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The Nature and Extent of π-Stabilization within Foiled Carbenes[†]

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Abstract: B3LYP/6-311+G(d,p) computations of the stabilization energies, singlet−triplet energy gaps, and lowest transition states for a set of cyclic alkenylidenes were performed in order to find the strongest interactions between the C−C double bond and the carbene center. The results suggest that among the alkenylidenes investigated in this study, those with a norbornenylidene structure represent strongly stabilized carbenes with a reduced reactivity toward intermolecular reactions. Further stabilization is found when the double bond is electron-rich or pyramidalized. Thus, for the rearrangement of *syn*-**34** to take place, an activation barrier of about 22 kcal/mol needs to be overcome. The inclination to undergo a retro-Skattebøl rearrangement, which to our knowledge has never been observed experimentally, is characteristic for highly stabilized foiled carbenes.

Introduction

Long-lived triplet carbenes have been generated with a half-life of up to 14.5 days.[1] In another development, stable carbenes have been produced by placing heteroatoms adjacent to the divalent carbon.[2] Moreover, it has been shown that singlet fluorophenoxycarbene can be entrapped within hemicarcerands and kept for days at room temperature.[3] One possibility is to shut off the energetically easiest intramolecular reaction paths, i.e., C−H insertions and alkyl shifts, as suggested by Nicolaides[4] for his heptacycloalkylidenes. Another way suggested by Gleiter and Hoffmann[5] deals with a special kind of cyclic alkenylidenes,[6] which were coined "foiled carbenes". Cyclic alkenylidenes are especially interesting, if double bonds and carbene centers are disposed in such a way that they can interact.[7] Foiled carbenes were defined as "systems where a stabilization is obtained by the inception of a facile carbene reaction which is foiled by the impossibility of attaining the final product geometry,"[5] e.g., cyclopropanation. Foiled carbenes are stabilized by a π-complex formed by an interaction between the π-orbital of the double bond (highest occupied molecular orbital, HOMO) and the empty p orbital of the divalent carbon (lowest unoccupied molecular orbital, LUMO), forming a 3-center-2-electron bond.[8] Cyclopropane rings can also engage in this kind of stabilization.[6,9−11] This interaction only occurs with singlet carbenes. Cyclopentylidenes possess a singlet ground state, and additional stabilization by a double bond leads to a large singlet−triplet splitting; therefore, in this study, only the singlet manifold was considered. In their original work,[5] Gleiter and Hoffmann used norbornenylidene **4** and norbornadienylidene (**31**) as examples. However, other systems can also be conceived. For example, in cyclobutenylidene,[12] strong interactions with the double bond are present and the formation of bicyclo[1.1.0]but-1-ene is sterically impossible. Moreover, the geometry of cyclobutenylidene is extremely distorted and it possesses a high π-stabilization (π-SE) and a large barrier toward rearrangement when compared with the related propenylidene. Here, we report our investigations of the structure of norbornenylidene-based foiled carbenes, their SE, and the most important reaction paths that they can undergo.

Computational Methods

Gaussian 03[13] was used for density functional theory calculations, employing Becke's[14] three-parameter hybrid method, and the exchange functional of Lee, Yang, and Parr (B3LYP).[15] Geometries were optimized at the B3LYP/6-31G(d) level of theory, and the stationary

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[†] Carbene Rearrangements. 65. For Part 64, see Rosenberg, M. G.; Brinker, U. H. *Eur. J. Org. Chem.* In press (DOI: 10.1002/ejoc.200600547).

(1) (a) Tomioka, H. *Acc. Chem. Res.* **1997**, *30*, 315. (b) Tomioka, H. *Pure Appl. Chem.* **2003**, *75*, 1041. (c) Iwamoto, E.; Hirai, K.; Tomioka, H. *J. Am. Chem. Soc.* **2003**, *125*, 14664. (d) Itoh, T.; Nakata, Y.; Hirai, K.; Tomioka, H. *J. Am. Chem. Soc.* **2006**, *128*, 957.

(2) (a) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (b) Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913.

(3) Liu, X.; Chu, G.; Moss, R. A.; Sauers, R. R.; Warmuth, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1994.

(4) Nicolaides, A. *J. Am. Chem. Soc.* **2003**, *125*, 9070.

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

(6) Brinker, U. H.; Fermann, M. In *Houben-Weyl (Methoden der Organischen Chemie)*; Regitz, M., Ed.; Thieme: Stuttgart, 1989; Vol. E 19b, pp 607−622.

(7) Mieusset, J.-L.; Brinker, U. H. *J. Org. Chem.* **2005**, *70*, 10572.

(8) Schoeller, W. W.; Brinker, U. H. *J. Am. Chem. Soc.* **1978**, *100*, 6012.

(9) (a) Freeman, P. K.; Hardy, T. A.; Raghavan, R. S.; Kuper, D. G. *J. Org. Chem.* **1977**, *42*, 3882. (b) Freeman, P. K.; Raghavan, R. S.; Kuper, D. G. *J. Am. Chem. Soc.* **1971**, *93*, 5288.

(10) Okumura, K.; Murahashi, S.-I. *Tetrahedron Lett.* **1977**, *18*, 3281.

(11) (a) Freeman, P. K.; Pugh, J. K. *J. Org. Chem.* **2000**, *65*, 6107. (b) Freeman, P. K. *J. Am. Chem. Soc.* **1998**, *120*, 1619.

(12) (a) Dyer, S. F.; Kammula, S.; Shevlin, P. B. *J. Am. Chem. Soc.* **1977**, *99*, 8104. (b) Nicolaides, A.; Matsushita, T.; Tomioka, H. *J. Org. Chem.* **1999**, *64*, 3299. (c) Nicolaides, A.; Matsushita, T.; Yonezawa, K.; Sawai, S.; Tomioka, H.; Stracener, L. L.; Hodges, J. A.; McMahon, R. J. *J. Am. Chem. Soc.* **2001**, *123*, 2870. (d) Takahashi, Y.; Nicolaides, A.; Tomioka, H. *J. Synth. Org. Chem., Jpn.* **2001**, *59*, 1070.

