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M_2E_2 four-member ring structure, $M_2(\mu\text{-}EH_2)_2(P2)_2$ (M = Pd or Pt; E = Si or Ge; P2 = $(PH_3)_2$ or $H_2PCH_2CH_2PH_2$) versus μ-disilene and μ-digermene-bridged structures, $M_2(\mu\text{-}E_2H_4)(P2)_2$. A theoretical study

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Abstract

$M_2(EH_2)_2(P2)_2$ (M = Pd or Pt; E = Si or Ge; P2 = $(PH_3)_2$ or diphosphinoethane ($H_2PCH_2CH_2PH_2$; dipe)) was theoretically investigated with the DFT method. Natural bond orbital (nbo) analysis and the laplacian of electron density indicate that $Pt_2(SiH_2)_2(P2)_2$ and $Pt_2(GeH_2)_2(P2)_2$ are characterized to be di(μ-silylene)- and di(μ-germylene)-bridged complexes, respectively, which involve M_2Si_2 and M_2Ge_2 four-member ring structures, respectively. In other words, they should be represented as $Pt_2(\mu\text{-}SiH_2)_2(P2)_2$ and $Pt_2(\mu\text{-}GeH_2)_2(P2)_2$. On the other hand, the palladium(0) analogs are understood in terms of μ-disilene- and μ-digermene-bridged complexes in which the Si–Si and Ge–Ge bonding interactions are maintained. Thus, they should be represented as $Pd_2(\mu\text{-}Si_2H_4)(P2)_2$ and $Pd_2(\mu\text{-}Ge_2H_4)(P2)_2$. The difference between platinum(0) and palladium(0) complexes is interpreted in terms of the difference in the strength of π-back donation interaction; in the platinum(0) complex, the π-back donation interaction is so strong that the Si–Si and Ge–Ge bonds are almost broken, while in the palladium(0) complex the π-back donation interaction is not so strong and thereby the Si–Si and Ge–Ge bonding interactions are still maintained. Also in the mononuclear disilene and digermene complexes, $M(E_2H_4)(P2)$ (M = Pd or Pt; E = Si or Ge), a similar difference between platinum(0) and palladium(0) complexes is observed; platinum(0) complexes are characterized to be a three-member metallacycle complex which involves an E–E single bond and two M–E covalent bonds, whereas the palladium(0) analogs are characterized to be the usual disilene and digermene complexes in which the Si=Si and Ge=Ge double bonds are maintained. This is because the π-back-donating interaction is stronger in platinum(0) complexes than in palladium(0) complexes. In $M(C_2H_4)(P2)$ and $M_2(\mu\text{-}C_2H_4)(P2)_2$, the C=C double bond is maintained, since the π-back donation is much weaker than those of Si and Ge analogs even in platinum(0) complexes. Thus, these complexes are characterized to be the ethylene complex in which the C=C double bond coordinates with the Pt(0) and Pd(0) centers and not the three-member metallacycle complex. © 2001 Published by Elsevier Science B.V.

Keywords: DFT; Molecules orbital calculations; Silylene; Germylene; Palladium; Platinum; μ-Silene; μ-Germene

1. Introduction

Reactions of transition-metal complexes with hydrosilane often yield transition-metal silyl and silylene species which play important roles as reactive intermediates in the transition-metal catalyzed hydrosilylation, dehydrocoupling reaction, and syntheses of organo-silicon compounds [1]. For instance, platinum(0) phosphine complexes react with hydrosilane to yield the

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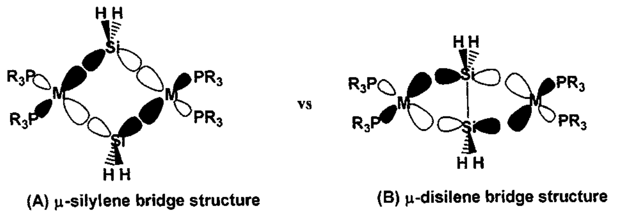
platinum(0) disilene complex, $Pt(Si_2R_4)(PR_3)_2$ [2], diplatinum di(μ-silylene)-bridged complex, $Pt_2(\mu\text{-}SiH_2)_2(PR_3)_4$ [3–5], diplatinum di(μ-silyl)-bridged complex, $Pt_2(\mu\text{-}SiHR_2)_2(PR_3)_4$ [4,6], and the simple platinum(II) disilyl complex, $Pt(SiR_3)_2(PR_3)_2$ [7,8]. Palladium(0) phosphine complexes also undergo similar reactions [9,10]. Hydrogermanes are also expected to undergo similar reactions with platinum(0) complexes [1f,11–13]. In those complexes, a conclusive discussion on the bonding nature of di(μ-silylene)-bridged diplatinum complex, $Pt_2(\mu\text{-}SiR_2)_2(PR_3)_4$ of those complexes has not been presented; for instance, it was suggested in some studies [3c,14] that the Si–Si bonding interaction did not exist and that one could understand this complex in terms of the di(μ-silylene)-bridged complex (see Scheme 1A). In Ref. [3d], however, it was proposed that this complex was understood in terms of the μ-disilene-bridged complex (Scheme 1B) which involved the Si=Si double bond.

In the chemistry of transition-metal complexes, the concept of σ-donation and π-back donation interactions [15] is very important and significantly useful for a detailed understanding of the coordinate bond nature and the electronic structure of many transition-metal complexes. We can expect that the concept of σ-donation and π-back donation interactions would be useful in investigating the bonding nature of $Pt_2(SiR_2)_2(PR_3)_4$. Electronic structure theory such as ab initio MO and DFT methods would provide valuable information for such discussions. However, to our knowledge a detailed theoretical study of these complexes has not been reported yet except for the pioneering semi-empirical MO studies [3c,14].

In this work, we theoretically investigated $M_2(ER_2)_2(P2)_2$ (M = Pd or Pt; E = Si or Ge; P2 = $(PH_3)_2$ or dipe ($H_2PCH_2CH_2PH_2$)) with the DFT method. In the present study, we wish to present a detailed knowledge on the geometries, bonding nature, and the electron distribution of these complexes. We also compare these complexes with the ethylene analogs, $Pt_2(\mu\text{-}C_2H_4)(P2)_2$, monomeric platinum(0)-disilene and digermene complexes, $Pt(E_2H_4)(P2)$, and their palladium(0) analogs, and elucidate a proper representation for these complexes, i.e. either a di(μ-silylene)-bridged (or di(μ-germylene)-bridged) four-member ring complex or a μ-disilene-bridged (or μ-digermene-bridged) complex.



Scheme 1.

2. Computational details

The geometries of all these complexes were optimized with the DFT method, where the B3LYP functional was adopted for the exchange-correlation term [16,17]. In geometry optimization, the following basis set system (BS-I) was adopted; core electrons of Pt (up to 4d); Pd (up to 3d); Si (up to 2p); P (up to 2p); and Ge (up to 3d) were replaced with effective core potentials (ECPs) [18,19], and their valence electrons were represented with split valence type basis sets, (311/311/111), (311/311/211), (21/21/1), (21/21/1) and (21/21/1), respectively, where a d-polarization function was added to Si, P and Ge [20]. For C and H, the usual 6-31G(d) sets [21] were employed, where a d-polarization function [22] was added to the C atom only that interacted with the metal center. Relative stabilities and electron distribution were investigated with a better basis set system (BS-II). In BS-II, valence electrons of Pt and Pd were represented with (541/541/111/1) and (541/541/211/1) sets, respectively [23,24], where the same ECPs as those of BS-I were adopted. For H and C, 6-311G(d,p) basis sets [25] were adopted, while a p-polarization function was not added to H that was involved in phosphine. For Si and Ge, (621111/52111/1) [26,27] and (63111111/3331111/411) sets [28] were employed, respectively, while the same ECPs and the same basis set as those of BS-I were adopted for P. All these calculations were carried out with the GAUSSIAN 98 program package [29] and contour maps were drawn with the MOLDEN program package [30].

3. Results and discussion

3.1. Geometries of $M(E_2H_4)(P2)$, $M_2(EH_2)_2(P2)_2$ (M = Pd or Pt; E = C, Si, or Ge; P2 = $(PH_3)_2$ or $H_2PCH_2CH_2PH_2$ (dipe))

As shown in Figs. 1 and 2, the E=E bond is much longer in $M(E_2H_4)(PH_3)_2$ than those in the free E_2H_4, as reported experimentally for ethylene complexes [31] and theoretically for ethylene and disilene complexes [32].

