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Ge$_2$H$_2$ a π-ligand in organometallic chemistry

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Abstract

η^2 π-Complexes of Ge$_2$H$_2$ with the organometallic fragments V(PH$_3$)$_2$(I)(CO)$_2$, Cr(CO)$_4$, Co(PH$_3$)$_2$(Cl) and M(PH$_3$)$_2$ (M = Ni, Pd, Pt) have been studied at the B3LYP level using the SBKJC relativistic effective core potentials and their associated basis sets on metals and iodine, and the 6-31G(d) basis set on all other elements. The transition metal fragments of V, Cr, Co, Ni, Pd and Pt were chosen based on known alkyne compounds. All the complexes are local minima for both the HGeGeH and GeGeH$_2$ isomers of the Ge$_2$H$_2$ ligand. The complexes containing GeGeH$_2$ isomer as a ligand are lower in energy than those with the HGeGeH ligand (except in the V complex in which the difference is only 1.0 kcal/mol). There is a net charge transfer from ligand to metal in complexes V–Co and from metal to ligand in late transition metal complexes (Ni–Pt).
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*Keywords:* π-Ligand; Ge$_2$H$_2$; Alkynyl complexes; DFT; FMO

1. Introduction

The η^2 π-complexes of C$_2$R$_2$ with various transition metals are well known [1]. Examples relevant to this study include [V(CO)$_2$(P(PhMe$_2$))$_2$(I)(MeC≡CMe)] (**1**), [Rh-(P(^{i}Pr)$_3$)$_2$(Cl)(Me$_3$SiC≡CC$_2$SiMe$_3$)] (**2**), and [Ni(PPh$_3$)$_2$-(HC≡CH)] (**3**) [2–4]. There are many theoretical studies available for these organometallic π-complexes [5]. The bonding between the alkyne and the transition metal is in general explained using the Dewar–Chatt–Duncanson (DCD) model [6]. In this model there are four types of interactions possible between the transition metal fragment and the alkyne ligand (Scheme 1). The most important ones are σ-donation from alkyne to metal and π-back donation from metal to alkyne (A and B in Scheme 1). If the majority of bonding is due to σ-donation then the complexes are referred as η^2 π-complexes, whereas if π-back donation is dominant, then the complexes are considered as metallacyclopropenes [5]. In some complexes where π-donation may be also important, the alkyne ligand is considered as a four

electron donor [5h]. Some computational studies have been reported for Si$_2$H$_2$ in organometallic complexes [7]. However, there are no studies available in the literature explaining bonding properties between Ge$_2$H$_2$ and transition metals.

Ge$_2$H$_2$ has been detected in the gas phase [8]. Theoretical studies have shown four minima on the singlet potential energy surface of Ge$_2$H$_2$ (Scheme 2) [9,10]. The global minimum is a dibridged isomer **7**. In the present study the π-ligand properties of isomers **4** and **5** are investigated. Isomers **6** and **7** were not considered further as they contain bridging hydrogen atom and it is likely that such isomers will not be as stable in the analogous RGeGeR systems [10].

We present here the results of a theoretical study on V(PH$_3$)$_2$(I)(CO)$_2$(Ge$_2$H$_2$) (**8a**), Cr(CO)$_4$(Ge$_2$H$_2$) (**9a**), Co(PH$_3$)$_2$(Cl)(Ge$_2$H$_2$) (**10a**), M(PH$_3$)$_2$(Ge$_2$H$_2$) (M = Ni (**11a**), Pd (**12a**), Pt (**13a**)) complexes, in which the Ge$_2$H$_2$ ligand is isomer **4**. The complexes which contain isomer **5** as a π-ligand are denoted as **8b**–**13b**. These complexes have been chosen based on the known alkyne analogues (**1**–**3**). Since, in the present study an attempt has been made to find the trends in a given row (3d transition metals) and

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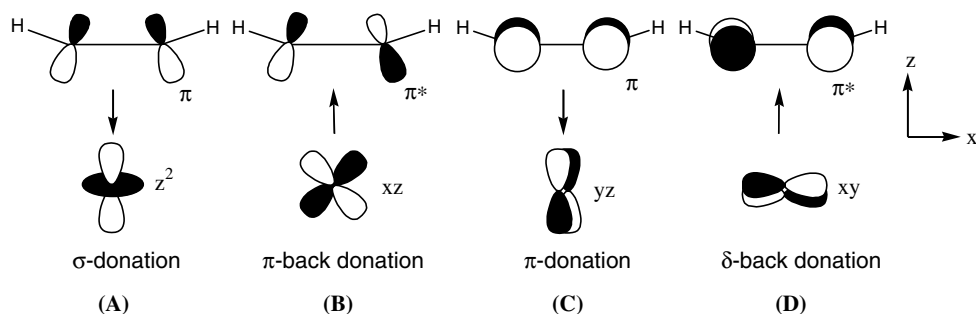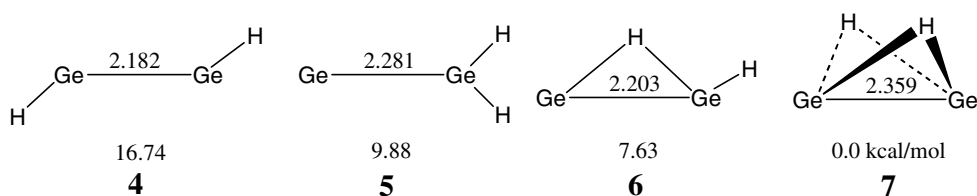
Scheme 1.