(13) Frisch, M. J.; et al. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

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

(15) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

10.1021/ja065595y CCC: $33.50 © 2006 American Chemical Society

Chart 1

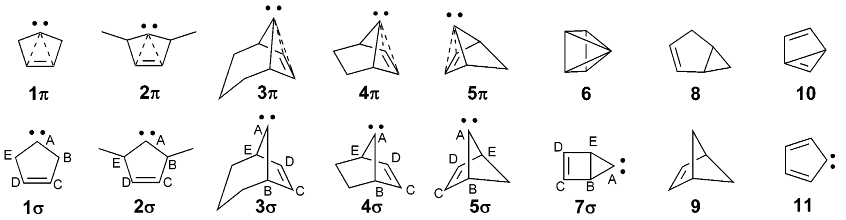
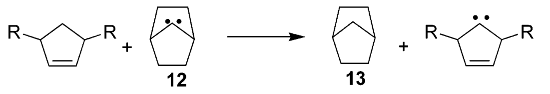


Table 1. Geometries, SEs, and Relative Energies of Mono- and Bicyclic Cyclopentenylidenes[a]

	$d(C_C–C_D)$ (pm)	$d(C_A–C_C)$ (pm)	bending angle	SE	ΔE ($E_\sigma - E_\pi$)	singlet–triplet gap
1π	136.0 (136.3)	196.5 (196.7)	100.2 (99.7)	−2.1 (−0.9)		−0.3 (−1.9)
1σ	133.4 (133.6)	244.6 (245.8)	180.0 (180.0)	7.0 (6.9)	−9.1 (−7.8)	8.8 (5.9)
1T	133.6 (133.8)	233.6 (231.0)	180.0 (180.0)	8.8 (9.1)		
2π	136.1 (136.4)	194.8 (193.9)	99.6 (98.2)	1.0 (2.2)		3.1 (1.6)
2σ	133.4 (133.6)	243.0 (244.3)	169.8 (171.5)	5.3 (4.9)	−4.3 (−2.7)	7.4 (4.3)
2T	133.6 (133.8)	229.4 (229.8)	179.6 (178.9)	8.5 (8.8)		
3π	136.1 (136.4)	196.7 (195.3)	100.8 (99.1)	5.1 (6.7)		12.1 (11.2)
3σ	133.5 (133.8)	241.0 (242.5)	150.7 (151.7)	5.0 (5.4)	0.1 (1.3)	12.0 (9.9)
3T	133.8 (134.1)	229.0 (229.3)	138.3 (138.4)	3.6 (3.7)		
4π	136.2 (136.6)	189.8 (189.3)	90.8 (90.0)	13.9 (15.6)		24.6 (23.7)
4σ	(134.1)	(241.4)	(141.9)	(2.4)	(13.2)	(10.5)
4T	134.3 (134.5)	229.7 (230.1)	127.8 (127.9)	−0.1 (0.0)		
5π	139.4 (139.5)	177.1 (177.8)	74.7 (74.9)	26.2 (28.4)		33.7 (33.3)
5σ						
5T	134.9 (135.0)	233.9 (234.5)	116.6 (116.8)	3.2 (3.2)		
6	145.0 (144.8)	165.3 (166.6)	60.8 (61.0)	31.3 (34.2)		
7σ	132.2 (132.5)	256.7 (258.9)	153.7 (153.4)	21.7 (22.0)	9.6 (12.2)	25.6 (23.7)
7T	134.8 (135.0)	244.8 (245.9)	119.3 (119.3)	6.7 (6.5)		

[a] The bending angle is defined as the angle between the plane formed by the divalent carbon C_A with its neighboring atoms ($C_E-C_A-C_B$) and the plane of the double bond ($C_B-C_C-C_D-C_E$). π stands for the foiled carbene, σ stands for the conformer, which is stabilized by hyperconjugation, and **T** stands for the triplet state. Energies in kcal/mol are as given by B3LYP/6-311+G(d,p); values in parentheses represent B3LYP/6-31G(d) computations.

Scheme 1. Isodesmic Reaction Used for the Calculation of Stabilization Energies



points were characterized by vibrational analysis. These geometries were refined at the B3LYP/6-311+G(d,p) level and also confirmed by vibrational analysis. All reported energies include zero-point corrections. Unless otherwise stated, all values in the text refer to B3LYP/6-311+G(d,p) calculations. For molecules that exist in several conformations, the most stable conformer was first determined using the semiempirical AM1 method (Chart 1).

The formation of a foiled carbene depends on the interplay between the stabilization due to the creation of a π-complex and the overcoming of steric repulsion. Table 1 shows that the strength of the interaction is a steric matter. The more bent the structure of the parent compound, the stronger is the interaction. The strength of this interaction can be followed by the distance between the carbene center and a carbon atom of the double bond (first column) or by the length of the double bond. It can also be evaluated by the energy difference ($E_\sigma - E_\pi$) of the two conformers, the π-complex (π), and the structure, which is stabilized by σ-bonds (σ) (Table 1). In addition, the isodesmic reaction depicted in Scheme 1 compares the energies of a cyclopent-3-en-1-ylidene and norbornanylidene (**12**) and gives the stabilization energy (SE) of the former carbene. A negative value of $E_\pi - E_\sigma$ means that the interaction is strong enough to generate a foiled carbene but that steric repulsion overrides the energetic gain due to π-complex formation.

The two conformers of cyclopentenylidene (**1**), i.e., **1σ** and **1π**, were first described using the semiempirical MINDO/3 method.[8] Later, these structures were computed again at the B3LYP/6-31G(d) level of theory.[16] According to our calculations, the flat conformer **1σ** is preferred over the nonclassical **1π** by 9.1 kcal/mol. Even if the bent conformer **1π** is of higher energy than **1σ** and also higher in energy than the transition state for the 1,2-H-shift leading to cyclopentadiene, **1π** can still be produced experimentally:[17] It has been shown to be a reactive intermediate in the Skattebøl rearrangement of vinylcyclopropylidenes.[18] Similarly, the foiled conformer **2π** of 2,5-dimethylcyclopent-3-en-1-ylidene (**2**) with 4.3 kcal/mol is also less stable than flat **2σ**. Although the difference is smaller than in **1**, it confirms that substitution with two alkyl groups in an α-position to the divalent carbon is not the main reason for the increased stability of the foiled conformation of norbornenylidene **4π**, which is 13.2 kcal/mol [B3LYP/6-31G(d)] more stable than **4σ**. The decisive point in favor for **4π** is the enforced conformational change due to the ring closure brought about by the connection of the C atoms of the two methyl groups in **2**.

Bicyclo[3.2.1]oct-6-en-8-ylidene[19] (**3**) shows two minima. Bent **3π** is the most stable conformer, but the energy difference with **3σ** is only 0.1 kcal/mol.

For bicyclo[2.1.1]hex-2-en-5-ylidente (**5**), only one conformer, i.e., foiled **5π**, was found. Starting with a classical geometry as given by AM1, the calculations converged directly to fulvene (**18**) with Gaussian and to a rotational transition state of **18** with Spartan, respectively. Because of the increase in strain, **5π** shows a higher SE (26.2 kcal/mol), when compared with **12**, and a very short distance between the carbene carbon and the carbon atom at the double bond (C_A-C_C =

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(16) Olivella, S.; López, N. *Chem. Eur. J.* **2001**, *7*, 3951.

(17) Kirmse, W.; Chiem, P. V.; Henning, P. G. *J. Am. Chem. Soc.* **1983**, *105*, 1695.

(18) (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.

(19) (a) Warner, P. M.; Chu, I.-S. *J. Am. Chem. Soc.* **1984**, *106*, 5366. (b) Warner, P.; Chu, I.-S. *J. Org. Chem.* **1984**, *49*, 3666. (c) Kirmse, W.; Richarz, U. *Chem. Ber.* **1978**, *111*, 1883.

