5200 *Organometallics* **2001,** *20,* 5200−5204

Theoretical Studies on $A_3H_3^+$ (A = C, Si, Ge) as π Ligands in Organometallic Chemistry

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Received July 10, 2001

η^3 π complexes of $A_3H_3^+$ (A = C, Si, Ge) with the organometallic fragments $Co(CO)_3$, $Rh(CO)_3$, $Ir(CO)_3$, $Ni(CO)_3$, $Co(PH_3)_3$, and $Ni(PH_3)_3$ have been studied at the B3LYP and B3P86 levels using the 6-31G(d) basis on ligands and SBKJC-21G relativistic effective core potential and their associated basis sets on metals. All the π complexes are minima. In Si and Ge complexes there is a ligand to metal charge transfer, making Si_3H_3 and Ge_3H_3 cationic ligands, whereas in C complexes there is a small charge transfer from metal to ligand, making C_3H_3 ligands anionic. These remarkable differences in electronic structure between carbon and its heavier analogues are explained using molecular orbitals and natural charges. All the π complexes for Si and Ge are considered viable targets for synthetic pursuit.

Introduction

There is a well-developed organometallic chemistry based on the smallest carbocyclic 2π ligand, $C_3R_3^+$.[1] The triphenylcyclopropenyl cation ($C_3Ph_3^+$) has proven to be a versatile ligand with transition-metal complexes.[2] In compounds such as $(C_3Ph_3)Co(CO)_3$ (**1**),[3] $(C_3Ph_3)Rh(CO)_3$ (**2**),[4] $(C_3Ph_3)Ir(CO)_3$ (**3**),[4] $[(C_3Ph_3)Ni(CH_3C(CH_2P(C_6H_5)_2)_3)]^+$ (**4**),[5] $(C_3Ph_3)NiCp$ (**5**),[6] $(C_3(t\text{-Bu})_2Me)WCp(PMe_3)Cl_2$ (**6**),[7] and $(C_3Ph_3)Mo(CO)_2(bipy)Br$ (**7**)[8] the three-membered carbocyclic ring bonds to the metal atom in a symmetrical η^3 fashion. Various theoretical analyses have been reported on these metallatetrahedrane complexes.[9] However, the number of η^3-cyclopropenyl complexes known is still relatively very small compared to the vast number of η^5-cyclopentadienyl complexes.[1] Will the η^3 coordination property also be favored for the heavier congeners $Si_3R_3^+$ and $Ge_3R_3^+$? We present here the results of a theoretical study on a series of organometallic complexes with $Si_3H_3^+$ and $Ge_3H_3^+$ ligands and show the remarkable differences in the bonding properties of C complexes and their heavier analogues.

$Si_3H_3^+$ has been detected in the gas phase.[10] Its ring structure (D_{3h}) is calculated to be the global minimum, and it has shown potential as an η^3 ligand in main-group pyramidal (Si_3H_3X, X = N, NH^+, PO; **8**, C_{3v}) and sandwich ($(Si_3H_3)_2X$, X = B^+, C^{2+}; **9**, D_{3h}) compounds.[11−13] Theoretical reports have shown that the trigermacyclopropenium ion (D_{3h}) is a stable minimum on the potential energy surface of $Ge_3H_3^+$.[14] The substituted analogue $Ge_3R_3^+$ (R = $t\text{-Bu}_3Si$) has been prepared experimentally and characterized by X-ray analysis.[15]

Comparison of ring sizes suggests that Si_3H_3 and Ge_3H_3 ligands may be more suitable π ligands than C_3H_3. For example, cyclopentadienyl is an excellent η^5 ligand due to the ideal claw size of its π framework for a range of transition-metal fragments.[16] The cyclopropenyl cation provides a much smaller span of orbitals, which is compensated by the large out-of-plane bending of the ring substituents away from the metal.[3−8] The longer Si−Si and Ge−Ge bond lengths in $Si_3H_3^+$ and $Ge_3H_3^+$ should reduce this orbital mismatch considerably. However, the cationic ligands $Si_3H_3^+$ and $Ge_3H_3^+$ might force the metal center to be less electropositive, giving a polarity reversed from that of the CpM complexes! We present here the results of a theoretical study on $(CO)_3Co(A_3H_3)$ (**10**, C_{3v}), $(CO)_3Rh(A_3H_3)$ (**11**, C_{3v}),