Scheme 2.

in a given group (Ni–Pt), the complex **2** has been replaced by **10a**.

2. Computational methods

All the computations were carried out with the GAUSSIAN 98 program package [11]. The geometries of the complexes **8a–13a** and **8b–13b** were optimized using the hybrid Hartree–Fock/DFT method B3LYP [12]. This method uses the combination of the three parameter Becke exchange functional with the Lee–Yang–Parr nonlocal correlation functionals. The default convergence criteria in GAUSSIAN 98 has been used for the optimization. The nature of the stationary points was determined by calculating the vibrational frequencies using analytical second derivatives of the energy. The local minimum structures were ascertained by the absence of imaginary frequencies. The SBKJC relativistic effective core potentials and their associated basis sets (V–Ni: [4211/4211/411], Pd: [4211/4211/311], Pt: [4111/4111/311]) were used for the transition metals and for Iodine ([41/41]). In these effective core potentials the core consists of all but the outermost electrons [13,14]. The standard 6-31G(d) basis set was used to describe all the other elements [15]. The combination of 6-31G(d) and SBKJC is represented as basis set B1 throughout this paper. We later performed calculations on some selected complexes (**11a–13a** and **11b–13b**) using another DFT method B3P86/B1 (which combines Becke's exchange functional with Perdew's nonlocal correlation functional method) for comparison [16]. The Ni complex (**11a**) has been further optimized using the all-electron correlation-consistent basis set cc-pVTZ (represented as basis set B2) on all the atoms at B3LYP level [17]. Fig. 1 shows the relevant structures, and the important geometrical parameters are given in

Table 1. Natural charges have been estimated using natural bond orbital (NBO) analysis [18]. The results at the B3LYP/B1 level are used in discussion unless specifically noted otherwise.

3. Results and discussion

3.1. Complexes with isomer 4

All of the complexes with isomer **4** displayed in Fig. 1 are minima. The optimized geometries of V (**8a**), Co (**10a**) and Ni (**11a**, and also for Pd and Pt) are similar to those of the experimental structures known for their carbon analogs **1** (pseudo octahedral), **2** and **3** (square planar). The Cr-complex (**9a**) has a pseudo-trigonal-bi-pyramidal (TBP) structure in which the Ge$_2$H$_2$ ligand has occupied an equatorial position.

The Ge–Ge distance (Table 1) is longest in the Co-complex (**10a**) and shortest in the V-complex (**8a**). Compared to the free ligand (**4**, Scheme 2), the Ge–Ge distance has been lengthened by 0.06, 0.08, 0.23 and 0.09 Å in V, Cr, Co and Ni complexes, respectively. It is interesting to note that the Ge–Ge distance in group 10 (Ni–Pt) complexes is lengthened systematically down the group (0.09, 0.10 and 0.11 Å, respectively, for Ni, Pd and Pt). The Ge–Ge distance in **8a**, **9a**, and **11a–13a** complexes is much shorter compared to the calculated distance in H$_3$GeGeH$_3$ (**14**, 2.401 Å), [19]. However, it is interesting to note that the Ge–Ge distance in the Co-complex (**10a**) is little longer than the single bond distance found in **14**. There are no specific trends found in the M–Ge distances of these complexes. The Pt–Ge distance in compound **13a** is slightly longer compared to the experimental values in cis-(Me$_2$PhGe)$_2$Pt-(PMe$_2$Ph)$_2$ (**15**, 2.445 Å) and cis-(MePh$_2$Ge)$_2$Pt-(PMe$_2$Ph)$_2$