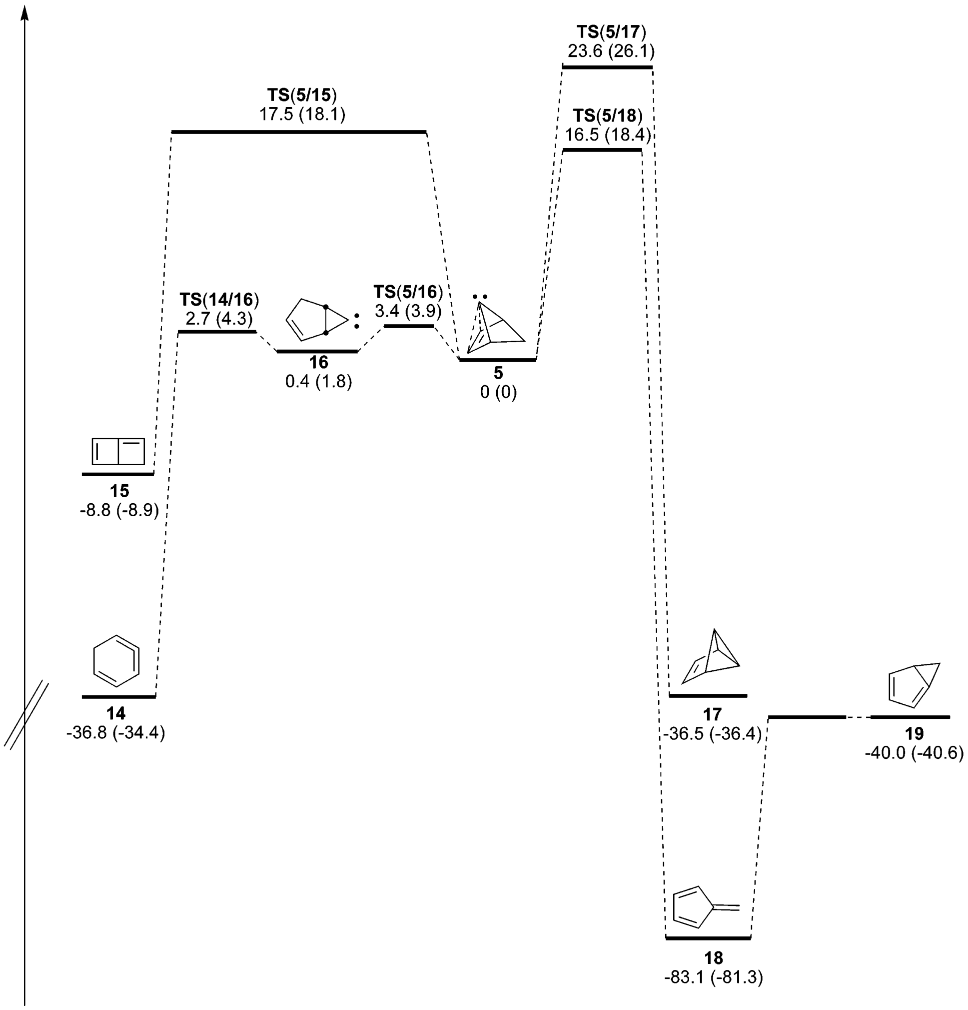

Figure 1. Decomposition of **5**. Energies in kcal/mol are as given by B3LYP/6-311+G(d,p); values in parentheses represent B3LYP/6-31G(d) computations.

177.1 pm) (Table 1). At the same time, C_A-C_B is strongly elongated (163.9 pm) and C_B-C_C is shortened (145.7 pm).

Besides the high SE of **5**, the kinetic stability of this compound was also investigated (Figure 1). Although cyclobutylidenes are known to easily rearrange to alkylidenecyclopropanes,[20] carbene **5** proved to be quite resistant toward this alkyl shift; that is, 16.5 kcal/mol is required for the transition **TS**(**5/18**). The resulting bicyclo[3.1.0]hexa-1,3-diene (**19**) is unstable and is not generated; instead, **5** rearranges directly to **18**. Diene **19** is known to rearrange easily by overcoming a barrier of only 0.3 kcal/mol to give **18**, a reaction that is exothermic by 41.3 kcal/mol [G2M(rcc,MP2) calculations].[21] The vinyl shift **TS**(**5/15**) requires 17.5 kcal/mol to take place. For the 1,3 C−H insertion to benzvalene **17**, a substantially higher activation energy of 23.6 kcal/mol is necessary. These results show that bicyclo[2.1.1]hexenylidenes are not only thermodynamically more stable than norbornenylidenes but also kinetically more stable, if only the known reactions of parent norbornenylidene are considered. Thus, the lowest transition state for **4** lies at only 10.8 kcal/mol, vide infra (after next paragraph). However, some attention should be given to the possibility of a retro-Skattebøl rearrangement **5** → **16**, since bicyclo[3.1.0]hex-2-en-6-ylidene (**16**) is only 0.4 kcal/mol higher in energy than **5**. The SE of **16** was found to be only 4.3 kcal/mol. This means that the double bond is not well-positioned to allow formation of a strong π-complex. In stark contrast to the corresponding alkenes, carbenes **16** and **5** possess about the same energy, whereas bicyclo[3.1.0]hex-2-ene (**8**) is about 21.5 kcal/mol more stable than bicyclo[2.1.1]hex-2-ene (**9**). This fact opens the way to the retro-Skattebøl rearrangement **5** → **16**. The transition state for this reaction is found to be only 3.4 kcal/mol and thus creates an easy way to benzene formation through opening of the cyclopropylidene ring to cyclohexa-1,2,4-triene (**14**)[22] and a concomitant rearrangement to benzene. This probably constitutes the only experimentally observable reaction of **5**.

With bicyclo[2.1.0]pent-2-en-5-ylidene (**7**), an even more strained analogue of **5** was investigated. In fact, the π-complex **7**π of this carbene corresponds to pyramidane **6**, a compound that computationally already has been thoroughly characterized[23] and predicted to be stable even at room temperature.[23f] However, this species has still not been prepared experimentally, although its precursor, tricyclo[2.1.0.0^{2,5}]-pentan-3-one,[24] and some of its derivatives were repeatedly synthesized. Carbene **7**σ was found as a minimum with B3LYP/6-31G(d). It was

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(20) For example, the transition state of the ring contraction of 2-methylcyclobutylidene is only 3.5 kcal/mol higher than the carbene as determined by B3LYP/6-31.G(d) calculations. (a) Nordvik, T.; Mieusset, J. L.; Brinker, U. H. *Org. Lett.* **2004**, *6*, 715. See also (b) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002. (c) Backes, J.; Brinker, U. H. In *Houben-Weyl (Methoden der Organischen Chemie)*; Regitz, M., Ed.; Thieme: Stuttgart, 1989; Vol. E 19b, pp 511−541. (d) Pezacki, J. P.; Pole, D. L.; Warkentin, J.; Chen, T.; Ford, F.; Toscano, J. P.; Fell, J.; Platz, M. S. *J. Am. Chem. Soc.* **1997**, *119*, 3191. (e) Schoeller, W. W. *J. Am. Chem. Soc.* **1979**, *101*, 4811. (f) Sulzbach, H. M.; Platz, M. S.; Schaefer, H. F., III; Hadad, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 5682.

