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Stabilization of Vinylidene-type and Acetylene-type Si_2H_2 Species by Coordination with Rhodium(I) and Platinum(0) Complexes. Theoretical Proposals

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Rh(I) and Pt(0) complexes of Si_2H_2 species were theoretically investigated. $RhCl(PMe_3)_2(Si_2H_2)$ (**2-Rha**) containing vinylidene-type Si_2H_2 species is the most stable among various Rh(I) complexes of Si_2H_2, while the vinylidene-type Si_2H_2 species (**2**) is much less stable than the most stable 2H-bridged Si_2H_2 species (**3**) by 11.5 kcal/mol, where the energy calculated by the DFT method is given hereafter. $RhCl(PMe_3)_2(Si_2H_2)$ (**1-Rh**) containing acetylene-type Si_2H_2 species easily isomerizes to the Rh complex (**4-Rh**) of the 1H-bridged Si_2H_2 species with a small activation barrier (2.6 kcal/mol). Complex **4-Rh** further isomerizes to **2-Rha** with a very small activation barrier (1.9 kcal/mol), while $RhCl(PMe_3)_2(Si_2H_2)$ (**3-Rh**) containing the 2H-bridged Si_2H_2 species isomerizes to **2-Rha** with a considerable activation barrier (11.8 kcal/mol). $Pt(PR_3)_2(Si_2H_2)$ (**3-Pt** or **3-Pt′** for R = H or Me, respectively) containing the 2H-bridged Si_2H_2 species has almost the same energy as the Pt complex (**2-Pta** or **2-Pta′**) of the vinylidene-type Si_2H_2 species; the energy difference is only 0.2−0.3 kcal/mol. $Pt(PR_3)_2(Si_2H_2)$ (**1-Pt** and **1-Pt′**) containing the acetylene-type Si_2H_2 species is moderately less stable than **3-Pt** and **3-Pt′** by 6.6 (4.9) kcal/mol, while the acetylene-type Si_2H_2 species (**1**) is much less stable than **3** by 20.0 kcal/mol, where the energy values for R = H and Me are given without parentheses and in parentheses, respectively. Complex **1-Pt** isomerizes to **4-Pt** with a moderate activation barrier (5.4 kcal/mol), which further isomerizes either to **2-Pt** with a very small activation barrier (1.9 kcal/mol) or to **3-Pt** with a moderately small activation barrier (4.1 kcal/mol). From these results, several theoretical predictions are proposed, as follows: (1) The vinylidene-type Si_2H_2 species is stabilized by Rh(I) and Pt(0) complexes. (2) The acetylene-type Si_2H_2 species is stabilized by the Pt(0) complex. And, (3) the vinylidene-type Si_2H_2 species can be isolated as the Rh(I) complex.

Introduction

One of challenging research subjects in the chemistry of group 14 elements is to synthesize Si_2R_2 species (R = H, alkyl, aryl, etc.) containing either a Si=Si double bond or a Si≡Si triple bond (see **1** and **2** in Scheme 1).[1] As a result of considerable efforts, compounds containing Si=Si,[2,3a,b] Si=Ge,[3b,c] Si=Sn,[3d] Ge=Ge,[4a] Ge=Sn,[3e,5] Sn=Sn,[4b,6] and Pb=Pb[1e,7] double bonds have been successfully synthesized by introducing bulky substituents on these group 14 elements. Similar compounds of group 15 elements containing P=P,[8,9] As=As,[10] Sb=Sb,[11] and Bi=Bi[11] double bonds have been synthesized by introducing bulky substituents as well. However, an

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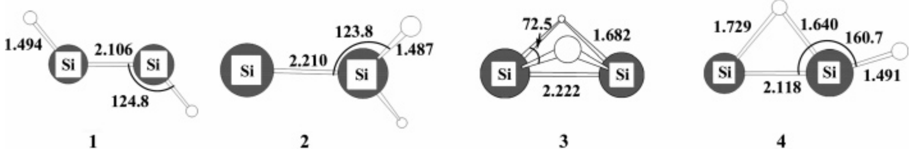
Scheme 1[a]



[a] The DFT/BS-I optimized bond distances and bond angles are given in angstroms and degrees, respectively.

acetylene-type Si_2H_2 species (**1** in Scheme 1) containing a Si≡Si triple bond has not been synthesized. This is because **1** is not stable and easily isomerizes to the valence isomer, 2H-bridged Si_2H_2 species (**3** in Scheme 1) through the 1H-bridged Si_2H_2 species (**4** in Scheme 1), as reported in many theoretical works.[12−15] Actually, **3** was spectroscopically detected.[16] Very recently, however, the acetylene-type Si_2R_2 species was successfully synthesized by introducing bulky substituents on the Si atoms.[17,18]

On the other hand, vinylidene-type Si_2H_2 species **2** containing a Si═Si double bond has not been isolated yet. No proposal has been presented for isolation of the vinylidene-type Si_2R_2 species, whereas introduction of bulky substituents on group 14 elements was effective to isolate the acetylene-type Si_2H_2 species, as recently succeeded experimentally[17,18] and proposed theoretically.[19] The other plausible method to stabilize the vinylidene-type Si_2R_2 and acetylene-type Si_2R_2 species is to coordinate these species with a transition-metal complex. Actually, similar Sb_2R_2 species coordinate with $Fe(CO)_4$ and $Pt(PEt_3)_2$ to form stable complexes, as experimentally reported.[20−22] In this regard, the transition-metal complexes of **1** and **2** are of considerable interest. Also, it is still interesting to isolate transition-metal complexes of the acetylene-type Si_2R_2 species and the vinylidene-type Si_2R_2 species without bulky substituents.

In this work, we wish to report a theoretical investigation of transition-metal complexes of various isomers of Si_2H_2, where $RhCl(PMe_3)_2$, $Pt(PMe_3)_2$, and $Pt(PH_3)_2$ were employed as transition-metal moieties. We selected these complexes for the following reasons: (1) $RhCl(PR_3)_2$ and $Pt(PMe_3)_2$ were reported to coordinate with dinitrogen[23] and distibene,[21] respectively, (2) it is likely that the coordinate bond of Sb_2R_2 is similar to that of Si_2H_2, and (3) because the dinitrogen ligand is labile, the transition-metal dinitrogen complex is expected to be a good precursor for the complex of Si_2H_2. Our intentions here are to present the first theoretical knowledge of transition-metal complexes with various Si_2H_2 species and to predict whether the transition-metal complex is useful to stabilize **1** and **2**.

Computations

Geometries were optimized by the DFT method with the B3LYP functional,[24,25] where a reasonable basis set system (BS-I) was employed. In BS-I, LANL2DZ[26] basis sets were used for Rh and Pt. For Cl and P atoms, LANL2DZ basis sets augmented with one d-polarization function were employed.[27,28] 6-311G(d, p)[29] and 6-31G(d)[30] were used for Si_2H_2 and the Me group of PMe_3, respectively. We ascertained that each equilibrium structure exhibited no imaginary frequency and each transition state had only one imaginary frequency; see Supporting Information Table S1 for the Cartesian coordinates of optimized geometries including transition states.