Also, the EH_2 plane is bent back away from the central metal, where the back-bending angels for E = C, Si, and Ge are 24, 25, and 24°, respectively, in the platinum(0) complexes, and 18, 24, and 23°, respectively, in the palladium(0) complexes. These geometrical features have been discussed in detail previously [31,32], and thereby, the detailed discussion is omitted here. In $M_2(EH_2)_2(PH_3)_4$, the following interesting geometrical features are observed: in both dinuclear palladium(0) and platinum(0) ethylene complexes, $Pd_2(C_2H_4)(PH_3)_4$ and $Pt_2(C_2H_4)(PH_3)_4$, the C=C bond distance is little different from that of $M(C_2H_4)(PH_3)_2$ and the M–C distance is much longer than that in $M(C_2H_4)(PH_3)_2$.

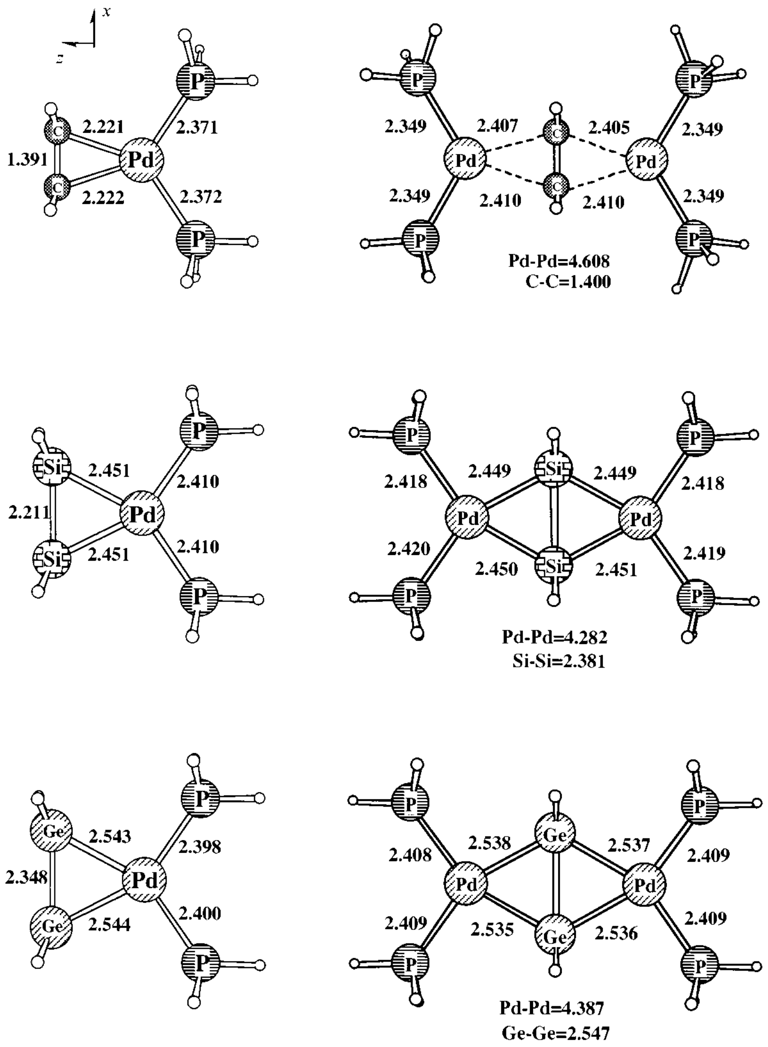


Fig. 1. Optimized geometries of $Pd(E_2H_4)(PH_3)_2$ and $Pd_2(EH_2)_2(PH_3)_4$ (E = C, Si, or Ge). Bond distances in Å and bond angles in °.

The ethylene moiety is completely planar. These features strongly suggest that the ethylene-bridged dinuclear platinum(0) and palladium(0) complexes are not very stable, as will be discussed below in detail. On the other hand, the Si–Si and Ge–Ge bond distances in $M_2(EH_2)_2(PH_3)_4$ are much longer and the M–Si and M–Ge bond distances are considerably shorter than those of $M(E_2H_4)(PH_3)_2$. In particular, it should be noted that the Si–Si and Ge–Ge distances in $Pt_2(E_2H_4)(PH_3)_4$ are even longer than the Si–Si (2.333 Å) and Ge–Ge (2.477 Å)[1] single bonds, respectively. In the palladium(0) complexes, the Si–Si bond is slightly longer than the usual Si–Si single bond but the Ge–Ge bond is slightly shorter than the usual Ge–Ge single bond. These features indicate that the Si–Si and Ge–Ge bonds are almost broken in the dinuclear platinum(0) complexes but their bonding interactions are still maintained in the dinuclear palladium(0) complexes. It should be mentioned here that although the dinuclear palladium(0) and platinum(0) complexes with C_2H_4 and Si_2H_4 are planar, only $Pt_2(GeH_2)_2(PH_3)_4$ is not planar in which a dihedral angle between the two $PtGe_2$ planes is 156°, as shown in Fig. 2.

In the dipe complexes, similar geometrical features are observed except that the E–E bond distance is longer and the M–E bond distance is shorter than those of the PH_3 complexes, as shown in Figs. 3 and 4. In addition, the dinuclear platinum(0) complexes of Si_2H_4 and Ge_2H_4 are non-planar in which the dihedral angle between the two PtE_2 planes are 166 and 155° for E = Si and Ge, respectively. These non-planar structures would be related to the bonding nature, as will be discussed below.

3.2. Binding energies

In Table 1, the binding energies of Si_2H_4 and Ge_2H_4 with platinum(0) and palladium(0) complexes are sum-

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[1] DFT/BS-I optimized values of Si_2H_6 and Ge_2H_6 are given.

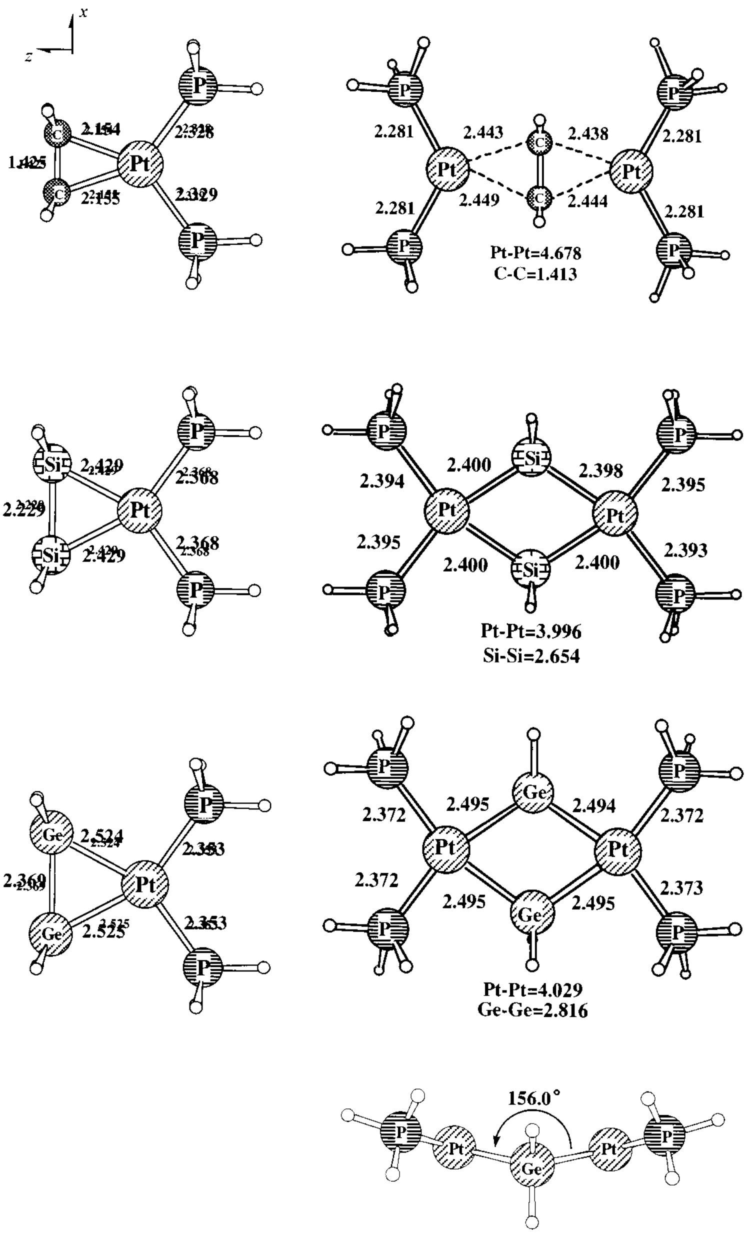
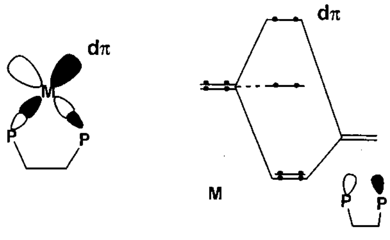


Fig. 2. Optimized geometries of $Pt(E_2H_4)(PH_3)_2$ and $Pt_2(EH_2)_2(PH_3)_4$ (E = C, Si, or Ge). Bond distances in Å and bond angles in °.

marized. The MP4(SDQ)-evaluated binding energies of C_2H_4 and Si_2H_4 with $Pt(PH_3)_2$ [32] are somewhat larger than the present values. However, we believe that a reliable discussion would be presented here based on the DFT method, since the relative stabilities of $Pt(C_2H_4)(PH_3)_2$ and $Pt(Si_2H_4)(PH_3)_2$ do not differ much between the DFT and MP4(SDQ) calculations and the DFT-calculated binding energies of $Pt(C_2H_4)(PH_3)_2$ and $Pt(Si_2H_4)(PH_3)_2$ are similar to the values calculated previously with the SD-CI method [32].