(21) (a) Madden, L. K.; Mebel, A. M.; Lin, M. C.; Melius, C. F. *J. Phys. Org. Chem.* **1996**, *9*, 801. (b) Bettinger, H. F.; Schreiner, P. R.; Schaefer, H. F., III; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1998**, *120*, 5741.

(22) (a) Christl, M.; Braun, M.; Müller, G. *Angew. Chem., Int. Ed.* **1992**, *31*, 473. (b) Janoschek, R. *Angew. Chem., Int. Ed.* **1992**, *31*, 476. (c) Musch, P. W.; Scheidel, D.; Engels, B. *J. Phys. Chem. A* **2003**, *107*, 11223.

Chart 2

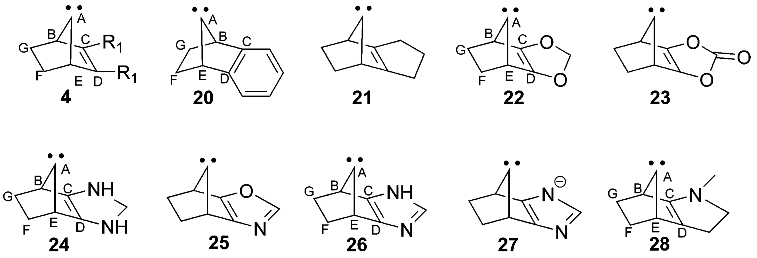

Table 2. Comparison of the Stability and the Geometry of Norbornenylidene Derivatives Bearing Substituents at the Double Bond[a]

	ΔE ($E_\pi - E_\sigma$)	singlet–triplet gap	*E* vinyl shift	SE	d(C_A–C_C) (pm)	d(C_C–C_D) (pm)
4 (R_1 = H)	(13.2)	24.6 (23.7)	10.8 (11.0)	13.9 (15.6)	189.8 (189.3)	137.2 (137.4)
20		16.9 (15.3)	10.2 (9.9)	6.2 (7.1)	204.0 (203.5)	141.2 (141.4)
4b (R_1 = CN)	4.2 (4.9)	16.1 (15.0)	4.5 (4.0)	3.6 (5.4)	199.2 (198.1)	137.7 (138.2)
4c (R_1 = CH_3)		27.2 (25.6)	12.0 (12.1)	17.2 (17.9)	191.0 (191.1)	138.0 (138.2)
4d (R_1 = Cl)	(11.5)	23.8 (21.7)	9.0 (9.3)	12.6 (13.5)	192.1 (192.2)	137.1 (137.3)
4e (R_1 = F)		28.8 (28.0)	12.4 (12.8)	17.5 (19.7)	185.5 (185.8)	137.1 (137.3)
4f (R_1 = OH)		33.2 (32.1)	14.3 (14.7)	22.7 (24.2)	187.4/188.6 (188.2/189.3)	138.0 (138.0)
4g (R_1 = NH_2)		33.8 (32.6)	15.3 (16.0)	24.6 (25.4)	187.4/195.7 (187.6/195.6)	138.7 (138.7)
21		30.6 (29.1)	19.1 (19.5)	20.5 (21.4)	185.4 (185.2)	138.0 (138.2)
22		37.5 (36.5)	22.8 (23.3)	24.4 (26.3)	183.1 (183.1)	137.1 (137.3)
23		32.8 (31.3)	21.0 (21.0)	19.6 (21.0)	181.4 (181.7)	137.0 (137.2)
24		35.2 (34.7)	20.7 (21.2)	24.2 (25.5)	189.0 (185.8)	137.7 (138.2)
25		27.8 (26.3)	21.2 (21.3)	16.7 (18.0)	184.6/186.7 (184.9/187.1)	138.3 (138.5)
26		27.7 (26.2)	21.4 (21.7)	17.2 (18.4)	188.7/189.7 (189.3/190.2)	139.8 (139.9)
27		33.3 (33.2)	27.5 (28.6)	31.5 (33.1)	191.9 (192.3)	141.7 (141.6)
28		34.7 (33.1)	24.9 (25.2)	24.0 (25.1)	179.1/191.8 (179.7/191.6)	138.8 (138.9)
29		34.0 (32.3)	21.9 (22.8)	23.4 (24.5)	180.1/188.1 (180.5/188.2)	137.8 (138.0)

[a] Energies in kcal/mol as are given by B3LYP/6-311+G(d,p); values in parentheses represent B3LYP/6-31G(d) computations.

already described at the HF/6-31G(d) and the MP2(FC)/6-31G(d) levels of theory.[23f] However, at the B3LYP/6-311+G(d,p) level, it represents a transition state. An intrinsic reaction coordinate calculation lead to structure **10**, a species that was already studied by Lewars at the MP2-(FC)/6-31G(d) level of theory as bicyclo[2.1.0]penta-2,4-diene.[23f] Remarkably, the C1−C4 bridge is extremely long (206.0 pm). At the B3LYP/6-311+G(d,p) level, **10** was not found by Maier and Endres[25] and was described as singlet cyclopentadienylidene (**11**), C_1,^1A by Mebel et al.[26] with B3LYP/6-311G(d,p). Further optimization of this structure with a spin multiplicity of 3 leads to triplet **11**,[25−27] a species that is 9.4 kcal/mol more stable than **10**.

These results show that a shortening of the distance between the double bond and the carbene carbon increases stabilization. This can be done by incorporating the divalent carbon into a bicyclic compound and by reducing the ring size. The second method to enhance the stability is to increase the electron density in the double bond by electron-releasing substituents. For this comparison, norbornenylidenes substituted in positions 2 and 3 were studied. In this case, not only the geometries of the molecules and their stabilization energies were investigated but also their kinetic stabilities toward the vinyl shift were studied, since it was found experimentally that this is the main reaction path for norbornenylidene **4** (R_1 = H). In carbene **4**, a 1,2-vinyl shift to bicyclo[3.2.0]hepta-1,6-diene and an alkyl shift to bicyclo[3.2.0]-hepta-1,3-diene take place to 67 and 7%,[28a] respectively.[28] This is also corroborated by the calculations: The vinyl shift needs an energy of 10.8 kcal/mol, whereas the alkyl shift requires 15.0 kcal/mol and the C−H insertion to give tricyclo[3.2.0.0^{2,7}]hept-3-ene, 25.3 kcal/mol. These are higher values than those calculated for **12** (9.3 for the alkyl shift and 12.3 kcal/mol for the C−H insertion). MP2, a method that tends to overestimate the interactions between the carbenic carbon and an electron donor, gives similar but slightly higher values: 11.9 kcal/mol for the vinyl shift in **4** and a SE of 21.2 kcal/mol. Accordingly, the distance between the divalent carbon and the double bond (182.0 pm) is shorter than at the B3LYP/6-311+G(d,p) level. Because of their increased stability toward isomerization, foiled carbenes are also expected to be intermolecularly less reactive than unstabilized ones. This was experimentally verified by Moss and Dolling, who compared the interception of norbornenylidene **4** and **12** with *cis*-4-methylpent-2-ene.[29] They found that **12** gives 23% of the cyclopropane adduct, whereas **4** affords only 0.067% of adduct.[29] This fact is another indication for a stabilization by the double bond (Chart 2).