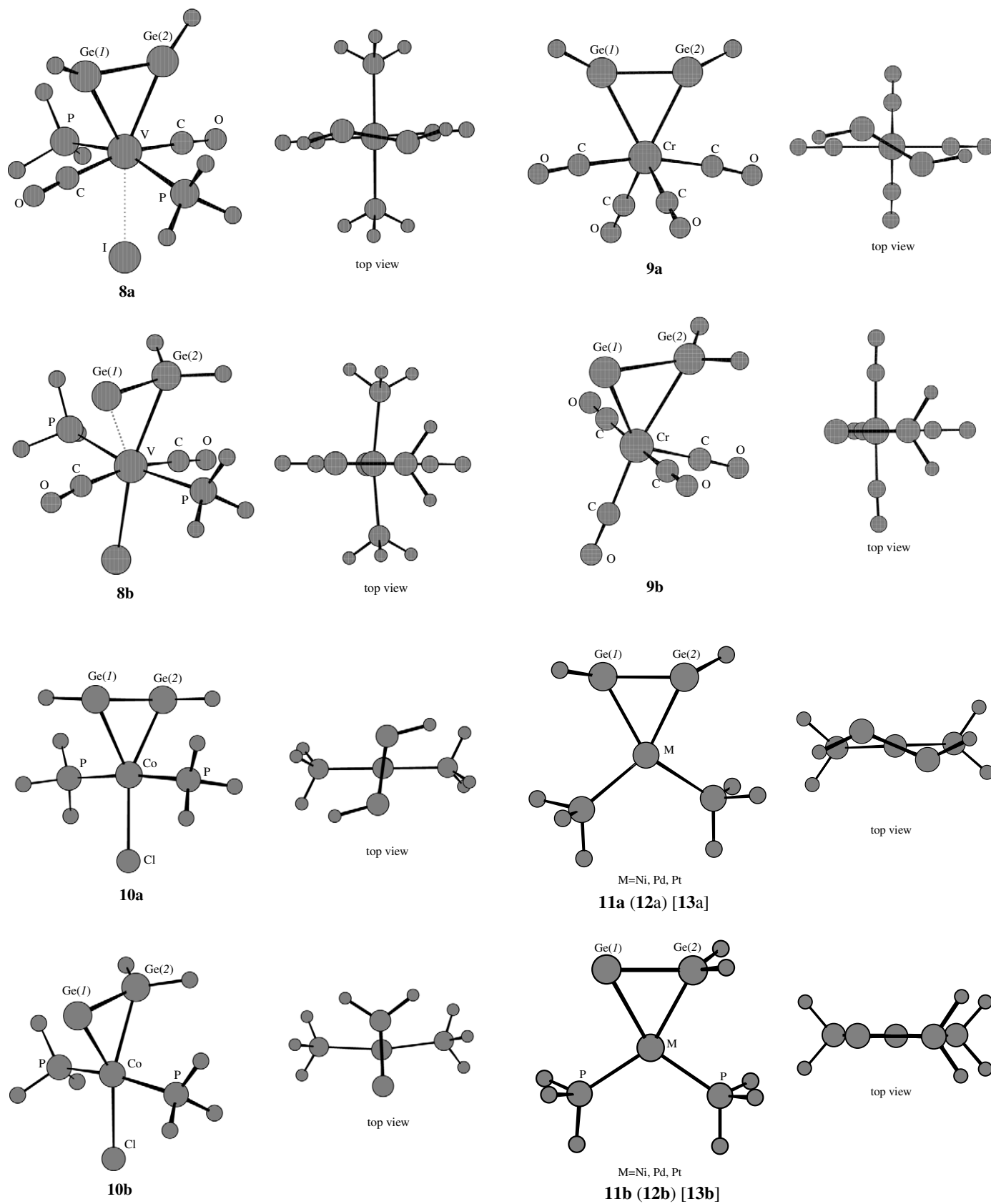Fig. 1. Optimized geometries of the complexes **8a**–**13a** and **8b**–**13b** at the B3LYP/B1 level. The top view shows the orientation of the Ge$_2$H$_2$ ligand with respect to the other ligands in each complex.

Table 1
Important geometrical parameters for **8a**–**13a** and **8b**–**13b** at the B3LYP/B1 level

Molecule	Ge(1)–TM[a]	Ge(2)–TM[a]	Ge–Ge	Ge–H	ϕ[b]
8a	2.513	2.513	2.241	1.540	49.5
8b	2.740	2.643	2.409	1.540	13.8
9a	2.490	2.490	2.263	1.540	33.4
9b	2.377	2.633	2.381	1.540	13.5
10a	2.379	2.379	2.410	1.580	3.5
10b	2.293	2.430	2.412	1.550	11.7
11a	2.359(2.330)[c]	2.359(2.330)	2.270(2.245)	1.560(1.550)	26.6(27.9)
11b	2.303(2.288)	2.473(2.424)	2.363(2.348)	1.550(1.550)	5.2(6.4)
12a	2.517(2.480)	2.517(2.480)	2.284(2.258)	1.560(1.550)	22.0(23.4)
12b	2.581(2.550)	2.521(2.490)	2.393(2.375)	1.550(1.540)	15.3(15.6)
13a	2.492(2.460)	2.492(2.460)	2.297(2.268)	1.560(1.550)	19.9(22.5)
13b	2.558(2.530)	2.500(2.470)	2.417(2.397)	1.550(1.540)	14.9(15.2)

[a] TM represents the transition metal, and refer to Fig. 1 for the atom numbering.
[b] Refer to the text for the definition of ϕ.
[c] The values in parenthesis are at the B3P86/B1 level.

