Relative Stabilities and Hydride Affinities of Silatropylium and Silabenzyl Cations and Their Isomers. Comparison with the Carbon Analogues Tropylium and Benzyl Cations

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Abstract: High-level ab initio calculations on silatropylium (**1-Si**) and silabenzyl (**2-Si**) cations and seven of their low-lying isomers (**3**−**8**), as well as on their carbon analogues, tropylium (**1-C**) and benzyl (**2-C**) cations, are reported. Heats of formation have been calculated at the G2(MP2) level of theory with the help of isodesmic and isogyric reactions. Relative stabilities and hydride affinities are reported using G2(MP2), G2(MP2,SVP), and density functional theory (B3-LYP, B-LYP, and B3-P86) procedures. The calculations confirm the experimental finding that tropylium cation is lower in energy than benzyl cation. The calculated heat of formation for benzyl cation ($\Delta H_{f\,298} = 907$ kJ mol^{-1}) is in good agreement with a value derived from recent experimental data but the calculated heat of formation for tropylium cation ($\Delta H_{f\,298} = 878$ kJ mol^{-1}) suggests that an experimental re-examination would be desirable. The stability ordering is reversed for the silicon analogues, silatropylium cation (**1-Si**, $\Delta H_{f\,298} = 980$ kJ mol^{-1}) and silabenzyl cation (**2-Si**, $\Delta H_{f\,298} = 942$ kJ mol^{-1}), with the latter lying lower in energy by 38 kJ mol^{-1}. Among the isomers that we have examined, the lowest in energy by a considerable margin is (η^5-methylcyclopentadienyl)silanium cation (**8**, $\Delta H_{f\,298} = 839$ kJ mol^{-1}). Two other isomers, δ-silabenzyl cation (**3**, $\Delta H_{f\,298} = 969$ kJ mol^{-1}) and (η^5-cyclohexadienyl)silanium cation (**7**, $\Delta H_{f\,298} = 965$ kJ mol^{-1}), lie intermediate in energy between **2-Si** and **1-Si**. The implications of our theoretical findings with regard to recent experimental results on the relative stabilities and hydride affinities of the $C_6SiH_7^+$ isomers in the gas-phase chemistry of silatoluene radical cation are discussed. Our calculated relative energies and hydride affinities suggest **8** as the most likely prospect for the second $C_6SiH_7^+$ isomer (in addition to **2-Si**) observed experimentally.

Introduction

In 1957 Meyerson *et al.*[1] suggested that, contrary to the belief held at the time, the $C_7H_7^+$ cation, produced during the unimolecular dissociation of the toluene radical cation, has the highly symmetrical structure of tropylium (**1-C**, Figure 1). Since then, numerous studies have appeared in the literature attempting to understand the structures and energetics of $C_7H_7^+$ ions.[2−4] As a result of these efforts, it is now known that hydrogen atom loss from the toluene radical cation yields both tropylium (**1-C**) and benzyl (**2-C**) cations. However, while the thermochemistry of **2-C** is quite well established, that of **1-C** is still quite uncertain. Tropylium cation is generally accepted to be more stable than benzyl cation, but the exact energy difference is controversial.

Interest in the heavier analogues of carbon,[5−8] and especially in the differences between silicon and carbon, has prompted both experimental and theoretical chemists to examine the effect

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(1) Rylander, P. N.; Meyerson, S.; Grubb, H. M. *J. Am. Chem. Soc.* **1957**, *79*, 842.

(2) For a recent review see: Lifshitz, C. *Acc. Chem. Res.* **1994**, *27*, 138.

(3) (a) McLafferty, F. W.; Winkler, J. *J. Am. Chem. Soc.* **1974**, *96*, 5182. (b) Dunbar, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 1382. (c) Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 7351. (d) Jackson, J.-A. A.; Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1977**, *99*, 7515. (e) Stapleton, B. J.; Bowen, R. D.; Williams, D. H. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1219. (f) McLafferty, F. W.; Bockhoff, F. M. *J. Am. Chem. Soc.* **1979**, *101*, 1783. (g) McLoughlin, R. G.; Morrison, J. D.; Traeger, J. C. *Org. Mass. Spectrom.* **1979**, *14*, 104. (h) Lifshitz, C.; Goldenberg, M.; Malinovich, Y.; Peres, M. *Org. Mass. Spectrom.* **1982**, *17*, 453. (i) Bombach, R.; Dannacher, J.; Stadelmann, J.-P. *Chem. Phys. Lett.* **1983**, *95*, 259. (j) Bombach, R.; Dannacher, J.; Stadelmann, J.-P. *J. Am. Chem. Soc.* **1983**, *105*, 4205. (k) Baer, T.; Morrow, J. C.; Shao, J. D.; Olesik, S. *J. Am. Chem. Soc.* **1988**, *110*, 5633. (l) Buschek, J. M.; Ridal, J. J.; Holmes, J. L. *Org. Mass. Spectrom.* **1988**, *23*, 543. (m) Olesik, S.; Baer, T.; Morrow, J. C.; Ridal, J. J.; Buschek, J.; Holmes, J. L. *Org. Mass. Spectrom.* **1989**, *24*, 1008. (n) Ohmichi, N.; Gotkis, I.; Steens, L.; Lifshitz, C. *Org. Mass. Spectrom.* **1992**, *27*, 383. (o) Lablanquie, P.; Ohashi, K.; Nishi, N. *J. Chem. Phys.* **1993**, *98*, 399.

(4) (a) Abboud, J.-L. M.; Hehre, W. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 6072. (b) Cone, C.; Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 372. (c) Katritzky, A. R.; Watson, C. H.; Dega-Szafran, Z.; Eyler, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 2471. (d) Lifshitz, C.; Gotkis, Y.; Ioffe, A.; Laskin, J.; Shaik, S. *Int. J. Mass Spectrom. Ion Processes* **1993**, *125*, R7. (e) Nicolaides, A.; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 9769.

(5) For recent reviews related to silicon compounds see, for example: (a) Baldridge, 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. For recent reviews that include germanium, see, for example: (g) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (h) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215. (i) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (j) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371. (k) Kudo, T.; Nagase, S. *Rev. Heteroat. Chem.* **1993**, *8*, 122. (l) Nagase, S. *Acc. Chem. Res.* **1995**, *28*, 469.

(6) For recent work related to silicon compounds see, for example: (a) Krogh-Jespersen, K.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* **1980**, *45*, 1608. (b) Chandrasekhar, J.; Schleyer, P. v. R.; Baumgärtner, R. O. W.; Reetz, M. T. *J. Org. Chem.* **1983**, *48*, 3453. (c) Nagase, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1121. (d) Baldridge, K. K.; Gordon, M. S. *Organometallics* **1988**, *7*, 144. (e) Wang, S. Y.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 7282. (f) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Am. Chem. Soc.* **1990**, *112*, 1710. (g) Grev, R. S.; Schaefer, H. F. *J. Chem. Phys.* **1992**, *97*, 7990. (h) Srinivas, R.; Hrusák, J.; Sülze, D.; Böhme, D. K.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 2802. (i) Jemmis, E. D.; Subramanian, G.; Prasad, B. V.; Tsuzuki, S.; Tanabe, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 865. (j) Trommer, M.; Sander, W.; Marquard, C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 766. (k) Nyulászi, L.; Kárpáti, T.; Veszprémi, T. *J. Am. Chem. Soc.* **1994**, *116*, 7239. (l) Apeloig, Y.; Müller, T. *J. Am. Chem. Soc.* **1995**, *117*, 5363. (m) Maier, G.; Pacl, H.; Reisenauer, H. P.; Meudt, A.; Janoschek, R. *J. Am. Chem. Soc.* **1995**, *117*, 12712.