The geometries of 16 norbornenylidenes bearing substituents at the double bond were optimized (Table 2). With **20**, comprising a benzene ring, a π-complex formed by the divalent carbon and the C_C−C_D can still be calculated, but it is one of the weakest that we found. At the B3LYP/6-31G(d) level of theory, only three of the norbornenylidenes

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(23) (a) Minkin, V. I.; Minyaev, R. M.; Zacharov, I. I.; Avdeev, V. I. *Zh. Org. Khim.* **1978**, *14*, 3. (b) Minyaev, R. M.; Minkin, V. I.; Zefirov, N. S.; Zhdanov, Y. A. *Zh. Org. Khim.* **1979**, *15*, 2009. (c) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781. (d) Minkin, V. I.; Minyaev, R. M.; Orlova, G. V. *THEOCHEM* **1984**, *110*, 241. (e) Bataji, V.; Michl, J. *Pure Appl. Chem.* **1988**, *60*, 189. (f) Lewars, E. *THEOCHEM* **1998**, *423*, 173. (g) Lewars, E. *THEOCHEM* **2000**, *507*, 165. (h) Kenny, J. P.; Krueger, K. M.; Rienstra-Kiracofe, J. C.; Schaefer, H. F., III. *J. Phys. Chem. A* **2001**, *105*, 7745. (i) Minkin, V. I.; Minyaev, R. M. *Dokl. Chem.* **2002**, *385*, 203.

(24) (a) Masamune, S. *J. Am. Chem. Soc.* **1964**, *86*, 735. (b) von E. Doering, W.; Pomerantz, M. *Tetrahedron Lett.* **1964**, *5*, 961. (c) Dowd, P.; Garner, P.; Schappert, R.; Irngartinger, H.; Goldman, A. *J. Org. Chem.* **1982**, *47*, 4240. (d) Maier, G.; Hoppe, M.; Reisenauer, H. P. *Angew. Chem., Int. Ed.* **1983**, *22*, 990. (e) Mehta, G.; Singh, S. R.; Priyakumar, U. D.; Sastry, G. N. *Tetrahedron Lett.* **2003**, *44*, 3101.

(25) Maier, G.; Endres, J. *J. Mol. Struct.* **2000**, *556*, 179.

(26) Nguyen, T. L.; Le, T. N.; Mebel, A. M. *J. Phys. Org. Chem.* **2001**, *14*, 131.

(27) (a) Platz, M. S.; Olson, D. R. *J. Phys. Org. Chem.* **1996**, *9*, 689. (b) Olson, D. R.; Platz, M. S. *J. Phys. Org. Chem.* **1996**, *9*, 759. (c) Zuev, P. S.; Sheridan, R. S. *J. Am. Chem. Soc.* **2001**, *123*, 12434. (d) Kassaee, M. Z.; Arshadi, S.; Acedy, M.; Vessally, E. *J. Organomet. Chem.* **2005**, *690*, 3427.

(28) (a) Moss, R. A.; Dolling, U.-H.; Whittle, J. R. *Tetrahedron Lett.* **1971**, *12*, 931. (b) Brinker, U. H.; Ritzer, J. *J. Am. Chem. Soc.* **1981**, *103*, 2116.

(29) Moss, R. A.; Dolling, U.-H. *Tetrahedron Lett.* **1972**, *13*, 5117.

Chart 3

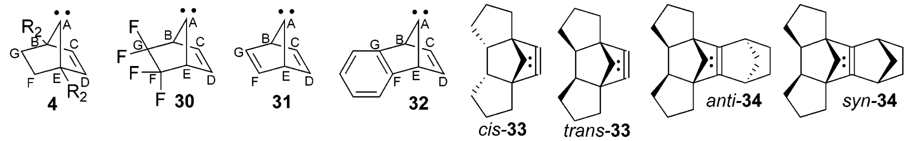

Table 3. Comparison of the Stability and the Geometry of Norbornenylidene Derivatives[a]

	singlet–triplet gap	E vinyl shift	SE	d(C_A–C_C) (pm)	d(C_C–C_D) (pm)
4 (R_2 = H)	24.6 (23.7)	10.8 (11.0)	13.9 (15.6)	189.8 (189.3)	137.2 (137.4)
4h (R_2 = NH_2)	26.9 (26.3)	7.5 (7.5)	15.7 (17.9)	188.0 (186.3)	137.6 (138.0)
4i (R_2 = CH_3)	24.9 (24.2)	10.0 (10.1)	14.6 (16.3)	189.0 (187.9)	137.1 (137.4)
4j (R_2 = CF_3)	24.3 (23.9)	13.5 (13.5)	9.2 (12.1)	192.0 (190.6)	136.5 (136.9)
4k (R_2 = F)	28.2 (27.1)	13.7 (13.2)	11.3 (13.9)	193.9 (191.3)	136.3 (137.1)
30	23.0 (21.9)	15.1 (15.1)	10.6 (12.5)	190.5 (190.0)	136.7 (137.1)
31	32.1 (31.6)	9.0 (8.9)	22.0 (24.0)	185.0 (184.7)	137.1 (137.3)
32	29.3 (28.8)	11.1 (9.9)	19.8 (21.1)	185.9 (185.3)	137.1 (137.4)
cis-**33**	23.3 (22.6)	7.1 (6.7)	14.1 (15.8)	190.7 (189.3)	136.4 (136.8)
trans-**33**	26.4 (26.0)	14.4 (14.9)	18.3 (20.5)	185.6 (184.5)	138.1 (138.5)
anti-**34**	34.6 (34.4)	22.2 (23.4)	29.5 (31.7)	184.5 (183.9)	139.0 (139.3)
syn-**34**	33.6 (32.9)	27.1 (28.1)	25.8 (27.7)	179.6 (179.4)	139.6 (139.8)

[a] Energies in kcal/mol as are given by B3LYP/6-311+G(d,p); values in parentheses represent B3LYP/6-31G(d) computations.