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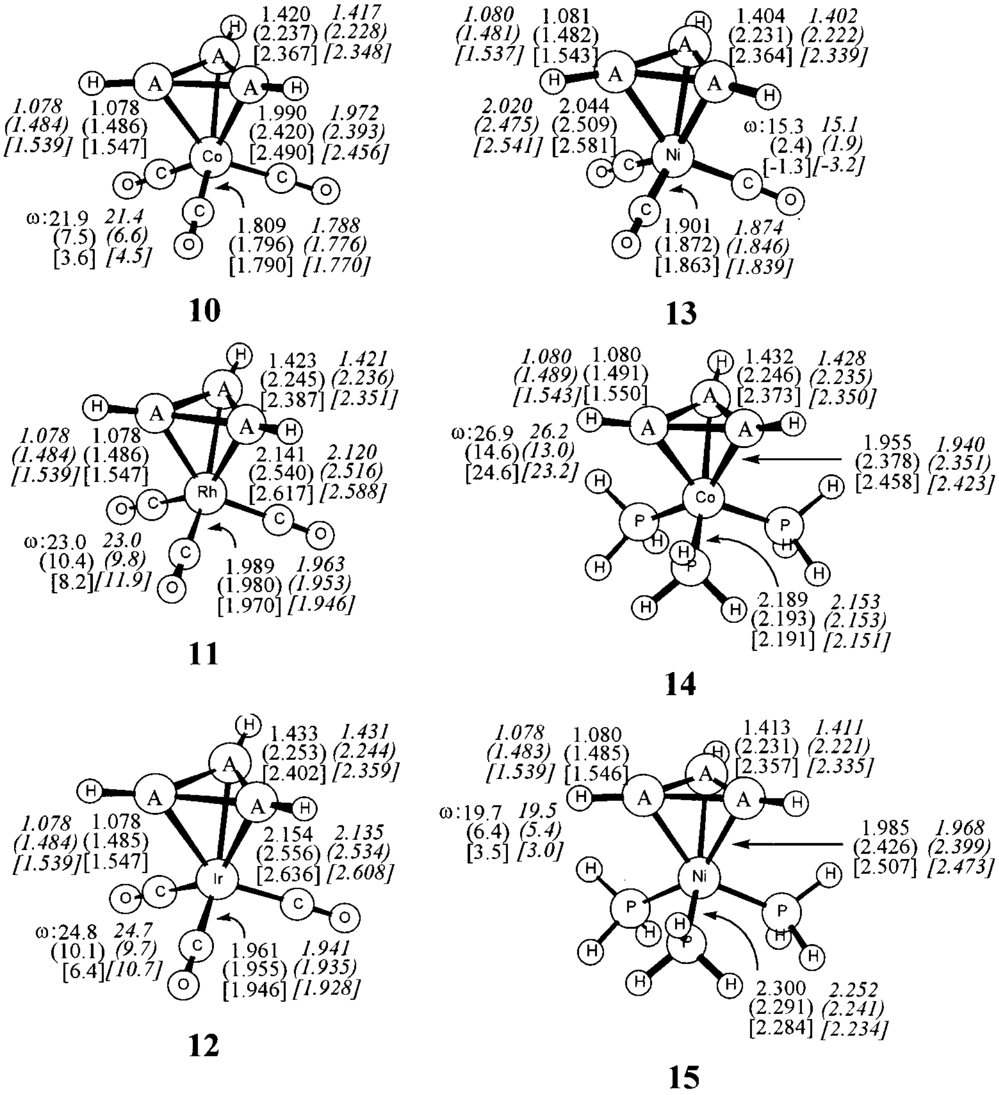

10 **13** **11** **14** **12** **15**

Figure 1. Optimized geometries and important bond distances for C, Si (in parentheses), and Ge (in brackets) complexes at the B3LYP/B1 level. The values in italics are at the B3P86/B1 level. Refer to the text for the definition of *ω*.