S0002-7863(96)00966-3 CCC: $12.00

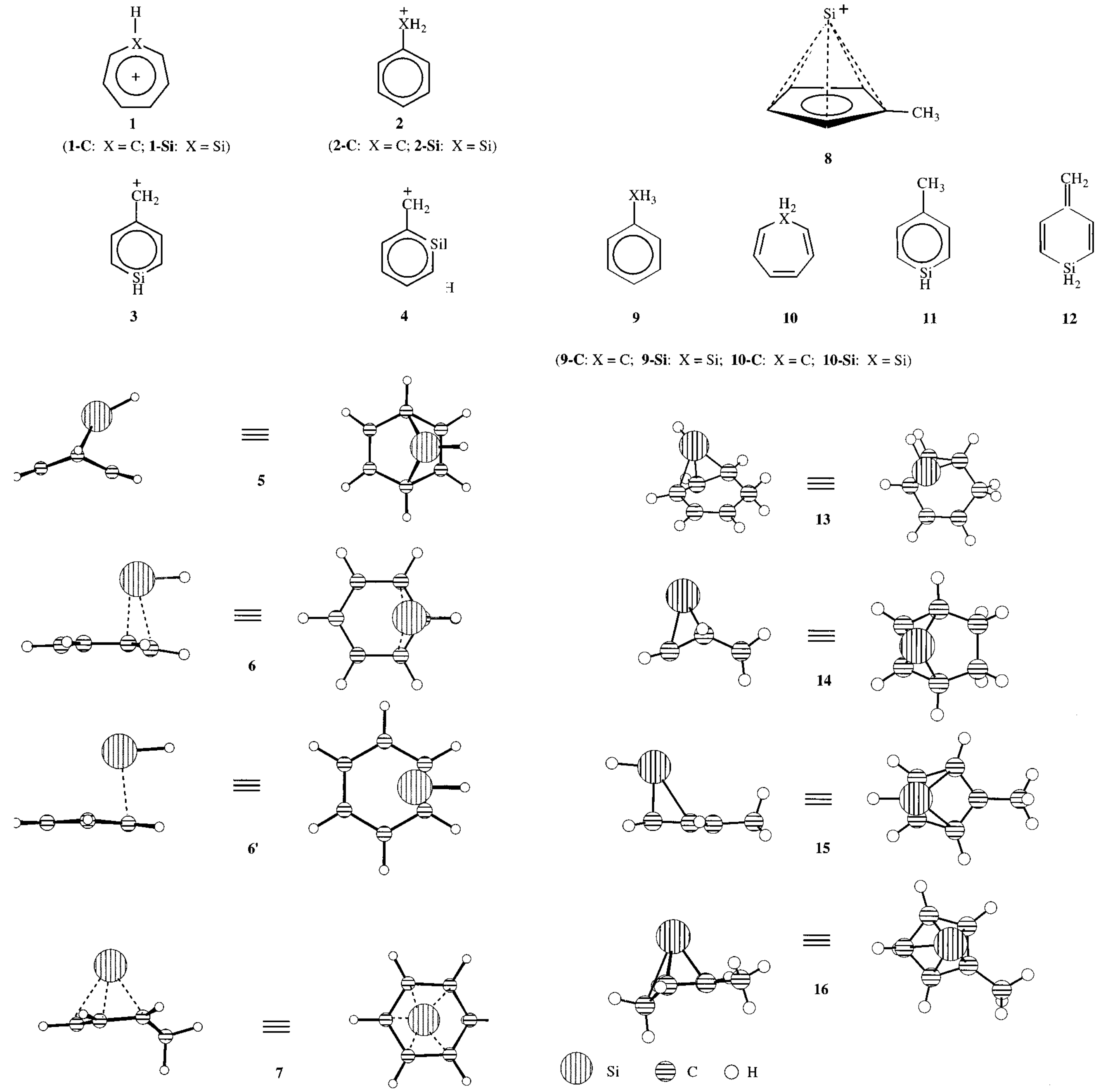

Figure 1. Schematic representation of structures **1**−**16**.

of substitution of carbon by silicon on the structures and energetics of various organic molecules. The recent gas-phase experiments of Beauchamp and co-workers[8] on silatoluene (**9-Si**) constitute an elegant effort to study the silicon-substituted analogues of benzyl and possibly tropylium cations. Their studies show that, as in the case of toluene radical cation, loss of a hydrogen atom from **9-Si**$^{\bullet+}$ results in the formation of two isomeric $C_6SiH_7^+$ cations. From the observed chemistry of the two isomers, they proposed the silatropylium cation (**1-Si**) and silabenzyl cation (**2-Si**) structures, with **1-Si** appearing to be thermodynamically more stable than **2-Si**. They also reported that **1-Si** does not react with cycloheptatriene, and therefore concluded that the hydride affinity of **1-Si** is lower than that of **1-C**, a remarkable result given that **1-C** has one of the lowest hydride affinities known for organic cations.

A useful tool in resolving conflicting experimental results or in shedding light in unexplored areas of gas-phase ion chemistry is provided by ab initio molecular orbital theory.[9] In a preliminary communication,[4e] we reported results of high-level ab initio calculations and noted that, at our highest levels of theory (G2 and G2(MP2)), **1-C** is indeed lower in energy than **2-C**, but by somewhat less than previously thought. However, our calculations showed that **1-Si** is thermodynamically *less*

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(7) For recent work that includes germanium see, for example: (a) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Chem. Soc., Perkin Trans. 2* **1990**, 417. (b) Reed, A. E.; Schleyer, P. v. R.; Janoschek, R. *J. Am. Chem. Soc.* **1991**, *113*, 1885. (c) Horner, D. A.; Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1992**, *114*, 2093. (d) Windus, T. L.; Gordon, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 9559. (e) Schleyer, P. v. R.; Kaupp, M.; Hampel, F.; Bremer, M.; Mislow, K. *J. Am. Chem. Soc.* **1992**, *114*, 6791. (f) Palágyi, A.; Schaefer, H. F.; Kapuy, E. *J. Am. Chem. Soc.* **1993**, *115*, 6901. (g) Leszczynski, J.; Huang, J. Q.; Schreiner, P. R.; Vacek, G.; Kapp, J.; Schleyer, P. v. R.; Schaefer, H. F. *Chem. Phys. Lett.* **1995**, *244*, 252. (h) Antoniotti, P.; Tonachini, G. *Organometallics* **1996**, *15*, 1307.

(8) (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.

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

stable than **2-Si**, raising some doubts as to the structure of the second isomer observed experimentally. In the present paper, in an attempt to reconcile our previous results[4e] with Beauchamp's conclusion that there is an isomer of energy lower than **2-Si**, we have expanded our computational studies to include a selection of other possible structures. We have also calculated hydride affinities of the various $C_6SiH_7^+$ isomers.

Computational Methodology

Ab initio molecular orbital calculations[9] were carried out using the GAUSSIAN 92,[10a] GAUSSIAN 94,[10b] MOLPRO,[11] and ACES II[12] programs. Geometry optimizations were carried out at the HF, MP2, B-LYP, B3-LYP, and B3-P86 levels with the 6-31G(d) basis set. Calculations at correlated levels of theory, other than MP2/6-31G(d), were carried out within the frozen-core approximation, unless otherwise specified.

Our best results were obtained at the G2, G2(MP2), and G2(MP2,SVP) levels of theory.[13,14] These all represent calculations effectively at the QCISD(T)/6-311+G(3df,2p) level on MP2/6-31G(d) optimized geometries, incorporating scaled HF/6-31G(d) zero-point energies (ZPE) and a so-called higher level correction. They differ in the additivity approximations that are used. G2 is found to perform slightly better than G2(MP2) but is computationally more demanding and so could not be applied to all of the systems examined in the present paper. G2(MP2,SVP)[14] performs comparably to the G2(MP2) method, but with substantial computational savings.

For the density-functional-theory (DFT) calculations, three different levels of theory were used: B-LYP (Becke's exchange functional[15] combined with the Lee, Yang, and Parr (LYP) correlation functional[16]), B3-LYP (an adaptation[10] of Becke's three-parameter exchange functional[17] combined with the LYP correlation functional), and B3-P86 (the B3 exchange functional combined with Perdew's gradient-corrected correlation functional[18]). All DFT calculations were carried out with GAUSSIAN 92/DFT and GAUSSIAN 94 using the FineGrid option for the numerical integration accuracy.

For ZPE corrections the calculated vibrational frequencies were scaled by the following factors: 0.893 (HF/6-31G(d)), 0.943 (MP2/6-31G(d), 1.013 (B-LYP/6-31G(d)), 0.891 (B3-LYP/6-31G(d)), and 0.976 (B3-P86/6-31G(d)).[19,20] Total energies at 298 K were derived from the corresponding energies at 0 K using the scaled HF/6-31G(d) frequencies and standard statistical thermodynamics formulas.

Results and Discussion

Evaluation of G2, G2(MP2), and G2(MP2,SVP) Theories for "Large" Systems. G2 and its simpler versions G2(MP2) and G2(MP2,SVP) have been designed for the accurate calculation of atomization energies and they have been found to be very successful in predicting a range of thermochemical properties for a variety of small and medium-sized molecules.[13,14,21,22] However, as we have recently pointed out,[23] the heats of formation of some (but not all) large hydrocarbons obtained using the standard approach based on the atomization reaction may be unreliable due to an unfavorable accumulation of errors. While G2 and G2(MP2) give rather similar overestimated results, G2(MP2,SVP) heats of formation of large hydrocarbons tend to be lower and surprisingly less prone to accumulation of errors.[23]

One such example is benzene, whose heat of formation is overestimated by 16 kJ mol^{-1} at G2 or 21 kJ mol^{-1} at G2(MP2), while it is underestimated by 8 kJ mol^{-1} using the G2(MP2,SVP) procedure.[23,24] However, the three methods are in much better agreement with one another and with experiment when the calculation of the heat of formation for benzene is based on isogyric and/or isodesmic reactions,[4e,23] such as those shown in Table 1. Thus, using the G2 (298 K) and G2(MP2) (298 K) energy changes for reactions 1−7, in conjunction with the experimental $\Delta H_{f\ 298}$ values for all the species involved except benzene, the $\Delta H_{f\ 298}$ of benzene is found to lie between 81 and 88 kJ mol^{-1}, resulting in our best theoretical estimate of 84 ± 4 kJ mol^{-1}. This is in excellent agreement with the experimental value[25] of 82.9 kJ mol^{-1}.