were calculated to exist in two different conformations at the carbene center, i.e., parent norbornenylidene **4** and the two electron-poor alkenes 2,3-dicyanobicyclo[2.2.1]hept-2-en-7-ylidene (**4b**) (R_1 = CN) and 2,3-dichlorobicyclo[2.2.1]hept-2-en-7-ylidene (**4d**) (R_1 = Cl). With the 6-311+G(d,p) basis set, only **4b** gives a minimum for a structure stabilized by σ-bonds. To the contrary, alkenes with electron-releasing substituents enhance the stabilization considerably. This can be followed by the shortening of the distance between the carbene center and the C_C or by the increase in SE. For example, in the case of 2,3-dihydroxybicyclo[2.2.1]hept-2-en-7-ylidene (**4f**) (R_1 = OH), the distance between the carbene carbon and the C_C is shortened from 189.8 pm in **4** to 187.4/188.6 pm in **4f**, whereas the SE increases from 13.9 to 22.7 kcal/mol. This increase in SE should lower the reactivity of the carbene especially toward intermolecular reactions. The stability of these alkyl carbenes toward intramolecular reactions is of even more importance. The activation energy E_a for the transition state for the vinyl shift is also increased by making the double bond more electron-rich. In the case of **4f** (R_1 = OH), E_a is enhanced from 10.8 to 14.3 kcal/mol. A further increase can be obtained by incorporating the double bond into an attached five-membered ring like in tricyclo[5.2.1.0^{2,6}]dec-2(6)-en-10-ylidene (**21**). This results in a deviation from planarity of the double bond, thereby enhancing its reactivity and its aptitude to interact with the carbenic carbon.[30] This causes the double bond substituents to move into the "*exo*" position. Remarkably, the pyramidalization in all alkenylidenes occurs in the opposite direction than in the corresponding alkene. Here, the substituents at the double bond are positioned in the "*endo*" position. The energy necessary for the vinyl shift in **21** for example is then increased to 19.1 kcal/mol. The energies needed for other intramolecular pathways follow the same trend: The alkyl shift already requires 21.5 kcal/mol, and the C−H-insertion needs 31.8 kcal/mol (see Supporting Information).

Aromatic heterocycles comprising the double bond of the norbornenylidene structure should be relatively easy to synthesize. They also provide a high kinetic stability, especially with an oxazol **25** or an imidazol ring **26**. The imidazol can easily be deprotonated (pK_b = 7) to **27**. This anion represents the most stable carbene investigated in this article (27.5 kcal/mol for the 1,2-vinyl shift and a SE of 31.5 kcal/mol) (Chart 3).

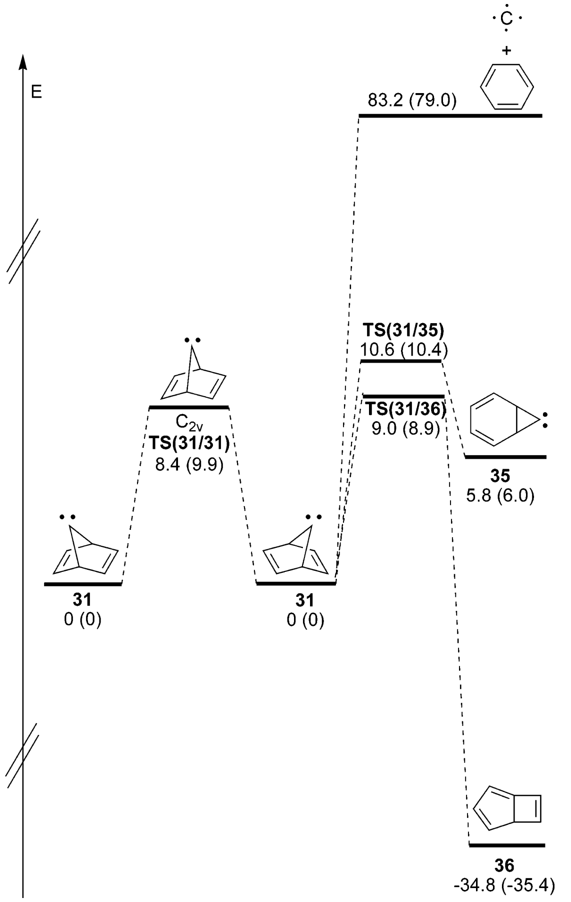

Figure 2. Reactions of **31**. Energies in kcal/mol are as given by B3LYP/6-311+G(d,p); values in parentheses represent B3LYP/6-31G(d) computations.

In a second step, the norbornenylidene derivatives **4h**−**k** and **30**−**33** were chosen to investigate the influence of substituents at the bridgehead carbons C_B and C_E and at C_F and C_G, respectively. Table 3 reveals that the divalent carbon bends even more with further electron-releasing groups attached to the bridgeheads. An increase in the SE is also observed. For example, with NH_2, the SE rises further from 13.9 for **4** to 15.7 kcal/mol for 1,4-diaminobicyclo[2.2.1]hept-2-en-7-ylidene

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(30) (a) Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095. (b) Holthausen, M. C.; Koch, W. *J. Phys. Chem.* **1993**, *97*, 10021. (c) Margtić, D.; Williams, R. V.; Warrener, R. N. *J. Org. Chem.* **2003**, *68*, 9186. (d) Can, H.; Zahn, D.; Balci, M.; Brickmann, J. *Eur. J. Org. Chem.* **2003**, 1111. (e) Vázquez, S.; Camps, P. *Tetrahedron* **2005**, *61*, 5147.

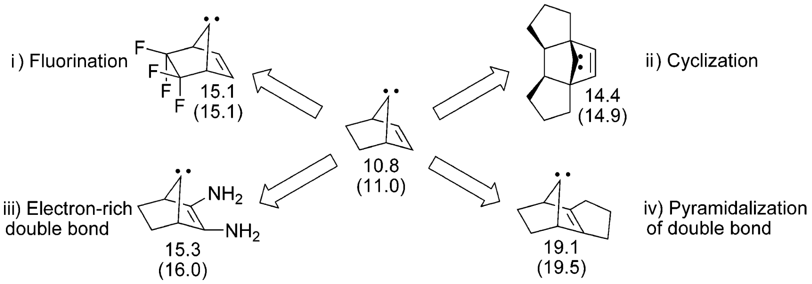

Figure 3. Strategies for the stabilization of norbornen-7-ylidene by substitution. Energies for the 1,2-vinyl shift in kcal/mol are as given by B3LYP/6-311+G(d,p); values in parentheses represent B3LYP/6-31G(d) computations.

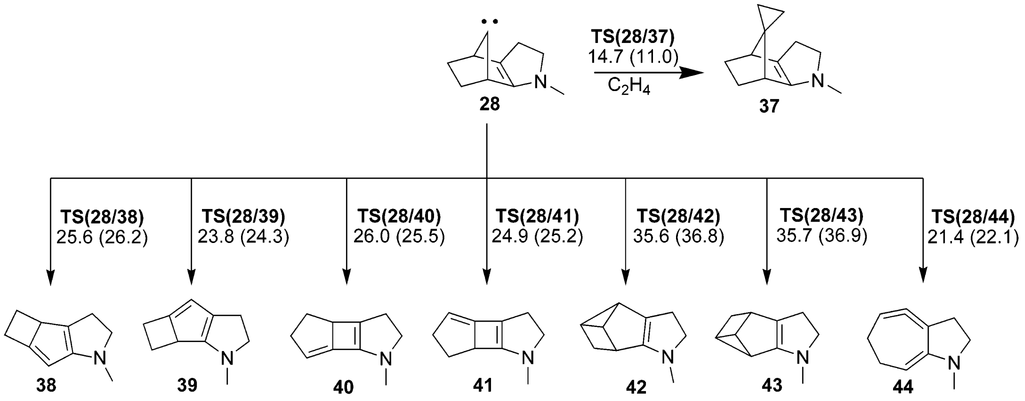

Figure 4. Rearrangements of **28**. Energies in kcal/mol are as given by B3LYP/6-311+G(d,p); values in parentheses represent B3LYP/6-31G(d) computations.

