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Foiled Carbenes Revisited: When *σ*-Stabilization Surpasses *π*-Stabilization†

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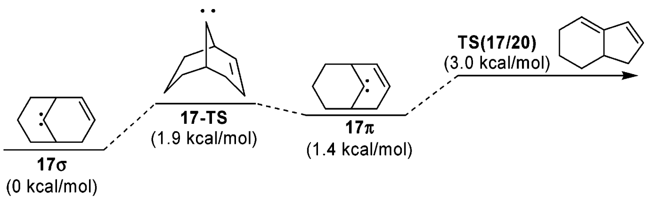

The bicyclic alkenylidenes **9** (bicyclo[3.2.1]oct-2-en-8-ylidene) and **17** (bicyclo[3.3.1]non-2-en-9-ylidene) were claimed to be stabilized foiled carbenes. Our B3LYP and MP2 computations confirm previous experimental data. Moreover, they show that these carbenes are very reactive and rearrange rapidly, mainly through a 1,2-vinyl shift by overcoming a low barrier (1.2 to 5.4 kcal/mol). This is in contrast to the high barriers (up to 30 kcal/mol) predicted for the same type of rearrangements in norborn-2-en-7-ylidene derivatives. In **17** and bicyclo[4.1.1]oct-2-en-7-ylidene (**23**), the divalent carbon atom is even bent *away* from the double bond!

Introduction

In singlet cyclic alkenylidenes, interactions between the divalent carbon and the double bond are predicted to stabilize the molecule,[1] making the carbene particularly reluctant toward rearrangements and intermolecular addition to alkenes.[2] This is especially the case in norbornen-7-ylidene derivatives, the most typical representatives of the foiled carbenes.[1,2] Carbenes are said to be foiled, when the completion of a normally feasible intramolecular reaction is prohibited by the fact that the resulting product would be excessively strained.[1,3] Usually, it concerns interactions between the LUMO of the divalent carbon with the HOMO of a double bond. Foiled carbenes are characterized by a high stabilization energy (SE), a large barrier toward rearrangement, and by major changes in their geometry.[2] On the basis of experimental results, other alkenylidenes have also been called foiled carbenes.[4] In bicyclic systems, this classification was mainly based on the predominance of 1,2-vinyl shifts taking place in these carbenes. Furthermore, a lack of products was observed resulting from 1,3-C−H-insertions, which are quite common for bicyclic compounds comprising a single carbon atom bridge. Yet, surprisingly, these assumptions were seldom supported by calculations. Indeed, the aforementioned reactive behavior can also be explained differently. In particular, *π*-complexation is not the only interaction that can cause bending of a divalent carbon. Carbene centers can also bend toward *σ*-bonds, due to hyperconjugative stabilization.[5−7] In contrast to the high SEs predicted for "true" foiled carbenes (up to more than 30 kcal/mol in comparison to norbornan-7-ylidene),[2] this hyperconjugative effect is much less potent. It is strong enough,

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† Carbene Rearrangements. 66. For Part 65, see: Mieusset, J.-L; Brinker, U. H. *J. Am. Chem. Soc.* **2006**, *128*, 15843.

(1) Gleiter, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 5457.

(2) Mieusset, J.-L; Brinker, U. H. *J. Am. Chem. Soc.* **2006**, *128*, 15843.

(3) In particular cases, these interactions can also lead to structures with a pyramidally coordinated carbon atom: Mieusset, J.-L; Brinker, U. H. *J. Org. Chem.* **2005**, *70*, 10572.

(4) (a) Brown, W. T.; Jones, W. M. *J. Org. Chem.* **1979**, *44*, 3090. (b) Brinker, U. H.; Ritzer, J. *J. Am. Chem. Soc.* **1981**, *103*, 2116. (c) Kirmse, W.; Chiem, P. V.; Henning, P. G. *J. Am. Chem. Soc.* **1983**, *105*, 1695. (d) Brinker, U. H.; König, L. *Chem. Lett.* **1984**, 45. (e) Baird, M. S.; Jefferies, I. *Tetrahedron Lett.* **1986**, *27*, 2493. (f) Fleischhauer, I.; Brinker, U. H. *Chem. Ber.* **1987**, *120*, 501. (g) Jones, D. W.; Marmon, R. J. *Tetrahedron Lett.* **1989**, *30*, 5467.

(5) Kaneno, D.; Tomoda, S. *Org. Lett.* **2003**, *5*, 2947.

