

Classical and Nonclassical Isomers of Tropylium, Silatropylium, and Germatropylium Cations. Descending the Periodic Table Increases the Preference for Nonclassical Structures

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Abstract: Ab initio calculations at the G2(MP2,SVP) level predict that there is a striking transition from a preference for classical isomers on the C₇H₇⁺ surface to a preference for nonclassical isomers on the C₆H₇Ge⁺ surface. The situation for C₆H₇Si⁺ is intermediate between these extremes, with classical and nonclassical isomers tending to have comparable energies despite their significant geometric differences.

Introduction

The similarities and differences between compounds of carbon and those of its heavier homologues have attracted considerable attention from both experimental and theoretical chemists.^{1–3} In this connection, recent suggestions that silatropylium cation (**1-Si**) might have been formed in the gas phase along with its isomer silabenzyl cation (**2-Si**)^{4,5} prompted us to carry out comparative studies of these two cations and their carbon analogues, tropylium (**1-C**) and benzyl (**2-C**) cations.^{6,7} Our computational studies indicated that most likely **1-Si** was not actually observed, and this has also been the conclusion of more recent experiments by Jarek and Shin.⁸ While our calculations⁷ predicted that the most stable isomer on the C₆H₇Si⁺ surface is the pyramidal **5-Si**, Jarek and Shin⁸ suggest that under their experimental conditions the observed species (besides **2-Si**) is a complex between benzene and HSi⁺ (with a structure similar to **7-Si**). Production of such a species from ionized silatoluene could be readily envisaged. Whatever the case may be, it is clear that there exist sufficient differences between the C₆H₇Si⁺ and C₇H₇⁺ surfaces that caution is needed when drawing analogies between the two.^{4,6,7} To better understand

these differences, we have extended our calculations in the present study to germatropylium (**1-Ge**) and its isomers. The new calculations provide further insights and more clearly delineated trends. In particular, we find that there is a transition from a preference for classical structures on the C₇H₇⁺ surface to a preference for nonclassical structures on the C₆H₇Ge⁺ surface, with the C₆H₇Si⁺ surface showing characteristics intermediate between these extremes.

Computational Procedures

Ab initio molecular orbital calculations⁹ were carried out with the GAUSSIAN 92,^{10a} GAUSSIAN 94,^{10b} and MOLPRO¹¹ programs. Optimized geometries were obtained for all species at the MP2(full)/6-31G(d) level of theory. Selected geometric parameters are displayed in Figures 1 and 2. Full geometries are presented in the form of GAUSSIAN archive files in Table S1 of the Supporting Information. In the case of tropylium cation (**1-C**), additional optimizations were carried out at the MP2(fc)/6-311+G(3df,2p) and QCISD(T)/6-31G(d) levels (also included in Table S1). Energies were obtained at the G2(MP2,SVP) level of theory,¹² which corresponds effectively to QCISD(T)/6-311+G(3df,2p) energy calculations at MP2(full)/6-31G(d) optimized geometries, incorporating scaled HF/6-31G(d) zero-point energies and a so-called higher level correction (see Table S2).¹³ In our previous work, we found this level of theory to be in very good agreement with the more accurate, but computationally more demanding, G2(MP2)^{14,15a} and G2^{14,15b} theories, at least as far as the relative energies of the C₇H₇⁺ and C₆H₇Si⁺ isomers are concerned.⁷ Unless

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(1) For recent reviews related to silicon compounds see, for example: (a) Baldrige, K. K.; Boatz, J. A.; Koseki, S.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1987**, *38*, 211. (b) Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989. (c) Bock, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1627. (d) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17. (e) Sekiguchi, A.; Sakurai, H. *Adv. Organomet. Chem.* **1995**, *37*, 1. (f) Tamao, K.; Kawachi, A. *Adv. Organomet. Chem.* **1995**, *38*, 1.

(2) For recent reviews that include germanium compounds see, for example: (a) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (b) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215. (c) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (d) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371. (e) Kudo, T.; Nagase, S. *Rev. Heteroat. Chem.* **1993**, *8*, 122. (f) Nagase, S. *Acc. Chem. Res.* **1995**, *28*, 469.

(3) For references to recent work related to silicon and germanium compounds, see ref 7.