Relative energies and binding energies of various isomers of $Pt(PR_3)_2(Si_2H_2)$ and $RhCl(PMe_3)_2(Si_2H_2)$ were evaluated by the DFT, MP2-MP4(SDTQ), and CCSD(T) methods[31] with a better basis set system (BS-II). In BS-II, (541/541/211/1) and (541/541/111/1) basis sets were used for Rh and Pt,[32,33] respectively, with the same effective core potentials as those of LANL2DZ. The cc-pVTZ basis sets[34] were employed for Si_2H_2. The same basis sets as those of BS-I were used for the other moieties. Relative energies of Si_2H_2 isomers calculated by the DFT/BS-II and CCSD(T)/BS-II methods are similar to those previously calculated by the CCSD(T) method with good basis sets[13] (see Supporting Information Table S2). These calculations were carried out with the Gaussian 98 program package.[35] Population analysis was carried out with the method proposed by Weinhold et al.[36] A contour map of the molecular orbital was drawn with the Molden package.[37]

Results and Discussion

Geometries of $Pt(PH_3)_2(Si_2H_2)$, $Pt(PMe_3)_2(Si_2H_2)$, and $RhCl(PMe_3)_2(Si_2H_2)$. As shown in Figures 1, 2,

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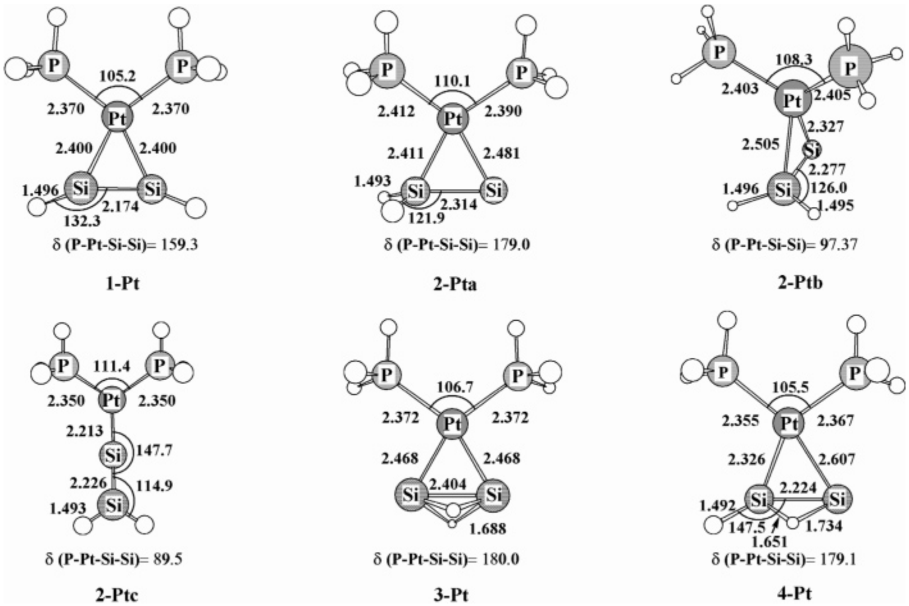


Figure 1. Optimized geometries of various isomers of $Pt(PH_3)_2(Si_2H_2)$. Bond lengths are in angstroms and bond angles in degrees.

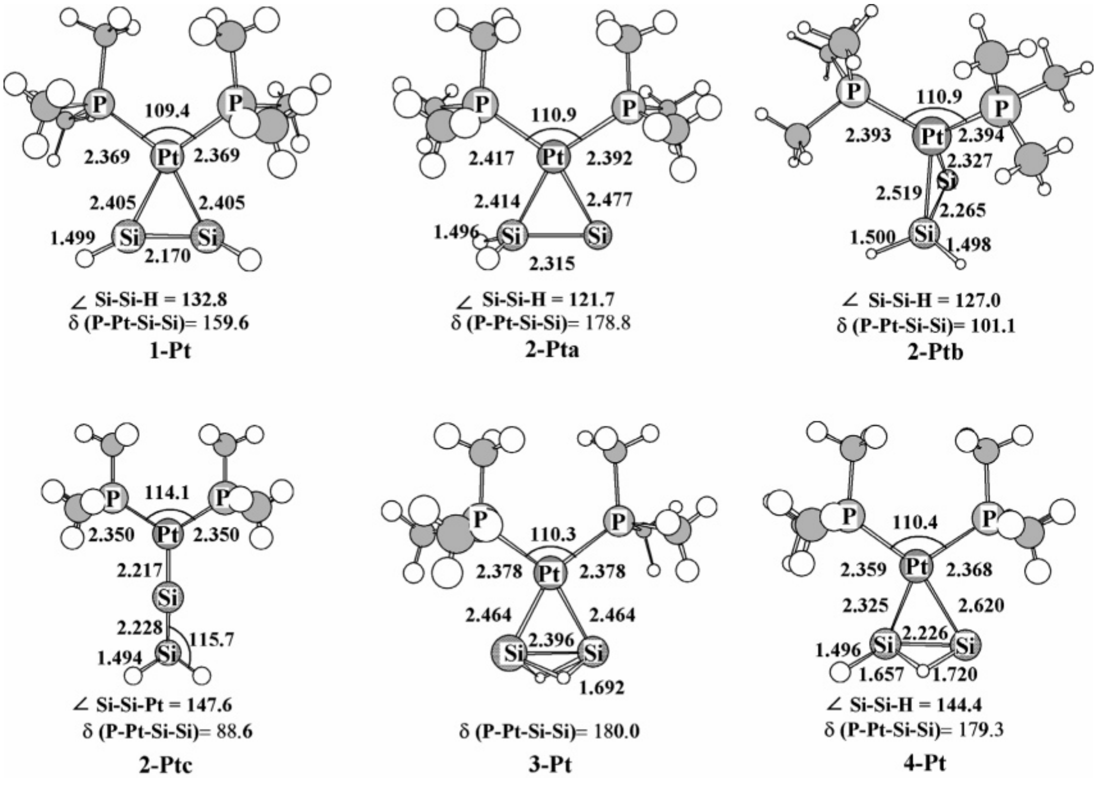
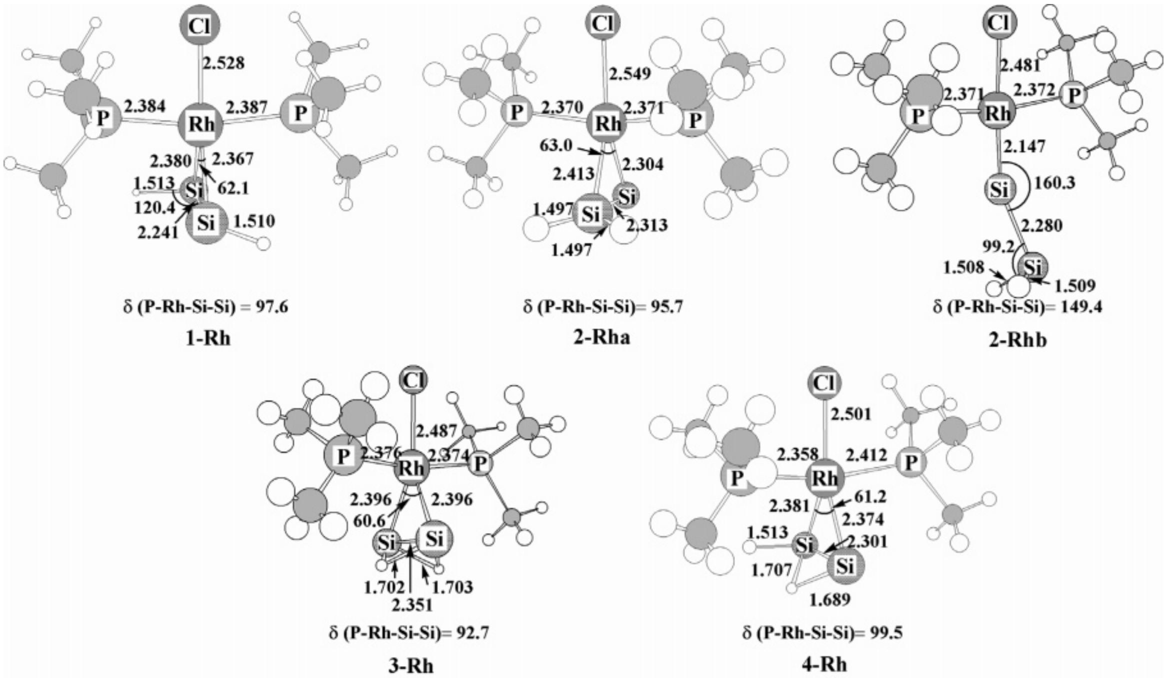