(6) (a) Hiršl-Starčević, S.; Majerski, Z. *J. Org. Chem.* **1982**, *47*, 2520. (b) Knoll, W.; Bobek, M. M.; Kalchhauser, H.; Rosenberg, M. G.; Brinker, U. H. *Org. Lett.* **2003**, *5*, 2943.

(7) (a) Tomioka, H; Sugiura, T; Masumoto, Y; Izawa, Y; Inagaki, S; Iwase, K. *J. Chem. Soc. Chem. Commun.* **1986**, 693. (b) Khodabandeh, S.; Carter, E. A. *J. Phys. Chem.* **1993**, *97*, 4360. (c) Armstrong, B. M.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 3685. (d) Lambert, J. B.; Liu, X. *Tetrahedron* **1997**, *53*, 9989. (e) Worthington, S. E.; Cramer, C. J. *J. Phys. Org. Chem.* **1997**, *10*, 755. (f) Hu, C.-H. *THEOCHEM* **2000**, *531*, 39. (g) Farlow, R. A.; Thamattoor, D. M.; Sunoj, R. B.; Hadad, C. M. *J. Org. Chem.* **2002**, *67*, 3257. (h) Baik, W; Yoon, C. H.; Koo, S.; Kim, B. H. *Bull. Korean Chem. Soc.* **2004**, *25*, 90. (i) Loncke, P. G.; Peslherbe, G. H. *Org. Biomol. Chem.* **2005**, *3*, 2191.

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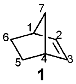
however, to control the regioselectivity of the carbene reaction. In this Article, we will reveal which of the purported singlet foiled carbenes really experience strong interactions between double bond and divalent carbon, and what kind of interaction dominates. Finally, it will be determined if those interactions cause a kinetic stabilization or destabilization.

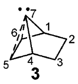


1


2π


2-TS


2σ



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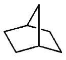
3-TS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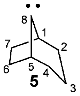

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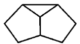
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Computational Methods

The Gaussian 03 program[8] was used for density functional theory calculations, employing Becke's[9] three-parameter hybrid method, and the exchange functional of Lee, Yang, and Parr (B3LYP).[10] Geometries were optimized at the B3LYP/6-31G(d) and the MP2-(FC)/6-31G(d) level of theory. The stationary points were characterized by vibrational analysis. The zero point vibrational energies (ZPE) were scaled by a factor of 0.9806 for B3LYP/6-31G(d) and 0.967 for MP2(FC)/6-31G(d).[11] All reported energies include zero-point corrections. Unless otherwise stated, all values in the text refer to B3LYP/6-31G(d) calculations. The electron population analysis was performed with the Atomic Polar Tensor (APT) model[12] because it is relatively independent of the level of theory. Furthermore, for C−H bonds, only a small negative charge is predicted for the hydrogen atom.[13] It is consistent with the bond dipole C^+-H^- observed in methane and ethane.[14] Thus, the carbon charges in hydrocarbons are less affected by the number of attached hydrogens and are more in line with the expectation of organic chemists than by the use of a conventional method. The obtained values were compared with results from a Natural Population Analysis (NPA).[15]

Results and Discussion

Gleiter and Hoffmann were the first to examine the stability of foiled carbenes using extended Hückel calculations.[1] They predicted norbornen-7-ylidene (**2**) to be bent and more nucleophilic than alkyl carbenes. **2** was reexamined by Freeman[16] concerning its potential homoaromaticity using B3LYP/6-311+G-(3df,2p)//B3LYP/ 6-31G(d) calculations. Moreover, **2** represents the first carbene, where the experimental results[17,18] were nicely corroborated by theory. Figure 1 represents the potential energy curves for the bending motion of C7 in norbornene (**1**), norbornen-7-ylidene (**2**), and norbornan-7-ylidene (**3**). It shows that the carbene center in **2** and **3** is more flexible than the bridging carbon atom in norbornene (**1**), thus proving the existence of interactions. But this is only true for the singlets, since **2** as a triplet has the same lack of flexibility as norbornene, because of the absence of an empty p orbital at C7. These calculations at the B3LYP/6-31G(d) level reveal a second minimum for norbornenylidene, **2**σ, lying 13.2 kcal/mol higher in energy than **2**π (see Supporting Information). Species **2**π denotes the conformer stabilized by the double bond, whereas **2**σ describes the conformer stabilized by hyperconjugation.