Apparently, binding energies of Si_2H_4 and Ge_2H_4 with $Pd(PH_3)_2$ and $Pt(PH_3)_2$ are considerably large, while those of C_2H_4 with $Pd(PH_3)_2$ and $Pt(PH_3)_2$ are small. The use of dipe instead of PH_3 leads to considerably larger binding energies in all the ethylene, disilene, and digermene complexes. Even the binding energy of C_2H_4 is considerably large in $Pd(C_2H_4)$(dipe). This is not surprising, because the chelate phosphine raises the



Scheme 2.

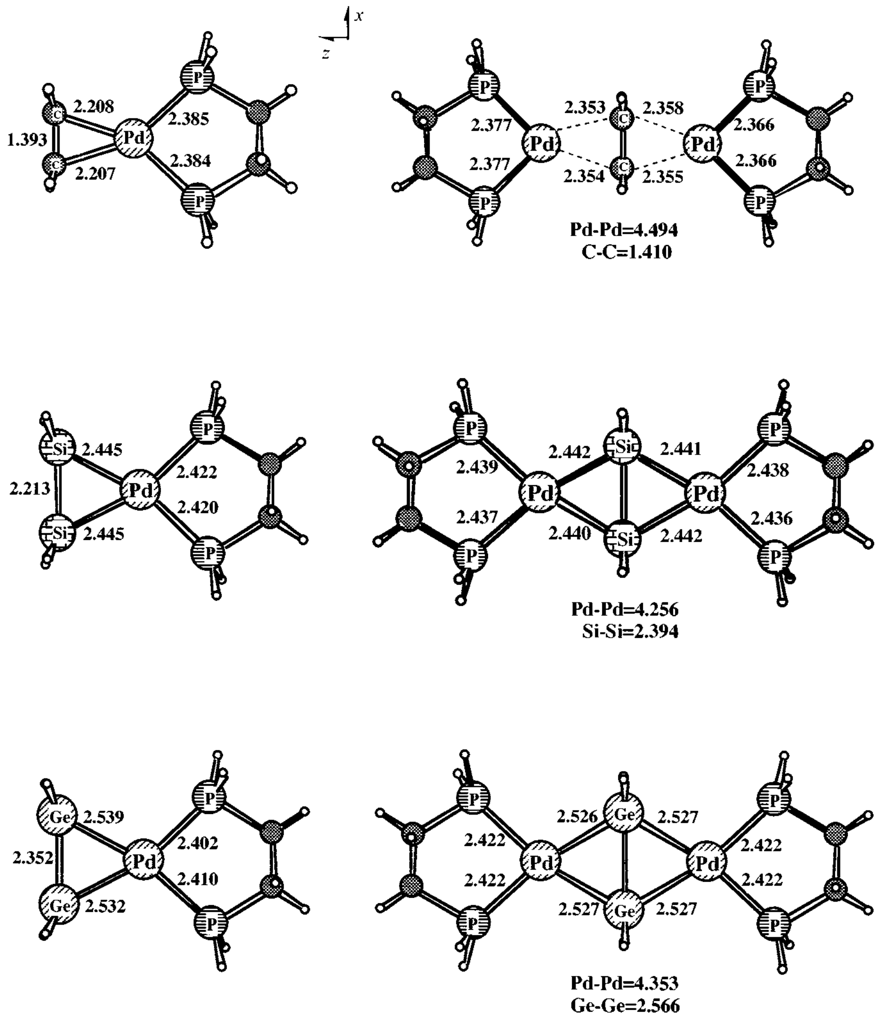


Fig. 3. Optimized geometries of Pd(E_2H_4)(dipe) and $Pd_2(EH_2)_2(dipe)_2$ (E = C, Si, or Ge; dipe = $H_2PCH_2CH_2PH_2$). Bond distances in Å and bond angles in °.

energy of the d_π orbital to enhance the π-back donation interaction [33,34], as shown in Scheme 2.

In the dinuclear complex, the binding energy can be defined as the stabilization energy either by Eqs. (1) or (2)

$$2\ M(P2) + E_2H_4 \rightleftarrows M_2(E_2H_4)(P2)_2 \qquad (1)$$

$$M(P2)(E_2H_4) + M(P2) \rightleftarrows M_2(E_2H_4)(P2)_2 \qquad (2)$$

In both definitions, the binding energies of C_2H_4 with the dinuclear palladium(0) and platinum(0) complexes are very small or slightly negative, when PH_3 is used as a ligand. These results indicate that $M_2(C_2H_4)(PH_3)_4$ is not stable and tends to convert into the monomeric complex, $M(C_2H_4)(PH_3)_2$. In the Si and Ge analogs, however, both binding energies are considerably large. The large binding energy for Eq. (2) indicates that $M_2(SiH_2)_2(P2)_2$ and $M_2(GeH_2)_2(P2)_2$ are formed as a stable species when M(P2) exists in excess in the solution. The dipe ligand provides a considerably larger binding energy than the PH_3 ligand in the dinuclear complexes, akin to that in the mononuclear complexes.

In both PH_3 and dipe ligands, the platinum(0) complexes are more stable than the palladium(0) complexes, as expected, because the Pt d_π orbital (−4.71 eV) is at a higher energy than the Pd d_π orbital (−6.83 eV), as discussed earlier [34,35], where orbital energies of M(dipe) calculated with the HF/BS-II method are in parentheses.

3.3. Electron distribution and bonding nature of palladium(0) complexes

The natural population analysis [36] was adopted here to investigate the electron distribution. In Table 2, total natural populations are shown, where their changes caused by the coordination of E_2H_4 with the Pd(0) center are in parentheses. Electron population of E_2H_4 increases upon the coordination with the Pd(0)