$(CO)_3Ir(A_3H_3)$ (**12**, C_{3v}), $[(CO)_3Ni(A_3H_3)]^+$ (**13**, C_{3v}), $(PH_3)_3Co(A_3H_3)$ (**14**, C_{3v}), and $[(PH_3)_3Ni(A_3H_3)]^+$ (**15**, C_{3v}) (where A = C, Si, Ge) complexes, which contain an η^3 coordination between the metal and the π ligand A_3H_3. The carbon compounds are included for comparison.

Computational Methods

All the structures were optimized and characterized by their Hessian signature using the hybrid Hartree–Fock/DFT method B3LYP.[17] 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.[18] The ligands were described by the standard 6-31G(d) basis set.[19] For metals the SBKJC-21G relativistic effective core potentials and their associated basis sets ([4211/4211/411]) were used.[20,21] 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 some structures (**10Si** and **13Si**) using all-electron triple-ζ and one f polarization basis set for metals and 6-311G(d) for ligands (represented as basis set B2).[22] All of the computations were carried out with the Gaussian98 program package on an NCSA supercomputer.[23,24] Figure 1 shows the relevant structures with selected geometrical parameters. We use natural charges obtained from natural bond orbital (NBO) analysis.[25] The results at the B3LYP/B1 level are used in the discussion unless specifically noted otherwise.

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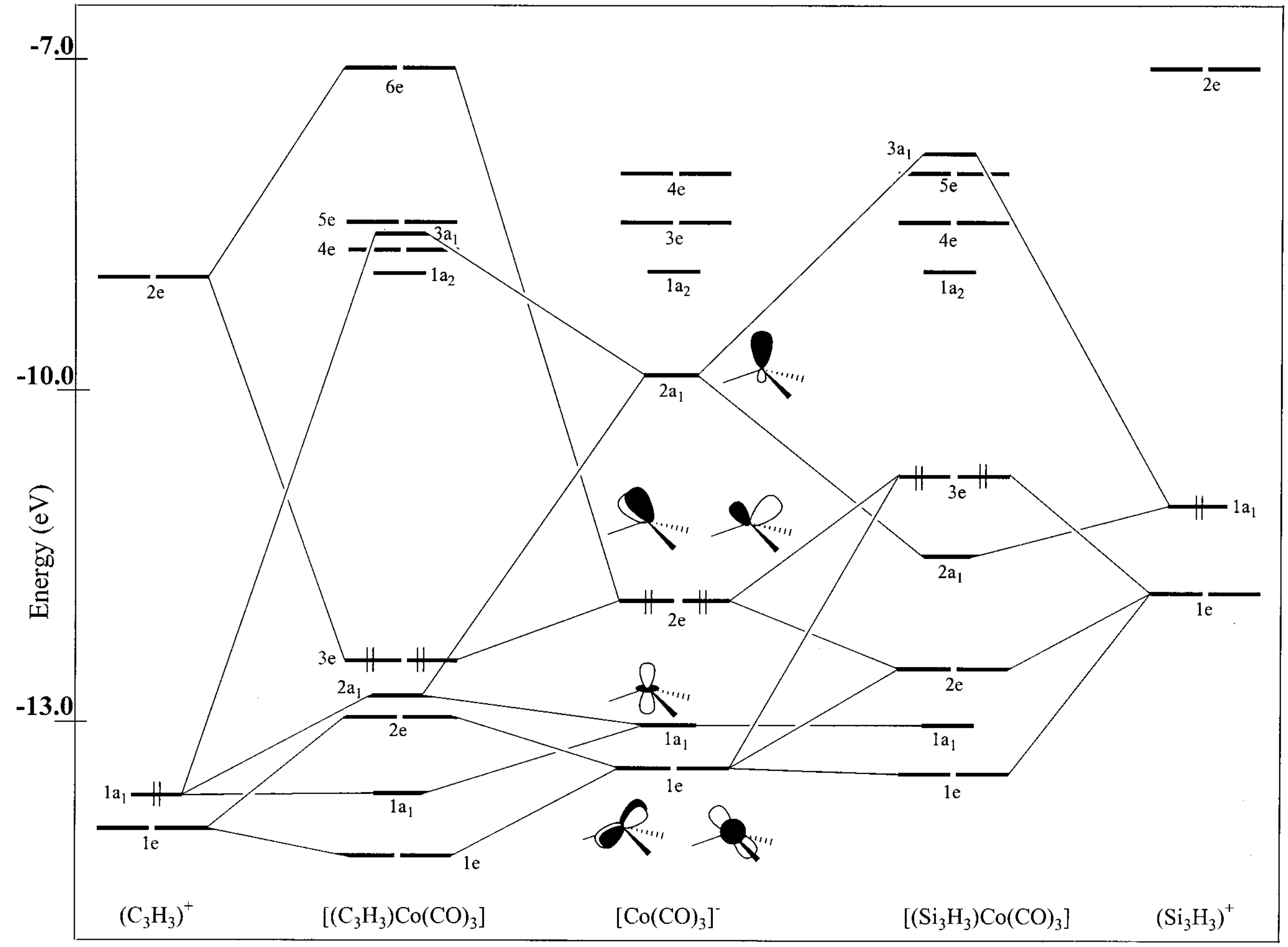