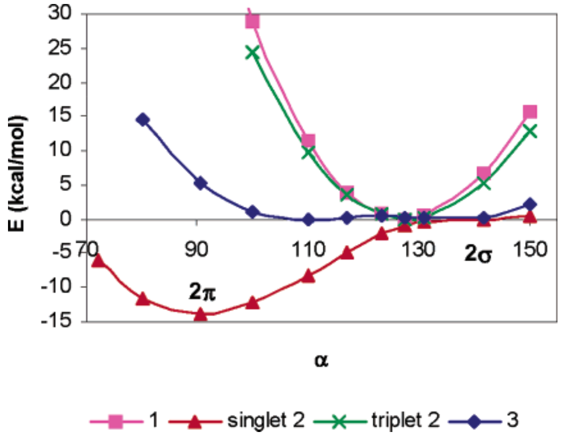

FIGURE 1. Potential energy curves for the bending motions of norbornene (**1**), singlet and triplet norbornen-7-ylidene (**2**), and norbornan-7-ylidene (**3**). *E* versus folding angle α (C2−C1−C4−C7). (C2−C1−C4−C7) and (C5−C1−C4−C7) were constrained, and the structures were optimized at the B3LYP/6-31G(d) level.

The bond lengths for **1**−**4** can be taken from Table 1. For singlet **2**σ, analysis of the bond lengths confirms the existence of interactions between the divalent carbon and the neighboring bonds, since the bonds C5−C6 (156.5 pm) and C1−C6 (160.0 pm) are elongated. In the same way, the distance C5−C7 is reduced to 218.6 pm corresponding to an angle of bending of 16° for **2**σ. The interactions in **2**π are characterized by an elongation of the double bond (137.4 pm) and of the bond leading to the carbenic center (d(C1−C7) = 155.9 pm), whereas the C1−C2 bond is strongly shortened (148.5 pm). These observations can be rationalized with the contributing structures shown in Figure 2. As will be seen later for higher analogues, the ability to form (c) is mandatory for obtaining a strong π complex. Formation of (c) also explains why highly stabilized foiled carbenes preferably react through a retro-Skattebøl rearrangement (a retro-vinylcyclopropylidene−3-cyclopentenylidene rearrangement)[19] than through a vinyl shift. Carbene **2**σ can be described using structures (a), (d), (e), and (f). Structure (a) remains by far the most important. Norbornanylidene **3**σ presents similar interactions than **2**σ. However, in contrast to

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[8] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. Gaussian 03, Gaussian, Inc., Pittsburgh PA, 2003.

[9] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[10] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

[11] Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

[12] Cioslowski, J. *J. Am. Chem. Soc.* **1989**, *111*, 8333.

[13] Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.* **1993**, *14*, 1504.

[14] Wiberg, K. B.; Wendoloski, J. J. *J. Phys. Chem.* **1984**, *88*, 586.

[15] (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. A. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. A. *Chem. Rev.* **1988**, *88*, 899.

[16] Freeman, P. K.; Dacres, J. E. *J. Org. Chem.* **2003**, *68*, 1386.

[17] (a) Moss, R. A.; Dolling, U.-H.; Whittle, J. R. *Tetrahedron Lett.* **1971**, *12*, 931. (b) Moss, R. A.; Dolling, U.-H. *Tetrahedron Lett.* **1972**, *13*, 5117.

[18] Moss, R. A.; Ho, C.-T. *Tetrahedron Lett.* **1976**, *17*, 1651.

[19] (a) Skattebøl, L. *Chem. Ind. (London)* **1962**, 2146. (b) Skattebøl, L. *Tetrahedron* **1967**, *23*, 1107. (c) Jones, W. M.; Brinker, U. H. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds. Academic: New York, 1977; p 169 ff. (d) Backes, J.; Brinker, U. H. In *Houben-Weyl (Methoden der Organischen Chemie)*; Regitz, M., Ed.; Thieme: Stuttgart, 1989, Vol. E 19b, pp 391−510.

TABLE 1. Optimized Geometries of Norbornane Derivatives 1−4 at the B3LYP/ 6-31G(d) Level of Theory[a]

	C1−C7	C1−C2	C2−C3	C1−C6	C5−C6	C2−C7	C5−C7	bending[b]
1	154.8	152.2	134.1	156.8	156.1	235.5	239.3	
2π	155.9	148.5	137.4	154.1	154.6	189.3	256.4	37.3
2-TS	151.1	151.7	134.1	159.1	156.3	239.2	224.7	10.1
2σ	150.6	151.6	134.1	160.0	156.5	241.4	218.6	15.8
3σ	150.9	154.9	155.9	156.6	157.2	246.6	224.3	13.2
3-TS	151.8	155.5	156.4	155.5	156.4	237.6	237.6	0.3
4	154.5	154.7	156.5	154.7	156.5	239.4	239.4	0

[a] All bond lengths in pm. [b] The angle of bending is defined as the difference in the dihedral angle C2−C1−C4−C7 between the carbene and the parent structure. The values are given in degrees.

