Stability

&

Reactivity

on the C_4H_4 PES

Adelina Nemirowski

Seminar *WS 05/06*

Contents

* effects on the **thermodynamic stability** of tetrahedrane
  - strain
  - spherical aromaticity

* **isolability** of tetrahedranes
  - substituted tetrahedranes
  - **un**substituted tetrahedrane

* **kinetic stability** of tetrahedrane
  - reactivity
  - accessability

Strain in cyclic structures:

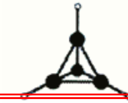
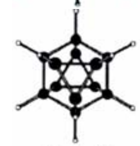
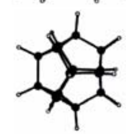
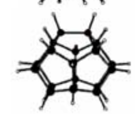
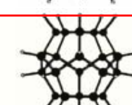
- A. v. Baeyer, *Chem. Ber.* **1885**, p. 2269: Cyclopropane should be the most and cyclopentane the least strained plane cycloalkane

- H.-S. Wu, X.-F. Quin, X.-H. Xu, H. Jiao, P. v. R. Schleyer, *JACS*, **2005**, p. 2334: Computation of the Baeyer-Strain in cage structures containing plane rings with B3LYP/6-311+G*//B3LYP/6-31G*

$$\boxed{(20/n)\ C_nH_n \longrightarrow C_{20}H_{20}}$$

but:
- Dodecahedrane is not completely strainless
- Tetrahedrane is stabilized by spherical aromaticity

↳ $\Delta_s E/CH$*(Tatrahedrane)* ≥ *30,7 kcal /mol*

n	PG	structure	N(R3	4	5	6)	$\Delta_s E$/CH [kcal/mol]
4	T_d		4				30,7
6	D_{3h}		2	3			20,8
8	O_h			6			16,8
10	D_{5h}			5	2		10,8
12	D_{3d}		2		6		4,4
12	T_d		4			4	6,6
14	D_{3h}			3	6		3,9
16	D_{4d}			2	8		2,2
18	C_{2v}			2	8	1	2,0
20	I_h				12		0,0

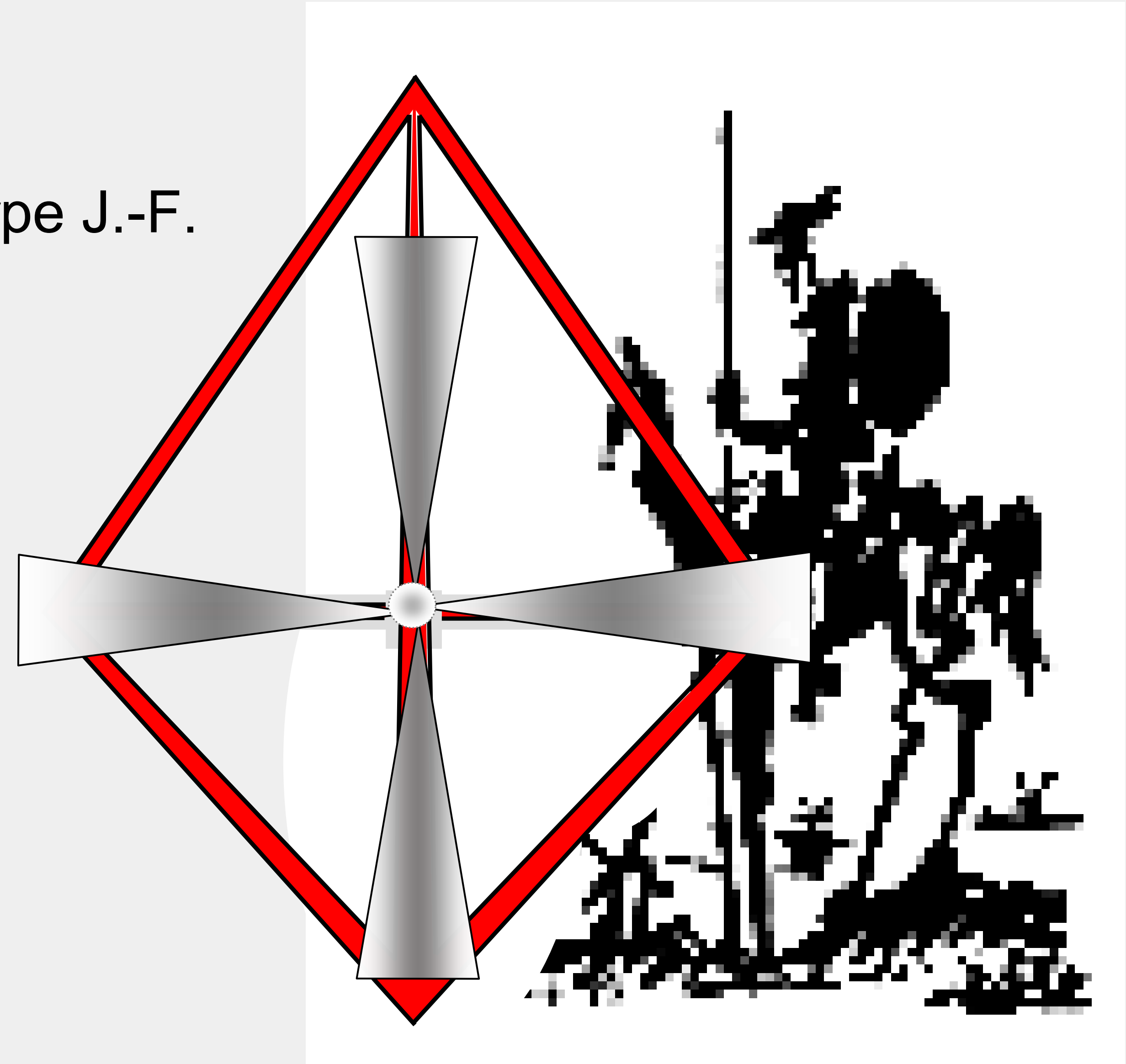
First notion of a structure of tetrahedral geometry:

Beesley, R. M.; Thorpe J.-F.