For the larger systems discussed in this paper, G2(MP2,SVP) heats of formation based on the atomization reaction are significantly smaller than the corresponding G2(MP2) values, in agreement with our previous experience[23] (see Tables S1 and S2 of the supporting information). However, we will see that the two procedures give essentially the same results for the hydride affinities of the $C_7H_7^+$ and $C_6H_7Si^+$ isomers, as well as for relative isomer energies. The significantly smaller computational expense of G2(MP2,SVP) as compared with G2(MP2) makes the former an attractive method for the study of quite large systems.

Heats of Formation and Relative Stabilities of Benzyl (2-C) and Tropylium (1-C) Cations. In the light of the above, we have chosen to use the isogyric approach to determine the heat of formation for **2-C**. From the isogyric reactions 8−13,

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(10) (a) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; 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. W.; 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 intio* 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) ACES II is an ab initio quantum chemical program system written by Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. It includes the VMOL integral and VPROPS property integral programs written by Almlöf, J.; Taylor, P., and a modified version of the integral derivative program ABACUS written by Helgaker, T. U.; Jensen, H. J. A.; Jørgensen, P.; Olsen, J.; Taylor, P. R. (b) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quantum Chem. Symp.* **1992**, *26*, 879.

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

(14) (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.

(15) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(16) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(17) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(18) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(19) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.

(20) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(21) See, for example: (a) Curtiss, L. A.; Kock, D. L.; Pople, J. A. *J. Chem. Phys.* **1991**, *95*, 4040. (b) Pople, J. A.; Curtiss, L. A. *J. Chem. Phys.* **1991**, *95*, 4385. (c) Smith, B. J.; Pople, J. A.; Curtiss, L. A.; Radom, L. *Aust. J. Chem.* **1992**, *45*, 285. (d) Curtiss, L. A.; Nobes, R. H.; Pople, J. A.; Radom, L. *J. Chem. Phys.* **1992**, *97*, 6766. (e) Chiu, S.-W.; Li, W.-K.; Tzeng, W.-B.; Ng, C.-Y. *J. Chem. Phys.* **1992**, *97*, 6557.

(22) See, for example: (a) Nobes, R. H.; Radom, L. *Chem. Phys. Lett.* **1992**, *189*, 554. (b) Wong, M. W.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 1507. (c) Nicolaides, A.; Radom, L. *J. Phys. Chem.* **1994**, *98*, 3092. (d) Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 3498.

(23) Nicolaides, A.; Radom, L. *Mol. Phys.* **1996**, *88*, 759.

(24) Nicolaides, A.; Radom, L. *J. Phys. Chem.* **1994**, *98*, 3092.

(25) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data Suppl. 1* **1988**, 17.

Table 1. Calculated and Experimental Heats of Isogyric Reactions (ΔH_{298}, kJ mol^{-1}) and Derived Heats of Formation ($\Delta H_{\mathrm{f}\ 298}$, kJ mol^{-1})

	ΔH_{298} (reaction)				
	expt[a]	G2(MP2)	G2	G2(MP2)	G2
				$\Delta H_{\mathrm{f}\ 298}(C_6H_6)$	
(1) $C_6H_6 + 6CH_4 \rightarrow 3CH_2{=}CH_2 + 3CH_3CH_3$	269	267	269	85	82
(2) $C_6H_6 \rightarrow 3C_2H_2$	601	603	601	81	83
(3) $C_6H_6 + 6CH_4 \rightarrow C_2H_2 + CH_2{=}CH_2 + 4CH_3CH_3$	308	308	310	83	82
(4) $C_6H_6 + 6CH_4 \rightarrow 1.5C_2H_2 + 4.5CH_3CH_3$	328	329	330	82	81
(5) $C_6H_6 + 4CH_4 \rightarrow$ (*s-trans*)-$C_4H_6 + CH_2{=}CH_2 + 2CH_3CH_3$	209	208	210	84	82
(6) $C_6H_6 + 6CH_3CH_3 \rightarrow 3CH_3CH_2CH_3 + 3CH_3CH{=}CH_2$	168	163	164	88	87
(7) $C_6H_6 + 3CH_3CH_3 \rightarrow 3CH_2{=}CH_2$ + cyclohexane	202	199	200	87	85
				$\Delta H_{\mathrm{f}\ 298}$(**2-C**)	
(8) **2-C** + $6CH_4 \rightarrow C_3H_5^+ + 2CH_2{=}CH_2 + 3CH_3CH_3$	335	343	345	902	900
(9) **2-C** + $2CH_4 \rightarrow C_6H_6 + CH_3^+ + CH_3CH_3$	331	331	333	910	908
(10) **2-C** + $CH_4 \rightarrow C_6H_6 + C_2H_5^+$	150	153	154	906	906
(11) **2-C** + $CH_3CH_3 \rightarrow PhCH_3 + C_2H_5^+$	126	127		909	
(12) **2-C** + $CH_4 \rightarrow PhCH_3 + CH_3^+$	308	306		912	
(13) **2-C** + $H^- \rightarrow PhCH_3$	−1005	−1005[b]		910	
				$\Delta H_{\mathrm{f}\ 298}$(**1-C**)	
(14) **1-C** + $H^- \rightarrow$ cycloheptatriene		−841[b]		879	
				$\Delta H_{\mathrm{f}\ 298}$(**2-Si**)	
(15) **2-Si** + $SiH_4 + CH_4 \rightarrow SiH_3^+ + CH_3SiH_3 + C_6H_6$		137		942[c]	
(16) **2-Si** + $CH_4 \rightarrow SiH_3^+ + PhCH_3$		159		951[c]	
(17) **2-Si** + $CH_4 \rightarrow$ **2-C** + SiH_4		75		944[d]	
(18) **2-Si** + $CH_3CH_3 \rightarrow$ **2-C** + CH_3SiH_3		27		938[d]	
(19) **2-Si** + $H^- \rightarrow PhSiH_3$	−961[e]	−962		941[b,f]	
(20) **1-Si** + $SiH_4 + CH_3CH_3 \rightarrow SiH_3^+ + CH_3SiH_2CH_3 + C_6H_6$		47		975[c]	
(21) **1-Si** + $CH_4 \rightarrow C_5SiH_6 + CH_3CH_2^+$		234		975[g]	
				$\Delta H_{\mathrm{f}\ 298}$(**3**)	
(22) **3** + $CH_4 \rightarrow C_5SiH_6 + CH_3CH_2^+$		245		964[g]	
(23) **3** + $C_6H_6 \rightarrow$ **2-C** + C_5SiH_6		92		968[d,g]	
(24) **3** + $SiH_4 + 6CH_4 \rightarrow SiH_3^+ + CH_3SiH_2CH_3 + 3CH_2{=}CH_2 + 2CH_3CH_3$		325		966[c]	
				$\Delta H_{\mathrm{f}\ 298}(PhSiH_3)$	
(25) $PhSiH_3 + 2CH_4 \rightarrow C_6H_6 + CH_3CH_3 + SiH_4$		57		126	
(26) $PhSiH_3 + CH_4 \rightarrow PhCH_3 + SiH_4$		32		128	
(27) $PhSiH_3 + CH_3CH_3 \rightarrow PhCH_3 + CH_3SiH_3$		−17		122	
(28) $PhSiH_3 + CH_4 \rightarrow CH_3SiH_3 + C_6H_6$		9		119	
				$\Delta H_{\mathrm{f}\ 298}(C_5SiH_6)$	
(29) $C_5SiH_6 + CH_4 \rightarrow SiH_4 + C_6H_6$		−44	−47	237	239
(30) $C_5SiH_6 + CH_3CH_3 \rightarrow CH_3SiH_3 + C_6H_6$		−92	−95	230	233
(31) $C_5SiH_6 + CH_3CH_2CH_3 \rightarrow CH_3SiH_2CH_3 + C_6H_6$		−132	−134	224	227
(32) $C_5SiH_6 + SiH_4 + 5CH_4 \rightarrow CH_2SiH_2 + CH_3SiH_3 + 2C_2H_4 + 2CH_3CH_3$		204	206	221[h]	219[h]
(33) $C_5SiH_6 + SiH_4 + C_2H_4 + CH_3CH_3 \rightarrow CH_2SiH_2 + CH_3SiH_3 + CH_4 + C_6H_6$		−63	−64	219[h]	220[h]

[a] Experimental values obtained using data from ref 25, unless otherwise noted. [b] Obtained using the exact value (−0.52539 hartrees) for the energy of H^-. [c] The experimental $\Delta H_{\mathrm{f}\ 298}$ for SiH_3^+ (985.4 kJ mol^{-1}) is based on $\Delta H_{\mathrm{f}\ 298}$ (SiH_3)[46a] and its ionization energy.[46b] See also discussion in ref 43a. [d] The experimental $\Delta H_{\mathrm{f}\ 298}$ for benzyl cation (**2-C**) (910 kJ mol^{-1}) is based on $\Delta H_{\mathrm{f}\ 298}$(benzyl radical) (210.5 kJ mol^{-1})[27] and IE(benzyl radical) (699.40 kJ mol^{-1}).[26] [e] From ref 8b. [f] For silatoluene ($PhSiH_3$) an estimated $\Delta H_{\mathrm{f}\ 298}$ of 124 ± 7 kJ mol^{-1} based on reactions 25−28 was used. [g] For silabenzene (C_5SiH_6) an esimated $\Delta H_{\mathrm{f}\ 298}$ of 233 ± 12 kJ mol^{-1} based on reactions 29−31 was used. [h] Using the experimental $\Delta H_{\mathrm{f}\ 298}$ of CH_2SiH_2 (179.9 kJ mol^{-1}) from ref 47.