(4) (a) Murthy, S.; Nagano, Y.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 3573. (b) Nagano, Y.; Murthy, S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 10805.

(5) For early papers dealing with C₆H₇Si⁺ isomers, see: (a) Bohlmann, F.; Koppel, C.; Schwarz, H. *Org. Mass Spectrom.* **1974**, *9*, 622. (b) Allen, W. N.; Lampe, F. W. *J. Am. Chem. Soc.* **1977**, *99*, 2943.

(6) Nicolaides, A.; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 9679.

(7) Nicolaides, A.; Radom, L. *J. Am. Chem. Soc.* **1996**, *118*, 10561.

(8) Jarek, R. J.; Shin, S. K. *J. Am. Chem. Soc.* **1997**, *119*, 6376.

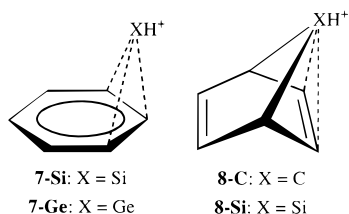
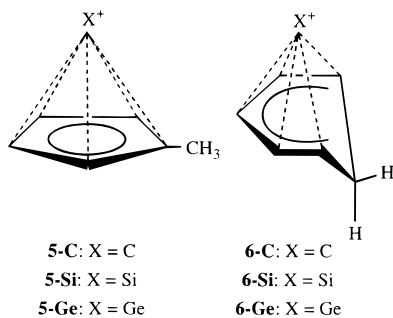
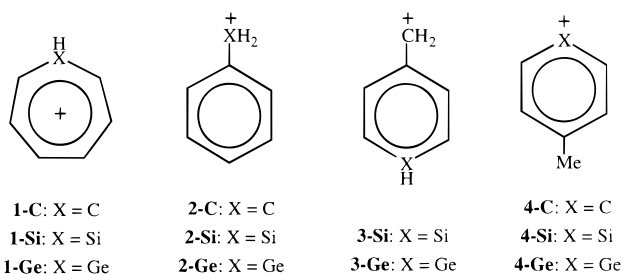
(9) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(10) (a) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN 92, Gaussian Inc.: Pittsburgh, PA, 1992. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. GAUSSIAN 94, Gaussian Inc.: Pittsburgh, PA, 1995.

(11) MOLPRO is a package of *ab initio* programs written by Werner, H.-J. and Knowles, P. J. with contributions by Almlöf, J.; Amos, R. D.; Deegan, M. J. O.; Elbert, S. T.; Hampel, C.; Meyer, W.; Peterson, K.; Pitzer, R. M.; Stone, A. J.; Taylor, P. R.; and Lindh, R.

(12) (a) Smith, B. J.; Radom, L. *J. Phys. Chem.* **1995**, *99*, 6468. (b) Curtiss, L. A.; Redfern, P. C.; Smith, B. J.; Radom, L. *J. Chem. Phys.* **1996**, *104*, 5148.

Chart 1



otherwise noted, all relative energies in this paper refer to G2(MP2,-SVP) values at 298 K (Table 1).

Results and Discussion

Assessment of Reliability. In our previous studies,^{6,7} we carried out calculations at a variety of levels of theory to gain some confidence in our predicted relative energies. In this section we report the results of some additional investigations in this regard. In the first instance, we have obtained the geometry of the highly symmetrical tropylium cation at levels of theory considerably higher than the standard MP2(full)/6-31G(d) level used in G2(MP2,SVP) theory. We find that MP2 optimization with a much larger basis set (MP2/6-311+G(3df,-2p)) shortens the C–C and C–H bonds by about 0.005 Å. On the other hand, if the optimization is carried out at the QCISD(T) level of theory (i.e. QCISD(T)/6-31G(d)), the C–C and C–H bonds are found to be longer by 0.005 and 0.003 Å, respectively. In other words, the effects of improving the basis set and the level of theory not only are rather small, but they also work in opposite directions. It is not surprising then that the G2(MP2,SVP) energy of **1-C** shows little sensitivity (less than 0.5 kJ mol⁻¹) as to which of the three geometries is used, with the MP2(full)/6-31G(d) geometry actually providing the lowest energy. The relative energies of **1-C** and **5-C** as a

(13) G2 basis sets for Ge and spin-orbit corrections for Ge and Ge⁺ may be found in the following: Curtiss, L. A.; McGrath, M. P.; Blaudeau, J. P.; Davis, N. E.; Binning, R. C.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104.