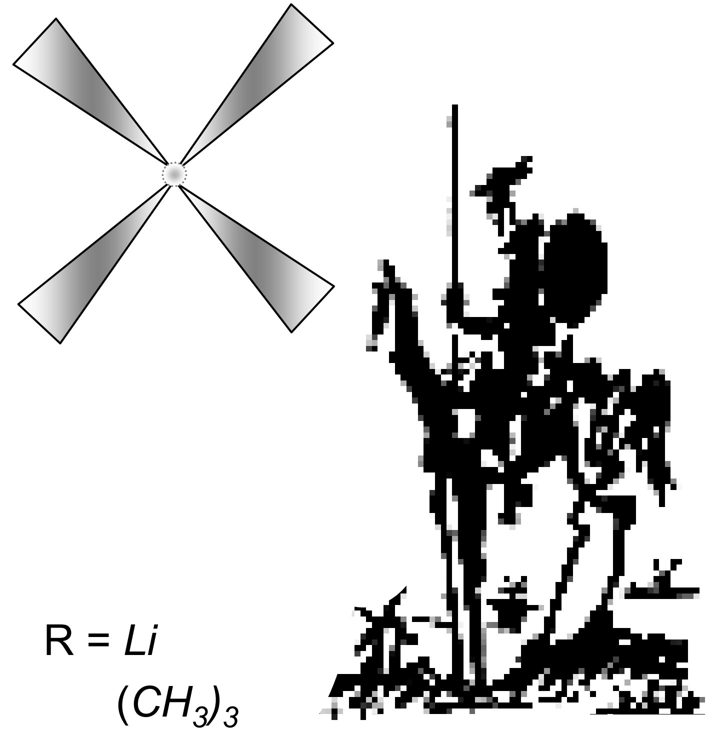
J. Chem. Soc.,

1913

p. 591



Chronology



R = *Si(CH$_3$)$_2$OiPr*

Si(SiH$_3$)$_3$

Si(CH$_3$)$_2$Ph

Si(CH$_3$)$_2$H

Ge(SiH$_3$)$_3$

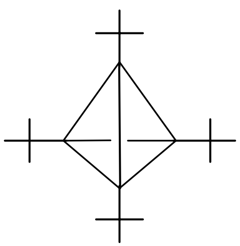
iPr

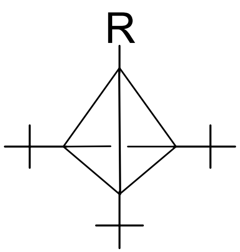
Ad

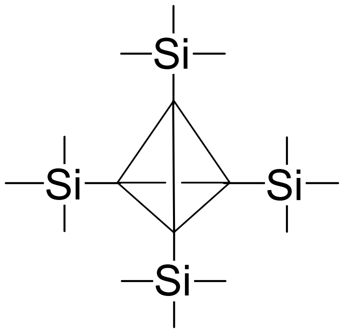
R = *Li*

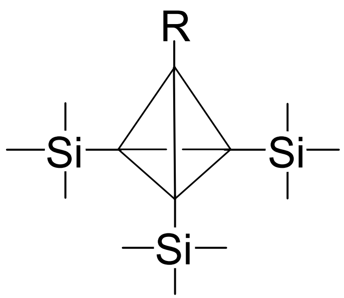
(CH$_3$)$_3$

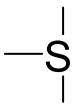
H

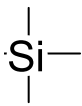








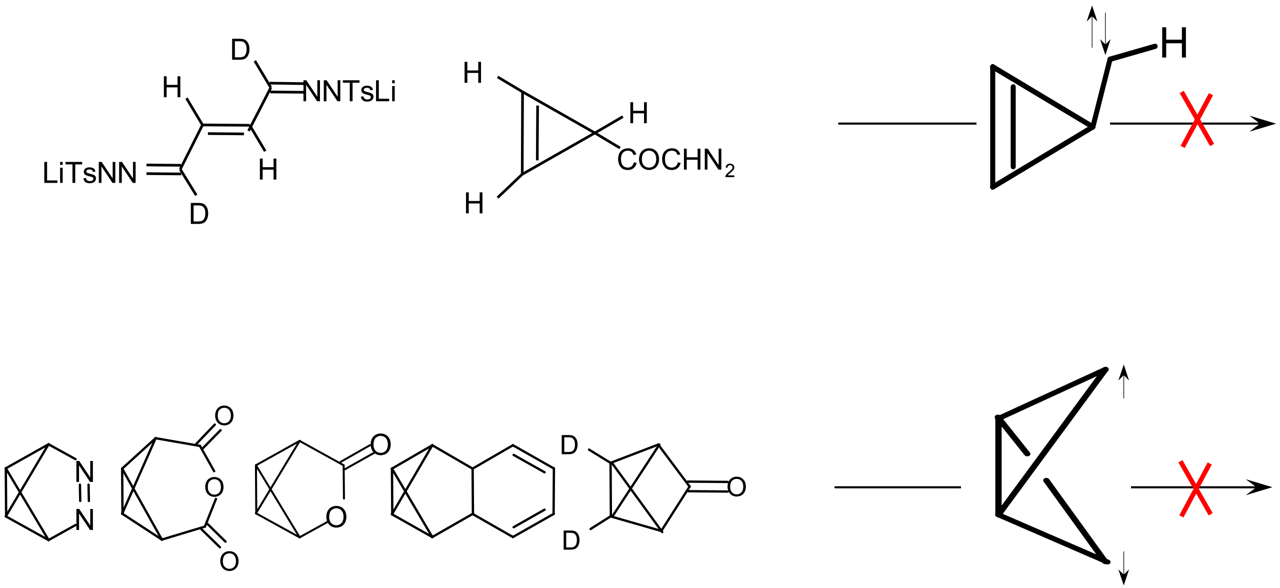


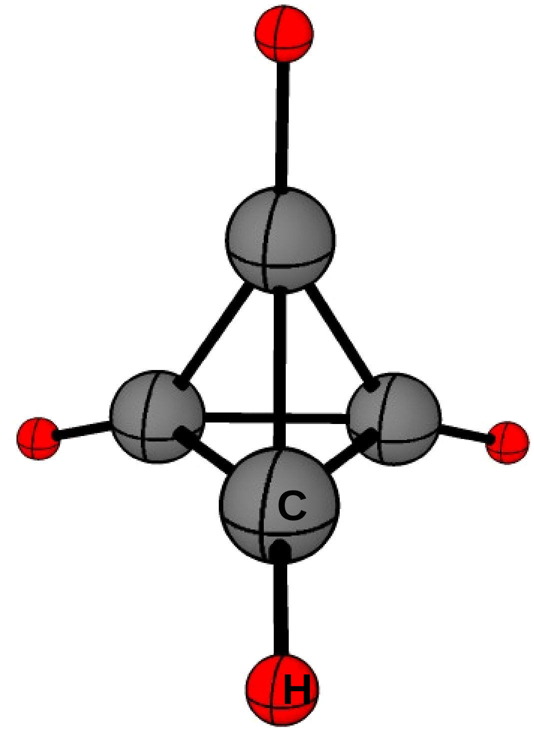


1913 | 1984 | 1989-1995 | 2001 | 2003 | 2005

G. Maier, S. Pfriem, U. Schaefer, R. Matusch, *Angew. Chem.* **1978**, *90*, 552
G. Maier, S. Pfriem, U. Schaefer, K. D. Malsch, R. Matusch, *Chem. Ber.* **1981**, *114*, 3965
G. Maier, R. Wolf, H. O. Kalinowski, *Angew. Chem.* **1992**, *104*, 764
G. Maier, F. Fleischer, H.-O. Kalinowski, *Liebigs Ann.* **1995**, 173
A. Sekiguchi, M. Tanaka, *J. Am. Chem. Soc.* **2003**, *125*, 12684
G. Maier, F. Fleischer, *Tetrahedron Lett.* **1991**, *32*, 57
G. Maier, D. Born, *Angew. Chem.* **1989**, *101*, 1085
G. Maier, R. Wolf, H.-O. Kalinowski, *Chem. Ber.* **1994**, *127*, 201
G. Maier, J. Neudert, O. Wolf, *Angew. Chem. Int. Ed.* **2001**, *40*, 1674

Unsubstituted tetrahedrane: Synthetic approaches



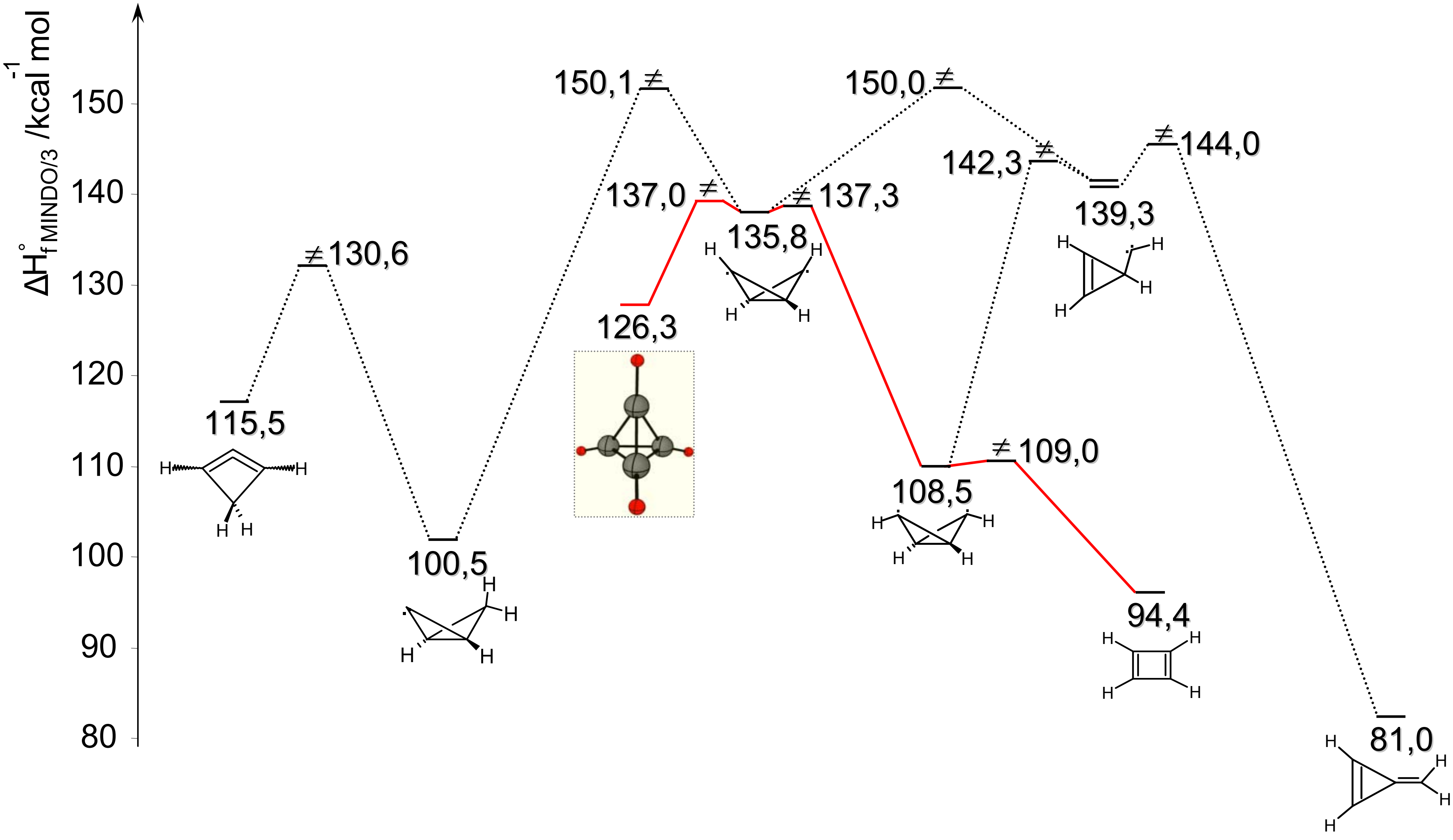


P. B. Shevlin & A. P. Wolf *JACS* **1970**, 406:

"...the data presented rule out all plausible mechanisms for the formation of acetylene other than VIA TETRAHEDRANE..."