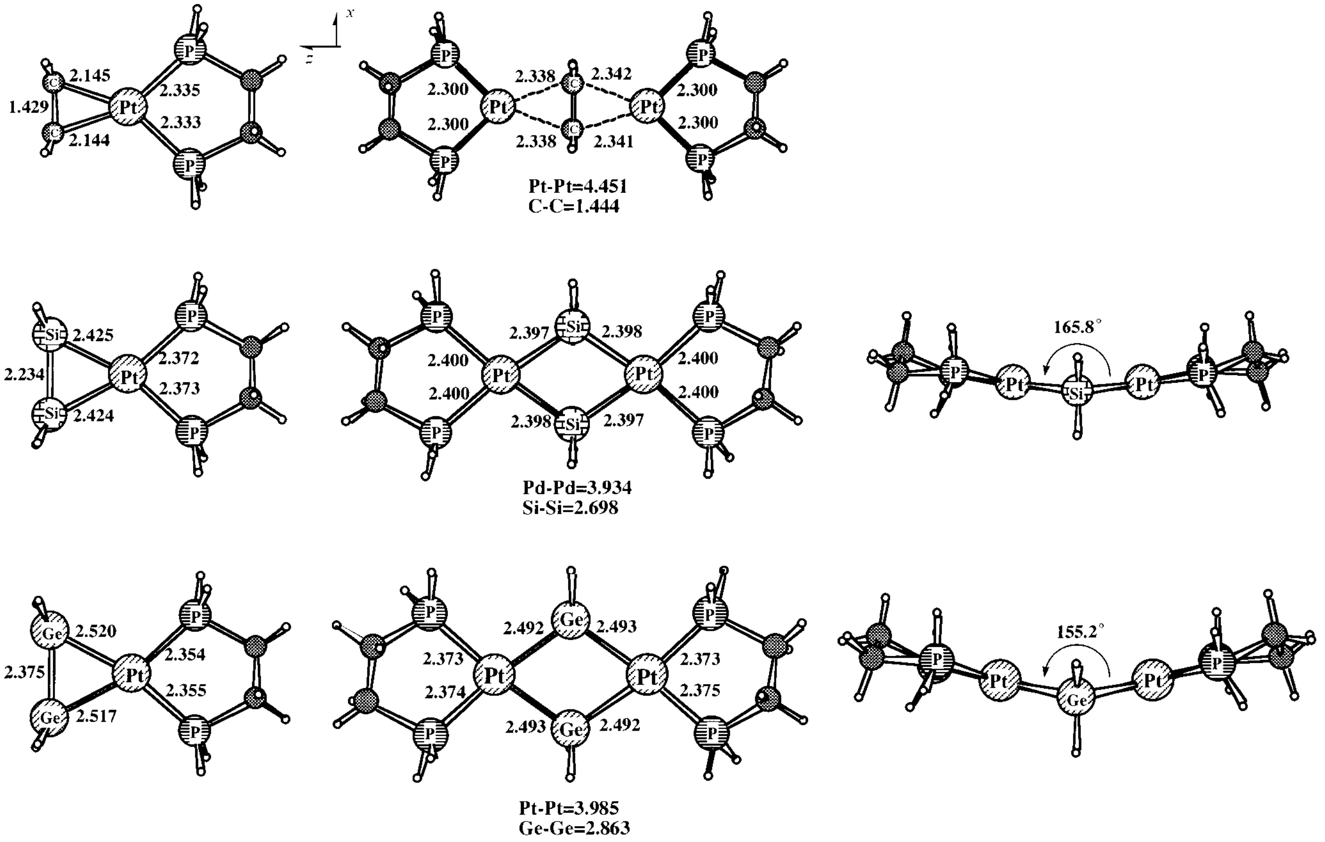


Fig. 4. Optimized geometries of $Pt(E_2H_4)(dipe)$ and $Pt_2(EH_2)_2(dipe)_2$ (E = C, Si, or Ge; dipe = $H_2PCH_2CH_2PH_2$). Bond distances in Å and bond angles in °.

Table 1
Binding energies (kcal mol^{-1}) [a] of C_2H_4, Si_2H_4, and Ge_2H_4 with palladium(0) and platinum(0) complexes

	C_2H_4		Si_2H_4		Ge_2H_4	
	Pd	Pt	Pd	Pt	Pd	Pd
$M(E_2H_4)(PH_3)_2$	10.4	13.4	41.8	52.1	33.2	41.2
$M(E_2H_4)(dipe)$	23.7	37.4	55.1	75.5	46.5	64.7
$M_2(EH_2)_2(PH_3)_4$ [b]	9.3	−0.7	68.1	89.6	56.5	74.3
	(1.1)	(−14.1)	(26.2)	(37.5)	(23.4)	(33.1)
$M_2(EH_2)_2(dipe)_2$ [b]	34.1	43.0	89.5	136.4	118.9	122.0
	(10.4)	(5.5)	(38.6)	(61.0)	(36.0)	(57.3)

[a] DFT/BS-II//DFT/BS-I.

[b] Out of parentheses: the binding energy for Eq. (1). In parentheses: the binding energy for Eq. (2) (see text for Eqs. (1) and (2)).

center and its increase becomes larger in the following order: $Si_2H_4 < Ge_2H_4 < C_2H_4$. Since the Pd d_{xz} orbital mainly participates in the π-back donation (see Fig. 1 for x and z-axes), its natural orbital population sheds some light on the extent of the π-back donation interaction, where the sum of natural orbital populations in valence and Rydberg spaces are given in Table 2. The Pd d_{xz} natural orbital population decreases in the order $C_2H_4 > Si_2H_4 > Ge_2H_4$, which clearly shows that the π-back donation interaction becomes stronger in the order $C_2H_4 < Si_2H_4 < Ge_2H_4$. However, this tendency is not consistent with the above-mentioned population changes of E_2H_4. These population changes are understood in terms that not only the π-back donation but the σ-donation also contributes toward the coordinate bond in $Pd(Si_2H_4)(P2)$ and $Pd(Ge_2H_4)(P2)$ more largely than that in the C_2H_4 analog.

In $Pd_2(E_2H_4)(PH_3)_4$, Pd d_{xz} natural orbital population decreases in the order $E_2H_4 = C_2H_4 > Si_2H_4 > Ge_2H_4$, which is consistent with the increasing order of electron population of E_2H_4, $C_2H_4 < Si_2H_4 < Ge_2H_4$. In these complexes, it is also suggested that the σ-dona-

Table 2
Natural populations [a] and their changes [b] by coordinations of C_2H_4, Si_2H_4, and Ge_2H_4 with mononuclear pallaium(0) and dinuclear palladium(0) complexes

	$Pd(E_2H_4)(PH_3)_2$			$Pd(E_2H_4)(dipe)$		
	C_2H_4	Si_2H_4	Ge_2H_4	C_2H_4	Si_2H_4	Ge_2H_4
M	45.956(−0.366)	46.099(−0.223)	46.069(−0.253)	45.948(0.086)	46.114(0.080)	46.081(0.047)
d_{xz} [c]	1.731(−0.183)	1.717(−0.197)	1.693(−0.275)	1.722(−0.201)	1.714(−0.209)	1.691(−0.232)
E_2H_4	16.225(0.225)	32.165(0.165)	68.203(0.203)	16.236(0.236)	32.174(0.174)	68.218(0.218)
	$Pd_2(E_2H_4)(PH_3)_4$			$Pd_2(E_2H_4)(dipe)_2$		
	C_2H_4	Si_2H_4	Ge_2H_4	C_2H_4	Si_2H_4	Ge_2H_4
M	46.005(−0.317)	46.089(−0.233)	46.067(−0.255)	45.966(−0.068)	46.107(0.068)	46.082(0.048)
d_{xz} [c]	1.834(−0.080)	1.759(−0.155)	1.734(−0.180)	1.813(−0.110)	1.759(−0.164)	1.731(−0.192)
E_2H_4	16.255(0.255)	32.292(0.292)	68.353(0.353)	16.298(0.298)	32.252(0.252)	68.329(0.329)

[a] Natural population analysis [36] was adopted.

[b] In parentheses are population changes. Positive values represent population increase, and vice versa.

[c] Sum of natural orbital populations in valence and Rydberg spaces.

tion is stronger in $Pd_2(Si_2H_4)(PH_3)_4$ than in $Pd_2(C_2H_4)(PH_3)_4$, since the Pd d_{xz} orbital population decreases by 0.075*e* but electron population of E_2H_4 increases by 0.037*e* on going from C_2H_4 to Si_2H_4. Also in $Pd_2(EH_2)_2(dipe)_2$, the Pd d_{xz} orbital population decreases in the order $C_2H_4 > Si_2H_4 > Ge_2H_4$, akin to that in $Pd_2(EH_2)_2(PH_3)_4$, while the electron population of Si_2H_4 is much smaller than that of C_2H_4. From these results, it should be concluded that the π-back donation increases in the order $C_2H_4 < Si_2H_4 < Ge_2H_4$ and that the σ-donation of Si_2H_4 is much stronger than that of C_2H_4 in all these complexes.

The increasing order of π-back donation, $C_2H_4 < Si_2H_4 < Ge_2H_4$, is easily understood in terms that the π* orbital energy becomes lower in energy in the order ethylene (4.43 eV) > disilene (0.10 eV) > digermene (0.06 eV), where the π* orbital energies calculated with the HF/BS-II method are shown in parentheses. In addition, the strong σ-donation of disilene comes from the fact that disilene π orbital (−7.56 eV) is at a much higher energy than that of ethylene (−10.23 eV) and at a slightly higher energy than that of digermene (−7.70 eV).

Natural bond orbital (nbo) analysis proposed by Weinhold [36a,37] provides the occupancy number of each nbo, which is expected to be useful for discussing the bonding nature. The occupancy numbers of several important natural bond orbitals are listed in Table 3, where the abbreviations of π-nbo, π*-nbo, σ-nbo, and σ*-nbo are adopted for the π-bonding E–E nbo, its anti-bonding counterpart, the σ-bonding E–E nbo, and its anti-bonding counterpart, respectively, hereafter.[2] The sum of occupancy numbers of all the E–E nbos is near 4.0 in free E_2H_4, which are consistent with our understanding that E_2H_4 involves the E=E double bond. In Si_2H_4 and Ge_2H_4, a small occupancy number is observed in the π*-nbo. This is probably because these molecules are slightly distorted from the planar [32,38]. Interestingly, the occupancy number of the π-nbo is significantly smaller but that of the π*-nbo is significantly larger in $Pd(E_2H_4)(P2)$ and $Pd_2(EH_2)_2(P2)_2$ than those of the free E_2H_4. These results are consistent with our understanding that E_2H_4 coordinates with the Pd(0) center through σ-donation and π-back donation interactions. The occupancy number of the π-nbo decreases in the order $E = C \gg Ge > Si$ in $Pd(E_2H_4)(P2)$ and $Pd_2(E_2H_4)(P2)$, while the occupancy number of the π*-nbo increases in the order $E = C < Si < Ge$. In Si_2H_4 and Ge_2H_4, the occupancy number of the π-nbo decreases in the order free $E_2H_4 > Pd(E_2H_4)(P2) > Pd_2(EH_2)_2(P2)_2$ but that of π*-nbo increases in the order free $E_2H_4 < Pd(E_2H_4)(P2) < Pd_2(EH_2)_2(P2)_2$. These tendencies clearly indicate that the σ-donation becomes stronger in the order $E = C < Ge < Si$ and the π-back donation becomes stronger in the orders $E = C < Si < Ge$ and $Pd(E_2H_4)(P2) < Pd_2(EH_2)_2(P2)_2$, which are consistent with the natural population changes dis-

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[2] In $M(E_2H_4)(P2)$, the π-orbital of E_2H_4 undergoes the orbital mixing of the σ-orbitals. This strictly means that the σ- and π-orbitals cannot be defined. In the present work, one of the E–E nbos is called π-nbo, when the s-component is very small and the p-component is very large. The E–E nbo is also called σ-nbo, when the ratio of s- and p-components is similar to sp^2. This is not unreasonable because such π-nbo and σ-nbo mainly arise from the π- and σ-orbitals of E_2H_4, respectively.