(14) (a) Curtiss, L. A.; Raghavachari, K. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer Academic Publishers: Dordrecht, 1995. (b) Raghavachari, K.; Curtiss, L. A. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995.

(15) (a) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221. (b) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

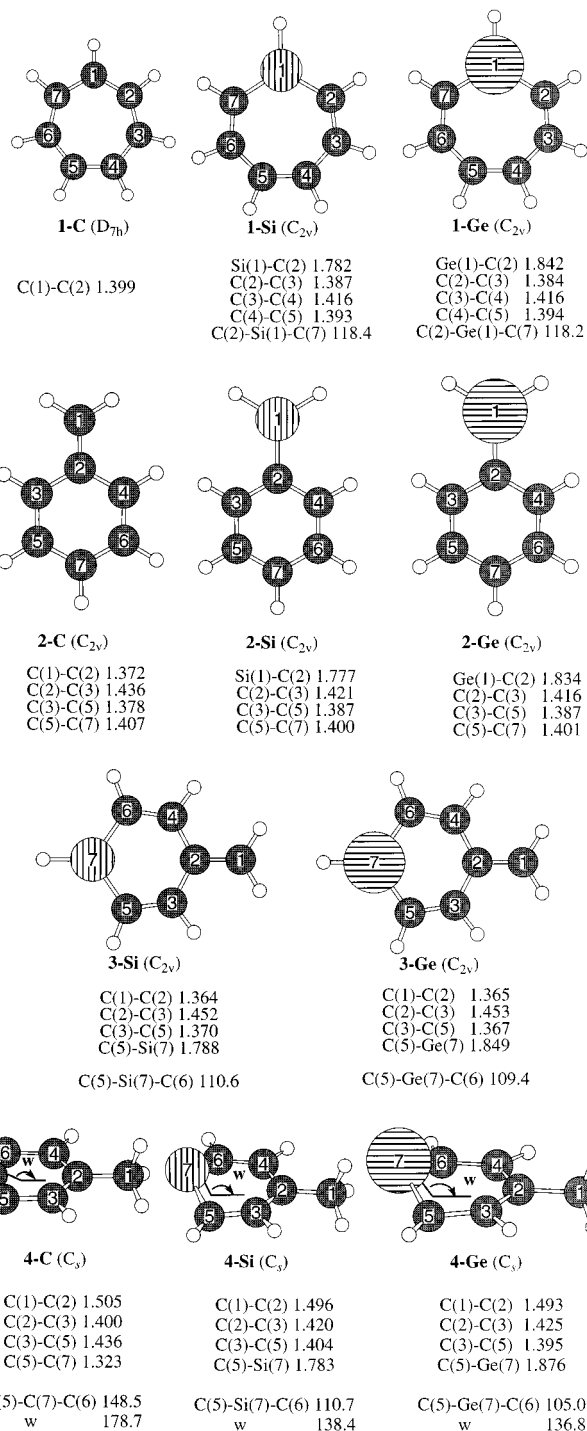


Figure 1. Selected bond lengths (Å) and bond angles (deg) for MP2/6-31G(d) optimized structures of the classical isomers **1–4**.

function of basis set and level of theory show a similar convergence behavior to the relative energies of **1-C** and **2-C** or **1-Si** and **2-Si**, discussed in our previous paper (see also Table S3).⁷ Therefore we believe that the G2(MP2,SVP) relative energies of the species examined in the present study will generally be reliable to within the established G2 target accuracy of 10 kJ mol⁻¹, and possibly to within 5 kJ mol⁻¹ in comparisons involving only the classical isomers.