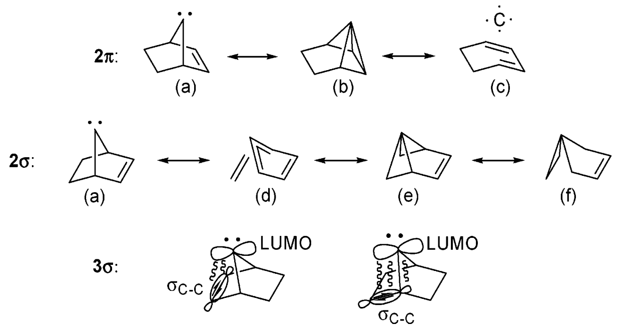

FIGURE 2. Contributing structures of **2**π and **2**σ and a frontier molecular orbital depiction of **3**σ.

2σ, the C5−C6 bond (157.2 pm) is more elongated than the C1−C6 bond (156.6 pm). The symmetrical **3-TS** is the transition state between the two bent conformers **3**σ. After zero-point correction, **3**σ and **3-TS** have the same energy**.** It shows that in **3**, C7 can flip back and forth very easily.

As illustrated in Figure 3, analysis of the electron population using the Atomic Polar Tensor model[12] reveals the presence of a negative charge (−0.118) on the divalent carbon atom of norbornenylidene **2**π due to the interactions between the LUMO of the carbene center and the HOMO of the double bond. In contrast, in **2**σ, there is almost no charge at C7 (+0.003).

The delocalization can also be tracked by a Natural Bond Orbital (NBO) analysis.[15] For **2**σ, only a small deviation from the Lewis structure is calculated. All valence NBOs are occupied by more than 1.95 e^- with the exception of C1−C6 and C4−C5 with an occupancy of only 1.91 e^-. Accordingly, the non-Lewis lone pair NBO (LP*) at the carbenic center is partly filled (0.16 e^-). A second-order perturbation theory analysis of the Fock matrix estimates the interaction between the donor NBOs (C1−C6 and C4−C5, respectively) and the acceptor NBO (LP*) to be 18.3 kcal/mol. In **2**π, the non-Lewis orbitals play a more important role. The NBO of the π bond possesses an occupancy of just 1.63 e^-. The compensation occurs mainly in the highly filled LP* at C7 (0.42 e^-). Furthermore, the antibonding NBO of the π bond is also significantly occupied (0.15 e^-). The SE associated with delocalization from the double bond C2−C3 to the carbenic center is estimated to be 156.5 kcal/mol. Secondary donating interactions to LP* comes from C1−C2 (respectively, C3−C4) with 26.8 kcal/mol and from the geminal bonds C1−C7 and C4−C7 with 9.8 kcal/mol.

What about Higher Homologues? Bicyclo[3.2.1]oct-2-en-8-ylidene (**9**)[20] and bicyclo[3.3.1]non-2-en-9-ylidene (**17**)[21] were also claimed to belong to the family of foiled carbenes. However, our calculations show that no strong internal π complex is formed in cases where the double bond is part of a six-membered ring due to an unfavorable orientation of divalent carbon and double bond orbitals. Nevertheless, the chemistry of **9** and **17** is still dominated by the ease of vinyl shifts.

Due to steric reasons, **9** can take on only one conformation. The carbene atom is bent toward the six-membered ring containing the double bond. However, the divalent carbon approaches the double bond only slightly and, with d(C8−C2) = 227.1 pm the distance remains quite long but considerably shorter than the distance to the allylic carbon atom (d(C8−C4) = 238.2 pm). Also, with d = 133.9 pm, the double bond is not elongated and the SE remains negative (−0.3 kcal/mol), if compared to bicyclo[3.2.1]octan-8-ylidene (**5**). In carbene **9**, a vinyl shift of C1−C2 to C8 takes place with a low activation barrier of 1.9 kcal/mol to afford bicyclo[3.3.0]octa-1,7-diene (**12**) (Figure 4). MP2(FC)/6-31G(d) calculations give a lower value of 0.2 kcal/mol. Experimentally, it was found that the vinyl shift counts for 97% of the isolated products (80−90% recovery).[20] In addition, we calculated other possible reaction pathways. The high-energy values obtained for these alternative transition states are in good agreement with the high selectivity of the reaction of carbene **9**. Indeed, the allyl shift to bicyclo-[3.3.0]octa-1,6-diene (**11**) requires an activation energy of 10.4 kcal/mol and the 1,3-C−H-insertion into the allylic C−H bond to afford tricyclooctene **10** even 12.2 kcal/mol. Compared with the reactions of bicyclo[3.2.1]octan-8-ylidene (**5**), the 1,2-alkyl shift requires a similar value (10.9 kcal/mol), whereas with 7.8 kcal/mol, the 1,3-C−H insertion to give **6** needs less energy to proceed. This change could probably be explained by the increase of the distance between the divalent carbon and the hydrogen atom at C−4 from 253.5 pm in **5** to 271.2 pm in **9**. Experimentally, **5** gives 98% tricyclooctane **6** as the product of a 1,3 C−H insertion.[20] Hence, **9** provides an excellent example for a carbene where the double bond has an important influence upon the reactive behavior of the divalent carbon; especially, the double bond is very well positioned to perform a vinyl shift. Nevertheless, **9** cannot be considered a foiled carbene, due to lack of stabilization and bending. Moreover, kinetically, **9** decomposes faster than **5**.