Table 3
Occupancies of nbos [a] of free E_2H_4, $Pd(E_2H_4)(P2)$, and $Pd_2(E_2H_4)(P2)_2$ ($E = C$, Si, or Ge; $P2 = (PH_3)_2$ or dipe)

Nbo [b]	Free-C_2H_4	$Pd(C_2H_4)(PH_3)_2$	$Pd(C_2H_4)$(dipe)	$Pd_2(C_2H_4)(PH_3)_4$	$Pd_2(C_2H_4)(dipe)_2$
σ(C–C)	1.999	1.994	1.997	1.992	1.988
σ*(C–C)	0.0	0.007	0.008	0.002	0.003
π(C–C)	1.998	1.862	1.854	1.872	1.856
π*(C–C)	0.0	0.342	0.361	0.382	0.445
(Pd–C)	–	0.0	0.0	0.0	0.0
(Pd–C)*					
	Free-Si_2H_4	$Pd(Si_2H_4)(PH_3)_2$	$Pd(Si_2H_4)$(dipe)	$Pd_2(Si_2H_4)(PH_3)_4$	$Pd_2(Si_2H_4)(dipe)_2$
σ(Si–Si)	1.993	1.981	1.981	1.842	1.819
σ*(Si–Si)	0.007	0.012	0.012	0.163	0.167
π(Si–Si)	1.971	1.675	1.663	1.607	1.586
π*(Si–Si)	0.019	0.416	0.437	0.521	0.533
(Pd–Si)	–	0.0	0.0	0.0	0.0
	Free-Ge_2H_4	$Pd(Ge_2H_4)(PH_3)_2$	$Pd(Ge_2H_4)$(dipe)	$Pd_2(Ge_2H_4)(PH_3)_4$	$Pd_2(Ge_2H_4)(dipe)_2$
σ(Ge–Ge)	1.941	1.967	1.967	1.823	1.798
σ*(Ge–Ge)	0.031	0.025	0.025	0.231	0.241
π(Ge–Ge)	1.951	1.685	1.674	1.610	1.589
π*(Ge–Ge)	0.029	0.449	0.476	0.537	0.554
(Pd–Ge)	–	0.0	0.0	0.0	0.0

[a] Natural bond orbital analysis [37] was adopted.

[b] The σ(E–E) and σ*(E–E) represent σ-type E–E natural bond orbital and its anti-bonding counterpart, respectively. The π(E–E) and π*(E–E) represent π-type E–E natural bond orbital and its anti-bonding counterpart, respectively. The (Pd–E) represents the Pd–E natural bond orbital.

Table 4
Natural populations [a] and their changes [b] by coordinations of C_2H_4, Si_2H_4, and Ge_2H_4 with mononuclear and dinuclear platinum(0) complexes

	$Pt(E_2H_4)(PH_3)_2$			$Pt(E_2H_4)$(dipe)		
	C_2H_4	Si_2H_4	Ge_2H_4	C_2H_4	Si_2H_4	Ge_2H_4
M	77.979(−0.539)	78.250(−0.268)	78.221(−0.297)	77.969(−0.196)	78.262(0.097)	78.228(0.063)
d_{xz} [c]	1.621(−0.267)	1.676(−0.212)	1.650(−0.238)	1.611(−0.278)	1.669(−0.220)	1.644(−0.245)
E_2H_4	16.337(0.337)	32.120(0.120)	68.168(0.168)	16.360(0.360)	32.137(0.137)	68.192(0.192)
	$Pt_2(E_2H_4)(PH_3)_4$			$Pt_2(E_2H_4)(dipe)_2$		
	C_2H_4	Si_2H_4	Ge_2H_4	C_2H_4	Si_2H_4	Ge_2H_4
M	78.119(−0.399)	78.262(−0.256)	78.223(−0.295)	78.029(−0.136)	78.281(0.116)	78.235(0.070)
d_{xz} [c]	1.798(−0.090)	1.679(−0.209)	1.657(−0.231)	1.756(−0.133)	1.674(−0.215)	1.650(−0.239)
E_2H_4	16.284(0.284)	32.189(0.189)	68.328(0.328)	16.400(0.400)	32.171(0.171)	68.332(0.332)

[a] Natural population analysis [36] was adopted here.

[b] In parentheses are population changes. Positive values represent population increase, and vice versa.

[c] Sum of natural orbital populations in valence and Rydberg spaces.

cussed above. It is also noted that the occupancy number of the M–E nbo is evaluated to be zero. From these occupancy numbers, it should be concluded that though the E=E bond becomes weaker in the palladium(0) complexes than in free E_2H_4, the π-bonding character is still maintained in the complex. Thus, the bonding nature of $Pd(E_2H_4)(P2)$ and $Pd_2(E_2H_4)(P2)_2$ is understood reasonably in terms that the E=E double bond coordinates with the Pd(0) center; in other words, these complexes should be represented as $Pd(E_2H_4)(P2)$ and $Pd_2(\mu\text{-}E_2H_4)(P2)_2$.

3.4. Electron distribution and bonding nature of platinum(0) complexes

In mononuclear platinum(0) complexes $Pt(E_2H_4)(PH_3)_2$, however, electron populations change in a completely different manner from those of the palladium(0) analogs, as follows: the Pt d_{xz} natural orbital population decreases in the order $Si_2H_4 > Ge_2H_4 > C_2H_4$, and the natural population of E_2H_4 increases in the order $Si_2H_4 < Ge_2H_4 < C_2H_4$, as shown in Table 4. These results suggest that the π-back donation of $Pt(C_2H_4)$-

(P2) is stronger than those of Pt(Si_2H_4)(P2) and Pt(Ge_2H_4)(P2). However, this suggestion is not consistent with our understanding that the π-back donation becomes stronger in the order $C_2H_4 < Si_2H_4 < Ge_2H_4$. This unexpected result would arise from the difference in the bonding nature between Pt(C_2H_4)(P2) and the others, as will be discussed below.

In Pt(C_2H_4)(P2), the occupancy number of the π-nbo decreases but that of the π*-nbo increases compared with those of free C_2H_4. In addition, the occupancy number of the M–C nbo is evaluated to be zero. All these features indicate that the C=C double bond is maintained and the coordinate bond is formed through σ-donation and π-back donation in this complex like the Pd analogs. In Pt(Si_2H_4)(P2) and Pt(Ge_2H_4)(P2), on the other hand, the occupancy number of the σ-nbo is somewhat smaller than 2 and the occupancy number of the π-nbo completely disappears, while the occupancy number is 1.75–1.86 for the Pt–S_2, Pt–Ge nbos and 0.38–0.56 for their anti-bonding counterparts. From these occupancy numbers, the PtE_2 moiety is characterized to be a three-member metallacycle structure in Pt(Si_2H_4)(P2) and Pt(Ge_2H_4)(P2), unlike Pt(C_2H_4)(P2) in which the PtC_2 moiety is understood in terms that the C=C double bond coordinates with the Pt(0) center. In other words, the C=C double bond is maintained, while the Si=Si and Ge=Ge double bonds change to the Si–Si and Ge–Ge single bonds in Pt(E_2H_4)(P2).

Now, let us return to the discussion on the Pt d_{xz} natural orbital population. Natural orbital population and nbo analysis involve diagonalization of the density matrix, and the difference in the bonding nature corresponds to the different eigenvector [36,37]. Since the bonding nature is completely different between Pt(C_2H_4)(P2) and the others, the eigenvector is different between them, which would lead to the above-mentioned unexpected population changes that Pt d_{xz} orbital population in Pt(C_2H_4)(P2) is smaller than those of Pt(Si_2H_4)(P2) and Pt(Ge_2H_4)(P2). Mulliken population analysis which does not involve such diagonalization provides a different tendency, as follows: Pt d_{xz} orbital population decreases in the order C_2H_4 (1.584*e*) > Si_2H_4 (1.503*e*) > Ge_2H_4 (1.464*e*) in Pt(E_2H_4)(P2) (the Pt d_{xz} orbital population based on Mulliken population analysis are in parentheses). This is consistent with our understanding that the π-back donation becomes stronger in the order $C_2H_4 < Si_2H_4 < Ge_2H_4$. These results suggest that the comparison of the natural orbital population between the two compounds is meaningful when they possess the similar bonding nature.