Figure 2. Interaction diagram for [$(C_3H_3)Co(CO)_3$] and [$(Si_3H_3)Co(CO)_3$]. Only the HOMO electrons are shown for each fragment.

Results and Discussion

All of the complexes **10**−**15** (C_{3v}) are minima, except **10Ge**, **11Ge**, and **12Ge**, which are transition states. The imaginary frequency corresponds to a twist of the hydrogens on the Ge_3H_3 ring, leading to a minimum with C_3 symmetry. However, the energies of the C_{3v} complexes are only ~0.1 kcal/mol higher than the twisted structures, which is negligible. The results at B3LYP/B2 also have shown that **10Si** and **13Si** are minima.

The electronic structure of the complexes **10**−**15** have been analyzed by the fragment molecular orbital (FMO) method.[26] The orbital interaction diagram of $[Co(CO)_3]^-$ with $C_3H_3^+$ and $Si_3H_3^+$ is shown in Figure 2 to illustrate the differences between C complexes and their heavier analogues. The frontier orbitals of $Co(CO)_3$ (ML_3 type) and C_3H_3 are well-known in the literature.[9a,26] The orbital interaction between the higher lying $2a_1$ orbital of the $Co(CO)_3$ fragment and the $1a_1$ (π) orbital of $C_3H_3^+$ is found to be very weak and, hence, is not shown in Figure 2. The HOMO of **10C** shows the contributions from 2e (π*) in the ligand and 2e in $Co(CO)_3$, leading to a charge transfer from the metal center to the ligand ring (Figure 2). This charge transfer makes C_3H_3 an anionic ligand, as suggested by Collman et al.[2] However, the NBO charges (−0.06, −0.28, and 0.26 e on Co, ring C, and H respectively; Table 1) shows this charge transfer to be very small. The valence MOs of the Si_3H_3 ligand are higher in energy than in C_3H_3, since these are formed from 3s and 3p orbitals. For example, the eigenvalues of the π MO are −18.05 and −12.30 eV for $C_3H_3^+$ and $Si_3H_3^+$, respectively, at the B3LYP/6-31G(d) level. Because of these high-energy valence MOs of Si_3H_3, the 2e orbital in $Co(CO)_3$ interacts with the 1e orbital on Si_3H_3. However, their bonding and antibonding (HOMO in **10Si**) combinations are filled. The HOMO-1 of **10Si** shows the contributions from $2a_1$ in $Co(CO)_3$ and $1a_1$ (π) in the Si_3H_3 ligand (Figure 2), leading to a charge transfer from ligand to metal, which

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Table 1. Total Energy (in au), Number of Imaginary Frequencies (NIM), and Natural Charge (in e) of Structures 10−15 (Figure 1) at the B3LYP/B1 Level