(**16**, 2.439 Å) [20]. Comparison of the Pd–Ge and Ni–Ge distances with $(Ph_3P)_2Pd(Ge(N(SiMe_3)_2)_2)$ (**17**, 2.328 Å), and $(Ph_3P)_2Ni(Ge(N(SiMe_3)_2)_2)$ (**18**, 2.206 Å) lead to similar conclusions [21,22].

The angle ϕ (Table 1) gives the non-planarity of the hydrogens on the coordinated Ge_2H_2 ligand from its ideal planar geometry found in free ligand **4** [23]. Larger value of ϕ represent greater bending of Hs away from the metal. The largest bending is found in the V-complex (**8a**, 49.5°) and the smallest bending is found in the Co-complex (**10a**, 3.5°).

3.2. Complexes with isomer 5

There are two types of ligand orientation possible for the π-complexes of isomer **5** with Ni–Pt. The in-plane orientation (**11b**–**13b**) complexes (where the Ge–Ge bond is in the molecular plane of P–M–P) are minima except for Ni, in which the complex is slightly twisted, whereas the perpendicular complexes (Ge–Ge bond is perpendicular to the molecular plane of P–M–P) are transition states. The energy difference between these two in-plane and perpendicular isomers is 0.7, 1.7 and 2.9 kcal/mol for Ni, Pd and Pt, respectively. The low energy difference between these two isomers also indicates that the germyne ligand might rotate like a propeller along the M-$(GeGeH_2)$ axis at room temperature. The alkyne complexes have a higher energy difference between the in-plane and perpendicular isomers (ΔE for $Pt(PH_3)_2(C_2H_2)$ is 18.1 kcal/mol). In the V (**8b**) and Co (**10b**) complexes the Ge–Ge bond is perpendicular to the P–M–P molecular plane (Fig. 1). Similar orientation has been observed experimentally for carbon complexes **1** and **2**. The Cr-complex (**9b**) has a TBP environment around the metal similar to that of **9a**, with the Ge_2H_2 ligand in an equatorial position. It is interesting to note that the Ge–Ge axis in **9b** is in the equatorial plane (Fig. 1), which is a minimum. The alternative arrangement in which the Ge–Ge axis is perpendicular to equatorial plane is a transition state and 18.22 kcal/mol higher in energy. The complexes **8b**–**13b** are found to be more stable than **8a**–**13a** (V: 1.0, Cr: 12.7, Co: 12.4, Ni: 7.0, Pd: 8.2, Pt: 8.8 kcal/mol).

In the case of complexes with isomer **5**, the Ge–Ge distance is longest in the Pt (**13b**) complex and shortest in the Ni (**11b**) complex. Compared to free ligand (**5**, Scheme 2), on average the Ge–Ge distance has been lengthened by 0.08–0.14 Å in **8b**–**13b**. Similarly, compared to the ethane like structure Ge_2H_6 (**14**), the Ge–Ge distance is shorter in Cr (**9b**), Ni (**11b**) and Pd (**12b**) complexes, and longer in V (**8b**), Co (**10b**) and Pt (**13b**) complexes. Similar to that of complexes with isomer **4**, there are no specific trends found in the M–Ge distances in complexes with isomer **5**. The Pt–Ge, Pd–Ge and Ni–Ge distances in **13b**, **12b** and **11b** are longer compared to the experimental values found in **15**–**18**. On average, the non-planarity of the hydrogens on Ge (ϕ, Table 1) varied from 5.2° to 14.9°. The largest non-planarity of hydrogens is found in Pt complex **13a** ($\phi = 14.9°$).

The complexes **11a**–**13a** and **11b**–**13b** are minima at the B3P86 level also. The bond distances in these complexes are calculated to be slightly shorter at the B3P86 level than at the B3LYP level (Table 1). Similar trends have been reported in the literature for organometallic complexes involving the Si and Ge based ligands [24]. The differences in bond distances between B3LYP/B1 and B3LYP/B2 levels are very small (on average ±0.007 Å) for the Ni complex (**11a**).

3.3. Electronic structure

The DCD model as shown in Scheme 1 has been widely used to explain the bonding between the acetylene and the transition metals. A similar model can be constructed for the explanation of bonding between ligand **4** and the transition metals, which is shown in Scheme 3. The difference in these two schemes is the perpendicular π and π* orbitals, which appear like lone-pair MOs in Ge_2H_2 due to the non-linear nature of isomer **4**. However, the feasibility of the bonding interactions that are shown
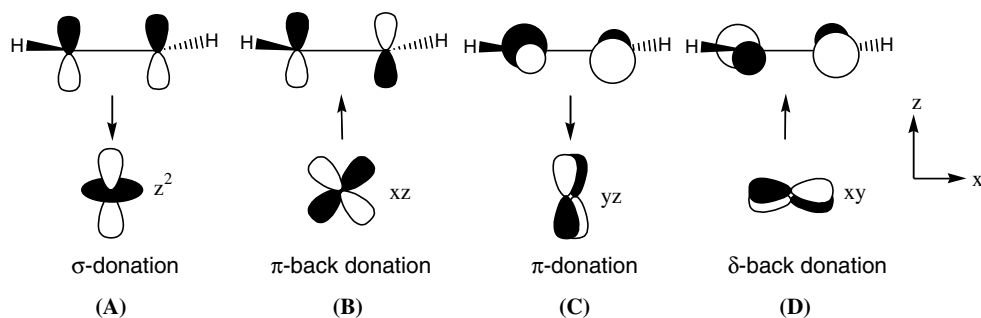
Scheme 3.