In the dinuclear platinum(0) complexes, the Pt d_{xz} natural orbital population decreases in the order E = C > Si > Ge,[3] and E_2H_4 electron population increases in the order E = Si < C < Ge. These results indicate that the π-back-donation becomes stronger in this order and the σ-donation of Si_2H_4 is stronger than that of C_2H_4, like those in $Pd_2(EH_2)_2(P2)_2$. Nbo analysis also provides interesting bonding features of these dinuclear platinum(0) complexes. In $Pt_2(C_2H_4)(P2)_2$, the occupancy number is 1.85–1.87 for the π-nbo, 0.38–0.45 for the π*-nbo, and zero for the Pt–C nbo (see Table 5). This result clearly shows that the C=C double bond is maintained in the complex and the coordinate bond of ethylene is formed through σ-donation and π-back donation. In $Pt_2(SiH_2)_2(P2)_2$ and $Pt_2(GeH_2)_2(P2)_2$, on the other hand, the occupancy numbers of all the Si–Si and Ge–Ge nbos are evaluated to be zero, while the occupancy number is evaluated to be 1.80–1.83 for Pt–Si and Pt–Ge bonding nbos and 0.42–0.45 for their anti-bonding counterparts (Table 5). These results mean that the Si–Si and Ge–Ge bonds are completely broken but the Pt–Si and Pt–Ge covalent bonds are formed in these complexes, unlike those in Pt(E_2H_4)(P2) in which the Si–Si and Ge–Ge single bonds are maintained. This is because the two d_{xz} orbitals participate in the π-back donation of $Pt_2(CH_2)_2(P2)_2$ and the electron population of E=E π* orbital in $Pt_2(EH_2)_2(P2)_2$ increases to a greater extent than that in Pt(E_2H_4)(P2). Thus, it should be clearly concluded that $Pt_2(EH_2)_2(P2)_2$ (E = Si or Ge) is characterized to be di(μ-silylene)- and di(μ-germylene)-bridged dinuclear complexes, $Pt_2(\mu\text{-}SiH_2)_2(P2)_2$ and $Pt_2(\mu\text{-}Ge_2H_4)_2(P2)_2$, which involve an M_2E_2 four-member ring structure.

3.5. Laplacian of electron density in $Pd(E_2H_4)(PH_3)_2$, $Pt(E_2H_4)(PH_3)_2$, $Pd_2(E_2H_4)(PH_3)_4$, and $Pt_2(E_2H_4)(PH_3)_2$

Since laplacian of electron density sheds meaningful light on the bonding nature [39], we compared the laplacian between $Pt_2(\mu\text{-}C_2H_4)(PH_3)_4$ and $Pt_2(\mu\text{-}SiH_2)_2(PH_3)_4$, as shown in Fig. 5, where the laplacians of the Ge analogs are omitted because of its similarity to those of the Si analogs. Apparently, the negative region is observed between the two C atoms of $Pt_2(\mu\text{-}C_2H_4)(PH_3)_4$, which clearly indicates that the C–C bonding interaction is involved in this complex. This result is consistent with the results provided by nbo analysis. In $Pt_2(\mu\text{-}SiH_2)_2(PH_3)_4$, on the other hand, the negative regions are not observed between the two Si atoms but are observed between Pt and Si atoms (see

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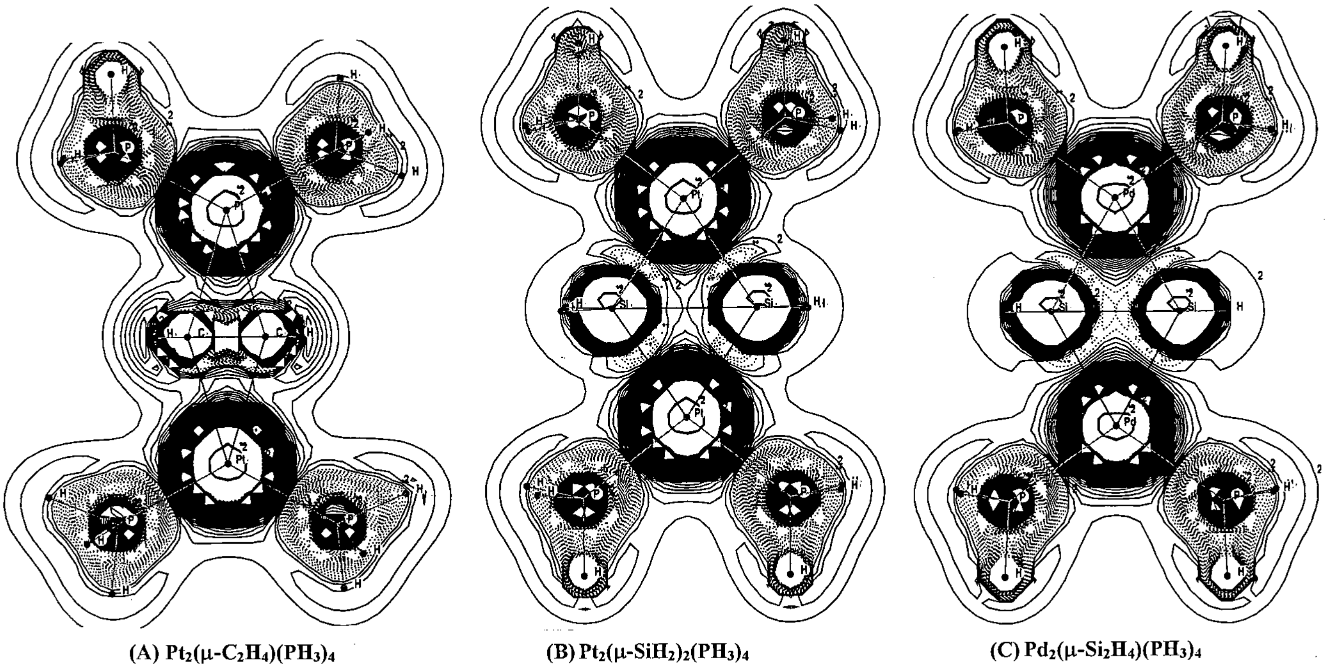
[3] Although $Pt_2(\mu\text{-}C_2H_4)(P2)_2$ has completely different bonding nature from those of Si and Ge analogs, Pt d_{xz} orbital population decreases in the order $C_2H_4 > Si_2H_4 > Ge_2H_4$, in this case, unlike that observed in Pt(E_2H_4)(P2). This is probably because the coordinate bond of C_2H_4 in $Pt_2(\mu\text{-}C_2H_4)(P2)_2$ is very weak and Pt d_{xz} orbital population does not decrease very much.

Table 5
Occupancies of natural bond orbitals[a] of free E_2H_4, $Pt(E_2H_4)(P2)$, and $Pt_2(E_2H_4)(P2)_2$ (E = C, Si, or Ge; P2 = $(PH_3)_2$ or dipe)

Nbo[b]	Free-C_2H_4	$Pt(C_2H_4)(PH_3)_2$	$Pt(C_2H_4)$(dipe)	$Pt_2(C_2H_4)(PH_3)_4$	$Pt_2(C_2H_4)(dipe)_2$
σ(C–C)	1.999	1.997	1.996	1.992	1.988
σ*(C–C)	0.0	0.011	0.013	0.002	0.003
π(C–C)	1.998	1.764	1.753	1.872	1.856
π*(C–C)	0.0	0.524	0.557	0.382	0.445
(Pt–C)	–	0.0	0.0	0.0	0.0
(Pt–C)*					
	Free-Si_2H_4	$Pt(Si_2H_4)(PH_3)_2$	$Pt(Si_2H_4)$(dipe)	$Pt_2(Si_2H_4)(PH_3)_4$	$Pt_2(Si_2H_4)(dipe)_2$
σ(Si–Si)	1.993	1.980	1.978	0.0	1.819
σ*(Si–Si)	0.007	0.012	0.013	0.0	0.167
π(Si–Si)	1.971	0.0	0.0	0.0	1.586
π*(Si–Si)	0.019	0.0	0.0	0.0	0.533
(Pt–Si)	–	1.801	1.828	1.804	1.834
(Pt–Si)*		0.441	0.433	0.431	0.416
	Free-Ge_2H_4	$Pt(Ge_2H_4)(PH_3)_2$	$Pt(Ge_2H_4)$(dipe)	$Pt_2(Ge_2H_4)(PH_3)_4$	$Pt_2(Ge_2H_4)(dipe)_2$
σ(Ge–Ge)	1.941	1.967	1.967	0.0	0.0
σ*(Ge–Ge)	0.031	0.024	0.025	0.0	0.0
π(Ge–Ge)	1.951	0.0	0.0	0.0	0.0
π*(Ge–Ge)	0.029	0.0	0.0	0.0	0.0
(Pt–Ge)		1.801	1.830	1.813	1.841
(Pt–Ge)*		0.461	0.465	0.445	0.434

[a] Natural bond orbital analysis [37] was adopted.

