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H-bridged $A_3H_3^+$ (A = Si and Ge): A π-ligand in organometallic chemistry †

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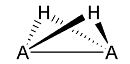
Organometallic complexes based on H-bridged $Si_3H_3^+$ and $Ge_3H_3^+$ ligands were studied at the B3LYP and B3P86 levels. Relativistic effective core potentials (SBKJC-21G and Stuttgart-RSC) and their associated basis sets were used on metals and the 6-31G(d) basis set was used on ligands. All the complexes $(A_3H_3)Co(CO)_3$ (**9**, C_{3v}), $(A_3H_3)Rh(CO)_3$ (**10**, C_{3v}) and $(A_3H_3)Ir(CO)_3$ (**11**, C_{3v}) (A = Si and Ge) are minima and more stable than the complexes based on $Si_3H_3^+$ and $Ge_3H_3^+$ ligands with terminal hydrogens (**9a**–**11a**). The stability of the bridged systems increases from Si to Ge. Isolobal and isosynaptic analogies connect these complexes with other organometallic complexes (*e.g.* $(\mu\text{-H})_3Fe_3(CO)_9(\mu_3\text{-CMe})$) and main group pyramidal systems (*e.g.* $(\mu\text{-H})_3B_3H_3(\mu_3\text{-CH})$).

Introduction

Interest in the differences of structure and bonding of C and its heavier analogs has been growing in recent years.[1–10] H-bridged structures are found to be stable and sometimes even global minima for Si and Ge compared to classical structures known for C. Some of the examples are: (i) Acetylene analogs Si_2H_2 and Ge_2H_2 prefer doubly bridged structure **1** (C_{2v}).[2,3] (ii) A triply H-bridged structure (**2**, C_{3v}) is a minimum for trisilacyclopropane and trigermacyclopropane.[4] (iii) The lowest energy structures of $Si_3H_5^+$ (**3**, C_s) and $Si_2H_3^+$ (**4**, D_{3h}) have two and three bridging H's respectively.[5,6] A similar trend is also found for the heavier analogs of the 2π-Hückel aromatic cyclopropenium ion.[7,8] The potential energy surface of $Si_3H_3^+$ has shown dramatic contrasts with that of the carbon analog.[7] $C_3H_3^+$ has four minima on its potential energy surface, whereas $Si_3H_3^+$ has twelve minima within a 46 kcal mol^{-1} range, though the classical trisilacyclopropenium ion is the global minimum (**5**, D_{3h}).[7,11] The triply H-bridged structure (**6**, C_{3v}) is also a minimum for $Si_3H_3^+$, but it is 30 kcal mol^{-1} higher in energy than **5-Si** at the B3LYP/6-31G(d) level.[7,8] In the case of Ge, **6** is also a minimum and its stability is competitive with **5**. **6-Ge** is 9.4 and 3.8 kcal mol^{-1} higher in energy than **5-Ge** at the B3LYP/6-31G(d) and G2 levels respectively.[8] $Si_3H_3^+$ has been detected in the gas phase and $Ge_3R_3^+$ (R = ^{t}Bu$_3$Si) has been prepared experimentally.[12,13] Pyramidal structures based on **5-Si** and **6-Si** have shown remarkable differences. The classical structures **7** (C_{3v}) are calculated to be less stable than the H-bridged isomers **8** (C_{3v}).[9] Though η^3-ligand properties of **5-Si** and **5-Ge** are studied in organometallics, there are no reports available regarding **6** as a ligand in organometallic chemistry.[14]

In view of the findings **1**–**4** and the relative stabilities of **7** and **8**, we reasoned that organometallic complexes with ligand **6** may also be stable. We report in this paper the results of a theoretical study on η^3 complexes ($(A_3H_3)Co(CO)_3$) (**9**, C_{3v}), ($(A_3H_3)Rh(CO)_3$) (**10**, C_{3v}) and ($(A_3H_3)Ir(CO)_3$) (**11**, C_{3v}) (where A = Si and Ge) (Fig. 1). The non-bridged isomers (**9a**–**11a**) are included for comparison. The present study shows that the bridged isomers (**9**–**11**) are indeed more stable than the non-bridged isomers (**9a**–**11a**).