in Scheme 3 depends on the relative energy gap between the ligand and metal fragment orbitals. The eigenvalues of the metal fragment MOs in turn depend on the ligand sphere on the metal. Hence, the electronic structure of the complexes **8a**–**13a** and **8b**–**13b** have been further analyzed using the fragment molecular orbital (FMO) method [25]. To compare the bonding in acetylene complexes with its heavier analogs, the vanadium complex **1** is included in the electronic structure analysis. All of the phenyl and methyl substituents in **1** are replaced by hydrogen atoms ([V(CO)$_2$(PH$_3$)$_2$(I)(HC≡CH)], **1H**) for the ease of calculations. Fig. 2a shows the orbital interaction diagram of V(CO)$_2$(PH$_3$)$_2$(I) with C$_2$H$_2$ and Ge$_2$H$_2$ (**4**). Though the carbon complex **1H** has higher symmetry, the C$_2$ symmetry notations have been used for consistency since the complex **8a** has C$_2$ symmetry (Fig. 1).

In accordance with the DCD model the in-plane π-orbital (1a) of C$_2$H$_2$ interacts with the 3a MO of the metal fragment, leading to σ-donation from ligand to metal (Scheme

1). However, this interaction is relatively weak due to the large energy gap between the metal 3a and the ligand 1a MOs. The in-plane π* MO (2b) of C$_2$H$_2$ interacts with the 3b of metal leading to π-back donation from metal to ligand. The orthogonal π MO (1b) of the ligand has an interaction with the 4b (yz) orbital on the metal. This interaction leads to π-donation of electrons from ligand to metal. The δ-back donation has not been observed between 2a of the ligand and the 2a of the metal fragment due to the large energy gap between them. Therefore, the bonding in **1H** can be summarized as σ and π donation from ligand to metal, which are weak, and a π-back donation from metal to ligand, which is strong. The NBO charges support this interpretation as the net charge on the C$_2$H$_2$ ligand is −0.05e (C: −0.27, H: 0.24e).

The valence MOs of the Ge$_2$H$_2$ (**4**) ligand are higher in energy than in C$_2$H$_2$, since these are formed from 4s and 4p atomic orbitals. For example, the calculated eigenvalue of the π MO (1a) for free Ge$_2$H$_2$ (**4**) is −5.5 eV as compared
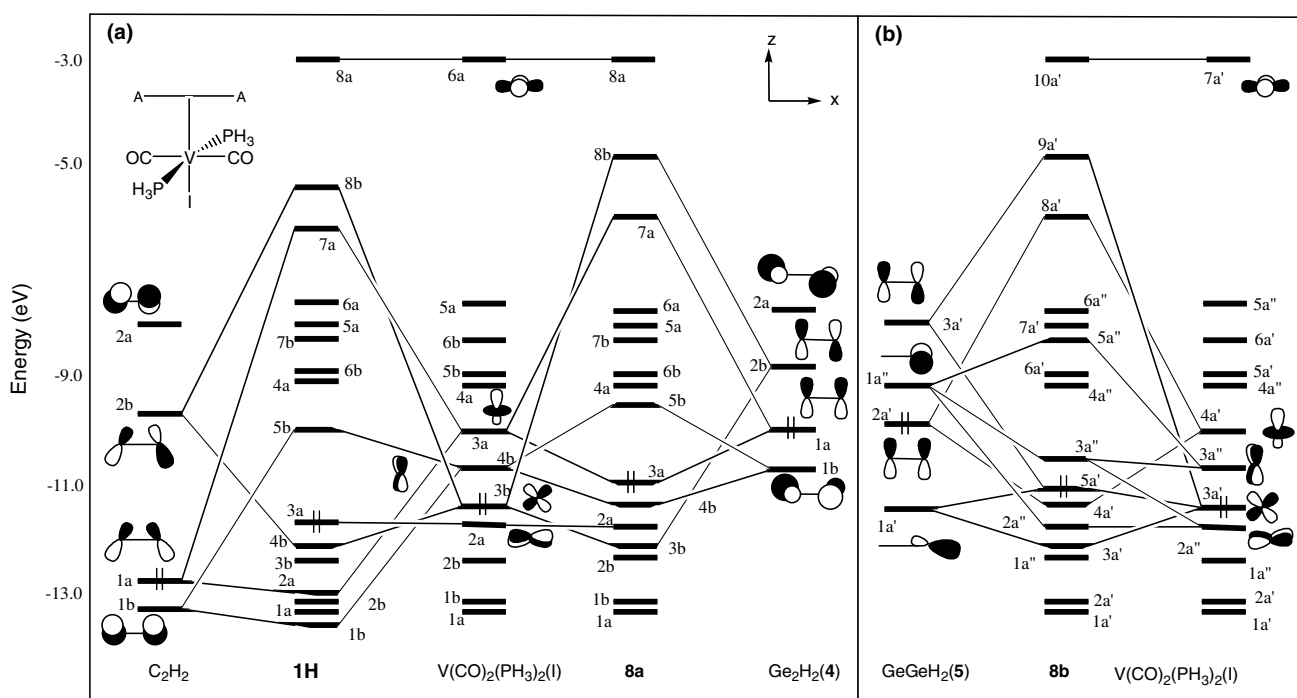