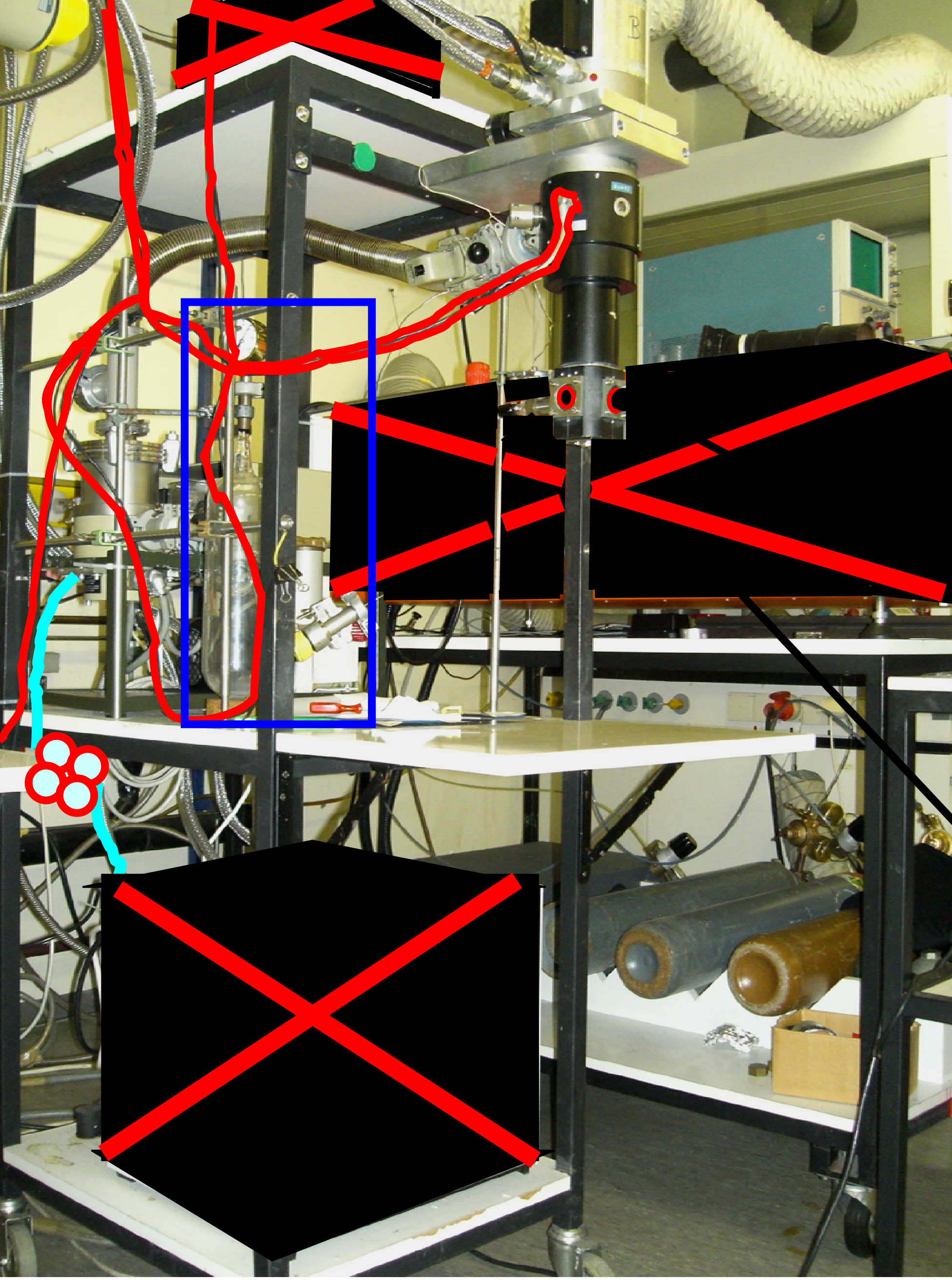
Peterson, R. F.; Baker, R. T. K.; Wolfgang, R. L. *Tetrahedron Lett.* **1969**, *54*, 4749.
Maier, G.; Hoppe, M.; Lanz, K.; Reisenauer, H. P. *Tetrahedron Lett.* **1984**, *25*, 5645
Reisenauer, H. P. zitiert in Christl, M.; Freund, S. *Chem. Ber.* **1985**, *118*, 979
Rodewald, L. B.; Lee, H. *J. Am. Chem. Soc.* **1973**, *95*, 623
Kaisaki, D. A.; Dougherty, D. A. *Tetrahedron Lett.* **1987**, *28*, 5263
Lage, H. W.; Reisenauer, H. P.; Maier, G. *Tetrahedron Lett.* **1982**, *23*, 3893
Maier, G.; Hoppe, M.; Reisenauer, H. P. *Angew. Chem.* **1983**, *95*, 1009

Previous computations: reactions of traditional synthons

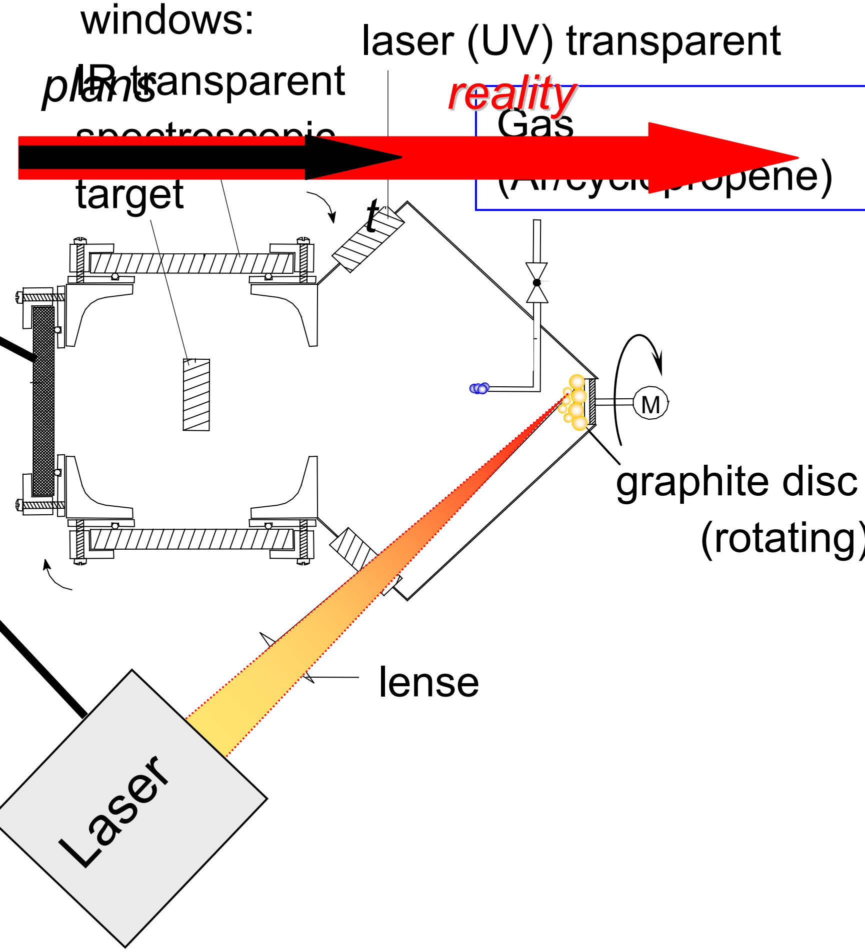


Kollmar, H.; Carrion, F.; Dewar, M. J. S.; Bingham, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 5292