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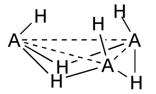

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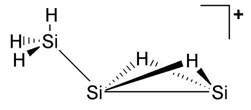

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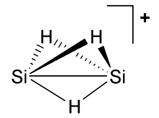

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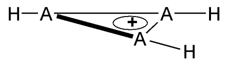

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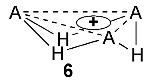

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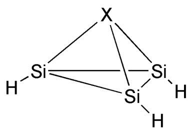

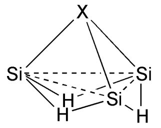

X=BH$^-$, CH, N, NH$^+$, NO, SiH, P, PH$^+$ and PO
7 **8**

Computational methods

The geometries of all the structures were optimized using the hybrid Hartree-Fock/DFT method B3LYP.[15] This method uses the combination of the three parameter Becke exchange functional with the Lee–Yang–Parr nonlocal correlation functionals. Another DFT method, which combines Becke's exchange functional with Perdew's nonlocal correlation functional method (B3P86) was also used for comparison.[16] The standard 6-31G(d) basis set was used for ligands and for metals the SBKJC-21G relativistic effective core potentials and their associated basis sets ([4211/4211/411]) were used.[17–19] In these effective core potentials, the core consists of all but the outermost electrons. The combination of 6-31G(d) and SBKJC-21G is represented as basis set B1 throughout this paper. We later optimized the geometries at the B3LYP level using the small core Stuttgart-RSC relativistic effective core potentials and their associated basis sets (Co: [311111/22111/411/1], Rh and Ir: [311111/22111/411]) on the metals and 6-31G(d) for ligands (represented as basis set B2).[18,20] The nature of the stationary points was determined from harmonic force constants and vibrational frequencies.[21] All of the computations were carried out with the Gaussian 98 program

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† Electronic supplementary information (ESI) available: Cartesian coordinates (at the B3LYP/B1 level), and total and zero point energies of structures **9**–**11**. See http://www.rsc.org/suppdata/dt/b1/b111172h/

Table 1 Relative energies (kcal mol^{-1})[a] and NBO charges (in e) of the isomers shown in Fig. 1.[b] The NBO charges for non-bridged systems are available in ref. 14

Structure	B3LYP/B1	B3LYP/B2	B3P86/B1	NBO charges
9-Si	0.0	0.0	0.0	Co: −0.47, Si: 0.35, H: −0.24, C: 0.48, O: −0.43
9a-Si	7.2	6.7	6.1	
10-Si	0.0	0.0	0.0	Rh: −0.30, Si: 0.30, H: −0.24, C: 0.47, O: −0.43
10a-Si	5.5	5.7	4.0	
11-Si	0.0	0.0	0.0	Ir: −0.13, Si: 0.28, H: −0.24, C: 0.43, O: −0.42
11a-Si	8.9	8.9	7.1	
9-Ge	0.0	0.0	0.0	Co: −0.42, Ge: 0.33, H: −0.22, C: 0.47, O: −0.43
9a-Ge	31.4	31.0	28.0	
10-Ge	0.0	0.0	0.0	Rh: −0.25, Ge: 0.28, H: −0.23, C: 0.46, O: −0.43
10a-Ge	30.6	30.8	27.0	
11-Ge	0.0	0.0	0.0	Ir: −0.07, Ge: 0.26, H: −0.23, C: 0.42, O: −0.43
11a-Ge	34.0	34.2	30.2	

[a] Relative energies are calculated after scaling the zero-point energy by 0.9806.[34] [b] All the compounds in Fig. 1 are minima.

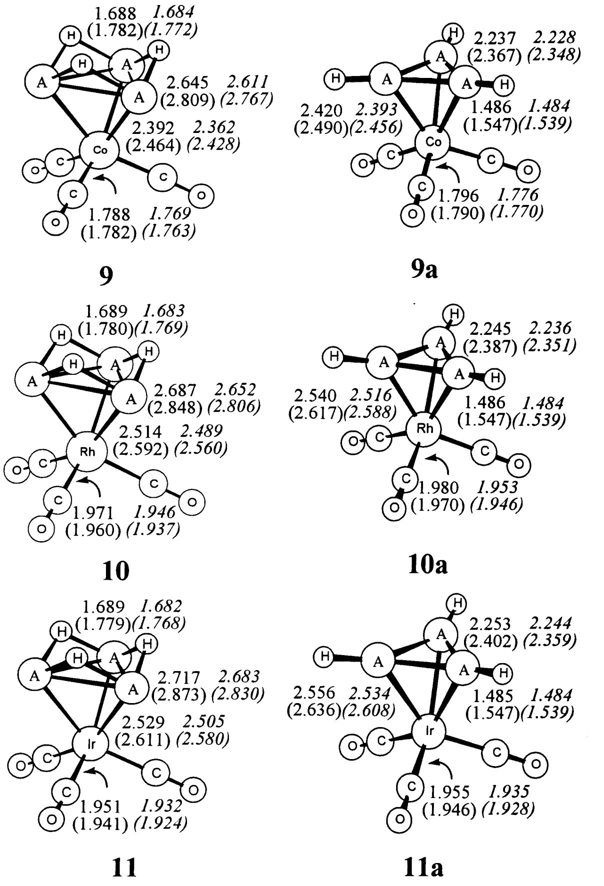

Fig. 1 Optimized geometries and important bond distances for Si and Ge (in parentheses) complexes at the B3LYP/B1 level. The values in italics are at the B3P86/B1 level. Structures **9a**–**11a** are given for comparison (ref. 14).

package on an NCSA supercomputer.[22,23] Fig. 1 shows the relevant structures with selected geometrical parameters. We use natural charges obtained from natural bond orbital (NBO) analysis.[24] The results at the B3LYP/B1 level are used in the discussion unless specifically noted otherwise.