Figure 2. Optimized geometries of various isomers of $Pt(PMe_3)_2(Si_2H_2)$. Bond lengths are in angstroms and bond angles in degrees.

and 3, all Si_2H_2 species (**1**, **2**, **3**, and **4**) coordinate with $Pt(PH_3)_2$, $Pt(PMe_3)_2$, and $RhCl(PMe_3)_2$ to afford stable Pt(0) and Rh(I) complexes. Hereafter, notations of **1-Pt**, **1-Pt′**, **1-Rh**, etc., are used to represent complexes of **1**, etc., with $Pt(PH_3)_2$, $Pt(PMe_3)_2$, and $RhCl(PMe_3)_2$, respectively. In the Pt(0) and Rh(I) complexes (**1-Pt**, **1-Pt′**, and **1-Rh**) of **1**, the Si−Si distance becomes longer than that of **1** by ca. 0.064 and 0.135 Å, respectively, as generally observed in the complexes of ethylene and acetylene with a transition-metal element. The Rh−Si distance is somewhat shorter than the Pt−Si distance, which is consistent with the longer Si−Si bond of **1-Rh** than those of **1-Pt** and **1-Pt′**. In the Pt(0) and Rh(I) complexes (**2-Pt**, **2-Pt′**, and **2-Rh**) of **2**, several coordination structures were optimized; the Si_2H_2 species interacts with the metal center with η^2-side-on coordination to afford **2-Pta**, **2-Pta′**, **2-Ptb**, **2-Ptb′**, and **2-Rha**, and with η^1-end-on coordination to afford **2-Ptc**, **2-Ptc′**, and **2-Rhb**. Several differences are observed between Pt(0) and Rh(I) complexes; the Si−Si bond is on the molecular plane in **2-Pta** and **2-Pta′** and perpendicular to the molecular plane in **2-Ptb** and **2-Ptb′**, while the Si−Si bond is not allowed to be on the molecular plane in **2-Rha** probably because of the steric



δ (P-Rh-Si-Si) = 97.6

1-Rh

δ (P-Rh-Si-Si)= 95.7

2-Rha

δ (P-Rh-Si-Si)= 149.4

2-Rhb

δ (P-Rh-Si-Si)= 92.7

3-Rh

δ (P-Rh-Si-Si)= 99.5

4-Rh

Figure 3. Optimized geometries of various isomers of $RhCl(PMe_3)_2(Si_2H_2)$. Bond lengths are in angstroms and bond angles in degrees.

repulsion between Si_2H_2 and the two PMe_3 ligands. The Si−Si bond becomes longer in the order **2** < **2-Ptc**, **2-Ptc′** < **2-Ptb**, **2-Ptb′** < **2-Pta**, **2-Pta′** < **2-Rhb** < **2-Rha**. It is noted that the Si−Si bond distance is much longer in the side-on complex than in the end-on complex. This geometry difference suggests that the coordinate bond is stronger in the side-on complex than in the end-on one, as will be discussed below.

In Pt(0) and Rh(I) complexes (**3-Pt**, **3-Pt′**, and **3-Rh**) of **3**, the Si−Si distance is considerably longer than that of **3**. The Pt−Si and Rh−Si distances of **3-Pt**, **3-Pt′**, and **3-Rh** are somewhat longer than those of **1-Pt**, **1-Pt′**, **2-Pta**, **2-Pta′**, **1-Rh**, and **2-Rha**, respectively, which suggests that the coordinate bond of **3** is weaker than those of **1** and **2**, as will be shown below. In the Pt(0) and Rh(I) complexes (**4-Pt**, **4-Pt′**, and **4-Rh**) of **4**, the geometrical features are similar to those of **3-Rh, 3-Pt**, and **3-Pt′** except for the position of one H atom.

Relative Stabilities of Various Isomers of $Pt(PH_3)_2(Si_2H_2)$, $Pt(PMe_3)_2(Si_2H_2)$, and $RhCl(PMe_3)_2(Si_2H_2)$. In $Pt(PH_3)_2(Si_2H_2)$, the relative stabilities of various structures were evaluated with the DFT, MP2 to MP4(SDTQ), and CCSD(T) methods, as shown in Table 1. Although the relative energy of **1-Pt** moderately fluctuates upon going to CCSD(T) from MP2, the relative energies of the other Pt(0) complexes fluctuate much less upon going from MP2 to CCSD(T). Also, it should be noted that the DFT and CCSD(T) methods provide similar relative energies in all isomers. Thus, the relative energies of various isomers were evaluated with the DFT method in such larger complexes as $Pt(PMe_3)_2(Si_2H_2)$ and $RhCl(PMe_3)_2(Si_2H_2)$. Energy values calculated by the DFT method are given hereafter unless another computation method is mentioned.

Important results are summarized, as follows: (1) Interestingly, **2-Pta**, **2-Ptb**, **3-Pt, 2-Pta′**, **2-Ptb′**, and **3-Pt′** have similar energies and are much more stable than **4-Pt** and **4-Pt′**, whereas **2** is much less stable than **3** by 11.5 kcal/mol. Because **2-Ptc** and **2-Rhb** are much less stable than **2-Pta** and **2-Rha**, respectively, **2-Ptc** and **2-Rhb** will not be discussed hereafter. (2) Although **1** is much less stable than **3** by 20.0 kcal/mol, **1-Pt** is moderately less stable than **3-Pt** by 4.9 kcal/mol (CCSD(T)) and 6.6 kcal/mol (DFT). Also, **1-Pt′** is moderately less stable than **3-Pt′** by 4.9 kcal/mol. These results indicate that **1** is much more stabilized by the coordination with the Pt center than **3**. (3) In the Rh(I) complexes, **2-Rh** is the most stable and **3-Rh** is the next most stable. (4) Complexes **1-Rh** and **4-Rh** are much less stable than **2-Rh** by 16.8 and 14.1 kcal/mol, respectively. From these results, it is concluded that $Pt(PR_3)_2$ stabilizes **1** and **2** and $RhCl(PMe_3)_2$ stabilizes **2**.