it is seen that the calculated G2(MP2) and G2 estimates of $\Delta H_{\mathrm{f}\ 298}$ of **2-C** range between 900 and 912 kJ mol^{-1}. If reactions 9 and 10 are combined with reactions 1−7, so that C_6H_6 does not appear in the former, then 14 additional isogyric reactions are obtained. This results in a slightly larger range (900−915 kJ mol^{-1}), leading to our best estimate for $\Delta H_{\mathrm{f}\ 298}$ of **2-C** of 907 ± 8 kJ mol^{-1}. This computational result is in reasonable agreement with the value of 910 kJ mol^{-1} that comes from combining recent measurements of the ionization energy of benzyl radical (699.40 ± 0.06 kJ mol^{-1})[26] and the $\Delta H_{\mathrm{f}\ 298}$ of benzyl radical (210.5 ± 2 kJ mol^{-1}).[27] Other recent experimental values lie somewhat further away, namely 897 ± 5[3k] and 916 ± 9 kJ mol^{-1}.[3j]

In agreement with previous theoretical and experimental work, tropylium cation is found to be the lower energy isomer (Table 2). Our computational results (see also Table S3 in the supporting information) show that electron correlation effects are important and that they favor the tropylium relative to the benzylic structure. This preference is exaggerated at the MP2 level, which predicts the largest energy difference between the two isomers. The energy difference between the two isomers seems to converge smoothly at higher levels of theory. The difference in ZPE, which has been included in all the relative energies in Table 2, favors the benzylic structure by 4 kJ mol^{-1}. Augmentation of the basis set also favors **2-C** but the magnitude of the correction beyond 6-311G(d,p) is only 2−4 kJ mol^{-1}, depending on the level of theory.[28]

All three DFT methods that we have examined give essentially the same energy difference between **1-C** and **2-C** and the results seem to be relatively insensitive to basis set. As with MP2, the DFT methods, which can be viewed as represent-

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(26) Eiden, G. C.; Weinhold, F.; Weisshaar, J. C. *J. Chem. Phys.* **1991**, *95*, 8665.

(27) Hippler, H.; Troe, J. *J. Phys. Chem.* **1990**, *94*, 3803.

(28) At all levels of theory that we examined, improvement in the basis set lowers "monotonically" the relative energy of **2-C** (see Table S3).

Table 2. Relative Stabilities (kJ mol^{-1}) of $C_7H_7^+$ and $C_6SiH_7^+$ Isomers at Various Levels of Theory

	E(**1-C**−**2-C**)	*E*(**1-Si**−**2-Si**)	*E*(**3**−**2-Si**)	*E*(**4**−**2-Si**)	*E*(**5**−**2-Si**)	*E*(**6**−**2-Si**)	*E*(**6′**−**2-Si**)	*E*(**7**−**2-Si**)[e]	*E*(**8**−**2-Si**)
HF/6-31G(d)[a]	−24	53	36	60	126	70	70	88	−62
MP2/6-31G(d)[b]	−49	43	49	68	50	47	50	13	−133
MP2/6-311+G(3df,2p)[b]	−42	48	47	69	49	48	50	23	−128
QCISD(T)/6-311G(d,p)[b]	−32	38	32	53	58	47	50	29	−110
G2(MP2-SVP) (0 K)	−29	39	28	51	52	42	44	23	−104
G2(MP2-SVP) (298 K)	−29	38	28	51	50	41	44	22	−105
G2(MP2) (0 K)	−28	38	27	50	53	43	46	24	−102
G2(MP2) (298 K)	−29	38	27	51	51	43	46	23	−103
B-LYP/6-31G(d)[c]	−38	26	35	52	[f]	58	[g]	63	−47
B3-LYP/6-31G(d)[c]	−38	33	38	57	[f]	58	[g]	57	−61
B3-P86/6-31G(d)[c]	−37	36	39	58	61	50	[g]	27	−93
B3-P86/6-311+G(3df,2p)[d]	−34	38	35	57	62	55		36	−87

[a] Including ZPE corrections based on scaled[19,20] HF/6-31G(d) frequencies. [b] At MP2/6-31G(d) optimized geometries, including ZPE corrections based on scaled[19,20] HF/6-31G(d) frequencies. [c] Including ZPE corrections based on scaled[20] B-LYP, B3-LYP, and B3-P86 frequencies. [d] Optimized geometries and ZPE corrections at the B3-P86/6-31G(d) level of theory. [e] The relative energies are increased by 3 kJ mol^{-1} if the ZPE corrections are based on the scaled[19,20] MP2/6-31G(d) frequencies.[37] [f] No minimum corresponding to structure **5** was found. Instead, optimizations starting from the MP2/6-31(d) geometry of **5** led to structure **6′**. [g] Structure **6′** is found to have one imaginary frequency with all three DFT methods.

ing an alternative means of including electron correlation, overestimate the stability of **1-C** relative to **2-C**. However, they perform better than MP2 in this case, yielding results comparable to those obtained at the MP3 level of theory.

At our best theoretical level (G2), we find that **1-C** is more stable than **2-C** by 29 kJ mol^{-1} at 298 K.[29] This value, in conjunction with our best estimate for $\Delta H_{f\,298}$ for **2-C** (907 ± 8 kJ mol^{-1}, see above), gives 878 ± 8 kJ mol^{-1} as the $\Delta H_{f\,298}$ for **1-C**. A very similar value (879 kJ mol^{-1}) is obtained from consideration of the G2(MP2) energy change for the isogyric reaction 14 in conjunction with the experimental heats of formation for H^- and cycloheptatriene (see Table 1).

Experimental heats of formation for tropylium cation (**1-C**) lie in the range 849−866 kJ mol^{-1} and are often indirect estimates. The discrepancy between theory and experiment of up to 30 kJ mol^{-1}, particularly in the more recent determinations,[3j,25] is sufficiently large that we believe the latter should be re-examined.

Silabenzyl (2-Si) and Silatropylium (1-Si) Cations. At the MP2/6-31G(d) level, the C−C bonds of the phenyl ring in **2-Si** vary between 1.387 and 1.421 Å while those in **2-C** vary between 1.378 and 1.436 Å (Table S4). This might be taken as an indication that less delocalization of the positive charge into the ring takes place in **2-Si** as compared with **2-C**. Such a result would be expected since silicon is more electropositive than carbon and is also more reluctant to form double bonds.[5a,30] The structure of **1-Si** is quite sensitive to the level of calculation. Whereas at the HF/6-31G(d) level of theory the C−C bonds are quite localized, varying between 1.355 and 1.440 Å, inclusion of electron correlation (MP2/6-31G(d)) tends to diminish the range of bond lengths (to between 1.387 and 1.416 Å).

The thermochemical data available for silicon compounds have improved greatly in recent years, partially due to a successful interplay between theory and experiment.[31] However, there are still several fundamental silicon-containing species for which reliable heats of formation are not available. Consequently fewer isodesmic reactions can be written that involve molecules with well-established heats of formation. This introduces a greater uncertainty in our predicted heats of formation for silabenzyl cation and its isomers. By using reactions similar to those used for **1-C** and **2-C**, the heat of formation of **2-Si** is estimated to be 942 ± 12 kJ mol^{-1} (reactions 15−19, Table 1). The analysis includes and agrees well with the value of 941 kJ mol^{-1} obtained by combining the calculated hydride affinity of the silabenzyl cation (reaction 19) with the heat of formation of H^- and our predicted heat of formation for silatoluene (124 ± 7 kJ mol^{-1}, reactions 25−28). We note in turn that the calculated hydride affinity of **2-Si** (962 kJ mol^{-1}) agrees well with the experimental value (961 kJ mol^{-1}).[8b]

In contrast to the carbon analogue case, we find that the seven-membered-ring structure **1-Si** lies significantly higher in energy than **2-Si** at all levels of theory (Tables 2 and S3). At the G2(MP2) level of theory, the energy difference amounts to 38 kJ mol^{-1}. Correlation effects are important and, as in the all-carbon case, they favor the seven-membered-ring structure. Due to the reversal in stability that accompanies substitution of carbon by silicon, correlation effects now tend to lower the energy difference between the two isomers. Unlike the all-carbon case, however, the MP series seems to converge quite rapidly to the QCISD(T) value (Table S3). The ZPE correction works in the opposite direction to electron correlation and, as in the case of **1-C** and **2-C**, favors the benzylic over the seven-membered-ring structure, in this case by 6 kJ mol^{-1}. Based on our estimated heat of formation for **2-Si** of 942 ± 12 kJ mol^{-1} (see above) and the G2(MP2) energy difference of 38 kJ mol^{-1}, we propose a $\Delta H_{f\,298}$ for **1-Si** of 980 ± 12 kJ mol^{-1}, which is consistent with the predictions based on reactions 20 and 21. Very similar values for $\Delta H_{f\,298}$ of 981 kJ mol^{-1} for **1-Si** and 943 kJ mol^{-1} for **2-Si** were reported in our preliminary communication[4e] on the basis of a smaller reaction set.