Results and discussion

All the complexes are minima and the bridged structures (**9**–**11**) are lower in energy than the non-bridged complexes **9a**–**11a**. In fact, the stability of bridged structures increases from Si to Ge (Table 1). On average the bridged Si complexes are 7.2 and 5.7 kcal mol^{-1} more stable than the non-bridged isomers at the B3LYP and B3P86 levels, respectively. Similarly, bridged Ge complexes are 32.0 and 28.4 kcal mol^{-1} more stable than the non-bridged isomers at the B3LYP and B3P86 levels. There is no significant change in relative energies obtained from the two basis set combinations (B1 and B2; Table 1). The energy difference between bridged and non-bridged structures is found to be slightly higher in Co and Ir complexes and less in Rh complexes (Table 1).

The structure and bonding properties of non-bridged isomers have been discussed previously;[14] hence, we restrict ourselves to bridged systems in this paper. The bond distances in **9**–**11** are calculated to be slightly shorter at the B3P86 level than at the B3LYP level. There is a variation of ±0.016 Å for bond distances between B3LYP/B1 and B3LYP/B2 levels. On average the Si–Si and Ge–Ge distances are 2.683 ± 0.038 Å and 2.843 ± 0.034 Å, respectively, at the B3LYP level. In accordance with the covalent radii of Co (1.16 Å), Rh (1.25 Å) and Ir (1.27 Å), the A–A distance is longest in the Ir complex (**11**) and shortest in the Co complex (**9**).[25] Similarly the metal(M)–A distance is longest in Ir complexes and shortest in Co complexes. The non-bridged complexes (**9a**–**11a**) were also reported to show similar trends in geometrical parameters.[14]

The A–A distances in **9**–**11** are longer than those in the free ligands (**6-Si**: 2.571 Å and **6-Ge**: 2.729 Å).[8] Similar results are found when comparing distances to those in **1** (**1-Si**: 2.221 Å and **1-Ge**: 2.358 Å) and **4** (**4-Si**: 2.417 Å and **4-Ge**: 2.611 Å).[2,3,6] The A–A distances in **9**–**11** are much shorter than in **2** (**2-Si**: 3.133 Å and **2-Ge**: 3.260 Å).[4] The M–A distances are slightly shorter in complexes **9**–**11** (by ~0.027 Å and ~0.025 Å for Si and Ge) than those in **9a**–**11a**, suggesting a strong metal–ligand bonding in **9**–**11**.

Comparison of the electronic structures of bridged and non-bridged isomers may give some insight into the stability of bridged isomers. A diagram showing the important interactions between **6-Ge** and $[Ir(CO)_3]^-$ leading to **11**, and **5-Ge** and $[Ir(CO)_3]^-$ leading to **11a** constructed by the fragment molecular orbital (FMO) method is shown in Fig. 2.[26] The frontier orbitals of $Ir(CO)_3$ (ML_3 type) and **5-Ge** (C_3H_3 type) are well known in literature.[26,27] The bonding in **11a-Ge** is explained due to the following interactions between $Ir(CO)_3$ and **5-Ge**. The 2e orbital of $Ir(CO)_3$ interacts with 2e (π^*) and 1e of the ligand leading to a three orbital interaction. Similarly, a second three orbital interaction between $1a_1$ (π) of the ligand and $1a_1$ (z^2), $2a_1$ (z) of the metal leads to $1a_1$, $2a_1$ and $3a_1$ in **11a-Ge**. The frontier orbitals in **6-Ge** are somewhat different than in **5-Ge**. The σ–π mixing due to the non-planar bridging hydrogens stabilizes both the $1a_1$ (π) and 2e (π^*) orbitals of **6-Ge**.[7,8,28] For example, the eigenvalues of the π MO are −11.92 and −13.36 eV for **5-Ge** and **6-Ge** ligands respectively, at the B3LYP/6-31G(d) level. Similarly, the eigenvalues of π^* MOs are −7.20 and −8.27 eV for **5-Ge** and **6-Ge**. Because of these low-energy valence MOs of **6-Ge**, the three orbital interaction between the metal $1a_1$ and $2a_1$, and ligand $1a_1$ is much more effective than that found with