Fig. 2. Interaction diagram for [V(CO)$_2$(PH$_3$)$_2$(I)(C$_2$H$_2$)] (**1H**) and [V(CO)$_2$(PH$_3$)$_2$(I)(Ge$_2$H$_2$)] (**8a** and **8b**). Only the HOMO electrons are shown for each fragment. The general molecular framework is shown in part (a), in which the ligand A$_2$ represents either C$_2$H$_2$, **4** or **5**.

to -7.7 eV for C_2H_2 at the B3LYP/6-31G(d) level. Because of the higher energy valence MOs of Ge_2H_2, the interaction between the metal 3a and ligand 1a orbitals is much more effective than that in C_2H_2. Similar to the carbon case, the π^* MO (2b) of **4** interacts with the 3b (xz) metal orbital leading to π-back donation (B in Scheme 3). The ligand MO 1b interacts with 4b on the metal leading to the 4b orbital of **8a** as predicted in Scheme 3. This kind of interaction is possible due to the non-linear nature of the ligand Ge_2H_2 (**4**) as shown in Fig. 1 (top view of **8a**) and Scheme 4 (which shows the top view of the interaction between yz of metal and 1b of the ligand). This bonding is similar to π-donation in the carbon case. Even though the valence MOs of **4** are higher in energy than that of the alkyne ligand, the energy gap between 2a of the ligand and the 2a of the metal fragment is large in complex **8a** (Fig. 2); hence, no δ-back donation has been observed. The bonding in **8a** can be described as σ and π donation from ligand to metal and π-back donation from metal to ligand. Unlike in the case of carbon (**1H**), both the σ and π donation in **8a** are strong. This should lead to a charge transfer from ligand Ge_2H_2 to the metal center. The NBO charges support this interpretation as the net charge on Ge_2H_2 ligand in **8a** is $+0.58e$ (Ge: $+0.37$, H: $-0.08e$). Therefore the bonding character of **8a** is predicted to be remarkably different from that of **1H**.

Fig. 2b shows the interaction diagram between the $GeGeH_2$ (**5**) ligand and the metal fragment $V(CO)_2(PH_3)_2$-(I). C_s symmetry has been used in this interaction diagram (Fig. 2b). Similar to that of complex **8a**, there is a σ-donation from ligand to metal due to the interaction from 2a′ of the ligand and 4a′ of the metal. However the metal 3a′ has a 3-orbital interaction with 3a′ (π^*) and 1a′ (σ-lone pair) of the ligand. This interaction can be viewed as a π-donation (from 1a′) and π-back donation (due to participation of 3a′). Similarly the 3-orbital interaction between metal 2a″ and 3a″ with the ligand 1a″ leads to a very low-lying LUMO in this complex **8b**. This interaction can be viewed as a δ-back donation (similar to that shown in Scheme 3). However, due to the low energy gap between the HOMO (5a′) and LUMO (3a″), the complex **8b** could be a high spin system. In fact, the stability analysis of **8b** leads to a UHF instability, whereas no such instability was found in **8a** [26].

PH₃

OC - - - - - - - - - - - CO

PH₃

π-donation
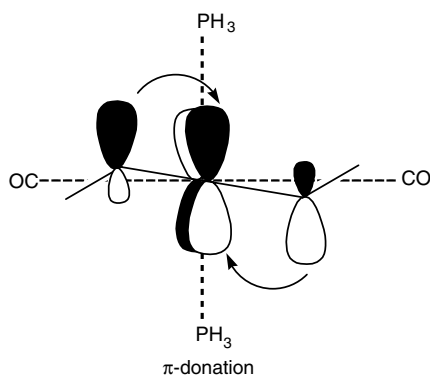
Scheme 4.

Further investigations have revealed that the complex **8b** is 8.1 kcal/mol more stable in the triplet state compared to its singlet state. The NBO analysis shows a net charge transfer from ligand **5** to the metal fragment (Ge: $+0.09$, Ge: $+0.44$ and H: $-0.01e$).

