond activation. This occurs via N---H hydrogen bonding of the second hydrazine to a hydrazine molecule that is already coordinated to germanium via a dative N---Ge bond. Experimental and computational data show that this hydrogen-bonding interaction is essential to the N-H bond activation, as the proton transfer to germanium becomes blocked by the use of N,N-dimethylhydrazine. In effect, the terminal methyl groups on the coordinated N,N-dimethylhydrazine ligand do not engage in N---H hydrogen bonding to the second molecule of NH2NMe2 and the adduct intermediate $(Ar^{Me_6})_2$ GeNH₂NMe₂ (3) is the only product formed (Scheme 1).

When the germylene $Ge(Ar^{Me_6})_2$ was treated with an excess of anhydrous hydrazine or methylhydrazine (ca. 3 mol equiv), the characteristic deep purple color of the solution faded, and slow cooling of the concentrated solution to ca. -20 °C

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Scheme 1. Reactions of the Diarylgermylene $Ge(Ar^{Me_6})_2$ with N_2H_4 , N_2H_3Me , and NH_2NMe_2



Figure 1. Thermal ellipsoid (30%) drawings of (left) 1 and (right) 2. Carbon-bound hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (deg): 1, Ge(1)-N(1) = 1.832(2), Ge(1)-H(1) = 1.52(2), N(1)-N(2) = 1.435(2), Ge(1)-N(1)-N(2) = 117.1(1); 2, Ge(1)-N(1) = 1.832(3), Ge(1)-H(1) = 1.48(2), N(1)-N(2) = 1.435(4), Ge(1)-N(1)-N(2) = 116.6(2).



Figure 3. Thermal ellipsoid (30%) drawing of 3. Carbon-bound hydrogen atoms and a flanking mesityl ring (C40–C48) are not shown for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)-N(1) = 2.110(4), N(1)-N(2) = 1.439(5), C(Ar)-Ge(1)-N(1) (av) = 94.3(1), Ge(1)-N(1)-N(2) = 118.7(3).

produced suitable single crystals of 1 or 2 for X-ray diffraction study. Complex 1 (Figure 1) was found to have a monomeric structure with distorted-tetrahedral coordination geometry at the germanium. Consistent with the higher germanium oxidation state, the Ge(1)–C(Ar) distances (1.981(2) and 1.984(2) Å) are shortened slightly with respect to those in Ge(Ar^{Me₆})₂ (cf. 2.033(4) Å), and the C(Ar)–Ge(1)–C(Ar) bond angle (113.0(1)°) is slightly narrower than the 114.4° in Ge(Ar^{Me₆})₂.²² The Ge(1)–H(1) and Ge(1)–N(1) bond distances are within the expected range for germanium(IV) hydrides and amides (1.52(2) and 1.832(2) Å, respectively),¹⁰ and the N–N distance in the hydrazido moiety is also shortened slightly to 1.435(2) Å from 1.45 Å.²³ The shortening of the N–N bond in 1 in comparison to that in free hydrazine and the higher degree of pyramidalization of the germaniumbound nitrogen ($\sum^{\circ} = 342.9^{\circ}$ for N(1) in comparison to $\sum^{\circ} =$



Figure 2. Calculated energy (kcal mol⁻¹) and drawings of intermediates and transition states with selected distances (Å) for the reaction of $Ge(Ar^{Me_6})_2$ with N_2H_4 via inter- and intramolecular proton transfer at the B3PW91 level.



Figure 4. Calculated energy (kcal mol⁻¹) and drawings of intermediates and transition states with selected distances (Å) for the reaction of $Ge(Ar^{Me_6})_2$ with NH₂NMe₂ at the B3PW91 level.

354.9° for N(2)) is consistent with a more covalent Ge-N bond and little to no interaction between the electron lone pair on nitrogen and the germanium atom. The FT-IR spectrum of 1 shows three weak bands at 3393, 3334, and 3259 cm^{-1} , assigned to the three N-H stretching modes of hydrazine. The germanium-bound hydrogen in 1 was located and freely refined from the X-ray data, and the presence of the hydride was further confirmed by absorptions in the FT-IR (2105 cm^{-1}) and ¹H NMR (5.45 ppm) spectra. Complex 2 (Figure 1) was isolated in a manner similar to that of 1, and ¹H NMR spectroscopy indicates that there was no formation of the structural isomer (Ar^{Me6})₂Ge(H)NMeNH₂. Apparently, steric effects disfavor the formation of a Lewis base complex to the methyl-substituted nitrogen and only the (Ar^{Me₆})₂GeNH₂NHMe adduct is observed. However, this species can also hydrogen bond via an N---H interaction to a second NH₂NHMe molecule and N-H bond activation is observed to afford 2.24

In order to gain a greater understanding of these reactions, the mechanism for the formation of 1 was studied computationally by DFT.²⁵ A transition state for intramolecular proton transfer (Figure 2, TS') was found on the potential energy surface (PES) for the reaction of N_2H_4 with $Ge(Ar^{Me_6})_{2}$; however, this pathway was deemed unlikely because its activation energy was calculated to be greater than 40 kcal mol⁻¹ above the starting materials. Consequently, we turned our attention to a mechanism involving intermolecular proton transfer. Transition state 1 (TS-1)²⁶ involves the initial approach of a hydrazine molecule to $Ge(Ar^{Me_{\delta}})_{2}$, which is immediately followed by the formation of the adduct intermediate (INT-1). The approach of the second molecule of hydrazine (INT-2) unexpectedly does not lead to an increase in energy. The energy required to overcome the conformational change in the molecule to accommodate the second molecule of N₂H₄ is offset by an intermolecular hydrogen bonding interaction, ca. 12 kcal mol^{-1.27} Transition state 2 (TS-2) represents the concerted proton migration of H2 from the

second hydrazine molecule to the electron-rich germanium atom with simultaneous transfer of H1 from the bound hydrazine to the second molecule of hydrazine. This transition state is related to that for the activation for ammonia by an analogous germanium species, and the total activation energy for the formation of 1 is similar at 23.0 kcal mol⁻¹ (cf. 17.0 kcal mol⁻¹ for $(Ar^{Me_6})_2Ge(H)NH_2$).¹⁰ We presume that 2 is obtained by a route that is similar to that of 1 to give the methyl-substituted species.