no.	structure	total energy	NIM	natural charge
10	C (C_{3v})	−601.242 66	0	Co, −0.06; ring C, −0.28; H, 0.26; C, 0.49; O, −0.45
	Si (C_{3v})	−1 355.441 65	0	Co, −0.40; Si, 0.23; H, −0.10; C, 0.45; O, −0.45
	Ge (C_3)[a]	−6 711.230 64	0	Co, −0.35; Ge, 0.19; H, −0.07; C, 0.45; O, −0.45
11	C (C_{3v})	−566.188 01	0	Rh, 0.13; ring C, −0.29; H, 0.26; C, 0.44; O, −0.44
	Si (C_{3v})	−1 320.401 47	0	Rh, −0.23; Si, 0.18; H, −0.10; C, 0.44; O, −0.44
	Ge (C_3)[a]	−6 676.188 40	0	Rh, −0.20; Ge, 0.14; H, −0.07; C, 0.44; O, −0.44
12	C (C_{3v})	−560.950 41	0	Ir, 0.31; ring C, −0.33; H, 0.26; C, 0.40; O, −0.44
	Si (C_{3v})	−1 315.171 73	0	Ir, −0.06; Si, 0.16; H, −0.10; C, 0.40; O, −0.44
	Ge (C_3)[a]	−6 670.957 25	0	Ir, −0.02; Ge, 0.12; H, −0.07; C, 0.40; O, −0.44
13	C (C_{3v})	−625.312 14	0	Ni, 0.35; ring C, −0.19; H, 0.31; C, 0.46; O, −0.36
	Si (C_{3v})	−1 379.518 24	0	Ni, 0.08; Si, 0.32; H, −0.06; C, 0.42; O, −0.37
	Ge (C_{3v})	−6 735.310 86	0	Ni, 0.12; Ge, 0.28; H, −0.03; C, 0.42; O, −0.37
14	C (C_{3v})	−1 290.660 47	0	Co, −0.25; C, −0.32; ring H, 0.24; P, 0.18; H, 0.00
	Si (C_{3v})	−2 044.858 05	0	Co, −0.66; Si, 0.16; ring H, −0.12; P, 0.17; H, 0.01
	Ge (C_{3v})	−7 400.644 39	0	Co, −0.58; Ge, 0.10; ring H, −0.09; P, 0.17; H, 0.01
15	C (C_{3v})	−1 314.800 55	0	Ni, 0.27; C, −0.24; ring H, 0.28; P, 0.06; H, 0.04
	Si (C_{3v})	−2 068.994 40	0	Ni, −0.06; Si, 0.25; ring H, −0.08; P, 0.06; H, 0.04
	Ge (C_{3v})	−7 424.783 27	0	Ni, −0.03; Ge, 0.21; ring H, −0.05; P, 0.05; H, 0.04

[a] These structures are transition states under C_{3v} symmetry (refer to the text).

is reversed flow compared to **10C** and cyclopentadienyl complexes. The NBO charges −0.40, 0.23, and −0.10 e on Co, Si, and H, respectively, support this interpretation (Table 1). The electronic structure of **10Ge** is also found to be similar to that of **10Si**. NBO charges on Co, Ge, and H are −0.35, 0.19, and −0.07 e, respectively, in **10Ge** (Table 1). Therefore, the bonding character of **10Si** and **10Ge** is remarkably different from that of **10C**. The electronic structures of Si and Ge complexes **11**−**15** are found to be similar to that of **10Si**, and those of **11C**−**15C** are similar to that of **10C**.

The bond distances in **10**−**15** are calculated to be slightly shorter at the B3P86 level than at the B3LYP level. The differences in bond distances between B3LYP/B1 and B3LYP/B2 levels are very small (±0.009 Å). On average the C−C, Si−Si, and Ge−Ge distances are 1.421 ± 0.017, 2.240 ± 0.013, and 2.375 ± 0.027 Å, respectively, at B3LYP/B1. The A−A distance is the longest in Ir complexes (**12**) and the shortest in Ni complexes (**13** and **15**). These findings are in accord with covalent radii of Ni (1.15 Å), Co (1.16 Å), Rh (1.25 Å), and Ir (1.27 Å).[27] Similarly, the metal (M)−A distance is the longest in Ir complexes. In general, the M−A distance is shorter in complexes containing PH_3 ligands than in complexes containing CO ligands (comparing **10**, **13**, **14**, and **15**). The shortest M−A distance is found in Co complex **14**. In comparison to the free ligand ($C_3H_3^+$, 1.366 Å; $Si_3H_3^+$, 2.206 Å; $Ge_3H_3^+$, 2.300 Å), the A−A distance is elongated due to charge transfer between the metal and ligand as discussed above.[11,14,28] The lengthening is found to be large in Ge (0.057−0.102 Å) and C complexes (0.038−0.067 Å) and small in Si complexes (0.025−0.047 Å). A comparison of the A−A bond length with typical cyclopropane-like structures (C_3H_6, 1.509 Å; Si_3H_6, 2.345 Å; Ge_3H_6, 2.422 Å) reveals a shortening of bond lengths in **10**−**15**.[29] Comparison with ethane-like structures A_2H_6 (C_2H_6, 1.531 Å; Si_2H_6, 2.350 Å; Ge_2H_6, 2.401 Å) leads to similar conclusions.[30] Due to the differences in A_3H_3 ring size, ω (the nonplanarity of ring hydrogens in the A_3 ring) is much smaller in Si and Ge complexes than in C complexes (ω is positive if hydrogens are tilted away from the metal).[31] The exceptional case is **14**, in which all the C, Si, and Ge rings have large positive ω. This is mainly due to the combination of short M−A distances and sterically large PH_3 ligands.