In particular, $RhCl(PMe_3)_2$ is interesting because its vinylidene-type Si_2H_2 complex **2-Rh** is the most stable in various Rh(I) complexes of Si_2H_2 species. Because $RhCl(N_2)(PR_3)_2$ is experimentally isolated[23b,c] and the

Table 1. Relative Stabilities (kcal/mol) and Various Geometries of $Pt(PH_3)_2(Si_2H_2)$, $Pt(PMe_3)_2(Si_2H_2)$, and $RhCl(PMe_3)_2(Si_2H_2)$[a]

	1	2a	2b	2c	3	4
(a) $Pt(PH_3)_2(Si_2H_2)$						
DFT	6.6	0.2	1.6	14.5	0.0	3.7
MP2	2.1	2.9	−4.8	21.4	0.0	0.9
MP3	8.0	0.6	3.8	20.0	0.0	2.2
MP4(DQ)	6.7	−0.5	−2.5	19.3	0.0	2.4
MP4(SDQ)	6.4	−1.0	−4.4	18.3	0.0	2.8
MP4(SDTQ)	2.5	0.5	-	17.8	0.0	1.8
CCSD	7.2	−1.2	−0.2	19.3	0.0	2.6
CCSD(T)	4.9	0.0	−1.5	18.8	0.0	2.0
(b) $Pt(PMe_3)_2(Si_2H_2)$						
DFT	4.9	−0.3	0.1	9.7	0.0	3.6
(c) $RhCl(PMe_3)_2(Si_2H_2)$						
DFT	11.3	−5.5	9.3	0.0	8.6	

(d) Si_2H_2	1	2	3	4
DFT	20.0	11.5	0.0	10.3
CCSD(T)	17.7	12.3	0.0	10.0

[a] Relative energy in kcal/mol and orbital energy in eV.

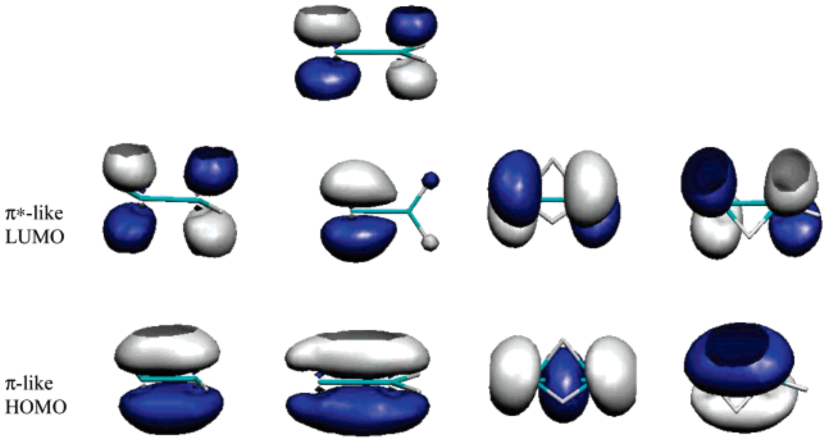


Figure 4. HOMO and LUMO of various Si_2H_2 species.

dinitrogen ligand is labile, we expect that $RhCl(N_2)(PR_3)_2$ is useful as a precursor complex to synthesize the Rh(I) complex of **2**. Thus, we examined the substitution reaction of N_2 for Si_2H_2 in $RhCl(N_2)(PMe_3)_2$.

$$RhCl(N_2)(PMe_3)_2 + Si_2H_2\ (\mathbf{2}) \rightarrow RhCl(Si_2H_2)(PMe_3)_2\ (\mathbf{2\text{-}Rha}) + N_2 \quad (1)$$

The reaction of eq 1 was evaluated to be extremely exothermic; the total energy change is −53.1 kcal/mol, $\Delta H°$ is −52.3 kcal/mol, and $\Delta G°$ is −49.5 kcal/mol at 298 K, where the vibration frequencies were evaluated with the DFT/BS-I method. This result strongly suggests that $RhCl(N_2)(PMe_3)_2$ is useful to stabilize **2**.

Coordinate Bonding Nature of Si_2H_2 with $Pt(PR_3)_2$ and $RhCl(PMe_3)_2$. It is of considerable importance to clarify the reasons why **2** is stabilized by the coordination with the Pt(0) and Rh(I) centers relative to **3** and why **1** is stabilized by the coordination with the Pt(0) center relative to **3**. The fundamental picture of the coordinate bonding nature is indispensable to clarify the reason. Here, we wish to discuss the coordinate bonding nature of Si_2H_2 with the metal center. The Rh atomic population considerably increases by the coordination of Si_2H_2 in all complexes examined here, while the Pt atomic population decreases, as shown in Table 2. Consistent with these population changes, the electron population of Si_2H_2 decreases in the Rh(I) complexes but increases in the Pt(0) complexes. These results indicate that the σ-donation mainly participates in the coordinate bond of the Rh(I) complexes, but the π-back-donation mainly participates in the coordinate bond of the Pt(0) complexes.

To inspect the bonding nature in more detail, we need the knowledge of the frontier orbitals of **1** to **4**. In **1**, π and π* orbitals are calculated at −5.75 and −3.57 eV, respectively, with the DFT/BS-II method, where Kohn−Sham orbitals are given hereafter (see Figure 4).[38] In **2**, π-, π*-, and π-type empty p orbitals participate in the coordinate bond with the metal center in the side-on coordination complexes. Their orbital energies are calculated to be −5.65, −1.84, and −3.65 eV, respectively. Although the LUMO (empty p orbital) is at considerably low energy, it does not overlap well with the d_π orbital of the metal center because it is perpendicular to the coordinate bond (see Figure 4). Thus, **2** does not form the strong π-back-donation unlike **1**. In **3**, the shape of the LUMO resembles that of the π* orbital, while it is at the highest energy (−0.01 eV) in the LUMOs of these Si_2H_2 species. Although its HOMO is of similar energy to those of the other Si_2H_2 species, the shape of the HOMO is much different from the usual π orbital and expands much less toward the metal center (see Figure 4). Interestingly, **4** possesses π- and π*-like orbitals at −5.79 and −2.20 eV, respectively.