Reaction: Cyclopropene + ^3C practical aspects

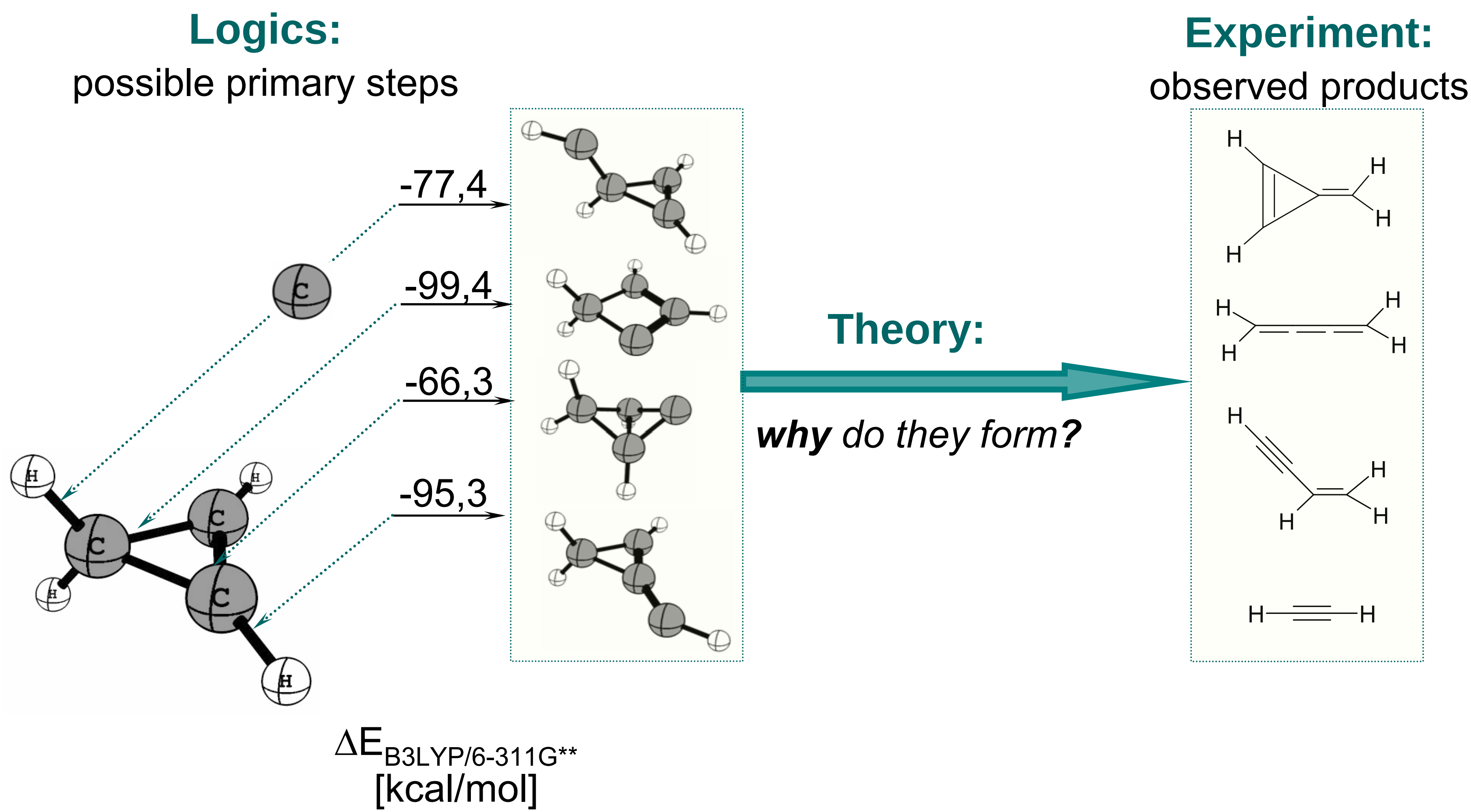


reaction chamber



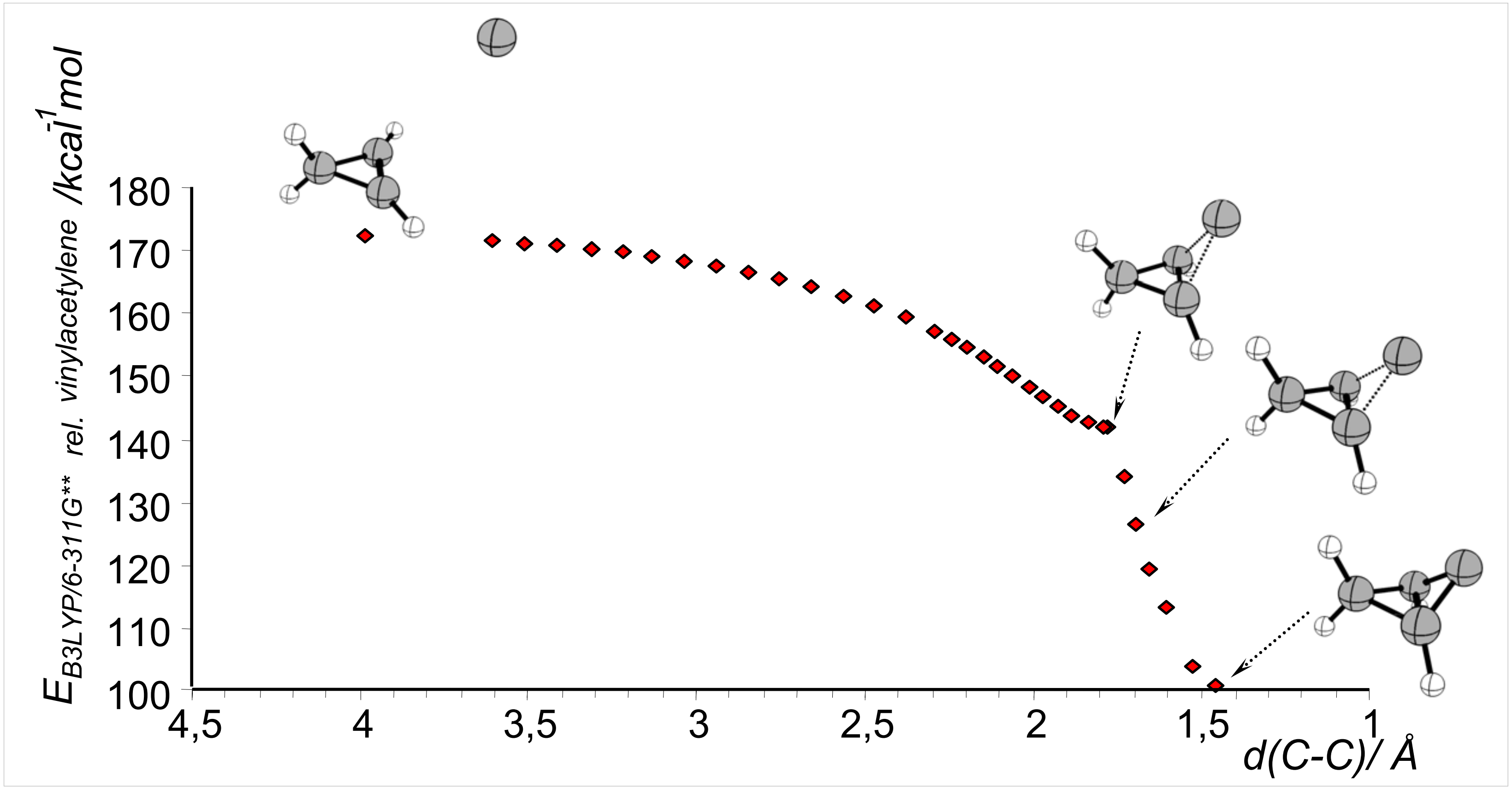
detection: IR-spectroscopically

Reaction: Cyclopropene + ^{3}C



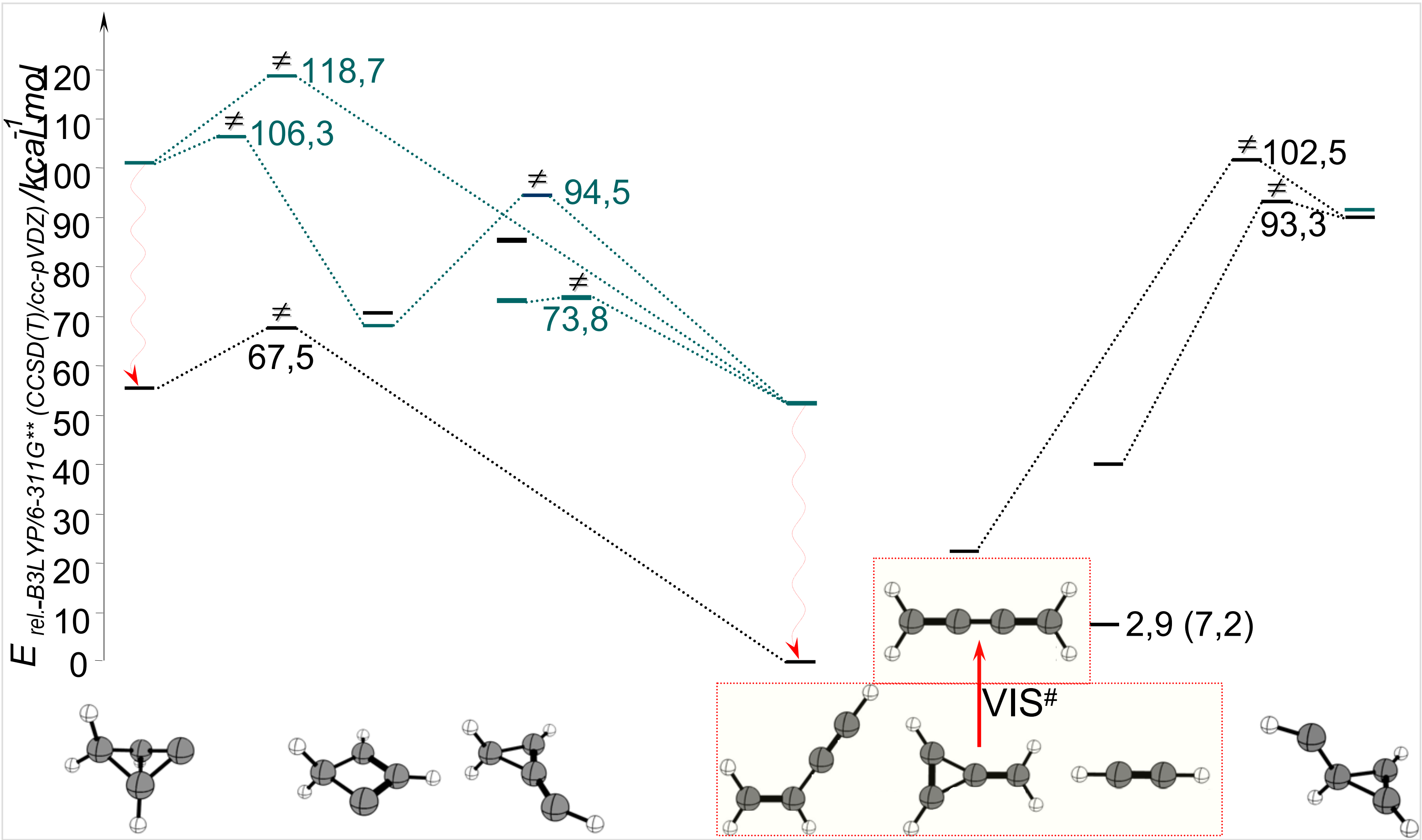
Energetics of the primary step:

e. g. double bond addition to Bicyclobutene



as expected according to the *Bell-Evans-Polanyi-principle*,
all primary steps are predicted to occur *activationless*

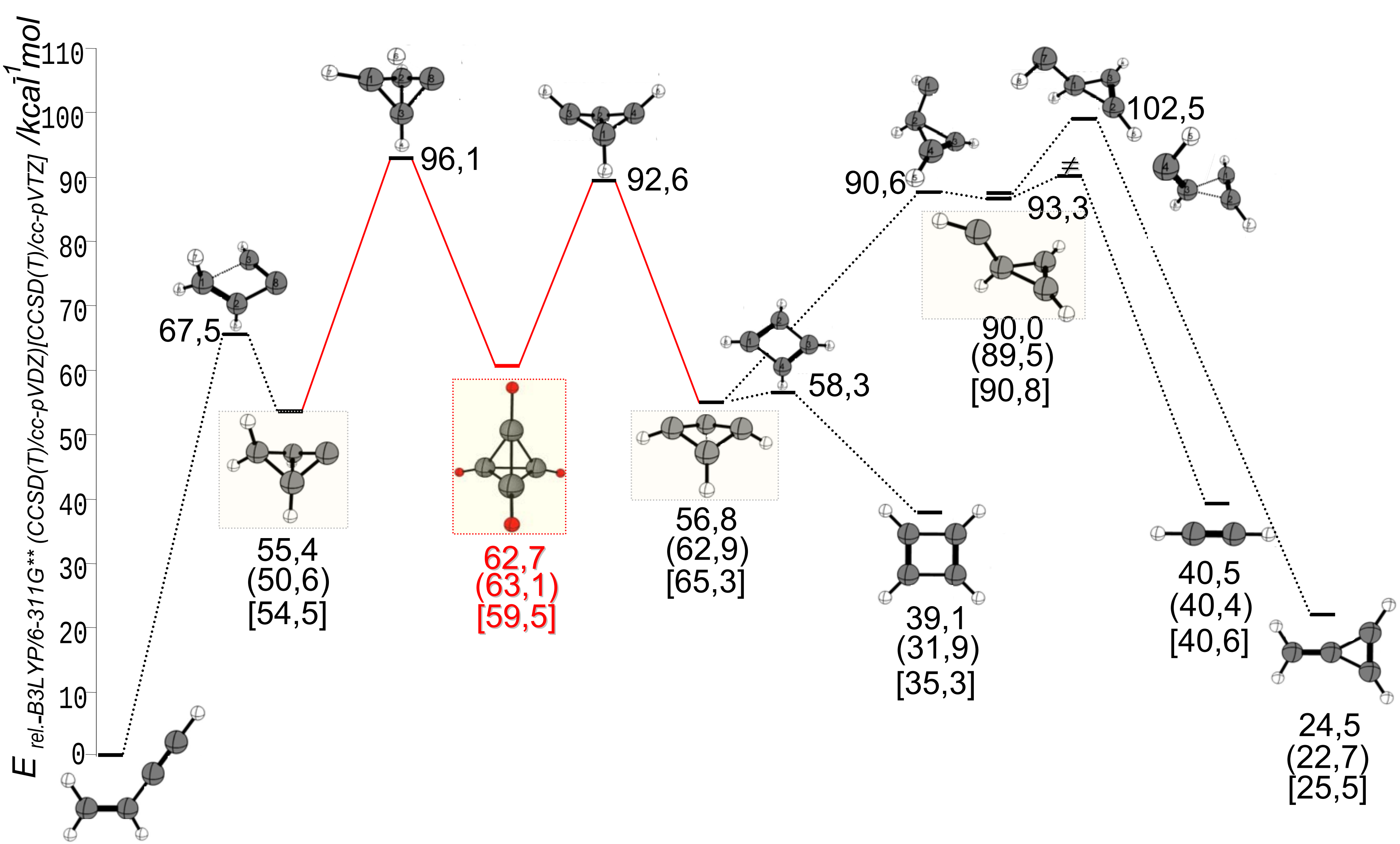
Energetically favoured reactions of primary products:



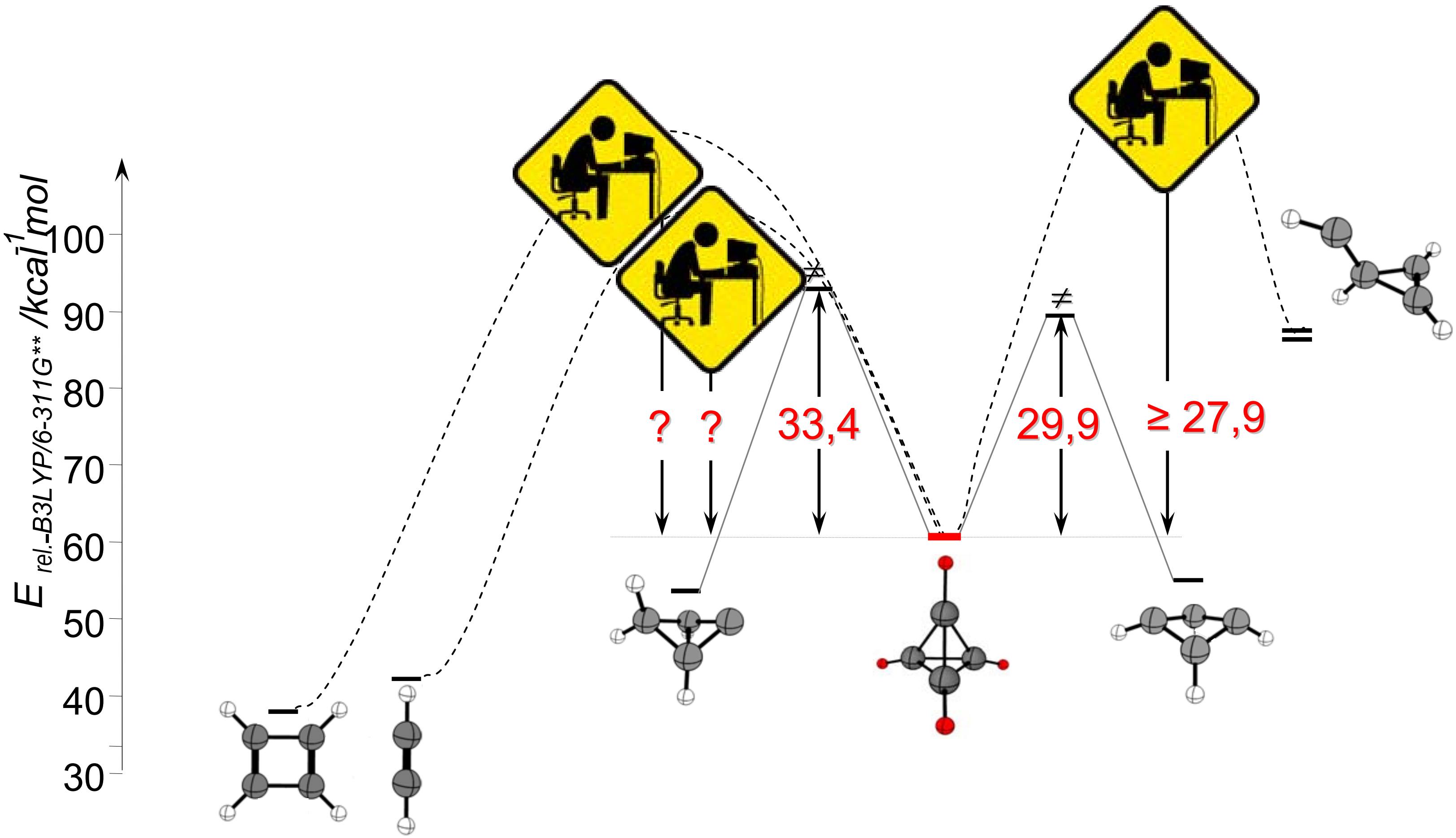
T	101,1(96,6)	70,7(70,3)	72,1(75,6)	52,5 (56,5)	22,7(24,5)	40,4(40,5)	90,0(89,4)
S	55,4(50,6)	68,0(66,5)	85,3	0,0 (0,0)			90,0(89,5)

#Wrobel, R.; Sander, W.; Cremer, D.; Kraka, E. *J. Phys. Chem. A* **2000**, *104*, 3819

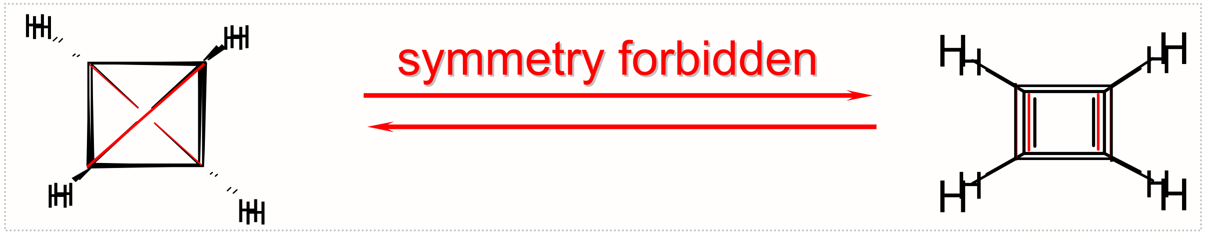
Reactions of traditional tetrahedrane synthons