Classical Isomers. Selected geometrical features of the classical isomers **1–4** are displayed in Figure 1, and corresponding relative energies are shown in Table 1. Tropylium cation (**1-C**) lies 29 kJ mol⁻¹ lower in energy than the isomeric benzyl cation (**2-C**).^{6,7} On the other hand, substitution of one carbon atom by silicon reverses the stability ordering, and **2-Si**

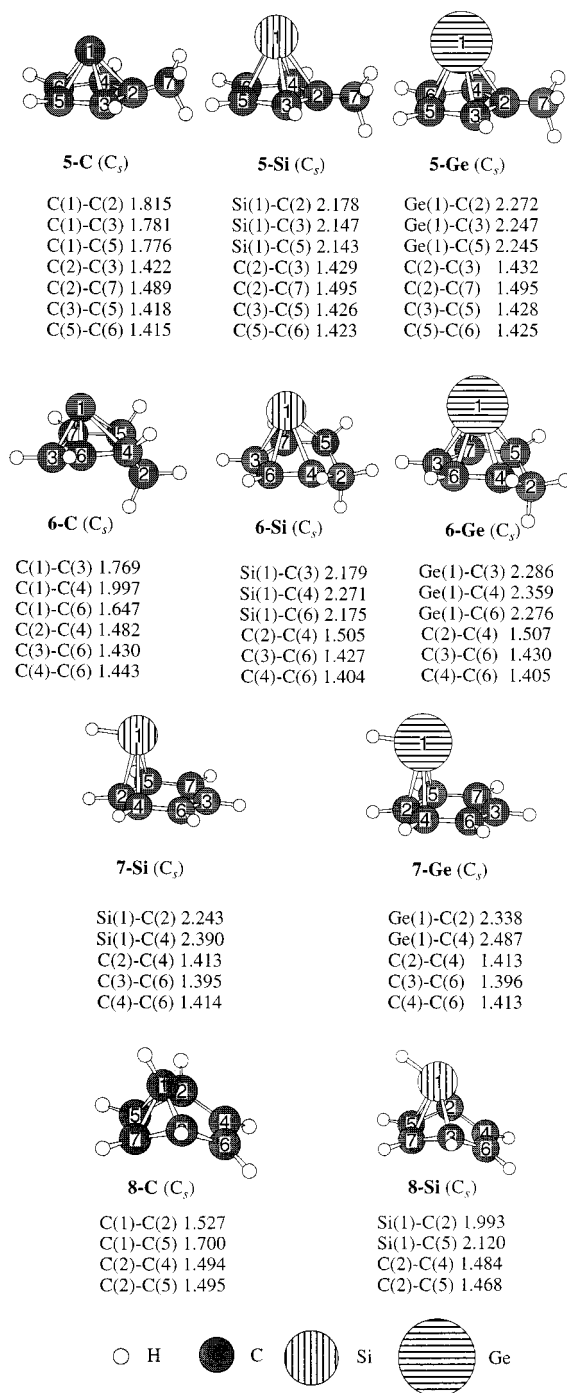


Figure 2. Selected bond lengths (Å) and bond angles (deg) for MP2/6-31G(d) optimized structures of the nonclassical isomers 5–8.

is calculated to be more stable than **1-Si** by 38 kJ mol⁻¹.^{6,7} A continuation of this trend is found for germanium, with germabenzyl cation (**2-Ge**) being more stable than germatropylium (**1-Ge**) by 67 kJ mol⁻¹. The greater stability of the seven-membered-ring structure (**1**) as compared with the benzylic structure (**2**) seems only to apply to the all-carbon system, and may be attributed in part to its aromaticity.¹⁶ In addition, since silicon and germanium are more electropositive than carbon and they do not form strong multiple bonds,^{1b,17} less electron delocalization might be expected in **1-Si** and **1-Ge**¹⁸ and this, together with the greater ability of Si and Ge to hold

Table 1. Relative G2(MP2,SVP) Isomer Energies (kJ mol⁻¹) at 298 K

X	1-X	2-X	3-X	4-X	5-X	6-X	7-X	8-X
C	0 ^a	29 ^b	c	210	277 ^b	406	d	154 ^b
Si	143	105	133	284	0 ^e	127	146	154
Ge	234	167	221	330	0 ^f	117	135	g

^a Relative to -270.10297 hartrees. ^b G2 relative energies are 29 (**2-C**) and 277 (**5-C**) kJ mol⁻¹. G2(MP2) relative energies are 28 (**2-C**), 276 (**5-C**), and 152 (**8-C**) kJ mol⁻¹. ^c Identical to **2-C**. ^d No minimum corresponding to the loose π -complex (**7-C**) was found on the HF/6-31G(d) surface. ^e Relative to -521.16545 hartrees. ^f Relative to -2307.56240 hartrees. ^g No minimum corresponding to the "tight" complex (**8-Ge**) was found on the HF/6-31G(d) or MP2(full)/6-31G(d) surfaces.

the positive charge in **2**, could also contribute to the reversal in the ordering of the stabilities of **1** and **2** in the case of the heavier analogues.

