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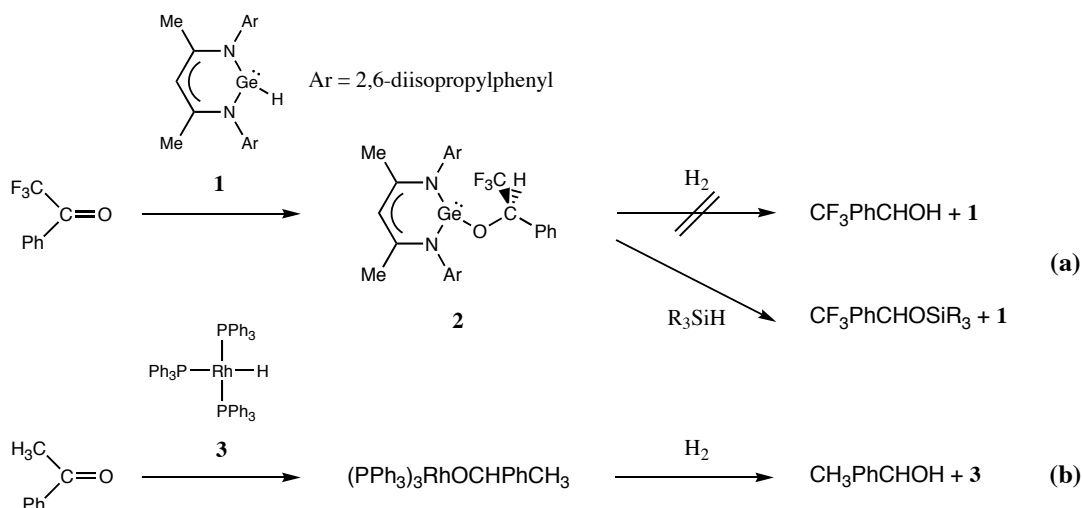
Theoretical Study of Ketone Insertion into Ge(II)-H Bond:
Comparison with that into Rh(I)-H Bond

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INTRODUCTION

Activation of small molecules is one of the fundamental characteristics of transition metal complexes, which is very important as the initial step of various catalytic reactions. The partially occupied valence *d* orbitals of a transition metal which are usually very close in energy play a key role in such reactions. On the other hand, it has been believed that main-group elements cannot play such a role and cannot be a catalyst in general. This is because their valence *s* and *p* orbitals are far apart in energy. However, successful synthesis and isolation of novel heavier main-group compounds, for instance heavier homologues of ethylene, acetylene, benzene, ketone or carbene, opened a new area of chemistry. The recent experiments report that some of such heavier homologues exhibit reactivity toward dihydrogen and some small molecules containing C=O, C≡C, N=N, and C=N bonds without any external catalysts.

In this work, we focus on activation of ketone by the Ge(II) hydride **1** producing the relevant germylene alcoxide **2** (Scheme 1a).¹ It is noted that this reaction resembles well the initial step of the hydrogenation reaction of ketone by the Rh(I) hydride **3** (Scheme 1b). We wish to disclose the mechanism of these reactions, discuss the essential similarity/dissimilarity between Ge(II) and Rh(I), and assess the potential for activating small molecules with a main-group-based catalyst.



Scheme 1

COMPUTATIONAL DETAILS

All geometries were optimized by the DFT method with B3PW91 functional. For

the energy evaluation and the analysis of the electronic structure, a triple- ζ basis set with $2d$ and $1f$ polarization functions was employed for Ge with the ECPs of Stuttgart-Dresden-Bonn group. A triple- ζ basis set with $2f$ polarization functions was employed for Rh with the same ECPs. The 6-311G(d) basis sets were employed for the other elements, where a diffuse function was added to O and one p polarization function was added to H of hydride, dihydrogen, and silane. The Gibbs energy in solvent was calculated incorporating with the polarized continuum model (PCM), where the translational entropy was corrected with the method developed by Whitesides et al. The relative energy was evaluated up to the MP4(SDTQ) and CCSD(T) levels for the model molecules and the MP2 and SCS-MP2 levels for the real molecules.

RESULTS AND DISCUSSION

The theoretical calculations show that the reaction of **1** with $\text{CF}_3\text{PhC=O}$ occurs in one-step process via four-membered transition state $\text{TS}_{1,2}$, where the Ge-H σ -bonding MO of **1** interacts with the C=O π^* -antibonding MO of ketone (Figure 1). The experimental fact that $(\text{CH}_3)_2\text{C=O}$ and $\text{Ph}_2\text{C=O}$ cannot react with **1** is explained in terms of their higher-lying C=O π^* -antibonding MO. To construct catalytic cycle with main-group-based catalyst, the regeneration process of **1** is investigated with several substrates. When silane is employed as the second reagent, **1** is regenerated with formation of silylether. However, further reaction is very difficult, when dihydrogen is employed.

The characteristic features of heavy main-group-based catalyst as well as the mechanism of the hydrogenation reaction of **3** will be presented in the symposium.

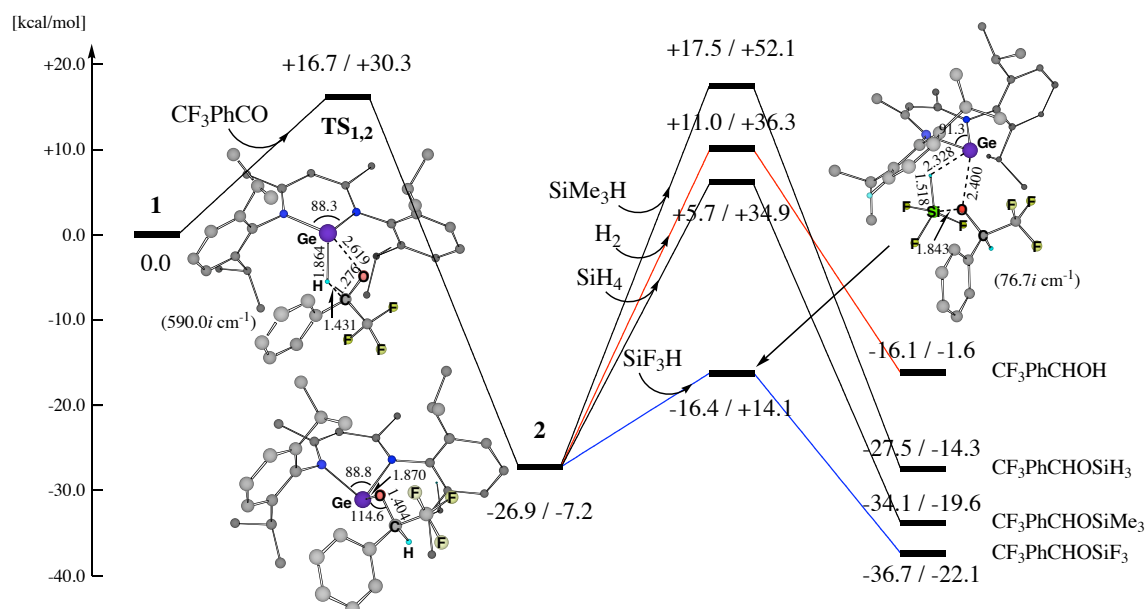


Figure 1. Optimized structures and relative energy ($\Delta E^0 / \Delta G_{\text{sol}}^0$) for the reaction shown in Scheme 1a. Energies, distances, and angles are in kcal/mol, Å, and degree, respectively.

¹ S. K. Mandal, H. W. Roesky, *Acc. Chem. Res.*, **2012**, *45*, 298.