(**4h**). However, because the transition state for the vinyl shift is even lower, this kind of substituent cannot be recommended. Hence, this barrier decreases from 10.8 in **4** to 7.5 kcal/mol in **4h**. The same observation can be made, if a double bond is present between C_F and C_G. Therefore, nonconjugative electron-withdrawing substituents at the bridgehead carbons as in **4j** and **4k** are preferable to enhance the kinetic stability of foiled carbenes. Moreover, the transition state for the vinyl shift of norbornenylidene **30** comprising four fluorine atoms at C_F and C_G is even 4.3 kcal/mol higher in energy than the one for **4**.

Compound **31** was originally calculated by Gleiter and Hoffmann[5] using extended Hückel calculations and more recently by Wong and Wentrup.[31] Both groups found a nonclassical geometry. MP2/6-31G-(d) calculations gave a short distance of 179.4 pm between C_A and C_C.[31] It is worth mentioning that MP2 computations tend to overestimate the interactions between the carbene center and the double bond. Our calculations [B3LYP/6-311+G(d,p)] found a longer distance of 185.0 pm. The SE was also determinated to be 22.0 kcal/mol (this work) with a transition state between both bent conformers of **31** of 8.4 kcal/mol (Figure 2). With 9.0 kcal/mol, the transition state for the vinyl shift is only slightly higher. A retro-Skattebøl rearrangement to bicyclo-[4.1.0]hepta-2,4-dien-7-ylidene (norcaradienylidene) should also be considered, since the transition state for this reaction is only 10.6 kcal/mol higher in energy than **31**. Once again, these findings show that a second double bond in **4** leads to a higher SE, but at the same time, the transition states for intramolecular rearrangements are lowered. Hence, even if a higher thermodynamic stabilization is obtained, the kinetic stability is not enhanced. Experimentally, by pyrolysis of the corresponding *N*-nitrosourea at 200 °C, it was suggested that carbene **31** competitively loses carbon to give benzene or gives rise to pentacyclo[7.5.0.0.^{1,12}0.^{2,5}0^{2,8}]tetradeca-3,6,10,13-tetraene.[32] At a higher temperature (350 °C), heptafulvalene is also formed.[32] The former product derives from a dimerization of bicyclo[3.2.0]hepta-1,3,6-triene, a compound resulting from **31** by a vinyl shift. The latter may be formed either via conversion of bicyclo[3.2.0]hepta-1,3,6-triene[31,32] to cyclohepta-1,2,4,6-tetraene or via a retro-Skattebøl rearrangement of carbene **31** to norcaradienylidene **35** followed by a cyclopropylidene−allene rearrangement. Our calculations speak against the generation of atomic carbon from **31**.

An enhancement of both interactions discussed can be observed in tetracyclic *trans*-**33** (Table 3). This effect can be explained best by an increase in ring strain, especially in the product of the vinyl shift. This fact is reflected in the reduced exothermicity of the reaction (−22.0 kcal/mol for the singlet; −48.5 kcal/mol starting from the triplet state: See Supporting Information) in comparison to norbornenylidene **4** (−31.1 kcal/mol; −55.7 kcal/mol for the triplet: See Supporting Information). Interestingly, the *cis*-isomer *cis*-**33** reveals just the opposite effect with reduced interactions. The double bond is only slightly elongated to 136.4 pm, and the vinyl shift occurs particularly easily (7.1 kcal/mol). This is due to an excessive ring strain in *cis*-**33** caused by the connection of the five-membered rings. Hence, a value of 14.8 kcal/mol (see Supporting Information) is obtained for this strain energy by comparison of the total energies of triplets *cis*-**33T** and *trans*-**33T**.

In summary, *four* strategies can be followed to enhance the stability of norbornenylidenes (see Figure 3). On the saturated moiety, (i) fluorination and (ii) steric constraints enhance the barrier for intramolecular rearrangement. On the unsaturated part of the molecule, (iii) a more electron-rich double bond and (iv) pyramidalization of the double bond lead to a loss of reactivity of these foiled carbenes. Combinations of these four strategies can be used in one molecule; their individual contributions to the stability are additive. For example, enamine **28** (Figure 4) combines approaches iii and iv.

Therefore, the reaction pathways of 3-methyl-3-azatricyclo[5.2.1.0^{2,6}]-dec-2(6)-en-10-ylidene (**28**) were investigated. Surprisingly, **28** is predicted to react preferentially through a combination of retro-Skattebøl reaction and cyclopropylidene−allene rearrangement to **44** (21.4 kcal/mol). However, a few intramolecular reactions may still be competi-

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[31] Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 7022.
[32] Brown, W. T.; Jones, W. M. *J. Org. Chem.* **1979**, *44*, 3090.

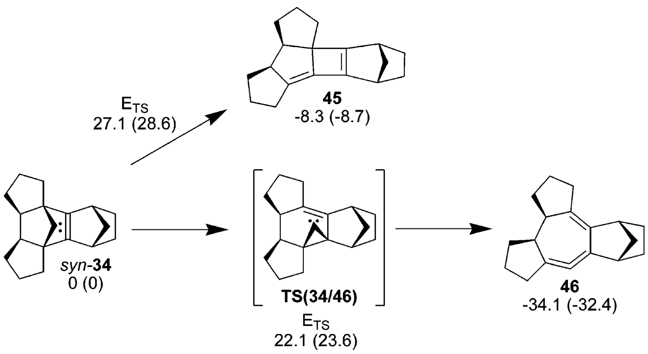

Figure 5. Reactions of *syn*-**34**. Energies in kcal/mol are as given by B3LYP/6-311+G(d,p); values in parentheses represent B3LYP/6-31G(d) computations.

tive: Possible rearrangements are the alkyl shift to **39** with 23.8 kcal/mol followed by the vinyl shift to **41** with 24.9 kcal/mol and formation of **40** (26.0 kcal/mol) and **38** (25.6 kcal/mol). Insertion into C−H bonds to **42** or **43** requires substantially higher energies (35.6 and 35.7 kcal/mol). However, **28** also possesses a high singlet−triplet gap of 34.7 kcal/mol (Table 2). This large value reflects the high SE (24.0 kcal/mol) of **28**, since triplet carbenes cannot be stabilized by interactions with double bonds.

We also tried to estimate the propensity of foiled carbenes toward intermolecular reactions, because the obtained high stabilization energies of these species suggest a decreased reactivity. Indeed, the addition of **28** to ethene to afford **37** has a high calculated barrier of 14.7 kcal/mol (G_{298} = 25.1 kcal/mol), although usually the addition of alkyl carbenes to alkenes occurs barrierless. This can be compared with the 8.4 kcal/mol (G_{298} = 19.6 kcal/mol) obtained for the addition of norbornenylidene **4** to ethene. Similarly, the insertion of **4** into the C−H bond of methane requires substantially more energy (20.8 kcal/mol) than the equivalent reaction with **12** (8.8 kcal/mol).