In the heterosubstituted systems (X = Si and Ge), there are four benzyl-type isomers in addition to **2**, with the heteroatom occupying different positions in the phenyl ring. The most stable of these on the C₆H₇Si⁺ surface is δ -silabenzyl cation (**3-Si**), which was found to lie 10 kJ mol⁻¹ lower in energy than silatropylium (**1-Si**).⁷ **3-Ge** is also found to be more stable than **1-Ge** by a similar amount. However, in both cases the lower energy benzyl-type isomer is **2**, which has an "intact" phenyl group, and in which the positive charge is more localized on the electropositive Si or Ge atoms.

The final classical structure that we examined for these cations corresponds to analogues of the 4-methyl-substituted phenyl cation. In the case of **4-C**, all the carbon atoms lie essentially in the same plane²⁰ and, as for the unsubstituted phenyl cation,²¹ the angle at the carbon bearing the formal charge is quite large (148.5°), resulting in considerable ("in-plane") deformation of the benzene ring. In the case of the heavier analogues, however, the six-membered ring is distorted toward a half-boat conformation with the heteroatom lying considerably out-of-plane (see Figure 1). This results in a much smaller CXC angle (110.7° and 105.0° for **4-Si** and **4-Ge**, respectively). Structures **3** and **4** formally differ by a hydride shift from X to the methylene group. As the electropositivity of X increases, the relative energy of structure **4** decreases, but even in the case of Ge, structure **3** is preferred over the germaphenyl cation (**4-Ge**) by 109 kJ mol⁻¹.

Overall among the classical structures **1–4**, the most stable structure is the one in which the maximum number of carbons is incorporated in the ring, while the heteroatoms prefer to occupy positions external to the ring. The latter is in agreement with the "heavy atom exclusion" rule.²²

Nonclassical Isomers. Selected geometrical features of the nonclassical isomers **5–8** are displayed in Figure 2, while corresponding relative energies are included in Table 1. On the C₆H₇Si⁺ and C₆H₇Ge⁺ surfaces, the lowest energy structures that we have found correspond to the nonclassical isomer **5**. Such "half-sandwich" compounds of group IV elements are known both experimentally²³ and computationally.²⁴ The

(18) This expectation is in accordance with the finding that the aromatic character of heterosubstituted benzenes gradually decreases upon descending the rows of the main group elements.^{16,19}

(19) Baldrige, K. K.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 4204.

(20) Structure **4** has C_s symmetry, but the plane of symmetry runs parallel to the π -system, and therefore symmetry does not require all ring atoms to lie in the same plane (see also Figure 1).

(21) Dill, J. D.; Schleyer, P. v. R.; Binkley, J. S.; Seeger, R.; Pople, J. A.; Haselbach, E. *J. Am. Chem. Soc.* **1976**, *98*, 5428.

(22) Epiotis, N. D. *Deciphering the Chemical Code: Bonding Across the Periodic Table*; Chapter 15, VCH: New York, 1996.

(23) See: Jutzi, P.; Köhl, F.; Hofmann, P.; Kruger, C.; Isay, Y.-H. *Chem. Ber.* **1980**, *113*, 757 and references therein.

(16) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity*; Wiley: New York, 1994.