The electronic structure of **9a** is similar to that of **8a**. There is a σ and π donation from ligand to metal and π-back donation from metal to ligand. Similarly, the bonding in **9b** is found to be close to that of **8b**. The only difference between **9b** and **8b** is that the 3-orbital interaction between ligand 1a″ and metal xy and yz is missing due to the large energy gap ($\sim$3 eV) between them. Therefore, there is no low lying LUMO in complex **9b**, and it can be stable in the low spin state. In fact the stability analysis of both **9a** and **9b** did not produce any UHF instability. The NBO charges on the Ge_2H_2 ligand are $+0.48$ and $+0.58e$ in **9a** and **9b**, respectively.

The electronic structure of complex **10a** is found to be different than those of early transition metal complexes from groups 5 (**8a**) and 6 (**9a**). The major difference is that both the bonding and anti-bonding combinations deriving from ligand 1b and metal 4b MOs are filled. Hence, there is no π-donation from ligand to metal. This is because the late transition metal Co has four extra d-electrons compared to V. Therefore the electronic structure of **10a** consists of a σ-donation from ligand to metal and a π-back donation from metal to ligand. Similar to **9b**, **10b** also missing the 3-orbital interaction due to 1a″ on ligand and 2a″ and 3a″ on the metal fragment. Therefore, the bonding in **10b** consists of σ-donation from ligand to metal and the π-back donation from metal to ligand. The net NBO charges on Ge_2H_2 ligand are $+0.18$ and $+0.09e$ in **10a** and **10b** complexes.

The transition metal fragment $Ni(PH_3)_2$ has all of the d-orbitals occupied unlike the systems V–Co. All of the complexes of Ni, Pd and Pt have shown bonding features close to each other. Fig. 3 shows the bonding interactions for Pt complexes (**13a** and **13b**), which is also applicable to both Ni and Pd complexes. The σ-donation from ligand to metal in complex **11a** is due to the interaction between the ligand's π MO (1a) and the metal p_z orbital. However, since the metal p_z orbital is higher in energy (-1.50 eV), this interaction is very weak. Similar to that of **10a**, the π-donation is also absent in complex **11a**. Therefore the bonding in complex **11a** is mainly due to the π-back donation from metal to ligand. The NBO charges support this interpretation as the net charge on Ge_2H_2 ligand is calculated to be $-0.22e$ (Ge: 0.01, H: $-0.12e$) in the complex **11a**. The compound **11b** has also shown bonding features similar to that of **11a**. Therefore the bonding in **11b** is also mainly due to the π-back donation from metal to ligand. The net NBO charge on the Ge_2H_2 ligand in **11b** is $-0.18e$ (Ge:0.01, Ge:0.07, H:$-0.13e$). Similarly, the net NBO charges on the ligand in **12a**, **12b**, **13a** and **13b** are -0.17, -0.11, -0.16 and $-0.10e$, respectively.

The bonding in Ge_2H_2 π-complexes of ligand type **4** is mainly due to: (i) σ-donation from the ligand's π MO; (ii) π-donation from the ligand's σ-lone-pair type MO
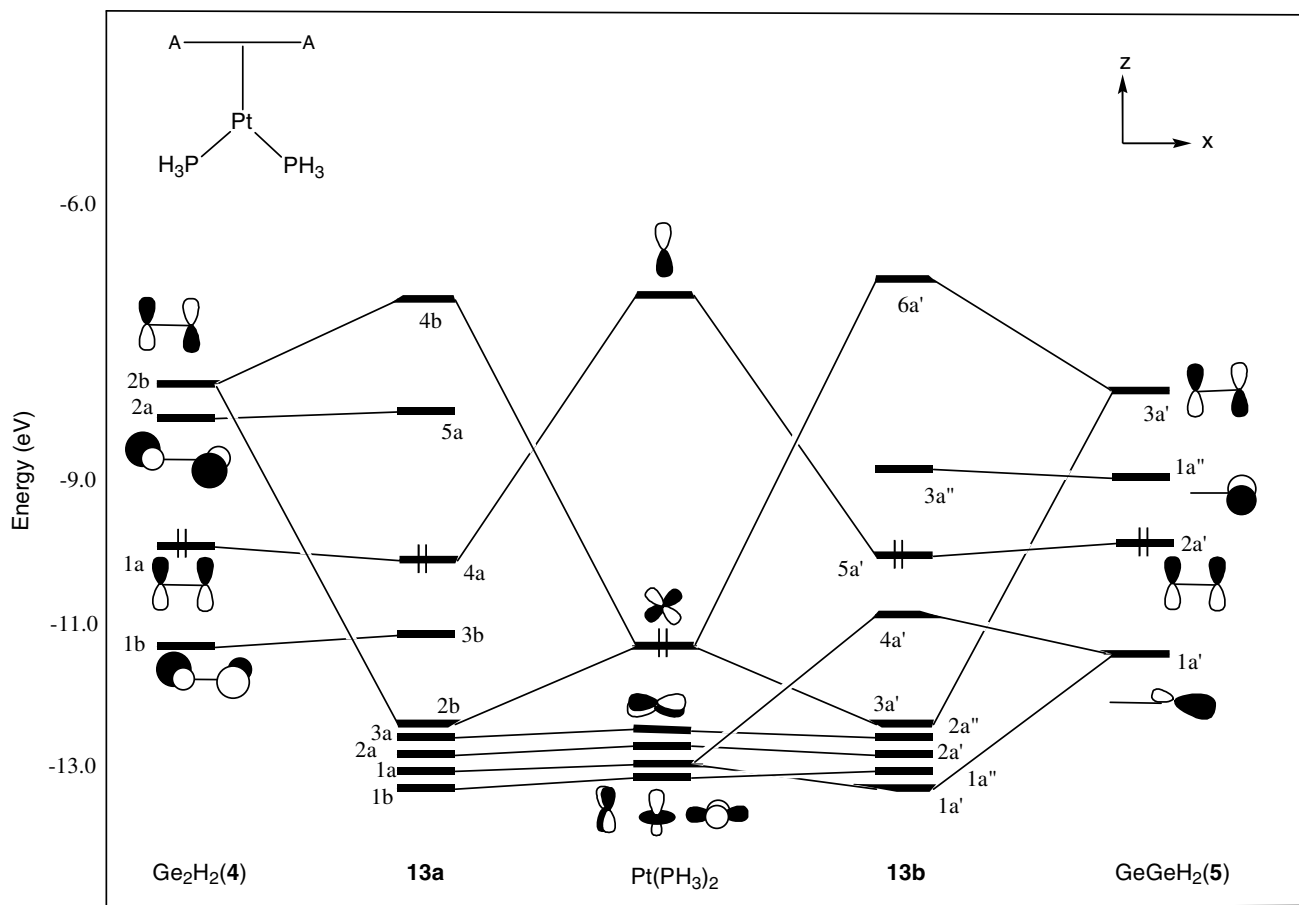
Fig. 3. Interaction diagram for [Pt(PH$_3$)$_2$(Ge$_2$H$_2$)] (**13a** and **13b**). Only the HOMO electrons are shown for each fragment. The A$_2$ in the molecular framework represents either **4** or **5**.