The calculated C−C distances in **10C**−**15C** are very close to average C−C bond distances determined experimentally in **1** (1.42 Å), **3** (1.43 Å), **4** (1.41 Å), and **5** (1.43 Å).[3−6] However, the Co−C, Ir−C, and Ni−C distances are shorter by 0.02, 0.03, and 0.04 Å in **10C**, **12C,** and **15C** as compared to those in **1**, **3**, and **4**. The Si−Si distances in **10**−**15** are shorter compared to that in **8** (2.308 and 2.343 Å for N, NH^+ and PO).[12] The Co−Si distance in **10Si** is slightly longer than the 2.25 Å value in $Cl_3SiCo(CO)_4$ and 2.38 Å in $H_3SiCo(CO)_4$.[32] Similarly, the Ni−Si distances in **13Si** and **15Si** are also longer than 2.15, 2.21, and 2.29 Å, found in Ni(silylene)$_3$, Ni{(*t*-Bu)NCH=CHN(*t*-Bu)Si}$_2$(CO)$_2$, and $Ni(SiH_2C_6H_4SiH_2)_2(PMe_2C_2H_4PMe_2)$, respectively.[33] Such a lengthening of M−Si distances indicates the π bonding character.

The π complexes **10**−**15** of Si and Ge may be reasonable synthetic targets, if they are substituted with adequately large groups. The experimental preparation and X-ray analysis of $Si_3R'_4$ (R′ = SiMe(*t*-Bu)$_2$),[34] Si_4R_4 (R = Si(*t*-Bu)$_3$),[35] and $Ge_3R_3^+$ [15] illustrate the importance of bulky substituents in stabilizing small-ring systems. One of the methods used in the literature to synthesize the η^3 π complexes of C is addition of a cyclopropenyl cation to a solution containing metal carbonyl anions.[36]

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A similar procedure might be worth trying for Si and Ge, since the $Si_3H_3^+$ and $Ge_3R_3^+$ species are known experimentally. To provide a closer connection to experimentally feasible systems, the permethylated structures of **10Si** and **10Ge** were studied at the B3LYP/B1 level and found to be minima. If anything, silyl substituents will only increase the donation of electron density into the Si_3 (Ge_3) ring and strengthen the π bonding.[37] Therefore, we feel that any of the π complexes **10**−**15** for Si and Ge are intriguing targets for experimental pursuit.

Conclusions

Calculations at B3LYP/B1 and B3P86/B1 levels show the following. The η^3 π complexes of A_3H_3 (A = C, Si, Ge) are minima. The electronic structure analysis reveals that there is a charge transfer from the metal to the ligand in C complexes. Si and Ge complexes exhibit charge transfer from the ligand to the metal, which is a reversed electron flow compared both to C complexes and cyclopentadienyl complexes. Calculations on permethylated complexes of **10Si** and **10Ge** show these structures to be minima, providing evidence that substituted A_3R_3 complexes similar to the A_3H_3 complexes reported here should also be stable.

Acknowledgment. This work was supported by Grant B-657 from the Robert A. Welch Foundation.

Supporting Information Available: Tables giving Cartesian coordinates of the structures in Figure 1. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010616C

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