Dimerization of carbenes is also expected to be a facile reaction, which is usually barrierless. However, this is rarely observed in solution, because the carbene tends to react fast, especially with its precursor, for example, a diazo compound or a diazirine, leading to the formation of azines. These reactions prevent a higher carbene concentration that is necessary to allow dimerization to occur. However, in the photolysis of the sodium salt of benzocyclobutenone *p*-toluenesulfonylhydrazone in benzene,[33] a condition where the generation of a π-stabilized benzocyclobutenylidene is expected, dimers were indeed observed as the major products. Therefore, we tried to estimate the barrier for the dimerization of a foiled carbene. For symmetry reasons, **31** was chosen as a model compound; however, a transition state could not be found. Next, a geometry optimization was performed on the dimer, constraining the distance between the two former carbenic centers at values ranging between 225 and 350 pm. These computations indicate that there is no barrier for the dimerization of **31**.

A combination of approaches ii, iii, and iv leads, for example, to the heteroatom-free *syn*-sesquinorbornenylidene derivative *syn*-**34**. The bending of the framework is *exo*,*exo* as for the corresponding cation,[34] the opposite as for *syn*-sesquinorbornene.[30a] It represents the most stable alkyl carbene described in this article, since 27.1 kcal/mol (Figure 5) is required for the isomerization through a vinyl shift. Interestingly, *anti*-sesquinorbornenylidene *anti*-**34** is much less stable (22.2 kcal/mol for the vinyl shift, Table 3). The difference in the stability between *syn*- and *anti*-sesquinorbornenylidene **34** confirms that the reason for the increase in stability is due to pyramidalization. The reluctance toward the vinyl shift is also partly caused by an increase in ring strain of the resulting diene **45**. Compound **45** is only 8.3 kcal/mol more stable than *syn*-**34** (and 41.9 kcal/mol more stable than triplet *syn*-**34T**). Therefore, with 22.1 kcal/mol, the retro-Skattebøl rearrangement **TS(34/46)** is predicted to be more competitive, because of the formation of a less-strained product. In this case, the resulting vinylcyclopropylidene is not found as a global minimum. Instead, the reaction directly leads to allene **46**.

Table 4. Comparison of the Properties of a Series of Carbenes[a]

	proton affinity	ionization potential[b,c]	HOMO[c]	LUMO[c,d]	SE
12	254.7	180.3 (7.82)	−123.4 (−5.35)	−39.4 (−1.71)	23.8
4σ	276.3	176.7 (7.66)	−122.5 (−5.31)	−36.0 (−1.57)	26.2
4π	263.0	175.4 (7.60)	−119.9 (−5.20)	22.8 (+0.99)	39.3
homopyramidane **5**	256.6	179.9 (7.80)	−124.3 (−5.39)	49.3 (+2.14)	52.1
34	278.2	156.3 (6.78)	−113.2 (−4.91)	43.8 (+1.90)	51.5
imidazolylidene	258.2	189.1 (8.20)	−125.4 (−5.44)	38.0 (+1.65)	107.9
CCl_2	209.0	232.8 (10.10)	−169.7 (−7.36)	−81.8 (−3.55)	46.4

[a] Energies in kcal/mol are as given by B3LYP/6-31G(d). [b] Vertical energies.[35] The energies of the radical cations were calculated at the carbene geometry. [c] Values in parentheses are given in eV. [d] LUMO of the carbenic center.

Norbornenylidene-based foiled carbenes usually present interactions solely between the LUMO of the carbene and the HOMO of the double bond. In the case of *syn*-**34**, the C−H bond of the secondary bridge is sufficiently well-positioned to interact slightly with the HOMO of the divalent carbon. However, because of the presence of the double bond, the system is too rigid to allow a 1,5-C−H insertion and it is even questionable whether this reaction is concerted or whether it proceeds via a zwitterionic intermediate. The resulting highly pyramidalized alkene is even 9 kcal/mol less stable than carbene *syn*-**34**.

The geometric changes, the enhanced stability, the high-energy barrier for isomerization, and the high triplet−singlet gaps suggest that the carbenes described in this study are homoaromatic. The diamagnetic susceptibility exaltation ($\Delta\chi$ = 22.7 cgs-ppm)[11a] calculated previously by Freeman for norbornenylidene **4** at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level of theory supports this interpretation.

A comparison of the frontier molecular orbitals of **4**σ and **4**π confirms that the energy of the HOMO remains practically unchanged, whereas the LUMO of **4**π (+0.99 eV) is significantly higher in energy than the LUMO of **4**σ (−1.57 eV) (Table 4). Like other alkyl carbenes, the foiled carbenes **4**π, homopyramidane **5**, and **34** possess a high-lying HOMO. These results are corroborated by their low ionization potentials and also by their high proton affinities, making them strong bases. The obtained values are similar to the values calculated for imidazolylidene, a nucleophilic carbene. The main difference resides in the SE, which can be compared with the one of dichlorocarbene.

Conclusion

Foiled carbenes belong to the most stable alkyl carbenes. Their stability is optimized, when the carbene center is included in a norbornenylidene structure and when the double bond is electron-rich and incorporated within another five-membered ring to enforce pyramidalization. A further stabilization can be obtained, if the norbornenylidene structure is substituted with electronegative atoms like fluorine at C5 and C6. For their decomposition, the vinyl shift is one of the energetically lowest pathways. However, this predominance disappears in highly stabilized foiled carbenes, where other reactions become competitive, like alkyl shifts (i.e., in **28**). However, more often, also a retro-Skattebøl rearrangement can take place. This is conceivable in the case of *syn*-**34** and **5** because of release of strain and in the case of norbornadienylidenes, due to the formation of “almost aromatic compounds”. Foiled carbenes are

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(33) Frimer, A. A.; Weiss, J.; Rosental, Z. *J. Org. Chem.* **1994**, *59*, 2516.

(34) (a) Eckert-Maksić, M.; Antol, I.; Margetić, D.; Glasovac, Z. *J. Chem. Soc., Perkin Trans. 2* **2002**, 2057. (b) Antol, I.; Glasovac, Z.; Eckert-Maksić, M. *New J. Chem.* **2004**, *28*, 880.

(35) Sander, W.; Kötting. C.; Hübert, R. *J. Phys. Org. Chem.* **2000**, *13*, 561.

relatively stable toward rearrangements, since in some species (i.e., **27**, **28**, and *syn*-**34**) an activation barrier of at least 21 kcal/mol needs to be overcome. For intermolecular reactions, because of the high SEs (SE = 24−32 kcal/mol) of the carbenes **27**, **28**, and **34**, their reactivities are also reduced. This is in contrast to methylene, perfluoroadamantanylidene, or the heptacycloalkanylidenes of Nicolaides[4] (SE = 8.8 kcal/mol for heptacyclo-[10.3.1.1.^{3,7}1.^{5,9}1.^{10,14}0.^{1,10}0.^{3,9}]nonadecan-2-ylidene), a group of molecules that are expected to still be really reactive, despite their lack of intramolecular reaction pathways.

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

Supporting Information Available: Complete ref 13 and Cartesian coordinates and energies for all relevant stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

JA065595Y