Bicyclo[3.3.1]non-2-en-9-ylidene (**17**) can take on conformations **17**σ and **17**π with **17**σ to be the most stable! In **17**σ, no foiled carbene structure is formed, the stabilization is due to hyperconjugation. The divalent carbon is bent away from the double bond, despite the fact that there is practically no difference in steric hindrance on both sides. Figure 5 shows the LUMO of **17**σ; the p orbital of the carbene center presents mixing with the neighboring σ bonds at C6 and C8. A second contribution arises from conjugation between the double bond at C2−C3 and the shortened C1−C9 bond (149.2 pm), thus providing a more planar arrangement. In **17**π, the carbene carbon is slightly bent toward the cyclohexene ring, but the carbene

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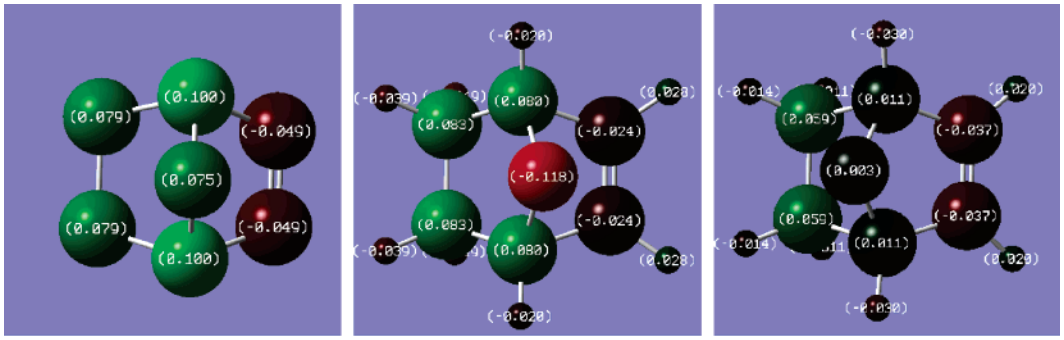
(20) Fickes, G. N.; Rose, C. B. *J. Org. Chem.* **1972**, *37*, 2898.



1 **2π** **2σ**

FIGURE 3. Atomic charges in **1**, **2***π*, and **2***σ* as given by the APT model (B3LYP/6-31G(d)). For this representation, a fixed charge range from +0.200 (green) to −0.200 (red) was chosen.

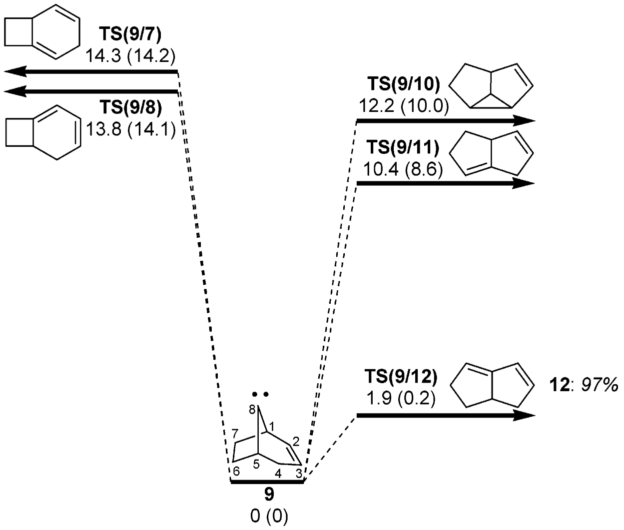


FIGURE 4. Rearrangements of **9**. Energies in kcal/mol are as given by B3LYP/6-31G(d); values in parentheses represent MP2(FC)/6-31G(d) computations. Values in italics represent yields given in % that were obtained by the sodium methoxide catalyzed decomposition of the tosylhydrazone of bicyclo[3.2.1]oct-2-en-8-one.[20]