In contrast to 1 and 2, treatment of the germylene with an excess of N,N-dimethylhydrazine affords the Lewis adduct 3 (Figure 3), and no formation of a germanium(IV) hydrazide is observed. The lack of formation of the germanium(IV) hydrazide is in sharp contrast to the facile nature of the reactions of $Ge(Ar^{Me_6})_2$ with N₂H₄ and N₂H₃Me, which cleanly yield the Ge(IV) N-H bond activated products. The coordination of the -NH₂ end of N,N-dimethylhydrazine molecule to the germanium can be described as a simple dative bond between the lone pair of nitrogen and the empty p orbital on the germylene. The Ge(1)-N(1) bond (2.103(4) Å) is more than 0.2 Å longer than those observed in 1 or 2 and is coordinated at a 97.6° angle with respect to the $Ge-C(ipso)_2$ plane. This bond angle is considerably less than those in 1 (128.8°) and 2 (127.6°) and is consistent with angles observed in other known neutral σ adducts of germylenes.²

The calculated reaction pathway for the reaction of $\text{Ge}(\text{Ar}^{\text{Me}_6})_2$ with *N*,*N*-dimethylhydrazine (Figure 4) displayed transition states and intermediates, albeit with larger energy differences, similar to those in the reaction pathway for the formation of **1**. Transition state 1 (TS-1) is higher in energy, ca. 5 kcal mol⁻¹, with respect to the starting materials in comparison to the reaction pathway for **1** (Figure 2), where the two are nearly degenerate. As in **1**, a hydrogen-bonding interaction is predicted to stabilize INT-2, but in this case, steric repulsion between the terminal methyl groups of the hydrazine ligand and the adjacent molecule of *N*,*N*-dimethylhydrazine significantly increases the energy required

for a second molecule of NH_2NMe_2 to approach INT-1 (3); thus, INT-2 is less stable relative to INT-1 by ca. 9 kcal mol^{-1} . The activation energy for the formation of the theoretical product, (Ar^{Me₆})₂Ge(H)N(H)NMe₂, is only 3.1 kcal mol⁻¹ higher than that for 1 (26.1 kcal mol^{-1}), but the transition state is 21.9 kcal mol⁻¹ higher in energy than the fully dissociated starting materials, whereas in 1 the energy difference is just 8.3 kcal mol⁻¹ higher. These differences may be rationalized in terms of the increased steric strain of the -NMe2 end of the bound hydrazine decreasing the dissociation energy of the Ge-N dative bond and preventing subsequent hydrogen bonding with the second molecule of hydrazine. Thus, there is a steep rise in energy of the key transition state (TS-2) with respect to $Ge(Ar^{Me_6})_2$ and free NH₂NMe₂. This inhibits the N-H bond activation of N,N-dimethylhydrazine, and the adduct 3 is the only product isolated.

In conclusion, we have prepared the first Ge(IV) hydrazides by facile N-H bond activation of hydrazine and methylhydrazine by the diarylgermylene $Ge(Ar^{Me_{\delta}})_2$. DFT calculations indicate that these reactions proceed with closely related intermediates and transition states in comparison to analogous reactions between germylenes and ammonia. The intermolecular N-H bond activation is dependent upon auxiliary hydrogen bonding between a germylene-hydrazine adduct intermediate (Figure 2, INT-1) with a second molecule of hydrazine (Figure 2, INT-2). This auxiliary interaction is inhibited when the germanium species is treated with N,Ndimethylhydrazine, and only the σ adduct 3 was formed. The inhibition of N-H bond activation, in this case, was calculated to be largely caused by the increased steric bulk of the terminal methyl groups of the hydrazine ligand preventing the close association, i.e. hydrogen bonding, of a second molecule of NH₂NMe₂ necessary for intermolecular proton transfer.

ASSOCIATED CONTENT

S Supporting Information

Text and figures giving synthesis details and characterization data for 1-3, tables giving crystallographic data and details of DFT calculations and atom coordinates, and CIF files giving crystal data for 1-3. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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(24) A full account of the structural and spectroscopic details of 2 can be found in the Supporting Information.

(25) See the Supporting Information for a full account of the computational methods.

(26) The activation energy was calculated to be very small, which means that this step would not be rate-determining. See the Supporting Information for further details.

(27) Single-point calculations using a larger basis set (6-311G(2d) for germanium and 6-31G(d,p) for all other atoms) were performed to determine the total energy required to reconfigure the molecule so that association with the second equalent of N₂H₄ was possible.

(28) We have recently reported a germylene-isocyanide complex which features similar bond angles with respect to the aryl-germanium plane. See: Brown, Z. D.; Vasko, P.; Fettinger, J. C.; Tuononen, H. M.; Power, P. P. J. Am. Chem. Soc. **2012**, *134*, 4045-4048.