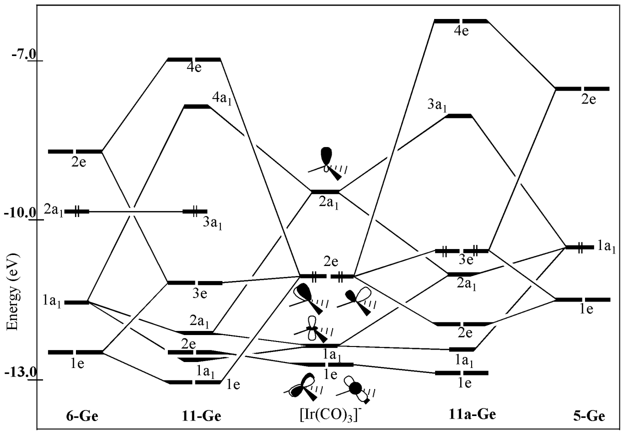

Fig. 2 Interaction diagram between **6-Ge** and [Ir(CO)$_3$]$^-$ leading to [(Ge$_3$H$_3$)Ir(CO)$_3$] (**11-Ge**, on left) and between **5-Ge** and [Ir(CO)$_3$]$^-$ leading to [(Ge$_3$H$_3$)Ir(CO)$_3$] (**11a-Ge**, on right). Only the HOMO electrons are shown for each fragment.

5-Ge. A similar effect is also found for the three orbital interactions between metal 2e and ligand 2e and 1e. These bonding features reveal that the low-energy valence MOs of the bridged ligand form better bonding with Ir(CO)$_3$ than those of the non-bridged ligand. Though it is difficult to pinpoint exactly what makes the bridged system **11-Ge** more stable than the non-bridged system **11a-Ge**, the relative stabilities discussed above are plausible contributing factors. Similar results were found for **9-Ge** and **10-Ge**. The silicon systems **9-Si**, **10-Si** and **11-Si** have also shown similar results, though to a lesser extent. The above discussed bonding features also reveal that there is a charge transfer from ligand to metal. The NBO charges (Table 1) in **9-Si** and **9-Ge** support this interpretation. Similar trends are found in **10-Si**, **10-Ge**, **11-Si** and **11-Ge**. The non-bridged systems have been reported to shown similar trends.[14] Therefore, both bridged and non-bridged ligands **5** and **6** behave as π donor ligands. The systematic decrease in the NBO charges on the metal and Si/Ge ligands down the group shows that the electron transfer from ligand to metal is decreasing from Co to Ir complexes. Since the CO is a σ donor and a π acceptor, whereas the Si/Ge ligands are only π donor ligands, the reduced Mulliken overlap population between M–C(carbonyl) is higher than M–Si/Ge (for example, the overlap populations are Co–C: 0.41, Co–Si: 0.08e in **9-Si** and Co–C: 0.41, Co–Si: 0.03e in **9a-Si**). The NBO analysis also reveals that the lone pairs on the A$_3$H$_3$ ring contains mainly s (~84%) character, which leaves maximum p-character (~94%) on A for other bonds.

It is interesting to note that isosynaptic and isolobal analogies connect the present bridged structures with other organometallic complexes like (μ-H)$_3$Fe$_3$(CO)$_9$(μ$_3$-CMe) and (μ-H)$_3$Os$_3$(CO)$_9$(μ$_3$-CH).[29–32,26] Using an isosynaptic analogy, Fe(CO)$_3$ and Os(CO)$_3$ can be replaced by Si or Ge and an isolobal analogy replaces CMe and CH by Co(CO)$_3$. Now the resulting structures are **9-Si** and **9-Ge** which are stable. Similarly, isomer **9-Si** can also be derived from **8**. The isolobal analogy between trivalent boron and divalent silicon connects **9-Si** with the theoretically predicted pyramidal system (μ-H)$_3$B$_3$H$_3$(CH).[30,33]

Conclusions

Calculations at the B3LYP and B3P86 levels show the following: η^3 organometallic complexes (**9**–**11**) based on the H-bridged A$_3$H$_3$$^+$ (A = Si and Ge) ligand are minima. Compared to complexes (**9a**–**11a**) based on the classical A$_3$H$_3$$^+$ ligand, **9**–**11** are more stable, and their average stability increases from Si (B3LYP: 7.2 and B3P86: 5.7 kcal mol^{-1}) to Ge (B3LYP: 32.0 and B3P86: 28.4 kcal mol^{-1}). Isomers **9-Si** and **9-Ge** are connected to other organometallic complexes and main group pyramidal systems through isolobal and isosynaptic analogies.

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