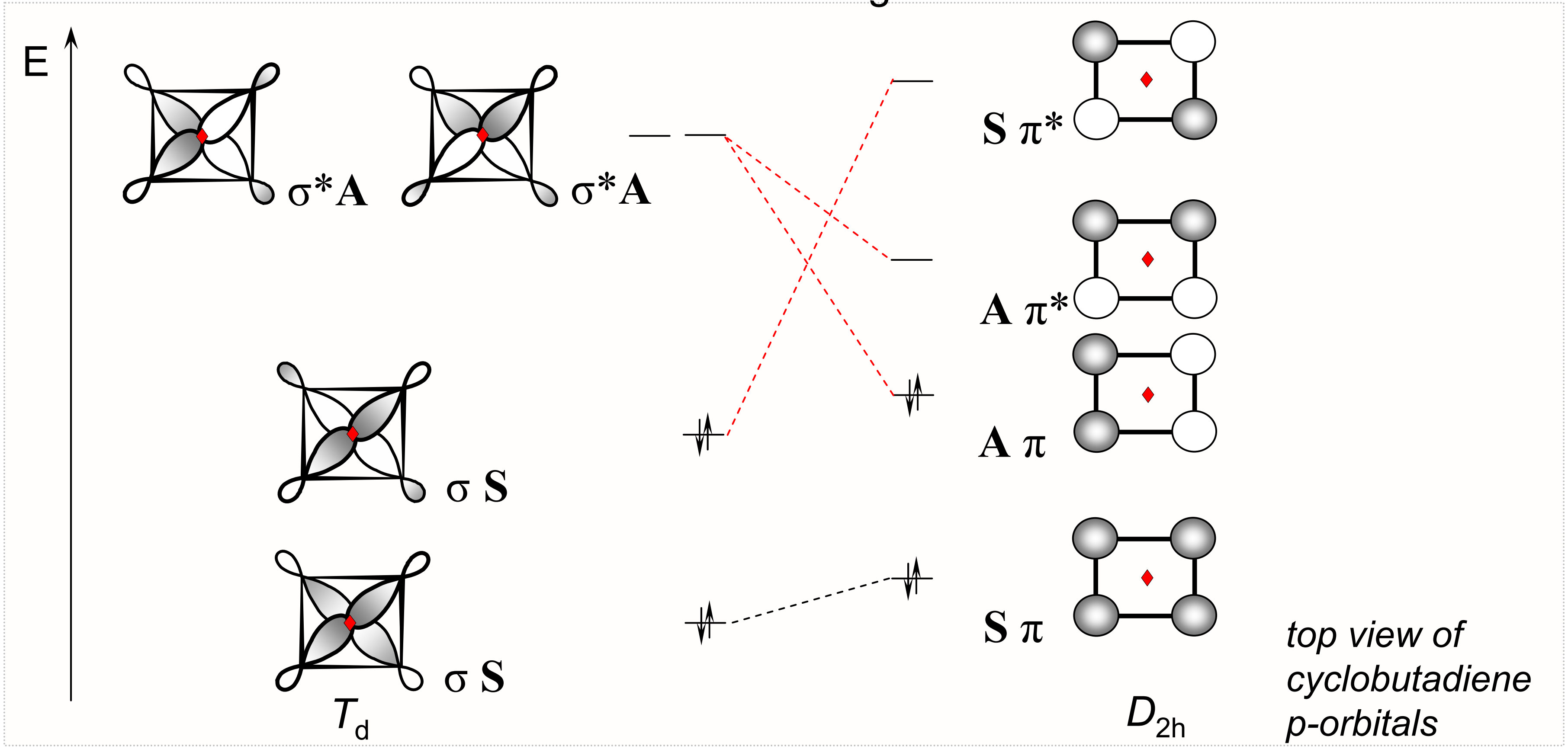
Kinetic stability of tetrahedrane

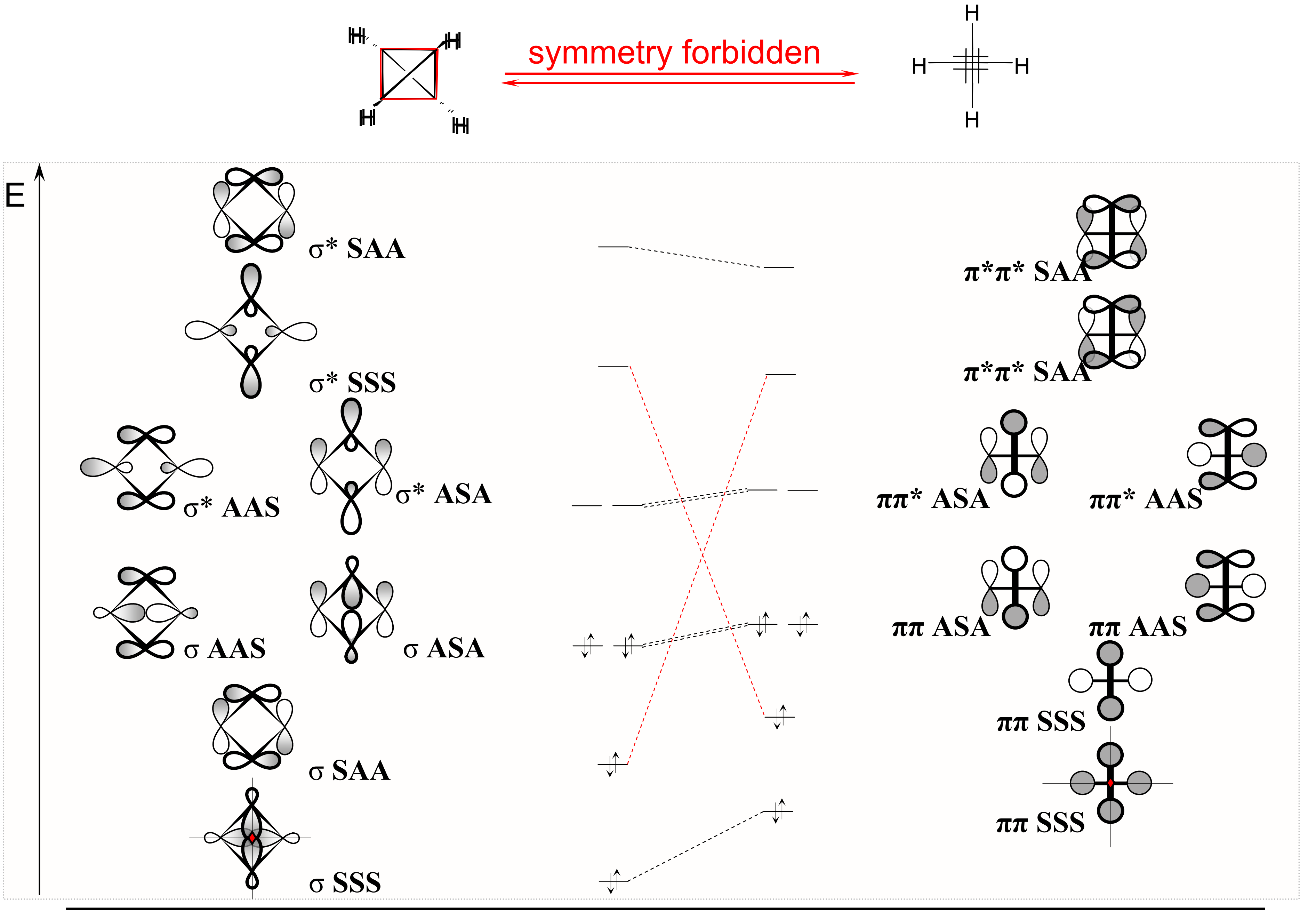


Concerted interconversion:



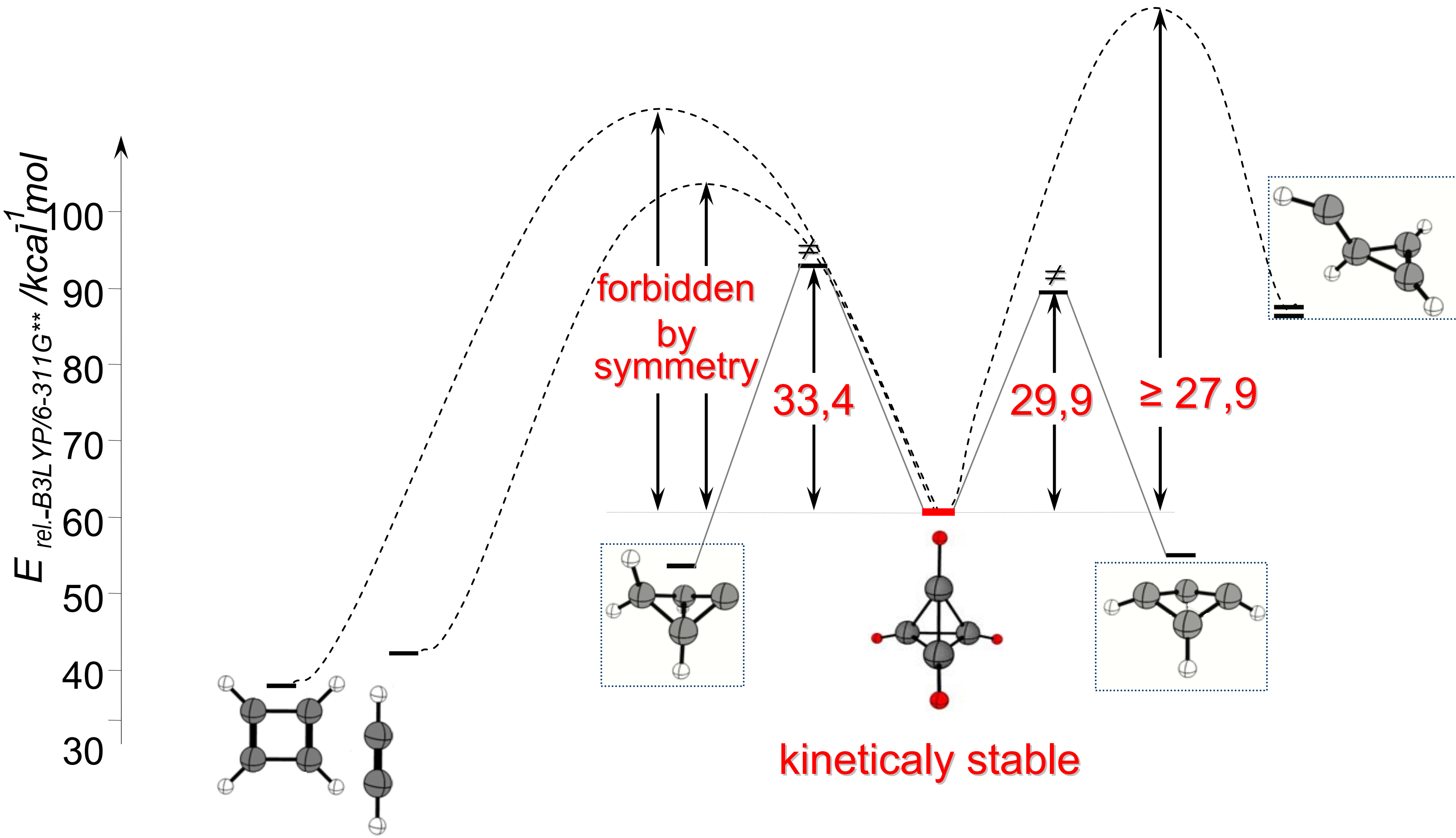
Correlation diagram





Concerted interconversion: Correlation diagram

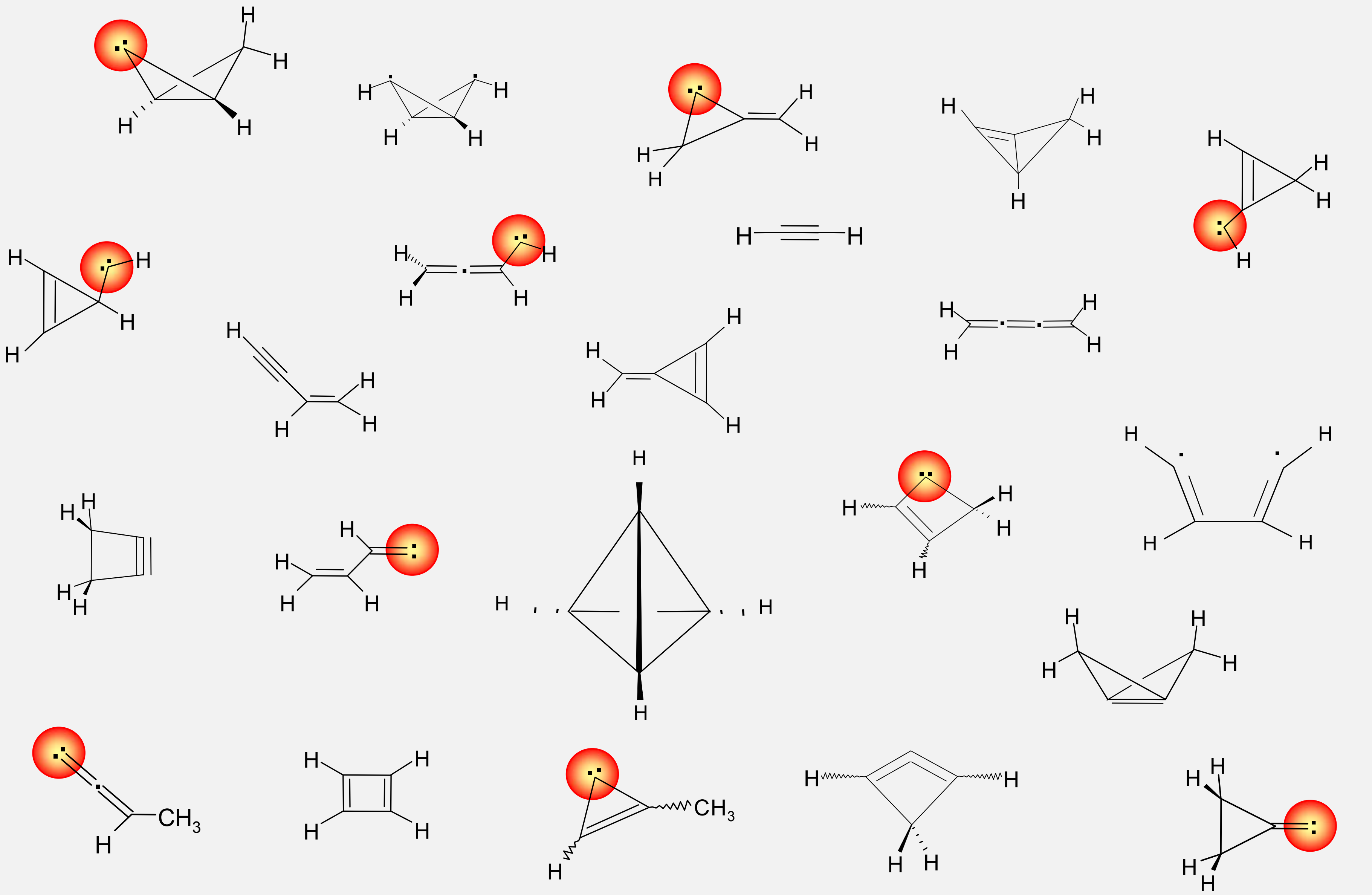
Kinetic stability of tetrahedrane



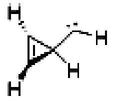
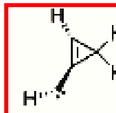
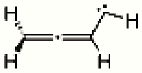
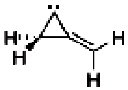
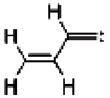
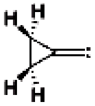
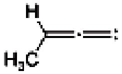
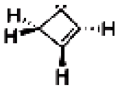
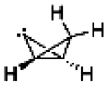
- formation from the classic precursors: **E_A**'s are of the **same order of magnitude**
- after formation: further rearrangements take place readilly if the excess E not removed

in general isoliable, but: not from the listed precursors

Studied structures



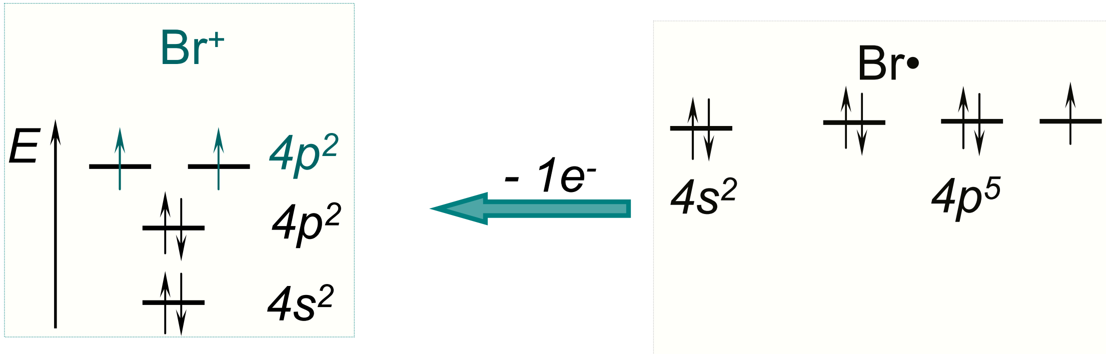
Thereof Triplet Carbenes:

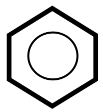
Structure	PG	ΔE_{ST} [kcal mol^{-1}] B3LYP-/6–311G**	CCSD(T)-/cc-pVDZ	CCSD(T)-//cc-pVTZ
	C_s C_s	−1.8	−0.1	−4.1
	C_s C_1	13.9	−2.1	−3.9
	C_s C_s[a]	6.6	5.7	4.6
	C_s C_s	−3.4	−6.0	−6.5
	C_s C_s	−51.6	−42.4	−51.5
	C_{2v} C_s	−55.3	−50.1	−65.4
	C_s C_s	−32.0	−32.6	−34.1
	C_s C_1	−14.8	−20.9	−22.6
	C_s C_1	−49.3	−56.0	−52.6
	C_s C_s	−45.7	−46.1	−47.6

Point groups, PG, (first entry for T, second for S) and singlet−triplet energy separations for carbenes of C_4H_4 stochiometry; according to the IUPAC convention the ΔE_{ST} values for the triplet ground state carbenes are positive

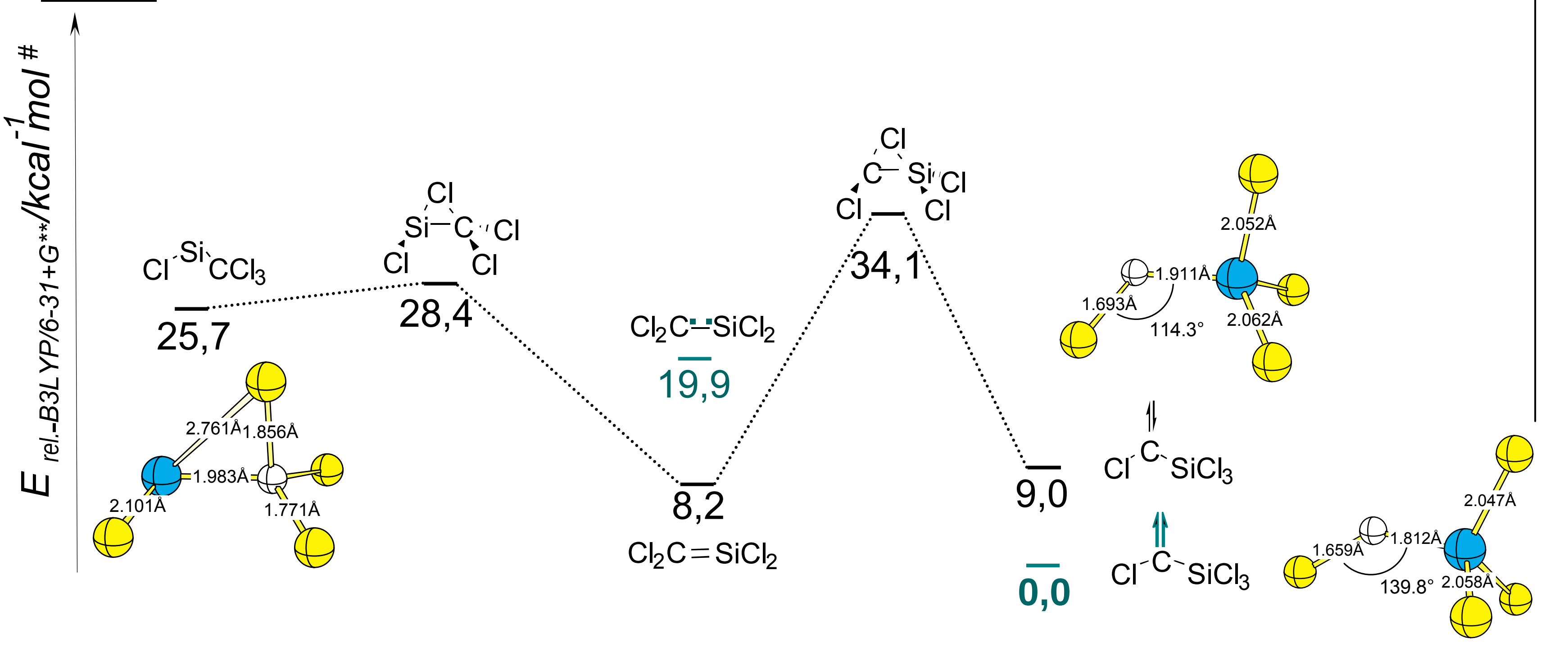
Triplet species: Organic magnets ?

- ubiquious
  - * O_2
  - * $AlBr_4^-$ +





- stable



#Reisenauer, H. P.; Schreiner, P. R. unpublished results to be continued...