(17) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

stability of such species has been attributed to three-dimensional aromaticity, with the bonding between the “cap” (i.e. the apical C or heteroatom) and the “ligand” (i.e. the substituted cyclopentadienyl moiety) obeying the “ $4n + 2$ interstitial electron” rule.^{16,25} The essence of this rule as applied in this case is that the “ π ” system of the ligand, which has three low-lying MOs, can be stabilized via interaction with three appropriate atomic orbitals of the cap.²⁵ Since the total number of “interstitial” electrons (that is the electrons that bind the cap and ligand together) is six, this interaction is strongly stabilizing in character.²⁶ In this respect, it is not so surprising that **5-C**, despite its unusual structure, is predicted to be a minimum on the $C_7H_7^+$ surface, albeit with a high energy. Consistent with the above, we find **5** to be thermodynamically very stable with respect to dissociation. For **5-C** and **5-Si**, the lower energy dissociation channel corresponds to formation of X (X = C or Si) plus the methylcyclopentadienyl cation and is calculated to require 556 and 609 kJ mol⁻¹, respectively. For **5-Ge**, the lower energy dissociation channel corresponds to formation of Ge⁺ plus the methylcyclopentadienyl radical and requires 511 kJ mol⁻¹.

Closely related to isomer **5** is another pyramidal structure (**6**), which is formally a five-coordinated cationic complex between X and cyclohexadienyl. The relatively low energy of isomer **6** may also be attributed to three-dimensional aromaticity. This can easily be seen by noting that cyclopentadienyl and cyclohexadienyl groups have the same number of π -electrons. Furthermore, the five methine carbons in **6** are approximately coplanar, as is also the case with **5**. Therefore one may apply the same arguments as above to show that **6** also satisfies the “ $4n + 2$ interstitial electron” rule. Once more the expected stability of such compounds is reflected in the finding that **6-X** is calculated to lie lower in energy than separated X plus the cyclohexadienyl cation by 303, 358, and 281 kJ mol⁻¹ for X = C, Si, and Ge, respectively.

In all three cases, the energy content of isomer **6** is higher than that of **5** by approximately the same amount (120–130 kJ mol⁻¹). In the case of Ge, **5-Ge** and **6-Ge** are the lowest energy isomers. In the case of Si, however, the benzylic isomer (**2-Si**) is more stable than **6-Si**, whereas for C both pyramidal isomers are considerably higher in energy than **2-C**.

Another interesting feature on the $C_6H_7Si^+$ surface is the existence of “loose” (**7-Si**) and “tight” (**8-Si**) [$SiH \cdots C_6H_6$]⁺ complexes. The former, which is best regarded as a π -complex, was actually found to be slightly more stable.⁷ We were not able to find a similar loose structure (**7-C**) on the $C_7H_7^+$ surface, but the tight complex (**8-C**) corresponds to the well-known norbornadienyl cation.²⁷ This isomer (**8-C**) lies significantly higher in energy than both the tropylium and benzyl cations (e.g. 154 kJ mol⁻¹ above **1-C**). On the other hand, on the $C_6H_7Ge^+$ surface we were able to locate only the loose π -complex [$GeH \cdots C_6H_6$]⁺ (**7-Ge**), which lies 18 kJ mol⁻¹ higher in energy than **6-Ge**. This is very close to the energy difference (19 kJ mol⁻¹) between **6-Si** and **7-Si**.

Jarek and Shin⁸ have generated $C_6H_7Si^+$ ions from ionized silatoluene and have proposed that a structure that is vibra-

tionally averaged between **7-Si** and the corresponding η^4 -complex can explain their key experimental observations, namely exchange with external labeled benzene and the absence of hydrogen abstraction from cycloheptatriene. It is interesting that they reject the “tight” **8-Si**, presumably because of its high (calculated) hydride affinity relative to that of tropylium cation. They estimate that their proposed structure (related to **7-Si**, as noted above) has a low hydride affinity, partly because they assume that the product is separated $C_6H_6 + SiH_2$. Since **7-Si** and **8-Si** are closely related energetically (they have the same energy content within our estimated uncertainty of 10 kJ mol⁻¹) and the barrier for the transformation of **7-Si** to **8-Si** is rather small (14–17 kJ mol⁻¹),⁷ it is not clear why interconversion of **7-Si** and **8-Si** would not lead to the lower-energy product 7-silanorbornadiene, as a result of hydride abstraction. In such a case, hydride transfer from cycloheptatriene would be exothermic, and the lack of reactivity with cycloheptatriene would require a kinetic barrier. This seems quite a plausible scenario given the significant electronic reorganization required for the formation of (planar) tropylium cation. On the other hand, if **7-Si** and **8-Si** do not interconvert under the experimental conditions then Jarek and Shin’s suggestion that **7-Si** has a low hydride affinity is essentially correct. We have characterized an $SiH_2 \cdots C_6H_6$ complex theoretically and find it to be bound by 36 kJ mol⁻¹ (with respect to separated C_6H_6 and SiH_2) (see Table S2). Despite this significant binding energy, the hydride affinity of **7-Si** to give $SiH_2 \cdots C_6H_6$ is still 26 kJ mol⁻¹ less than the hydride affinity of tropylium cation, consistent with the lack of reactivity with cycloheptatriene.