The predicted G2(MP2) energy difference of 38 kJ mol^{-1} between the two isomers **1-Si** and **2-Si** is substantial and we believe that it is unlikely that a reversal in the relative stabilities will take place at still higher levels of theory.

***δ*-Silabenzyl Cation (3) and *β*-Silabenzyl Cation (4).** In the carbon analogue case, experiments[3j] have shown that interconversion of the two $C_7H_8^{\bullet+}$ ions, toluene radical cation (**9-C**$^{\bullet+}$) and cycloheptatriene radical cation (**10-C**$^{\bullet+}$), requires less energy than dissociation to either **2-C** or **1-C.** A mechanism for this isomerization has been proposed based on semiempirical[32] and ab initio[2,4d] calculations. Furthermore, scrambling of hydrogens in **10-C**$^{\bullet+}$, which results in all carbons and hydrogens becoming equivalent, is predicted to be even more facile than the above-mentioned isomerization process.[32] To the extent that these observations are transferable to the silicon system, it is

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(29) G2 energies at 298 K for **1-C** and **2-C** are −270.10699 and −270.09585 hartrees, respectively.

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

(31) See, for example: (a) Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: New York, 1989. (b) Gordon, M. S.; Francisco, J. S.; Schlegel, H. B. In *Advances in Silicon Chemistry*; JAI Press Inc.: Hampton Hill, UK, 1993; Vol. 2.

(32) Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 2446.

reasonable to expect that interconversion between **9-Si**$^{•+}$ and **10-Si**$^{•+}$ is possible under Beauchamp's experimental conditions.[8] In this case, however, scrambling of the silicon atom can give rise to up to four isomers of the type **11**$^{•+}$ with the silicon residing at different positions in the six-membered ring. These four isomers can give rise, after loss of a hydrogen atom from the methyl group, to four different cations of the benzylic type. We have explored all these possible structures at the HF and MP2 levels of theory. As might have been expected from simple resonance considerations, the α- and γ-silabenzyl cations are found to lie much higher in energy (by 130−150 kJ mol^{-1} as compared with **2-Si**) and therefore were not considered any further.

The geometries of δ-silabenzyl (**3**) and β-silabenzyl (**4**) are quite similar. In both cases, the benzene ring is somewhat distorted to accommodate the larger silicon atom. At the MP2/6-31G(d) level of theory, the bond lengths between the carbons of the ring vary between 1.370 and 1.452 Å for **3** and 1.367 and 1.449 Å for **4**. A natural population analysis (NPA) (using the SCF wave function at the MP2/6-31G(d) geometry) finds the Si−H moiety to have a charge of +1.54 in both **3** and **4** (compared with +1.48 in **1-Si**).

The heat of formation for **3** may be obtained from our best estimated $\Delta H_{f\,298}$ value for **2-Si** (942 kJ mol^{-1}) together with the G2(MP2) relative energy of **3** (27 kJ mol^{-1}) giving 969 kJ mol^{-1}. Alternatively we can calculate $\Delta H_{f\,298}$ for **3** with the help of isogyric reactions 22−24, in conjuction with experimental data (where available). The required heat of formation of silabenzene may itself be obtained with the help of isogyric reactions 29−33. However, unlike benzene, the resultant $\Delta H_{f\,298}$ of silabenzene varies between 219 and 239 mol^{-1}. This wide range, which could be associated with uncertainties in several of the experimental heats of formation (see below), introduces a larger uncertainty in the results based on reactions 22 and 23. Nevertheless, the $\Delta H_{f\,298}$ for **3** based on reactions 22−24 is in good agreement with our best estimate of 969 kJ mol^{-1}, lending additional confidence to the reliability of the calculated heats of formation.

7-Silanorbornadienyl Cation (5) and [HSi···C$_6$H$_6$]$^+$ (6 and 6′). Like its parent 7-norbornadienyl cation,[33] 7-silanorbornadienyl cation (Figure 1, **5**) was found to prefer a C_s structure to the more symmetric C_{2v}. The silicon atom in **5** lies quite close to the bridgehead carbons (1.923 Å at HF/6-31G(d), 1.993 Å at MP2/6-31G(d)). These values are only slightly greater than the typical lengths of single Si−C bonds (∼1.8−1.9 Å), indicating a considerable amount of bonding. This is supported by the considerable calculated puckering of the benzene ring.[34] However, in the case of the silicon compound the tilt of the bridge is much less pronounced and the pyramidalization at the Si center is greater than and in the opposite direction to the corresponding distortions at the C$_7$ center in the 7-norbornadienyl cation.

In contrast to **5**, isomers **6** and **6′** are characterized by longer Si−C bonds (2.243 and 2.302 Å, respectively, at MP2/6-31G(d)) and the benzene ring is calculated to be almost planar. This suggests that **6** and **6′** can be regarded as geometrically loose [HSi···C$_6$H$_6$]$^+$ π-complexes. Despite the large silicon−carbon distances, a natural population analysis (using the SCF wave function at the MP2/6-31G(d) geometry) finds the Si−H moiety in **6** and **6′** to have charges of only +0.68−0.69.[35] The two structures **6** and **6′** differ with respect to the orientation of the Si−H bond relative to the benzene ring. Both **6** and **6′** are predicted to be minima on the HF/6-31G(d) surface, with **6** marginally (<1 kJ mol^{-1}) higher in energy than **6′**. However, inclusion of electron correlation (at MP2/6-31G(d) or using any of the three DFT methods) reverses this energy ordering, and **6′** is found to have one imaginary frequency in a mode that apparently interconverts two structures of the type **6**.

Interestingly, isomer **6** is calculated to be slightly more stable than **5** (Table 2). The binding energy of **6** with respect to dissociation to HSi$^+$ and C$_6$H$_6$ is calculated (at the G2(MP2) level) to be 214 kJ mol^{-1}. This modest binding energy is consistent with Beauchamp's expectation[8] that a complex like **6** (or **5**) should be able to react with a molecule of C$_6$H$_6$ (or C$_6$D$_6$) in a reaction that exchanges the benzene ligand.

Isomers **5** and **6** display an interesting form of isomerism. Both may be regarded as [HSi···C$_6$H$_6$]$^+$ complexes, with the SiH moiety lying at differing distances from the benzene ring. Interestingly, at the HF/6-31G(d) level of theory, the (geometrically) *tight* complex (or 7-silanorbornadienyl cation) **5** lies considerably higher in energy than the *loose* complex **6**. At this level of theory the transition structure separating **5** and **6** is, as expected, quite similar in geometry to **5**, and lies only 7 kJ mol^{-1} (reduced to 6 kJ mol^{-1} after accounting for ZPE corrections) higher in energy than **5**. At the MP2/6-31G(d) level of theory, the geometry of the transition structure lies somewhere between the geometries of **5** and **6** and its energy content is calculated to be 10 kJ mol^{-1} higher than that of **5** (reduced to 9 kJ mol^{-1} after accounting for ZPE corrections). Our best calculations (G2(MP2)) predict that **6** lies 8 kJ mol^{-1} lower in energy than **5** at 298 K. At the B-LYP/6-31G(d) and B3-LYP/6-31G(d) levels, we were unable to find a minimum in the surface corresponding to **5**. C_s-symmetry constrained optimizations starting from the MP2/6-31G(d) structure for **5** led directly to **6′**.

(η^5-Cyclohexadienyl)silanium Cation (7) and (η^5-Methylcyclopentadienyl)silanium Cation (8). These two isomers have no hydrogens attached to the silicon and their structures might initially appear surprising. (η^5-Cyclohexadienyl)silanium cation (**7**) (Figure 1, Table S4) formally resembles an ion−molecule complex involving a silicon atom and a cyclohexadienyl (C$_6$H$_7$) moiety. At the HF/6-31G(d) level, **7** is found to have C_1 symmetry, but when electron correlation is included in the calculation a more symmetric C_s structure results.[36,37] At the C_s minimum, the five methine carbons are essentially coplanar and the methylene carbon is strongly tilted in the opposite direction to the silicon atom. The silicon lies 2.17−2.27 Å away from the five near-planar carbons. These distances are significantly longer than normal single silicon−carbon bond lengths (1.8−1.9 Å). On the other hand, since both C$_6$H$_7$$^+$ and C$_6$H$_7$$^•$ are calculated to have C_{2v} structures, the strong out-of-plane tilt of the methylene group in **7** indicates an appreciable

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[33] (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.

[34] The flap angle of the benzene ring is approximately 131° in the HF/6-31G(d) structure and 135° in the MP2/6-31G(d) structure. For 7-norbornadienyl cation the respective values are 127° and 127.5°.[33c]

[35] In comparison, the NPA charge of the Si−H moiety in **5** is calculated to be +1.21. The significant charge transfer from silicon to the benzene ring in isomers **6** and **6′** is reminiscent of that calculated for the [H$_3$Si−C$_6$H$_6$]$^+$ and [H$_3$Si−toluene]$^+$ complexes: Schleyer, P. v. R.; Buzek, P.; Müller, T.; Apeloig, A.; Siehl, H.-U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1471.