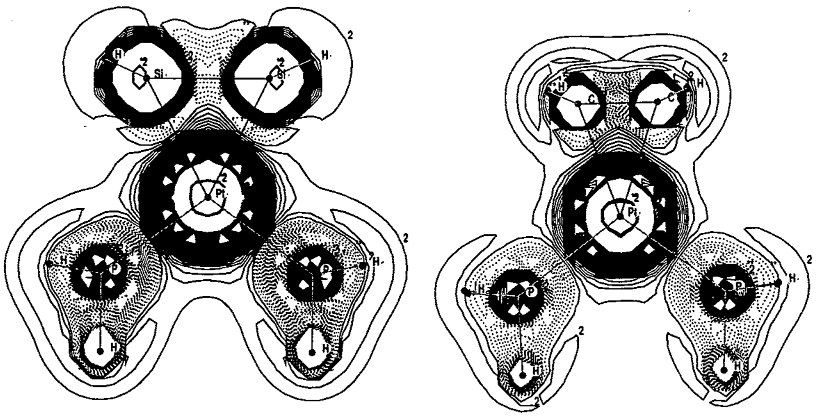
[b] The σ(E–E) and σ*(E–E) represent σ-type E–E natural bond orbital and its anti-bonding counterpart, respectively. The π(E–E) and π*(E–E) represent π-type E–E natural bond orbital and its anti-bonding counterpart, respectively. The (Pt–E) and (Pt–E)* represent the Pt–E natural bond orbital and its anti-bonding counterpart, respectively.



(A) $Pt_2(\mu\text{-}C_2H_4)(PH_3)_4$ **(B) $Pt_2(\mu\text{-}SiH_2)_2(PH_3)_4$** **(C) $Pd_2(\mu\text{-}Si_2H_4)(PH_3)_4$**

Fig. 5. Laplacian of electron density in $Pt_2(C_2H_4)(PH_3)_4$, $Pt_2(SiH_2)_2(PH_3)_4$, and $Pd_2(SiH_2)_2(PH_3)_4$. Solid lines and dotted lines represent the positive and negative values, respectively, where the interval of values is 0.025 a.u.

Fig. 5B). These negative regions clearly represent that this complex involves the four Pt–Si bonding interactions but the Si–Si bonding interaction is broken in this complex. In the palladium analog, however, the laplacian is rather similar to that observed in $Pt_2(\mu\text{-}C_2H_4)(PH_3)_4$ and the negative region exists between the



(A) $Pt(Si_2H_4)(PH_3)_2$ (B) $Pt(C_2H_4)(PH_3)_2$

Fig. 6. Laplacian of electron density in $Pt(Si_2H_4)(PH_3)_2$ and $Pt(C_2H_4)(PH_3)_2$. Solid lines and dotted lines represent the positive and negative values, respectively, where the interval of values is 0.025 a.u.

two Si atoms (Fig. 5C). Moreover, the negative value between the two Si atoms is larger than that between Pd and Si atoms by about 0.025 a.u. These results indicate that the Si–Si bonding interaction is maintained in $Pd_2(\mu\text{-}Si_2H_4)(PH_3)_4$. Thus, the laplacian of electron density shows that $Pt_2(\mu\text{-}SiH_2)_2(PH_3)_4$ is characterized to be a Pt_2Si_2 four-member ring complex but the palladium analog is characterized to be a μ-disilene-bridged complex, $Pd_2(\mu\text{-}Si_2H_4)(PH_3)_4$. Again, these features are consistent with our discussion based on the nbo analysis (vide supra).

Interesting differences are also observed between $Pt(C_2H_4)(PH_3)_2$ and $Pt(Si_2H_4)(PH_3)_2$, as shown in Fig. 6. In $Pt(C_2H_4)(PH_3)_2$, the considerably large negative region is observed between the two C atoms and the other negative regions are observed between Pt and C atoms. In $Pt(Si_2H_4)(PH_3)_2$, on the other hand, the negative region between the two Si atoms is less dense than that of $Pt(C_2H_4)(PH_3)_2$ and the other negative region exists at an almost intermediate area between Pt and Si atoms. The negative region between the two Si atoms exhibit similar values to that between Pt and Si atoms in $Pt(Si_2H_4)(PH_3)_2$, while the negative region between the two C atoms is much more dense than that between Pt and C atoms in $Pt(C_2H_4)(PH_3)_2$. These features are consistent with our understanding that $Pt(Si_2H_4)(PH_3)_2$ is considered to involve a three-member metallacycle structure but $Pt(C_2H_4)(PH_3)_2$ is characterized to involve the coordination of the C=C double bond with the Pt(0) center.

3.6. Contour maps of important molecular orbitals

Since the contour map of the molecular orbital also provides meaningful information on the bonding nature, we investigated the contour maps of several important molecular orbitals of $Pt_2(\mu\text{-}SiH_2)_2(PH_3)_4$, $Pd_2(\mu\text{-}Si_2H_4)(PH_3)_4$, and $Pt_2(\mu\text{-}C_2H_4)(PH_3)_4$, where contour maps of $Pt(C_2H_4)(PH_3)_2$ and $Pt(Si_2H_4)(PH_3)_2$ are omitted since they were discussed in detail earlier [32]. As shown in Fig. 7, both $Pt_2(\mu\text{-}SiH_2)_2(PH_3)_4$ and $Pd_2(\mu\text{-}Si_2H_4)(PH_3)_4$ exhibit almost the same contour maps, unexpectedly, whereas the nbo analysis and the laplacian of electron density provide a completely different bonding nature between them. For instance, the 41st orbital of the platinum(0) complex and the 43rd orbital of the palladium(0) complex involve a typical d_π–π^* back-donating interaction between the metal and silylene (or disilene), in which the bonding overlap between M and Si atoms is similar between the palladium(0) and platinum(0) complexes. Interestingly, HOMO (the 50th orbital) of both palladium(0) and platinum(0) complexes involves the π-bonding overlap between the two Si atoms and the M–Si bonding overlap outside of the M–Si line. Important differences between the palladium(0) and platinum(0) complexes are found in the 48th orbital. This orbital of the platinum(0) complex consists of the larger d_π–d_π bonding overlap between the two Pt atoms and the larger anti-bonding overlap between the two Si atoms than those of the palladium(0) analog. This difference in the 48th orbital is considered as one of the origins of the difference in the bonding nature between $Pt_2(\mu\text{-}SiH_2)_2(PH_3)_4$ and $Pd_2(\mu\text{-}Si_2H_4)(PH_3)_4$, since the 48th orbital leads to a weaker Si–Si bonding interaction and a stronger Pt–Si bonding interaction in the platinum(0) complex than those in the palladium(0) complex. This orbital also provides the driving force for the non-planar distortion of the M_2E_2 moiety, since the non-planar distortion increases the d_π–d_π bonding overlap.[4]