atom remains too far away from the double bond (d(C9−C2) = 232.0 pm) to profit from strong stabilizing interactions. The MP2 results are in good agreement with the B3LYP/6-31G(d) results. As expected, MP2 predicts slightly stronger interactions, e.g., a shorter distance between C2 and C9 (225.1 pm). Figure 6 shows that carbene **17** is rather stabilized by hyperconjugation effects[5,6,7] than by π complex formation. With only 1.7 kcal/mol, the energy difference between both conformers is small. However, this difference is large enough to explain the selectivity observed experimentally during the thermal decomposition of the sodium salt of the tosylhydrazone of bicyclo[3.3.1]non-2-en-9-one.[21] In addition to 31% of **20**, the product deriving from the vinyl shift, a characteristic reaction of cyclic alkenylidenes, Fisch and Pierce observed 18% of **15** and **16**, respectively, two products resulting from insertion into the C−H bonds of the saturated ring.[21] However, products deriving from an allyl shift such as **19** or from insertion into the allylic C−H bond such as **18** were not found. This finding was interpreted as evidence for a foiled carbene, but is more in line with the fact that **17***σ* is the most stable conformation of bicyclo[3.3.1]non-2-en-9-ylidene (**17**). It is also worth noticing that after consideration of zero-point energies, the barrier preventing **17***π* to be transformed into **17***σ* disappears completely at the B3LYP/6-31G(d) level of theory, but not with MP2(FC)/6-31G(d). The remaining products consisted of 11% of bicyclo[3.3.1]non-2-ene, 8% indane, and at least three additional compounds. The formation of bicyclo[3.3.1]non-2-ene is in accordance with a relatively low calculated singlet−triplet gap of 2.6 kcal/mol (see Supporting Information). This low value is in stark contrast to those obtained for foiled norbornenylidene derivatives which are ranging between 24 and 35 kcal/mol.[2] As expected, the triplet does not show any interaction with the double bond and has a more symmetrical structure (d(C9−C2) = 243.0 pm).

The calculated activation energies for the reaction of singlet **17** confirm the predominance of the vinyl shift **17** → **20** (5.4 kcal/mol) and the C−H insertions **17** → **16** and **17** → **15** into the cyclohexane ring (8.9 and 9.3 kcal/mol) over the insertion into the allylic C−H bond (13.6 kcal/mol). However, the calculations also predict the formation of products **13** and **14** deriving from alkyl shifts (10.5 and 9.5 kcal/mol). Nevertheless, these two compounds were not observed experimentally, since they might be responsible for the formation of indane.

The results of a population analysis with the APT method on the conformers **17***σ* and **17***π* of carbene **17** are shown in Figure 7. Although the carbene center C9 in **17***π* is expected to interact with the double bond, no negative charge arises at C9 (+0.013). Interestingly, in **17***σ*, C9 is even slightly more negative (−0.015) than in **17***π* (0.013). However, the most striking feature in the charge repartition of **17***σ* is the slightly positive charge (+0.155; +0.152) to be observed on C6 and C8. Compared with **17***π*, it represents a change of ca. +0.02 e. The same trends were obtained from a natural population analysis (NPA)[15] (see Supporting Information).

These results suggest that this kind of carbene does not belong to the family of stabilized carbenes. However, the proximity of the π electrons from the double bond with the electron deficient carbene center leads to an enhanced reactivity of these species. Indeed, even if cyclopropanation remains impossible due to excessive strain, other reactions become more favorable, like vinyl shifts or the Skattebøl rearrangement.

This suggestion is confirmed by the rearrangements of bicyclo[4.1.1]oct-2-en-7-ylidene **23**[22] yielding a complex mix-

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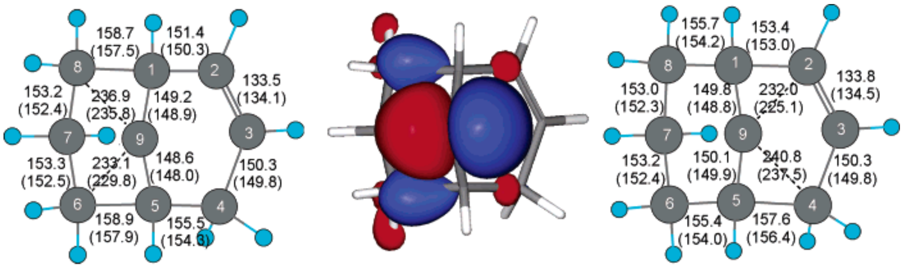
[21] Fisch, M. H.; Pierce, H. D. *J. Chem. Soc. Chem. Commun.* **1970**, 503.