[36] A C_s-constrained HF/6-31G(d) optimization leads to a stationary point (one imaginary frequency) that lies only 1 kJ mol^{-1} higher in energy than the C_1 minimum.

[37] For the G2(MP2) energy of **7**, the scaled HF/6-31G(d) frequencies calculated at the C_1 geometry were used. If scaled MP2/6-31G(d) frequencies (obtained at the C_s MP2/6-31G(d) geometry) are used, then the total energy of **7** is increased by 1 kJ mol^{-1}. (In the case of **1-Si** and **2-Si**, using scaled MP2/6-31G(d) frequencies decreases their total energies by 1 and 2 kJ mol^{-1}, respectively.)

interaction between silicon and the organic fragment. At the G2(MP2) level of theory, Si has a higher ionization energy than $C_6H_7^•$. Thus the dissociation of **7** into Si + $C_6H_7^+$ lies 123 kJ mol^{-1} lower than the Si^+ + $C_6H_7^•$ channel. Quite remarkably, **7** is bound with respect to Si + $C_6H_7^+$ by 358 kJ mol^{-1}, which is significantly larger than the calculated binding energy of 214 kJ mol^{-1} for **6** (with respect to HSi^+ and C_6H_6) and indicative of a strong bonding situation.

Electron correlation is extremely important in calculating the relative energy of **7**. At the MP2/6-31G(d) level of theory, **7** is actually found to be *more* stable than **2-Si** by 2 kJ mol^{-1}. However, the ZPE for **7** is calculated to be 16 kJ mol^{-1} (scaled HF/6-31G(d) frequencies) or 19 kJ mol^{-1} (scaled MP2/6-31G-(d) frequencies) higher than that of **2-Si**, so that overall **2-Si** is predicted to be more stable (Table 2). It is interesting and rather unusual that (at correlated levels of theory) the relative stability of these two isomers is largely determined by their ZPEs. Almost half of the differences in the ZPEs between **7** and **2-Si** can be traced to the fact that **7** has two C−H bonds in place of the two Si−H bonds present in **2-Si**. This is reminiscent of the case of methylsilylene and its isomer silaethylene where ZPE corrections are also quite significant in determining their relative stabilities.[38] According to the available data,[38a] approximately one third of the difference in the ZPEs between methylsilylene and silaethylene may be attributed to the difference in the zero-point vibrational energies between a C−H and an Si−H bond.

Whereas the three DFT methods are generally in reasonable agreement with one another and with the conventional ab initio results in describing the relative energies of most of the species in Table 2, this does not seem to be the case with isomer **7**. Of the three DFT methods, only B3-P86 seems to describe the relative energy of **7** adequately, although this may of course be fortuitous. It should also be noted that, in contrast to the situation for the other isomers, the DFT results for **7** are quite sensitive to the basis set used.

(η^5-Methylcyclopentadienyl)silanium cation (**8**) (Figure 1, Table S4) is geometrically similar to **7**. The apical Si atom in **8** lies a little closer to the carbon atoms of the five-membered ring (2.14−2.18 Å), which is essentially flat. One noticeable difference between these two pyramidal isomers is the position of the hydrogens. In the case of **7** the methine hydrogen atoms are quite strongly tilted toward the apical atom, whereas in **8** they are essentially in the plane of the ring. **8** has a higher ZPE energy than **2-Si** for the same reason as noted above for **7**. However, in this case the electronic factors strongly override the differences in ZPEs and **8** is calculated to be 103 kJ mol^{-1} lower in energy than **2-Si**, making **8** by far the most stable isomer among the possibilities that we have studied. Another manifestation of the remarkable stability of **8** is that its dissociation to Si plus $CH_3-C_5H_4^+$ is endothermic by 607 kJ mol^{-1} at the G2(MP2) level.

Electron correlation is also very important in calculating the relative stability of **8**, in a manner very similar to that seen for **7**. For example, at the QCISD/(T)/6-31G(d) level the energy of **8** (relative to **2-Si**) is found to be 48 kJ mol^{-1} lower than at the HF/6-31G(d) level, which is comparable to the 49 kJ mol^{-1} change in the case of **7**. This similarity, which is presumably due to the similarity in the structures of **7** and **8**, is also found with the DFT methods where, as before, the B3-P86 method appears to perform better than B-LYP and B3-LYP.

Structures analogous to **8** have been examined computationally in the past and their stability has been attributed to the "magic" number of six interstitial electrons involved in the bonding between the apical atom and the cap (ligand).[6a,39] The term three-dimensional aromaticity has been proposed to describe this special stability.[6a,39] Experimentally, analogous compounds of Ge and Sn have been synthesized and have been shown spectroscopically to have pyramidal structures.[40,41] The stability of **7** can be understood in a similar manner. However, in this case the presence of the methylene bridge increases the size of the cap, and presumably this can explain the tilting of the hydrogens atom toward the apical atom in **7**.[39a] Furthermore, this difference in the positions of the hydrogens is consistent with the order of the relative stabilities of **7** and **8**.[39b]

Heats of Formation and Relative Stabilities of the $C_6SiH_7^+$ Isomers. Electron correlation is found to be crucial for predicting the relative stabilities of the $C_6SiH_7^+$ isomers, especially for the non-classical structures (Table 2). In addition, the MP2 level of theory does not always describe the relative energies of the $C_6SiH_7^+$ isomers well. For example, in the case of **1-Si** and **3**, the relative stabilities at the MP*n* levels of theory oscillate, with MP2 and MP4 favoring **1-Si** whereas MP3 favors **3**.[42] In such cases, it is highly desirable to obtain QCISD(T) results.

The three DFT methods are generally found to perform quite similarly (Table 2). However, among the three methods only B3-P86 predicts the existence of **5** as a minimum on the $C_6SiH_7^+$ surface, and it also describes the relative energies of **7** and **8** adequately. With the exception of isomers **7** and **8**, the DFT results are less sensitive to basis set than are the MP2 results.

The heats of formation of **3**−**8** can be obtained from the estimated $\Delta H_{f\ 298}$ for **2-Si** in conjunction with the G2(MP2) relative energies of the other isomers (Table 2). The fact that the heats of formation of the $C_6SiH_7^+$ isomers are anchored on our estimated $\Delta H_{f\ 298}$ for **2-Si** makes it important to ask how reliable are the experimental data for the species involved in the isogyric reactions 15−18. As has already been noted,[31b] G2 heats of formation for silicon compounds tend to be lower than the experimental values by 0−8 kJ mol^{-1}. However, it has been recently suggested[43] that the experimental heat of formation for the silicon atom is too low by approximately 6 kJ mol^{-1} and we have used this revised value (Table 3).[44] Since G2 heats of formation are based on atomization energies, this upward revision of the heat of formation of the silicon atom increases the G2 heats of formation of silicon-containing molecules by the same amount, bringing most of them into better agreement with experiment.

In the light of the above, our finding that G2 overestimates the heats of formation of 2-silapropane and silaethylene by more than 10 kJ mol^{-1} (Table 3) might be an indication that the

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[38] (a) Köhler, J. H.; Lischka, H. *J. Am. Chem. Soc.* **1982**, *104*, 5884. (b) Schaefer, H. F. *Acc. Chem. Res.* **1982**, *15*, 283. (c) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270.

[39] (a) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781. (b) Reference 9, p 375.

[40] Jutzi, P.; Kohl, F.; Hofmann, P.; Kruger, C.; Isay, Y.-H. *Chem. Ber.* **1980**, *113*, 757.

[41] We have also examined the $C_6H_7Ge^+$ isomers and we find that structures like **8** and **7** are the most stable isomers in that case also. Nicolaides, A.; Radom, L. To be submitted for publication.

[42] With the 6-311G(d,p) basis set, the MP2(frozen-core), MP3, and MP4 energies (in hartrees) of **1-Si** are −520.92395, −520.92012, and −520.98130, respectively. The corresponding energies for **3** are −520.88169, −520.92518, and −520.98067, respectively.

[43] (a) Grev, R. S.; Schaefer, H. F. *J. Chem. Phys.* **1992**, *97*, 8389. (b) Ochterski, J. W.; Petersson, G. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1995**, *117*, 11299.

[44] Calculated heats of formation reported in Table 3 and in Tables S1 and S2 were obtained from the atomization reaction. The required experimental heats of formation for the atoms were taken from ref 25, except in the case of Si ($\Delta H_{f\ 0}(Si_{(g)})$ = 452.3 kJ mol^{-1}).[43]

Table 3. Deviations from Experimental Values of G2(MP2) and G2 Heats of Formation (kJ mol^{-1}) for Selected Silicon Compounds[a]

	expt(298 K)[b]	$\Delta\Delta H_{f\,298}$(G2(MP2))[c]	$\Delta\Delta H_{f\,298}$(G2)[c]
SiH_4	35.0	−2.8	−3.6
CH_3SiH_3	−29.0	5.4	3.9
$CH_3SiH_2CH_3$	−95.0	12.5	10.1
$CH_2{=}SiH_2$	179.9[d]	13.0	13.9
SiH_3^+	985.4[e]	−9.0	−7.1

[a] Calculated heats of formation obtained from the atomization reaction in conjunction with experimental data for the heats of formation of the atoms (C and H from ref 25, Si from ref 43).[44] [b] Experimental values obtained using data from ref 25, unless otherwise noted. [c] The differences are defined as: $\Delta\Delta H_{f\,298} = \Delta H_{f\,298}(\text{calc}) - \Delta H_{f\,298}(\text{expt})$. [d] From ref 47. [e] Table 1, footnote *c*.