Table 2. Electron Populations of Pt(0) and Rh(I) Complexes of Si_2H_2 and Frontier Orbital Energies of Si_2H_2

	1	2a	2b	3	4
(a) $Pt(PH_3)_2(Si_2H_2)$					
$\Delta\rho$(Pt)	−0.306	−0.214	−0.278	−0.209	−0.277
$\Delta\rho$(Pt d)	−0.117	−0.083	−0.107	−0.055	−0.092
$\Delta\rho(Si_2H_2)$	0.126	0.024	0.018	0.033	0.107
(b) $Pt(PMe_3)_2(Si_2H_2)$					
$\Delta\rho$(Pt)	−0.410	−0.309	−0.301	−0.375	
$\Delta\rho$(Pt d)	−0.136	−0.102	−0.067	−0.108	
$\Delta\rho(Si_2H_2)$	0.260	0.142	0.141	0.233	
(c) $RhCl(PMe_3)_2(Si_2H_2)$					
$\Delta\rho$(Rh)	0.243	0.314	0.319	0.292	
$\Delta\rho$(Rh d)	0.575	0.637	0.655	0.625	
$\Delta\rho(Si_2H_2)$	−0.153	−0.198	−0.237	−0.201	

(d) Si_2H_2	1	2	3	4
$\epsilon(\pi^*)$	-3.57	−1.84 -3.65^a	−0.01	−2.20
$\epsilon(\pi)$	−5.75	−5.65	−5.78	−5.79

[a] The empty p orbital on the terminal Si atom.

Frontier orbitals of the metal moiety are also important for discussion of the interaction between Si_2H_2 and the metal center. $RhCl(PMe_3)_2$ possesses one unoccupied d_σ orbital at −2.07 eV, but $Pt(PR_3)_2$ does not have such an unoccupied d orbital.[39a] The HOMO of $RhCl(PMe_3)_2$ is at −4.70 eV, and that of $Pt(PH_3)_2$ is at −4.44 eV.[39b]

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(38) Hartree−Fock orbital energies of π and π* orbitals are −7.59 and 1.29 eV, respectively, for **1**, −7.69 and −0.89 eV, respectively, for **2**, −7.95 and 1.27 eV, respectively, for **3**, and −7.64 and 1.37 eV, respectively, for **4**. Several differences are observed between the Hartree−Fock and Kohn−Sham orbitals; for instance, the LUMO of **1** is the lowest in Kohn−Sham orbital, but that of **2** is the lowest in Hartree−Fock orbital. The LUMO of **3** is the highest in Kohn−Sham orbital, but that of **4** is the higherst in Hartree−Fock orbital. Kohn−Sham orbital energies fit well with the relative stabilities of the Pt(0) and Rh(I) complexes.

(39) (a) In $Pt(PH_3)_2$, the empty 6s orbital is the LUMO, which is calculated at −1.69 eV. Although this orbital energy is not very high, the electron population indicates that the σ-donation to the Pt(0) center does not occur effectively. (b) The energies of the HOMO and LUMO were calculated with the distorted geometry of $Pt(PH_3)_2$, which is taken in **1-Pt**.

Thus, the σ-donation interaction is strongly formed between the HOMO of Si_2H_2 and the unoccupied d_σ orbital of the Rh(I) complex, but it is weak in the Pt(0) complex, while the π-back-donation is more strongly formed in the Pt(0) complex than in the Rh(I) complex.

It is noted that the HOMO of **2** is at much higher energy than that of **3** and the LUMO and π^* orbitals of **2** are at much lower energies than the LUMO of **3**. Thus, **2** much more strongly interacts with the metal center through the σ-donation and π-back-donation interactions than does **3**. As a result, **2-Rh** is more stable than **3-Rh** by 5.5 kcal/mol and **2-Pt** has a similar energy to **3-Pt**, though **2** is much less stable than **3** by 11.5 kcal/mol. We examined here how the coordination of Si_2H_2 changes the electron distribution, to confirm that the above discussion is correct. In **2-Rha**, the Rh atomic population increases by 0.314*e* and the electron population of the Si_2H_2 moiety decreases by 0.198*e* upon coordination of Si_2H_2, while in **3-Rh** the Rh atomic population increases by 0.319*e* and the electron population of the Si_2H_2 moiety decreases by 0.237*e*. These population changes do not clearly explain the reason that **2-Rha** is more stable than **3-Rh**. This is because the σ-donation and π-back-donation induce the opposite population changes. However, each d orbital population strongly supports the above discussion. In **2-Rha**, the $d_{x^2-y^2}$ orbital mainly participates in the σ-donation, the population of which increases (by 0.539*e*) to a greater extent than that (0.452*e*) in **3-Rh**.[40] The d_π orbital mainly contributes to the π-back-donation in **2-Rha**, the population of which decreases by 0.350*e* in **2-Rha** and by 0.242*e* in **3-Rh**. These population changes indicate that the σ-donation and π-back-donation are stronger in **2-Rha** than in **3-Rh**, as suggested above. In **2-Pt**, the d_π orbital population decreases more (by 0.239*e*) than that (0.132*e*) in **3-Pt**, while the other d orbital populations hardly change. These results clearly show that the π-back-donation is stronger in **2-Pt** than in **3-Pt**, but the σ-donation contributes little to the coordinate bonds of **2-Pt** and **3-Pt**, as suggested above. As a result, **2** is more stabilized by the coordination with Rh and Pt centers than **3**.

In **1**, the HOMO is at similar energy to that of **3**, whereas the LUMO of **1** is at a much lower energy than that of **3** (see Table 1). These features suggest that the π-back-donation is stronger in **1-Pt** and **1-Rh** than in **3-Pt** and **3-Rh**, respectively. Actually, the electron population of Si_2H_2 increases more in **1-Pt** than in **3-Pt**. As a result, **1-Pt** is moderately less stable than **3-Pt** by 4.9 kcal/mol, although **1** is much less stable than **3** by 20.0 kcal/mol. In **1-Rh**, the electron population of Si_2H_2 decreases. This is because not only π-back-donation but also σ-donation participate in the coordinate bond of **1-Rh**. Actually, the Si_2H_2 coordination with the Rh center increases the $d_{x^2-y^2}$ orbital population by 0.514*e* in **1-Rh** compared with that (0.452*e*) in **3-Rh**. Thus, **1** is stabilized by the coordination with the Rh center, too; actually, the energy difference (11.3 kcal/mol) between **1-Rh** and **3-Rh** is much smaller than that (20.0 kcal/mol) between **1** and **3**.

The LUMO of **4** is at considerably lower energy than that of **3**. This feature suggests that the π-back-donation contributes more to the coordinate bond of **4** than that of **3**; actually, the Si_2H_2 coordination with the Pt center increases more the electron population of Si_2H_2 in **4-Pt** than in **3-Pt**. As a result, **4-Pt** is moderately less stable than **3-Pt** by 3.7 kcal/mol, although **4** is much less stable than **3** by 10.0 kcal/mol. In the Rh(I) complex, the π-back-donation is not strong, unlike that in the Pt(0) complex, as was discussed above. The σ-donation is not very much different between **3-Rh** and **4-Rh**, because the HOMO of **4** is at an energy similar to that of **3**, while the former orbital expands more toward the metal center than the latter one. As a result, the energy difference between **4-Rh** and **3-Rh** is not very much different from that between **4** and **3**.