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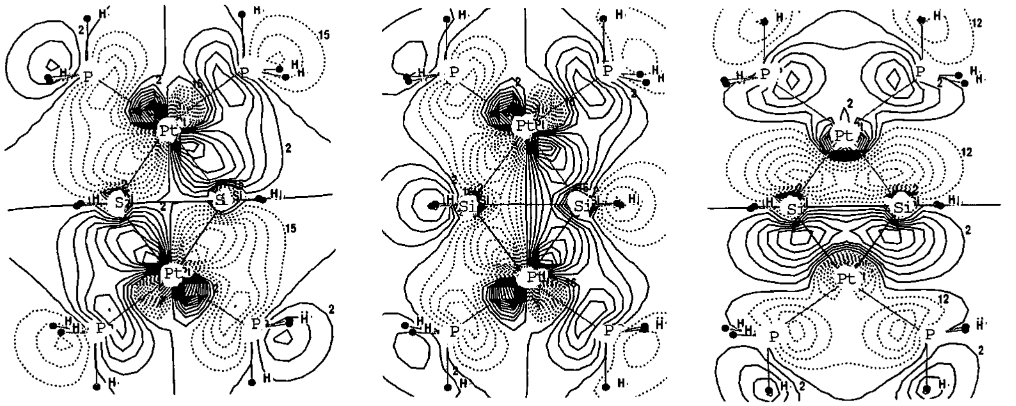
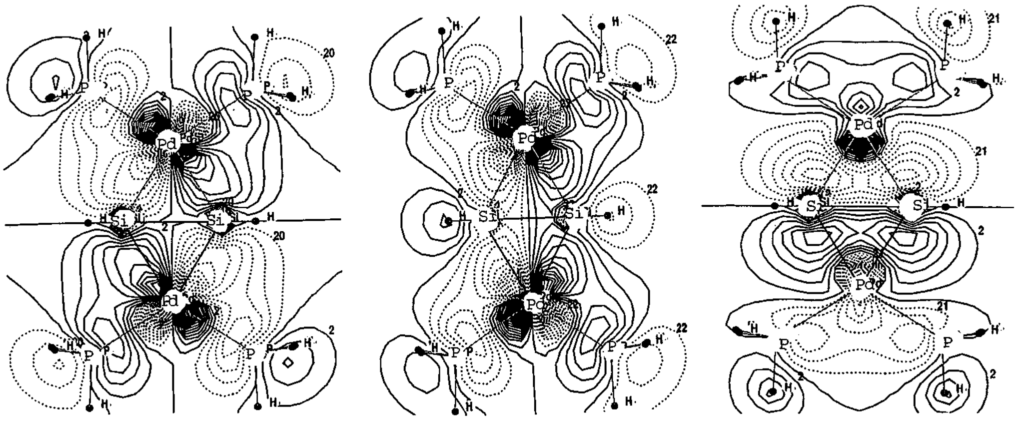
[4] The non-planar distortion, however, decreases the bonding overlap between M d_π and E_2H_4 π^* orbitals. The distortion angle would be determined by the balance of d_π–d_π and d_π–π^* bonding overlaps. The detailed investigation is now underway.

$Pt_2(\mu\text{-}C_2H_4)(PH_3)_4$, however, exhibits different contour maps, as shown in Fig. 8. For instance, the d_π–π^* (the 37th orbital) and the d_π–d_π (the 42th orbital) bonding overlaps are much smaller than those of $Pt_2(\mu\text{-}SiH_2)_2(PH_3)_4$ and $Pd_2(\mu\text{-}Si_2H_4)(PH_3)_4$. These features are consistent with our understanding that the C=C



(a) d_π-π^* (41 th MO) (b) d_π+d_π (48 th MO) (c) π (50 th MO)

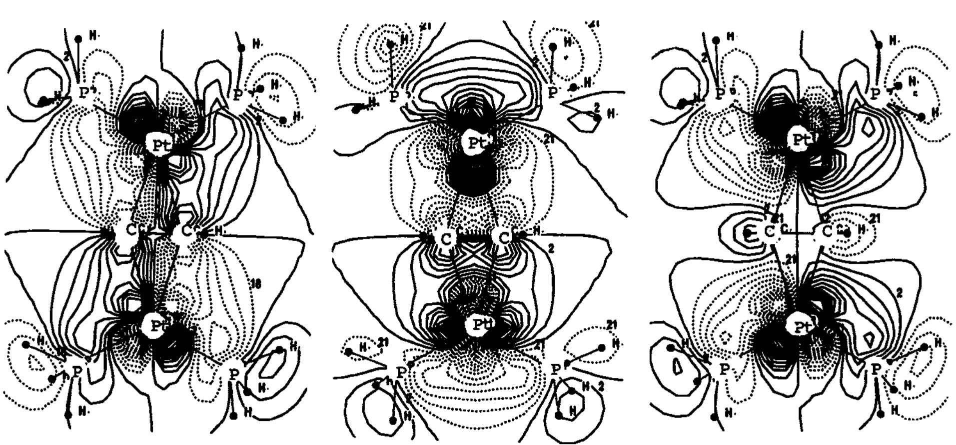
(A)$Pt_2(\mu\text{-}SiH_2)_2(PH_3)_4$



(d) d_π-π^* (43 th MO) (e) d_π+d_π (48 th MO) (f) π (50 th MO)

(B) $Pd_2(\mu\text{-}SiH_2)_2(PH_3)_4$

Fig. 7. Contour maps of important molecular orbitals of $Pt_2(\mu\text{-}SiH_2)_2(PH_3)_4$ and $Pd_2(\mu\text{-}Si_2H_4)(PH_3)_4$. Solid lines and dotted lines represent the positive and negative values, respectively, where the interval of values is 0.0125 a.u.



(a) d_π-π^* (37 th MO) (b) π (41 th MO) (c) d_π+d_π (42 th MO)

Fig. 8. Contour maps of important molecular orbitals of $Pt_2(\mu\text{-}C_2H_4)(PH_3)_4$. Solid lines and dotted lines represent the positive and negative values, respectively, where the interval of values is 0.0125 a.u.

double bond is maintained and the Pt–C bonding interaction is weak in this complex.

Since $Pt_2(\mu\text{-}SiH_2)_2(PH_3)_4$ and $Pd_2(\mu\text{-}Si_2H_4)(PH_3)_4$ have similar frontier orbitals, they are not considered very much different. Thus, we wish to propose following predictions: (1) $Pt_2(\mu\text{-}SiH_2)_2(PH_3)_4$ would change into the μ-disilene-bridged form by introducing the electron-accepting ligand, since such a ligand would suppress the expansion of the Pt d_{xz} orbital toward the other platinum center to decrease the d_π–d_π bonding overlap and the Si–Si anti-bonding overlap in the 48th orbital; and (2) $Pd_2(\mu\text{-}Si_2H_4)(PH_3)_4$ would change into the di(μ-silylene)-bridged structure by introducing the strongly electron-releasing ligand, since such a ligand increases the expansion of Pd d_π orbital toward the other palladium center.

4. Conclusions

In this work, $Pt_2(SiH_2)_2(P2)_2$ ($P2 = (PH_3)_2$ or dipe) and its Ge analogs are theoretically investigated with the DFT method. They are characterized to be di(μ-silylene)- and di(μ-germylene)-bridged dinuclear platinum(0) complexes, respectively, which involve the Pt_2E_2 ($E = Si$ or Ge) four-member ring structure. In these complexes, the occupancy numbers of σ- and π-nbos of the E–E bond are zero, while the occupancy number of the Pt–E bonding nbo is 1.80–1.84 and that of its anti-bonding counterpart is 0.42–0.46. The laplacian of electron density is also positive between the two E atoms but negative between Pt and E atoms. In other words, these complexes are represented to be $Pt_2(\mu\text{-}SiH_2)_2(P2)_2$ and $Pt_2(\mu\text{-}GeH_2)_2(P2)_2$. On the other hand, $Pd_2(SiH_2)_2(P2)_2$ and its Ge analogs are characterized as μ-disilene- and μ-digermene-bridged dinuclear palladium(0) complexes, respectively, since laplacian of electron density and nbo analysis clearly show that the E–E bond is maintained but the Pd–E interaction is not considered a covalent bond. In other words, they should be represented as $Pd_2(\mu\text{-}Si_2H_4)(P2)_2$ and $Pd_2(\mu\text{-}Ge_2H_4)(P2)_2$. This suggests that the border between the di(μ-silylene)-bridged structure and the μ-disilene-bridged structure exists between palladium(0) and platinum(0) complexes. The difference between palladium(0) and platinum(0) complexes is interpreted easily in terms of the energy level of the d orbital. Since the platinum(0) d orbital is at a higher energy than the palladium(0) d orbital, a π-back donation interaction between platinum(0) and disilene (or digermene) is much stronger than that between the palladium(0) complexes, and the E–E bond of the platinum(0) complexes is weakened by the π-back donation to a greater extent than that of the palladium(0) complexes.

The complex $M_2(C_2H_4)(P2)_2$ is characterized as an ethylene-bridged dinuclear complex in both M = Pd and Pt. In these complexes, ethylene π-bonding interaction is much less weakened by the π-back donation interaction than those of disilene and digermene, since the ethylene π* orbital is at a higher energy than those of disilene and digermene.

A similar difference between platinum(0) and palladium(0) complexes is observed in $M(E_2H_4)(P2)$ (M = Pd or Pt; E = Si or Ge). From the nbo analysis and the laplacian of electron density, $Pt(E_2H_4)(P2)$ is characterized to be a three-member metallacycle complex that involves the E–E single bond and the M–E covalent bond. However, the palladium(0) analogs are characterized to be disilene and digermene complexes in which the Si=Si and Ge=Ge double bonds coordinate with the Pd(0) center. In the ethylene complexes, the C=C bond is completely maintained in both platinum(0) and palladium(0) complexes, because the π-back donation to ethylene is weak.

In conclusion, we wish to emphasize that the concept of σ-donation and π-back donation [15] is very useful for understanding well the geometry and bonding nature of these μ-disilene- and di(μ-silylene)-bridged dinuclear complexes and their Ge analogs.

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