Table 4. Recommended Heats of Formation ($\Delta H_{f\,298}$, kJ mol^{-1})

		theory	expt
tropylium cation	**1-C**	878	853,[a] 859,[b] 866,[c] 849[d]
benzyl cation	**2-C**	907	910,[e] 897,[f] 916,[a] 899[d]
silatropylium cation	**1-Si**	980	
silabenzyl cation	**2-Si**	942	
δ-silabenzyl cation	**3**	969	
β-silabenzyl cation	**4**	993	
7-norbornadienyl cation	**5**	993	
$[HSi\cdots C_6H_6]^+$	**6**	985	
(η^5-cyclohexadienyl)silanium cation	**7**	965	
(η^5-methylcyclopentadienyl)-silanium cation	**8**	839	
silatoluene	**9**	124	
7-silanorbornadiene		246	
silabenzene		233	

[a] From ref 3j. [b] From ref 3g. [c] From ref 3c. [d] From ref 25. [e] Table 1, footnote *d*. [f] From ref 3k.

experimental heats of formation for these two molecules are slightly too low. This could in turn explain the lower heat of formation of silabenzene predicted by the isodesmic reactions 32 and 33 compared with that predicted by reactions 29−31. If a value of 220 kJ mol^{-1} (reactions 32 and 33) is used for $\Delta H_{f\,298}$ of silabenzene, then the energy gap between **2-Si** and **3**, based on reactions 15 and 22, is calculated to be considerably smaller than the one predicted by directly comparing the G2(MP2) energies of the two isomers, casting some doubt on this value. If all reactions 29−33 are taken into account, then $\Delta H_{f\,298}$ for silabenzene is estimated to be 229 ± 12 kJ mol^{-1}. However, based on the above discussion it seems better not to take into account reactions 32 and 33, leading to our best estimate of 233 ± 12 kJ mol^{-1} for $\Delta H_{f\,298}$ of silabenzene.

Our best estimates for the heats of formation of the $C_6SiH_7^+$ isomers that we have examined are summarized in Table 4, but due to the quite large uncertainty (±12 kJ mol^{-1}) in our estimated values, the exact ordering of their stabilities cannot be stated unequivocally in certain cases. The global minimum appears to be **8**, whose energy is well separated (by more than 100 kJ mol^{-1}) from the rest of the isomers. The other seven isomers are clustered in a rather narrow band of 50 kJ mol^{-1} with **2-Si** being the most stable among them. Approximately 25 kJ mol^{-1} higher in energy than **2-Si** lie **3** and **7**. These are followed by **1-Si** and **6**, and finally by **4** and **5**.

Hydride Affinities. At the G2(MP2) level, tropylium cation (**1-C**) has a hydride affinity (calculated as the negative of the enthalpy change in reaction 14) of 841 kJ mol^{-1}. This is consistent with the general view that tropylium cation has one of the lowest hydride affinities among organic molecules.[25] In this light, it is intriguing that Beauchamp[8] has concluded that one of the observed C_6SiH_7 isomers had a hydride affinity even lower than that of **1-C**, as indicated by its failure to react with cycloheptatriene. We have therefore carefully examined the hydride affinities of our various $C_6SiH_7^+$ isomers.

Table 5. Calculated Hydride Affinities (kJ mol^{-1})[a] Relative to That of Tropylium Cation (**1-C**)

cation		G2(MP2,SVP) (298 K)[b]	G2(MP2) (298 K)[b]
tropylium	**1-C**	0[c]	0[c]
benzyl	**2-C**	164	164
silatropylium	**1-Si**	46	48
silabenzyl	**2-Si**	119	121
δ-silabenzyl	**3**	67[d] (58)[e]	67[d] (59)[e]
β-silabenzyl	**4**	88	88
7-norbornadienyl	**5**	48	50
(η^5-cyclohexadienyl)-silanium cation	**7**	16[f] (−45)[g]	18[f]
(η^5-methylcyclopentadienyl)-silanium cation	**8**	−138[h] (−147)[i]	(−146)[i]

[a] Calculated hydride affinities were obtained using the exact value for the heat of formation of H^-.[25] [b] Total G2(MP2,SVP) and G2(MP2) energies are listed in Tables S1 and S2 of the supporting information. [c] Relative to 841 kJ mol^{-1}. [d] With respect to formation of **10**. [e] With respect to formation of **11**. [f] With respect to formation of **13**. [g] With respect to formation of **12**. [h] With respect to formation of **16**. [i] With respect to formation of **15**.

First we note that the hydride affinity of **2-C** is calculated at the G2(MP2) level to be 164 kJ mol^{-1} higher than that of tropylium cation (Table 5). It is interesting that this difference is mainly due to the higher energy of cycloheptatriene (**10-C**) compared with toluene (**9-C**) (135 kJ mol^{-1}, Table 6), rather than to the greater stability of **1-C** compared with **2-C** (only 29 kJ mol^{-1}, Table 2).

For the silicon analogues, silacycloheptatriene (**10-Si**) is found to be less stable than silatoluene (**9-Si**) by 112 kJ mol^{-1}, an amount not too dissimilar to that of the carbon systems. However, due to the *higher* energy content of **1-Si** relative to **2-Si** (by 38 kJ mol^{-1}), the hydride affinity of **1-Si** is only 73 kJ mol^{-1} lower than that of **2-Si**. As a consequence, even though the hydride affinity of **2-Si** is lower than that of **2-C**, that of **1-Si** is higher than that of **1-C** by almost 50 kJ mol^{-1}. In other words, the hydride-transfer reaction between cycloheptatriene and silatropylium cation is predicted to be quite exothermic and, in the absence of other complicating factors, this thermodynamic argument suggests that such a reaction should have been observed if **1-Si** were indeed present.

If H^- addition takes place at the exocyclic carbon in **3** to give **11**, the hydride affinity of **3** is calculated to be about 100 kJ mol^{-1} smaller than that of **2-C**, even though both isomers are formally benzylic cations. Clearly, the silicon substitution in the ring has a significant effect. Alternatively, since most of the charge in **3** lies on silicon and since **11** and **12** are of comparable stability (Table 6), it is possible that hydride abstraction by **3** might, for kinetic reasons, lead preferentially to the formation of **12** rather than **11**. The hydride affinity of **3** is then slightly smaller but it is still approximately 60 kJ mol^{-1} higher than that of **1-C**.

In the case of **7**, hydride attack at the silicon center, where the majority of the positive charge is calculated to reside, could give rise to **13** which is found to be located at a minimum on the C_6SiH_8 surface. This is a C_1-symmetry structure with the silicon atom lying above the ring and within 2.04−2.08 Å of three of the six carbons. It is a high-energy structure, calculated at the G2(MP2,SVP) level of theory to lie 185 kJ mol^{-1} above silatoluene. If **13** were to be used as the reference structure for the hydride affinity of **7** then the latter would have a hydride affinity 45 kJ mol^{-1} *lower* (at G2(MP2,SVP)) than that of **1-C**. However, there is a lower-lying structure (**14**) which may be thought of as resulting from a hydride attack at the carbon

Table 6: Thermochemical Stabilities (kJ mol^{-1}) of C_7H_8 and C_6SiH_8 Isomers Relative to Toluene and Silatoluene

molecule		G2(MP2,SVP) (298 K)[a]	G2(MP2) 0 K[a]	G2(MP2) 298 K[a]
toluene	**9-C**	0	0	0
cycloheptatriene	**10-C**	135	136	135
norbornadiene		185	187	185
silatoluene	**9-Si**	0	0	0
silacycloheptatriene	**10-Si**	111	111	112
δ-silatoluene	**11**	79	80	81
4-methylenesila-cyclohexadiene	**12**	89	88	89
[SiH$\cdots C_6H_7$]	**13**	185		
(η^4-cyclohexadiene)silicon	**14**	125	128	126
[SiH$\cdots C_5H_4Me$]	**15**	161	162	164
(η^4-methylcyclopentadiene)-silicon	**16**	152		
7-silanorbornadiene		121	124	122

[a] Total G2(MP2,SVP) and G2(MP2) energies are listed in Tables S1 and S2 of the supporting information.

adjacent to the methylene group in **7**. Since **14** is approximately 60 kJ mol^{-1} more stable than **13** (Table 6), the hydride affinity of **7** to give **13** is calculated to be higher than that of **1-C**, but only by a modest 16 kJ mol^{-1} (G2(MP2,SVP)) (or 18 kJ mol^{-1} at the G2(MP2) level of theory). The calculated small exothermicity for the reaction between **7** and **10-C** is not entirely inconsistent with the fact that this reaction was not observed. If hydride transfer from **10-C** to the second $C_6SiH_7^+$ isomer requires significant electronic reorganization, there may be a sufficiently large barrier associated with the process so as to inhibit the hydride-transfer reaction.