The differences between Rh(I) and Pt(0) complexes are of considerable interest. The difference between **2-Pta** and **2-Rha** is easily interpreted in terms of the frontier orbitals of $RhCl(PMe_3)_2$ and $Pt(PR_3)_2$. In the Rh(I) complex, both σ-donation and π-back-donation contribute to the coordinate bond, while the π-back-donation mainly contributes to the coordinate bond in the Pt(0) complex, as was discussed above. Because **2** can form both σ-donation and π-back-donation but **3** does not form well the σ-donation and π-back-donation interactions, **2** is much more stabilized by the coordination with the Rh(I) center than by the coordination with the Pt(0) center, but **3** is not stabilized very much by the coordination with both Pt(0) and Rh(I) centers. Thus, **2-Rha** is much more stable than **3-Rh**, but **2-Pta** has a similar energy to **3-Pt**. On the other hand, **1-Pt** is moderately less stable than **3-Pt** by 6.6 kcal/mol, but **1-Rh** is considerably less stable than **3-Rh** by 11.3 kcal/mol. It is interesting that **1** is more stabilized by the coordination with the Pt(0) center than by the coordination with the Rh(I) center, although **2** is more stabilized by the coordination with the Rh(I) center than by the coordination with the Pt(0) center. This difference between Pt(0) and Rh(I) complexes strongly suggests that the π-back-donation is necessary to stabilize the metal complex of **1**. This is not surprising, because the shape of the π^* orbital is different between **1** and **2**; **1** is the best for the π-back-donation because its π^* orbital is at low energy and its shape resembles well that of acetylene, which is favorable for the π-back-donation, while the LUMO of **2** is at an energy similar to that of **1**, but it does not overlap well with the d_π orbital of the metal center, as discussed above (also, see Figure 4). Thus, the π-back-donation is important to stabilize the metal complex of **1**, but the σ-donation is important to stabilize the metal complex of **2**. As a result, the Pt(0) complex is favorable for the stabilization of **1**, but the Rh(I) complex is favorable for the stabilization of **2**.

From the above discussion,[41] it is concluded that $RhCl(PMe_3)_2$ with an unoccupied d_σ orbital is useful to isolate **2** and $Pt(PR_3)_2$ with a doubly occupied d_π orbital at high energy is useful to stabilize **1**.

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(40) Strictly speaking, the σ and π orbitals cannot be defined, because these complexes are not symmetrical. However, the $d_{x^2-y^2}$ orbital mainly participates in the σ-donation and the d_{xz} or d_{xy} orbital mainly participates in the π-back-donation.

(41) (a) The qualitative discussion of bonding nature is presented here. More detailed discussion would be possible with the energy decomposition analysis if the complexes here had some symmetry to separate the σ-donation and π-back-donation, as reported recentely.[41b] (b) Frenking, G.; Wichmann, K.; Fröhlich, N.; Loschen, C.; Lein, M.; Frunzke, J.; Rayón, V. M. *Coord. Chem. Rev.* **2003**, *238*–*239*, 55. Petz, W.; Kutschera, C.; Heitbaum, M.; Frenking, G.; Tonner, R.; Neumüller, B. *Inorg. Chem.* **2005**, *44*, 1263, and references therein.

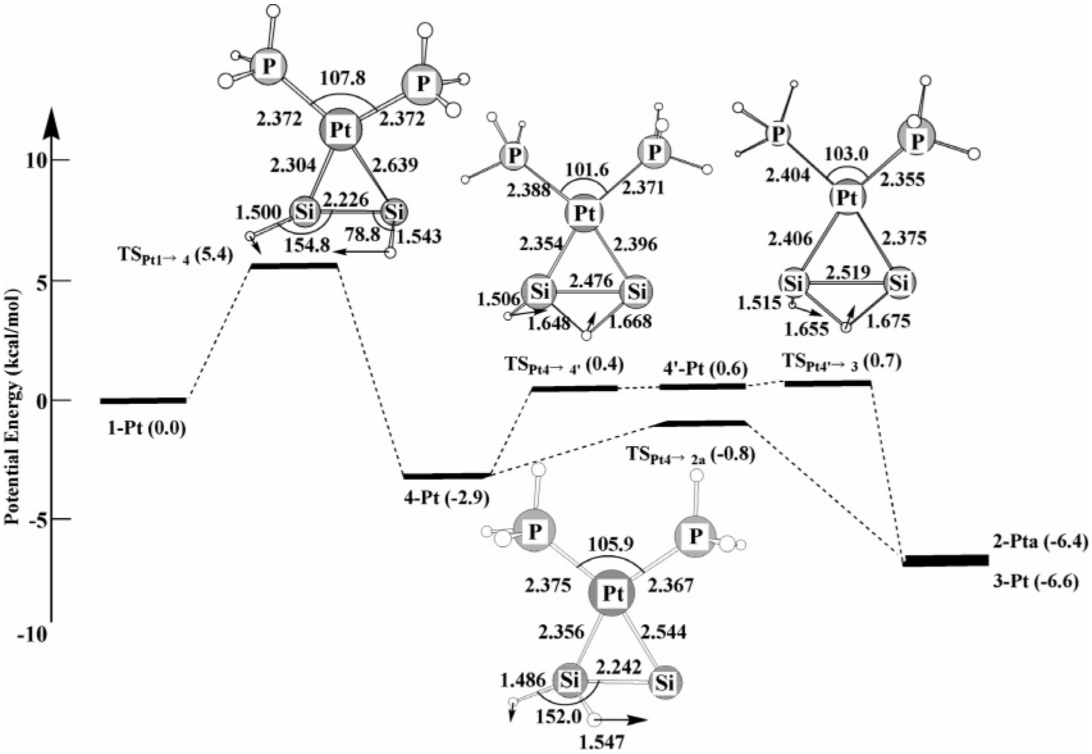

Figure 5. Transition states and relative energy (in kcal/mol) in the isomerization of $Pt(PH_3)_2(Si_2H_2)$. Bond lengths are in angstroms and bond angles in degrees. The DFT/BS-II method was employed.

Si−Si Bond of Si_2H_2 in Pt(0) and Rh(I) Complexes. It is of considerable interest whether the Si≡Si triple bond is kept in the Pt(0) and Rh(I) complexes of **1** and the Si=Si double bond is kept in the Pt(0) and Rh(I) complexes of **2**. In **1**, the occupation number of the NBO analysis is 2.00 for the Si−Si σ-bonding orbital and 1.879 and 1.873 for two Si−Si π-bonding orbitals, where the DFT/BS-II method was employed to evaluate the occupation number. In **2**, the occupation number is 2.00 for the σ-bonding orbital and 1.977 for the π-bonding orbital. These results suggest that the Si−Si bond is understood to be a triple bond in **1** and a double bond in **2**.

In **1-Pt**, on the other hand, the occupation number is 1.932 for the Si−Si σ-bonding orbital and 1.865 for the Si−Si π-bonding orbital. In **1-Rh**, the occupation number is 1.848 for the σ-bonding orbital and 1.760 for the π-bonding oribital. In **2-Pta** and **2-Pta′**, the occupation number of the Si−Si σ-bonding orbital is 1.981 and 1.982, respectively. In **2-Rha**, it is 1.968. However, the occupation number for the Si−Si π-bonding orbital disappears in **2-Pta**, **2-Pta′**, and **2-Rha**. These results indicate that the Si≡Si triple bond of **1** and the Si=Si double bond of **2** become a Si=Si double bond and a Si−Si single bond, respectively, by the Si_2H_2 coordination with the Pt(0) and Rh(I) centers. These features are not surprising because the σ-donation and the π-back-donation weaken the Si−Si π-bonding interaction to decrease the Si−Si bond order.