Gas-phase experiments have implied the existence of both (η^5 -cyclohexadienyl)yttrium (**6**, X = Y) and (hydrido)(benzene)yttrium (**7**, X = Y).^{28a} The experimental data suggest that either **6-Y** and **7-Y** are formed independently or their interconversion is facile.²⁸ Such an isomerization is interesting since it can be viewed as a partial hydrogenation of the benzene ring (**7** \rightarrow **6**) or as a C–H bond activation of the cyclohexadienyl system (**6** \rightarrow **7**). In the systems that we have examined, the G2(MP2,-SVP) barrier for the **7-Si** \rightarrow **6-Si** isomerization is 103 kJ mol⁻¹, while that for **7-Ge** \rightarrow **6-Ge** is 122 kJ mol⁻¹. Both barriers lie below the corresponding binding energies of 222 and 165 kJ mol⁻¹ for **7-Si** and **7-Ge**, respectively.²⁹

Conclusions

Our findings suggest that on the $C_7H_7^+$ surface the highly symmetrical tropylium cation is the global minimum, followed closely by the benzyl cation; nonclassical isomers lie significantly higher in energy. At the other end of the scale, on the $C_6H_7Ge^+$ surface the nonclassical isomers are preferred and the classical isomers lie significantly higher in energy. The situation for $C_6H_7Si^+$ is intermediate between these extremes, with classical and nonclassical isomers tending to have comparable energies despite their significant geometric differences. Indeed six of the eight $C_6H_7Si^+$ isomers lie within a narrow energy band of just 50 kJ mol⁻¹.

Acknowledgment. We gratefully acknowledge generous allocations of time on the Fujitsu VPP-300 supercomputer of the Australian National University Supercomputing Facility and the SGI Power Challenge of the Australian Cooperative Super-

(24) Krogh-Jespersen, K.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* **1980**, *45*, 1608.

(25) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781.

(26) There is also another pair of electrons on the cap, but this is regarded as nonbonding and occupying an orbital hybridized away from the ligand, and therefore not strongly affected by the interaction between the cap and the ligand.

(27) (a) Stroy, P. R.; Saunders, M. *J. Am. Chem. Soc.* **1962**, *84*, 4876. (b) Olah, G. A.; Liang, G.; Mateescu, G. D.; Riemenschneider *J. Am. Chem. Soc.* **1973**, *95*, 8698. (c) Bremer, M.; Schötz, K.; Schleyer, P. v. R.; Fleischer, U.; Schindler, M.; Kutzelnigg, W.; Koch, W.; Pulay, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1042.

(28) (a) Huang, Y.; Hill, Y. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 840. (b) For a similar transformation in solution but with a ligated metal, see: Kowalski, A. S.; Ashby, M. T. *J. Am. Chem. Soc.* **1995**, *117*, 12639.

(29) The binding energies are defined with respect to dissociation to C_6H_6 and HX^+ (X = Si, Ge).

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Supporting Information Available: Archive entries for MP2(full)/6-31G(d) optimized geometries and MP2(fc)/6-311+G(3df,2p) single-point energy calculations (Table S1), total G2(MP2,SVP) energies at 0 and 298 K and G2(MP2,-

SVP) heats of formation based on the standard atomization reaction (Table S2), and basis set dependence of the relative energies of **1-X** and **2-X** ($X = \text{C}, \text{Si}$) and of **2-C** and **5-C** (Table S3) (19 pages). See any current masthead page for ordering and Internet access instructions.

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