For **8**, as with **7**, there are several possible positions for hydride attack. Hydride attack at the Si center (to give **15**) is again found to be thermodynamically less favorable than hydride attack at the ring (to give **16**), even though in this case the preference for ring-attack is much smaller. Both paths are predicted to be highly endothermic when **10-C** is the hydride source. Overall, among the silicon cations that we have examined we find that **8** not only has the lowest hydride affinity, but its hydride affinity is significantly lower (by 138 kJ mol^{-1}) than that of tropylium, consistent with Beauchamp's observation of non-reaction with **10-C**.[8b]

Implications Regarding Recent Gas-Phase Experiments. It is useful at this stage to draw together the implications from our calculations regarding the identity of the $C_6SiH_7^+$ isomer observed, in addition to silabenzyl cation, in the recent gas-phase experiments of Beauchamp et al.[8]

In the first place, we note that the predicted difference in energy between **1-Si** and **2-Si** at the G2(MP2) level of theory is substantial and it is unlikely that a reversal in their relative stabilities will take place at even higher levels of theory. Furthermore, three other isomers (**3**, **7**, and **8**) are predicted to be more stable than **1-Si**. This, along with the fact that the hydride affinity of **1-Si** is almost 50 kJ mol^{-1} higher than that of **1-C**, makes it highly unlikely that silatropylium cation (**1-Si**) was the second $C_6SiH_7^+$ isomer observed in the recent mass spectrometry experiments.[8]

The δ-silabenzyl cation (**3**) is an attractive possibility for the second isomer mainly because its formation from **9-Si**$^{\bullet+}$ is not difficult to conceive. As discussed above, it is quite reasonable to assume that under the experimental conditions, **9-Si**$^{\bullet+}$ isomerizes to **11**$^{\bullet+}$, from which **3** can straightforwardly be formed. However, **3** is calculated to have a considerably higher hydride affinity than **1-C**, and it would be difficult to explain why it would not react with cycloheptatriene.

The 7-silanorbornadienyl cation (**5**) or the [HSi$\cdots C_6H_6$]$^+$ complex (**6**) are additional possibilities. However, we might expect that, under the experimental conditions, **5** or **6** would react with C_6D_6 to form the corresponding [HSi$\cdots C_6D_6$]$^+$ complexes.[8b,45] The fact that such an exchange was *not* observed, along with the fact that both **5** and **6** are found to lie 40−50 kJ mol^{-1} higher in energy than **2-Si**, makes it rather unlikely that **5** or **6** were present in Beauchamp's experiments.

(η^5-Cyclohexadienyl)silanium cation (**7**) is an interesting possibility. Its energy is only 23 kJ mol^{-1} higher than that of **2-Si** and its hydride affinity to produce **13** is just 16−18 kJ mol^{-1} above that of **1-C**. In addition, the hydride affinity of **7** to produce **12** is actually 45 kJ mol^{-1} below that of **1-C**. On the other hand, a high degree of bond reorganization is required for a structure like **7** to be produced from the radical cation of silatoluene (**9-Si**$^{\bullet+}$), which argues against its formation. However, it should be noted that under the experimental conditions, there are at least two different isomers of $C_6SiH_8^{\bullet+}$ present.[8b] Presumably one of them is **9-Si**$^{\bullet+}$, but the other has been postulated[8] to be a [$C_6H_6\cdots SiH_2$]$^+$ complex, based on its reactivity with C_6D_6. The available experimental evidence suggests that this radical cation does not undergo a direct H$^\bullet$ elimination to give rise to [$C_6H_6\cdots$SiH]$^+$ type complexes like **5** or **6**. It might be possible then, that it rearranges to some other isomer, perhaps **13**$^{\bullet+}$, which is a conceivable precursor of **7**. We have located a [$C_6H_6\cdots SiH_2$]$^{\bullet+}$ complex on the $C_6H_8Si^{\bullet+}$ surface and preliminary results at the MP2/6-31G(d) level of theory indicate that its rearrangement to **13**$^{\bullet+}$ is endothermic by 64 kJ mol^{-1}.

Overall the most likely candidate for the second observed $C_6SiH_7^+$ isomer is (η^5-methylcyclopentadienyl)silanium cation (**8**). It is by far the most stable isomer among those that we have examined and its hydride affinity is significantly less than that of tropylium cation, both of which are consistent with the experimental observations.[8] On the other hand, one might argue that its formation from **9-Si**$^{\bullet+}$ requires significant rearrangement of the silatoluene skeleton. However, as discussed above for **7**, this is not entirely inconceivable. If under the experimental conditions the formation of a species like **13**$^{\bullet+}$ is possible, little further rearrangement is required to arrive at a structure like **15**$^{\bullet+}$, from which **8** can be formed. Alternatively, it is also possible that cation **7** is first formed and subsequently it rearranges to **8**. The formation of **7** presumably requires less reorganization of the silatoluene skeleton and our computational results are not entirely inconsistent with its formation in the gas-phase experiments.[8] Thus it is possible that both isomers **7** and **8** are formed in addition to **2-Si** under the experimental conditions.

In summary, the calculated thermochemical properties of **8** (its stability relative to **2-Si** and its hydride affinity relative to that of **1-C**) are consistent with the experimental observations, making **8** the most likely candidate for the second observed $C_6SiH_7^+$ isomer. In addition, it is possible that **7** is also formed under the experimental conditions. Further experiments designed to detect such non-classical structures and possibly to differentiate between them are highly desirable.

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[45] (a) Cacace, F.; Crestoni, M. E.; Fornarini, S.; Gabrielli, R. *Int. J. Mass Spectrom. Ion Processes* **1988**, *84*, 17. (b) Cacace, F.; Attinà, M.; Fornarini, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 654.

[46] (a) Seetula, J. A.; Feng, Y.; Gutman, D.; Seakins, P. W.; Pilling, M. J. *J. Phys. Chem.* **1991**, *95*, 1658. (b) Johnson, R. D.; Tsai, B. P.; Hudgens, J. W. *J. Chem. Phys.* **1989**, *91*, 3340.

[47] Shin, S. K.; Irikura, K. K.; Beauchamp, J. L.; Goddard, W. A., III *J. Am. Chem. Soc.* **1988**, *110*, 24.

Concluding Remarks

Our ab initio calculations confirm that tropylium cation (**1-C**) lies lower in energy than benzyl cation (**2-C**). The heat of formation calculated for **2-C** is close to the value derived from recent experimental data. However, the heat of formation for **1-C** is not in particularly good agreement with literature experimental values. We believe that determination of a new experimental heat of formation for tropylium cation would be highly desirable.

Our calculations reveal a complicated but fascinating $C_6SiH_7^+$ surface. The global minimum on this surface is predicted to be (η^5-methylcyclopentadienyl)silanium cation (**8**). A cluster of seven other isomers (**1-Si**, **2-Si**, **3**−**7**) with distinctly different structure lies within a narrow energy band about 100−150 kJ mol^{-1} above **8**. Unlike the carbon analogue case, the seven-membered-ring silatropylium structure **1-Si** lies higher in energy than the silabenzyl isomer (**2-Si**). The δ-silabenzyl cation (**3**) and (η^5-cyclohexadienyl)silanium cation (**7**) lie intermediate in energy between **2-Si** and **1-Si**.

A point of considerable interest is the identification of the two $C_6SiH_7^+$ isomers observed in recent gas-phase experiments of Beauchamp et al. One of these is clearly silabenzyl cation (**2-Si**). However, our results do not support the experimental assignment of **1-Si** to the second isomer.

We believe that the (η^5-methylcyclopentadienyl)silanium cation (**8**) is the most likely candidate for the second isomer observed in the gas-phase experiments. Not only is it the most plausible from an energy point of view, but it is also calculated to have a hydride affinity considerably smaller than **1-C**, in accordance with the experimental observations. It is not clear how such a structure can be obtained from silatoluene radical cation (**9-Si**$^{\bullet+}$) in the light of the high degree of bond reorganization that would be required. However, it could be formed from a second $C_6SiH_8^{\bullet+}$ isomer that has been found to be present.

Clearly the issue of the structures and properties of the experimentally observed $C_6SiH_7^+$ isomers is not yet fully resolved and further experiments in this area are highly desirable. Calculations on the structures of the relevant $C_6SiH_8^{\bullet+}$ radical cations are in progress in order to gain insight into possible paths for forming the $C_6SiH_7^+$ cations.

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Supporting Information Available: Total G2(MP2) energies at 0 and 298 K and G2(MP2) heats of formation based on the standard atomization reaction (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), basis set dependence of the relative energies of **1** and **2** at various levels of theory (Table S3), selected bond lengths of **1**, **2**, **7**, and **8** at the HF/6-31G(d) and MP2/6-31G(d) levels of theory (Table S4), HF/6-31G(d) and MP2/6-31G(d) harmonic vibrational frequencies and intensities for **1**, **2**, **3**, **7**, and **8** (Table S5), and archive entries of the MP2/6-31G(d) optimized geometries and MP2(fc)/6-311+G(3df,2p) single-point calculations (Table S6) (33 pages). See any current masthead page for ordering and Internet access instructions.

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