Although the Si−Si bond is understood to be a Si=Si double bond in **1-Pt** and **1-Rh** and to be a Si−Si single bond in **2-Pta**, **2-Pta′**, and **2-Rha**, the Pt(0) and Rh(I) complexes of **1** and **2** are still worthy of investigation, as follows: Such Si−Si bonds in **1-Pt**, **2-Pta**, **1-Rh**, and **2-Rha** are perturbed by transition-metal complexes and their electronic structures become different from those of the Si_2H_2-free species. These features are interesting in both applied chemistry and fundamental chemistry. Also, it is expected that these Rh(I) and Pt(0) complexes are useful to trap such transient species as **1** and **2** and to utilize them in new chemical reactions.

Isomerization of the Si_2H_2 Moiety in $Pt(PH_3)_2$ and $RhCl(PMe_3)_2$.[42]As reported previously, **1** easily isomerizes to the most stable Si_2H_2 species **3** through **4**. It is of considerable interest to theoretically investigate how easily (or with difficulty) the isomerization of Si_2H_2 takes place in the Pt(0) and Rh(I) complexes. As shown in Figure 5, **1-Pt** isomerizes to **4-Pt** with a moderate activation barrier of 5.4 kcal/mol and small exothermicity of 2.9 kcal/mol. The activation barrier is similar to that of the isomerization of free Si_2H_2 species reported previously.[15,43] The exothermicity is much smaller than that of the isomerization of free Si_2H_2 species because the energy difference between **1-Pt** and **4-Pt** is much smaller than that between **1** and **4**. Complex **4-Pt** further isomerizes to **2-Pta** with a very small activation barrier of 2.1 kcal/mol and small exothermicity of 3.5 kcal/mol. Also, **4-Pt** isomerizes to **3-Pt** with a very small activation barrier of 1.7 kcal/mol and small exothermicity of 3.7 kcal/mol. This isomerization does not take place through one transition state but through intermediate **4-Pt′**, the geometry of which is given in Supporting Information Figure S2.

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[42] The isomerization reactions were not investigated in $Pt(PMe_3)_2(Si_2H_2)$ because we consumed a lot of CPU time to optimize the transition states of the isomerization of the smaller $Pt(PH_3)_2(Si_2H_2)$ complex. However, it is likely that the isomerization reactions similarly take place in $Pt(PMe_3)_2(Si_2H_2)$ because the relative stabilities of isomers of $Pt(PH_3)_2(Si_2H_2)$ are similar to those of $Pt(PMe_3)_2(Si_2H_2)$.

[43] The basis sets and method used are different between the previous work[15] and the present one. However, it is likely that a qualitative comparison can be made between the previous work and this work; actually, the relative stabilities of Si_2H_2 isomers presented here are similar to those reported in the previous work.

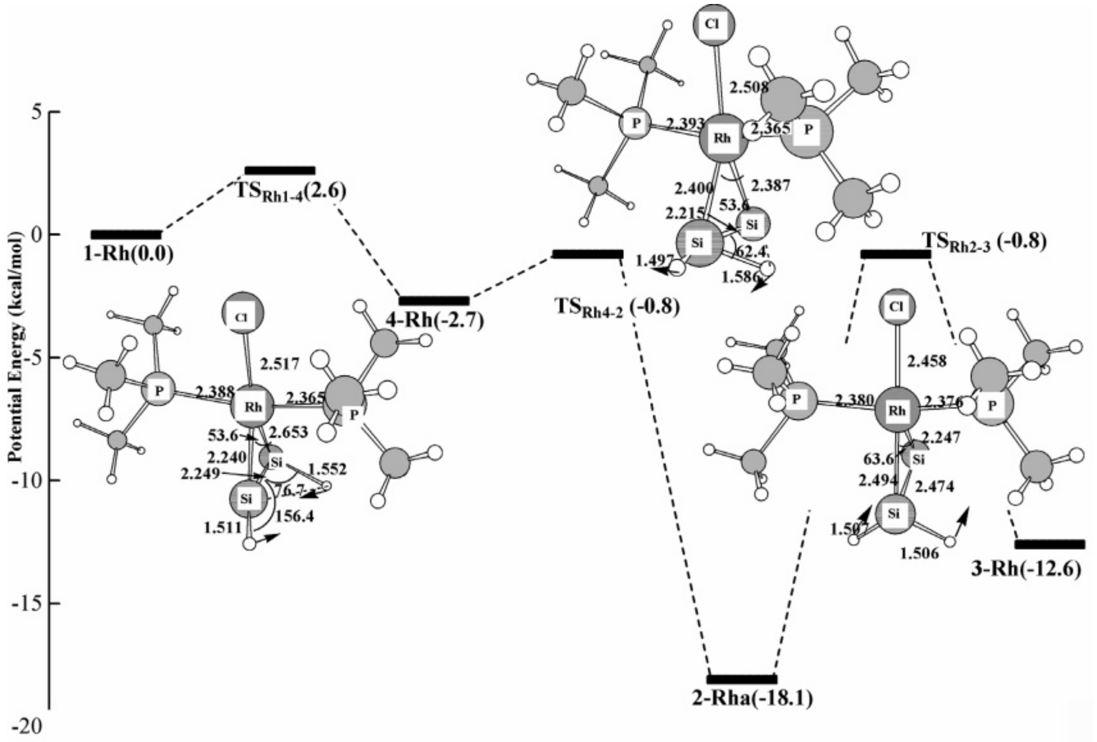

Figure 6. Transition states and relative energy (in kcal/mol) in the isomerization of Pt(PH_3)$_2$(Si_2H_2). Bond lengths are in angstroms and bond angles in degrees. The DFT/BS-II method was employed.

However, discussion of **4-Pt′** is omitted here because it takes a geometry similar to those of **TS$_{Pt4-4'}$** and **TS$_{Pt4'-3}$** and it has almost the same energy as **TS$_{Pt4-4'}$** and **TS$_{Pt4'-3}$**; in other words, **4-Pt′** is a transient species similar to **TS$_{Pt4-4'}$** and **TS$_{Pt4'-3}$**. These activation barriers and energies of reaction are smaller than those of the isomerizations of **4**; for instance, **4** isomerizes to **3** with a considerable activation barrier and exothermicity (6.0 and 9.0 kcal/mol, respectively) and isomerizes to **2** with a considerable activation barrier and endothermicity (7.0 and 5.1 kcal/mol, respectively). It is noted that although **4** isomerizes to **2** with a considerable activation barrier (7.0 kcal/mol), **4-Pt** easily isomerizes not only to **3-Pt** but also to **2-Pta** with a very small activation barrier. This is because **2-Pta** is more stable than **4-Pt**, but **2** is considerably less stable than **4**. Also, the opposite isomerization from **2-Pta** to **4-Pt** and that from **3-Pt** to **4-Pt** easily take place with small activation barriers. These results suggest that (1) **2-Pta** is produced from **1-Pt**, (2) **2-Pta** is in equilibrium with **3-Pt**, and (3) the interconversion between **2-Pta** and **3-Pt** easily occurs through **4-Pt**.