[22] (a) Brinker, U. H.; König, L. *J. Am. Chem. Soc.* **1981**, *103*, 212. (b) Brinker, U. H.; König, L. *Chem. Ber.* **1983**, *116*, 894.



17σ **17σ** **17π**

FIGURE 5. LUMO of **17**σ showing hyperconjugation with the neighboring σ bonds and optimized geometries for carbenes **17**σ and **17**π. Bond lengths in picometer are as given by B3LYP/6-31G(d); values in parentheses represent MP2(FC)/6-31G(d) computations.

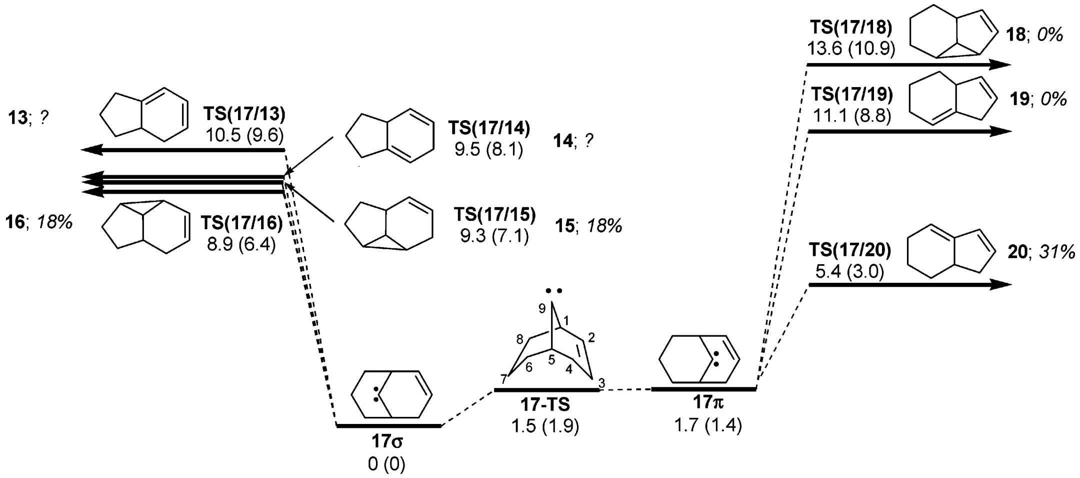
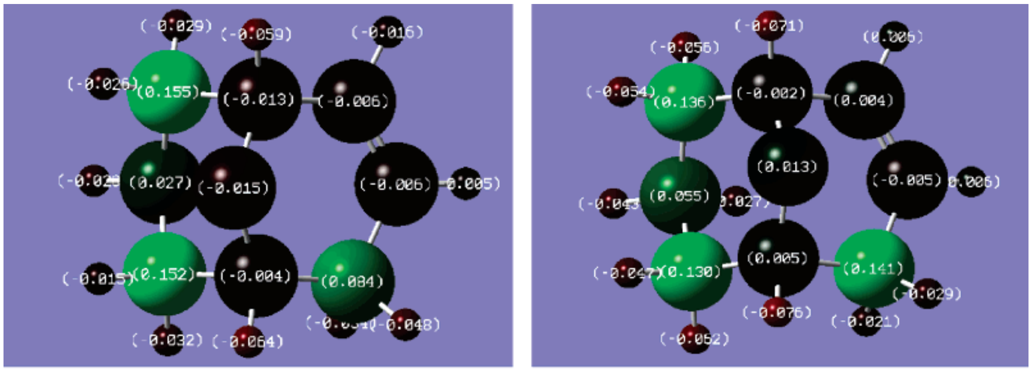


FIGURE 6. Rearrangements of **17**. Energies in kcal/mol are as given by B3LYP/6-31G(d); values in parentheses represent MP2(FC)/6-31G(d) computations. Values in italics represent yields given in % that were obtained by the thermal decomposition of the sodium salt of the tosylhydrazone of bicyclo[3.3.1]non-2-en-9-one.[21]



17σ **17π**

FIGURE 7. Atomic charges in **17**σ and **17**π are as given by the APT model (B3LYP/6-31G(d)). For this representation, a fixed charge range from +0.200 (green) to −0.200 (red) was chosen.