and (iii) π-back donation from the metal to the ligand's π*
MO. In the case of early transition metal complexes (e.g.
8a) all three bonding features are found to be important,
whereas in late transition metal complexes (**11a**) bonding
feature (iii) is predominant. Therefore, in the early transi-
tion metal complexes the charge transfer is from ligand
to metal, whereas in late transition metal complexes it is
from metal to ligand, due to the increase in d-electron
count of the metals. It is interesting to see that the net
NBO charge on the Ge$_2$H$_2$ ligand changes from a positive
value (+0.58e in **8a**) to a negative value (−0.22e in **11**) in
tune with the above conclusion. However, caution needs
to be exercised, as the charges are dependent on the ligand
sphere on the metal. The ligand **5** also has shown similar
features. The complexes with ligand **5** have δ-back dona-
tion from metal to ligand. This feature was found only in
the V-complex (**8b**), and it is absent when d-electron count
increases (**9b**, **10b** and **11b**).

The Ge$_2$H$_2$ π complexes studied here can be consid-
ered as reasonable synthetic targets, if they are substi-
tuted with adequately large groups. The experimental
preparation and X-ray analysis of Ar′GeGeAr′ (Ar′ =
C$_6$H$_3$-2,6(C$_6$H$_3$-2,6-^{i}Pr$_2$)$_2$) and [(Me$_3$P)$_2$Pt(Si$_2$R$_4$)] (R =
SiMe$_2$(t-Bu)) [27,28], and the computational studies on
Ge$_2$R$_2$ (R = 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl,

and 2,6-bis(2,4,6-triisopropylphenyl)phenyl) [10] illustrate
the importance of bulky substituents in stabilizing the
multiple bonds in heavier group 14 elements.

4. Conclusions

Calculations at the B3LYP level showed that the η^2-
complexes **8a**–**13a** and **8b**–**13b** of Ge$_2$H$_2$ ligands **4** and **5**
are local minima. The electronic structure analysis revealed
that there is a charge transfer from the metal to the ligand
in the alkyne complex of V (**1H**). The Ge complexes of V
(**8a** and **8b**) exhibit a charge transfer from ligand to metal,
which is a reversed electron flow compared to the C com-
plex (**1H**). However, in the late transition metal complex
(**11a** and **11b**) of Ge, the charge transfer is from metal to
ligand. Complexes with ligand **5** have shown a 3-orbital
interactions due to participation of either in-plane lone pair
(1a′) or the orthogonal p-orbital (1a″) on ligand. All the π
complexes with the ligand **5** are lower in energy than those
with the ligand **4**.

provided on the Research Cluster operated by UNT Academic Computing Services.

Appendix A. Supplementary material

Tables giving Cartesian coordinates and vibrational frequencies of the structures in Fig. 1. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.01.037.

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