Similarly, **1-Rh** easily isomerizes to **4-Rh** with a very small activation barrier of 2.6 kcal/mol and a very small exothermicity of 2.7 kcal/mol, as shown in Figure 6. Complex **4-Rh** further isomerizes to **2-Rha** with a very small activation barrier of 1.9 kcal/mol and a considerably large exothermicity of 15.4 kcal/mol. This is because **2-Rha** is much more stable than **4-Rh**. It is noted also that **2-Rha** isomerizes to **3-Rh** with a considerably large activation barrier of 17.3 kcal/mol and somewhat large endothermicity of 5.5 kcal/mol. From these results, it is reasonably concluded that **2-Rha** can be isolated from RhCl(PMe_3)$_2$ and Si_2H_2 if some of **1**, **2**, and **4** is produced. However, **2-Rha** cannot be produced from RhCl(PMe_3)$_2$ and **3**, because the isomerization from **3-Rh** to **2-Rha** needs a considerably large activation barrier of 11.6 kcal/mol.

At the end of this section, we wish to mention the absences of the **4-Rh** → **3-Rh** isomerization and the **2-Pta** → **3-Pt** isomerization. The transition state of the **2-Pta** → **3-Pt** isomerization was not found in the Pt(0) complexes. Similarly, the **2** → **3** isomerization was not presented in the Si_2H_2-free species.[15] This is easily understood, as follows: Because two H atoms must move in this isomerization, it is likely that this isomerization does not occur easily. The absence of the **2-Pta** → **3-Pt** isomerization corresponds to the result that the potential energy surface (PES) of Pt(PH_3)$_2$(Si_2H_2) is not very much different from that of the free Si_2H_2 species except that **2-Pt** has a similar energy to **3-Pt** and the PES is more flat than that of the free Si_2H_2 species. In the Rh(I) complexes, on the other hand, the transition state of this **3-Rh** → **2-Rha** isomerization was presented, but the transition state of the **4-Rh** → **3-Rh** isomerization could not be found (see Supporting Information Figure S3), unlike the Pt(0) complexes and the free Si_2H_2 species. This is easily understood by considering that **2-Rha** is much more stable than **3-Rh** and **4-Rh**, as follows: Usually, the **4** ↔ **2** and **4** ↔ **3** interconversions more easily take place than the **2** ↔ **3** interconversion because one H atom moves in the former interconversions, as observed in the free Si_2H_2 species and Pt(0) complexes (see above). In the Rh(I) complexes, however, **2-Rha** is much more stable than **3-Rh** and **4-Rh**. As a result, the **3-Rh** ↔ **4-Rh** interconversion tends to shift to the **3-Rh** ↔ **2-Rha** interconversion; in other words, if the geometry of **3-Rh** started to change toward **4-Rh** or if the geometry of **4-Rh** started to change toward **3-Rh**, the geometry changes shifted toward **2-Rha**. Thus, the **3-Rh** ↔ **2-Rha** and **4-Rh** ↔

2-Rha interconversions occur, but the **3-Rh** ↔ **4-Rh** interconversion does not.

Conclusions

Rh(I) and Pt(0) complexes of various isomers of Si_2H_2 species were theoretically investigated mainly with the DFT method, while MP2 to MP4(SDTQ) and CCSD(T) methods were used in several calculations. $RhCl(PMe_3)_2(Si_2H_2)$ (**2-Rha**) containing the vinylidene-type Si_2H_2 species is calculated to be the most stable in various Rh(I) complexes of Si_2H_2. This is very interesting because the vinylidene-type Si_2H_2 species (**2**) is much less stable than the most stable 2H-bridged Si_2H_2 species (**3**) by 11.5 kcal/mol, where the energy calculated by the DFT method is given hereafter. $RhCl(PMe_3)_2(Si_2H_2)$ (**1-Rh**) containing the acetylene-type Si_2H_2 species easily isomerizes to the Rh complex (**4-Rh**) of the 1H-bridged Si_2H_2 species with a small activation barrier (2.6 kcal/mol) and small exothermicity (2.7 kcal/mol). Complex **4-Rh** further isomerizes to **2-Rha** with a very small activation barrier (1.9 kcal/mol) and significantly large exothermicity (15.4 kcal/mol). On the other hand, $RhCl(PMe_3)_2(Si_2H_2)$ (**3-Rh**) containing the 2H-bridged Si_2H_2 species isomerizes to **2-Rha** with a considerable activation barrier (11.8 kcal/mol) and a moderate exothermicity (5.5 kcal/mol). From these results, it should be concluded that **2-Rha** can be isolated from $RhCl(PMe_3)_2$ and acetylene-type Si_2H_2, vinylidene-type Si_2H_2, and 1H-bridged Si_2H_2 species.

$Pt(PR_3)_2(Si_2H_2)$ (**3-Pt** or **3-Pt′** for R = H or Me, respectively) containing the 2H-bridged Si_2H_2 species has almost the same energy as the Pt(0) complex (**2-Pta** or **2-Pta′**) of the vinylidene-type Si_2H_2 species; the energy difference is only 0.2−0.3 kcal/mol. $Pt(PR_3)_2(Si_2H_2)$ (**1-Pt** and **1-Pt′**) containing the acetylene-type Si_2H_2 species is moderately less stable than **3-Pt** and **3-Pt′**, by 6.6 (4.9) kcal/mol, although the acetylene-type Si_2H_2 species (**1**) is much less stable than **3**, by 20.0 kcal/mol, where the energy value is given without parenthesis for R = H and in parentheses for R = Me. Complex **1-Pt** isomerizes to **4-Pt** with a moderate activation barrier (5.4 kcal/mol) and very small exothermicity (2.9 kcal/mol). Complex **4-Pt** further isomerizes either to **2-Pt** with a very small activation barrier (1.9 kcal/mol) and small exothermicity (3.5 kcal/mol) or to **3-Pt** with a moderately small activation barrier (4.1 kcal/mol) and small exothermicity (3.7 kcal/mol). These results lead to the conclusion that **1** and **2** are stabilized by coordination with the Pt(0) center. However, it is not easy to isolate **1-Pt** because **1-Pt** easily isomerizes to either **2-Pta** or **3-Pt** through **4-Pt**. Although the isolation of **1-Pt** is difficult, we wish to propose the possibility that **2-Pta** would be synthesized as a mixture with **3-Pt** because it has almost the same energy as **3-Pt** and the interconversion between **2-Pta** and **3-Pt** easily takes place through **4-Pt**.

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Supporting Information Available: Complete form of ref 35. Tables of optimized geometries of various isomers of $Pt(PH_3)_2(Si_2H_2)$, $Pt(PMe_3)_2(Si_2H_2)$, and $RhCl(PMe_3)_2(Si_2H_2)$ and relative energies of various Si_2H_2 species calculated with DFT, MP2-MP4(SDTQ), and CCSD(T) methods. Figures of optimized Si_2H_2 species and one isomer of $Pt(PH_3)_2(Si_2H_2)$ **Pt-4′**, which is an intermediate in the isomerization of **4-Pt** to **3-Pt**. Figure of energy and geometry changes starting from the preliminary optimized transition state of the isomerization from **4-Rh** to **3-Rh**. This material is available free of charge via the Internet at http://pubs.acs.org.

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