ture (Figure 8). The observed products result from: (1) a vinyl shift to **24** (1.2 kcal/mol, 23−28%), (2) a Skattebøl rearrangement to **9** (4.5 kcal/mol, 10%), and (3) a cyclobutylidene−methylenecyclopropane rearrangement to **21** and **22** (1.2 and 0.6 kcal/mol, respectively, 62−67%). Interestingly, carbene **23** also does not prefer the foiled structure, but the nonclassical cyclobutylidene conformation is favored. Alkenylidene **23** is so reactive that the characteristic reactions of foiled carbenes are able to compete successfully with the cyclobutylidene−methylenecyclopropane rearrangement, a reaction which is known to proceed very easily.[23] It is worth noticing that the reaction barriers toward all four products are lower than the barrier for the transition between the foiled structure **23**π and the hyperconjugated structure **23**σ (4.9 kcal/mol). This is also the case for the transition between the conformer in a pseudo-boat form **23σr** (relative to the carbenic carbon) and the conformer in the pseudo-chair form **23**σ. It means that the

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[23] (a) Sulzbach, H. M.; Platz, M. S.; Schaefer, H. F., III; Hadad, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 5682. (b) Nordvik, T.; Mieusset, J.- L.; Brinker, U. H. *Org. Lett.* **2004**, *6*, 715.

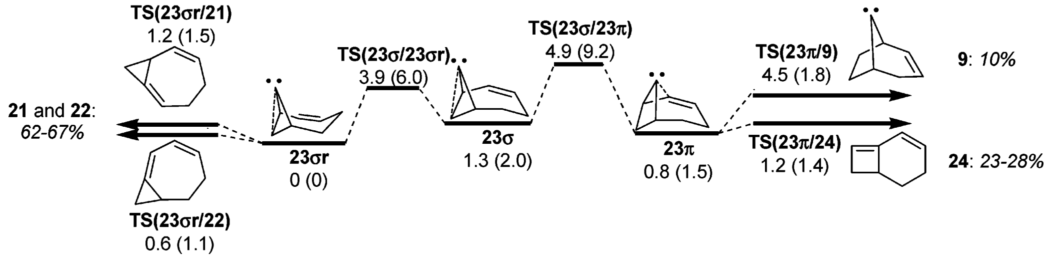

FIGURE 8. Rearrangements of **23**. Energies in kcal/mol are as given by B3LYP/6-31G(d); values in parentheses represent MP2(FC)/6-31G(d) computations. Values in italics represent the yields of the C_8H_{10} fraction and are given in %.[22]

outcome of the rearrangement of **23** is determined by the generation of three conformationally different carbenes.

Experimentally, **23** was generated by pyrolysis of the tosylhydrazone salt of bicyclo[4.1.1]oct-2-en-7-one.[22] Its immediate precursor is the corresponding diazo compound, 7-diazobicyclo-[4.1.1]oct-2-ene. According to our calculations, for its decomposition leading preferentially to the formation of **23*σ*r**, 29.3 kcal/mol are needed. However, formation of **23*σ*** and **23*π*** is only slightly disfavored (29.7 and 29.8 kcal/mol, respectively). Therefore, under the reaction conditions applied, all three carbenes, **23*σ*r**, **23*σ***, and **23*π***, should be generated.

Conclusion

It was found that in bicyclic alkenylidenes only the cyclopentenylidene subunit can produce strong interactions resulting in considerable bending of the carbenic carbon toward the double bond thereby affording high stabilization energies. If the double bond is included into a larger ring ($n \geq 6$), i.e., with a cyclohexenylidene or a cycloheptenylidene subunit, the interactions are of about the same magnitude than hyperconjugative effects and only a small distortion is observed. According to our calculations, in bicyclo[3.3.0]non-2-en-9-ylidene (**17**) and in bicyclo[4.1.1]oct-2-en-7-ylidene (**23**), the divalent carbon is even bent away from the double bond! However, the interactions between divalent carbon and double bond have an important effect on the transition state in every bicyclo[x.y.1]alk-2-enylidene investigated, since the vinyl shift is one of the energetically lowest pathways. In contrast to norbornenylidene with its cyclopentenylidene subunit, the carbenes investigated in this Article are much more prone to intramolecular rearrangement and less stable than their saturated counterparts. Hence, for such species, it would be better not to use the term “foiled carbene.”

Acknowledgment. Calculations with Gaussian 03 were performed on the Schrödinger III Linux cluster at the University of Vienna.

Supporting Information Available: Figures for the NPA atomic charges for **2** and **17**; Cartesian coordinates and energies for all relevant stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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