Violations to the Principle of Least Motion

Castiñeira Reis, Marta; Alajarín, Mateo; Marín-Luna, Marta

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Link to publication in University of Groningen/UMCG research database

ROYAL SOCIETY OF CHEMISTRY

REVIEW

Check for updates

Violations to the principle of least motion: the shortest path is not always the fastest

Marta Castiñeira Reis, [ID] [a] Mateo Alajarin [ID] [b] and Marta Marin-Luna [ID] *[b]

The reaction between two molecules is usually envisioned as following a least-motion path with both molecules travelling minimum distances to meet each other. However, the reaction path of lowest activation energy is not only determined by practicality but mainly by the orbital symmetry of the involved reactants and the efficiency of their mutual interaction. The term non-least-motion was born to design those reactions in which reactants follow, in their route to products, pathways longer than those intuitively expected. In this review we summarize the theoretical and experimental studies that describe and rationalize reactions following non-least-motion paths, starting with the dimerizations of carbenes and followed by additional processes of these and other reactive species (silylenes, carbynes) such as insertions into single bonds and additions to π-bonds. Other examples involving less reactive partners are also included.

Introduction

The principle of least motion (PLM) was first disclosed by Rice and Teller in 1938.[1] It refers to the intuitive idea that two or more reacting molecules approach each other following a pathway involving the minimum structural, electronic and configurational alterations.[2] Years later, this principle was split into two more specific subclasses: the principle of least nuclear motion (PLNM) and the principle of least change in electronic configuration.[3,4] Despite its sound basis, the PLM has been shown to be violated in a number of reactions in which following the least-motion path would result in disrespecting orbital symmetry or in an inefficient orbital interaction. As a result, in 1970, the term non-least motion (that is, the non-least motion principle, NLMP) was coined by Hoffman, Gleiter and Mallory in their computational study on the dimerization of methylene yielding ethene.[5] They reported that a coplanar approach of the two singlet carbenes following a minimal atomic displacement (least-motion trajectory) is symmetry forbidden and involves high activation energy (Fig. 1). On the contrary, they computed a barrierless reaction path where the reactants in singlet state approach each other by following a non-least-motion pathway through a non-planar trajectory. In this latter pathway, the two reacting partners are initially located perpendicular to each other with the lone pair (σ^2) of

the first methylene molecule interacting with the empty p-orbital (π^0) of the second one (Fig. 1). In this way, the electronic repulsion of the two lone pairs present in the least-motion trajectory is avoided, whereas a favourable nucleophile-electrophile interaction is thus established in such non-least-motion alternative. Notwithstanding, Basch *et al.* reported, one year later, that the coupling of two well-oriented bent methylenes in its triplet states should follow a least-motion trajectory.[6]

From these first examples, the least and non-least-motion terminology was quickly adopted by other researchers in the area of computational chemistry. Representative instances of such processes were reported in the 1970s and will be discussed in the following lines (Schemes 1 and 2). In 1972 Berson and Jenkins suggested that, according to the Woodward and Hoffmann rules, in the 1,n rearrangements (n = 4, 8, 12,...) of cyclic poly-enylium cations the migrating group should invert its configuration while in 1,m rearrangements (m = 2, 6, 10,...) it should be retained. The reason behind this stereochemical preference is the antara or suprafacial nature of the rearrangements. Thereby, they demonstrated by using deuterium-labelling experiments that the rearrangement of the homotropylium cation **1** towards **1′** takes

1970, Hoffman *et al.*

least motion   *non-least motion*

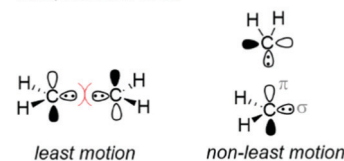Fig. 1 Least and non-least-motion of the $\sigma^2\pi^0$ methylene dimerization to form ethylene.

[a] *Stratingh Institute for Chemistry, University of Groningen, 9747 AG Groningen, The Netherlands*

[b] *Departamento de Química Orgánica, Facultad de Química, Regional Campus of International Excellence "Campus Mare Nostrum", Universidad de Murcia, E-30100 Murcia, Spain. E-mail: martamarin@um.es*
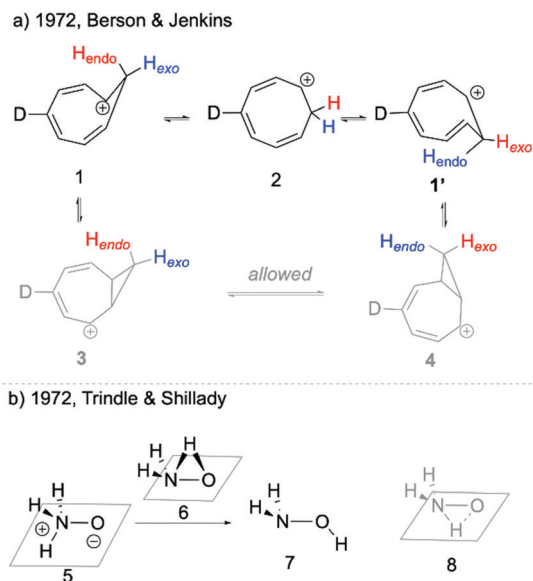
Scheme 1 (a) Rearrangement of the homotropylium cation **1** and (b) conversion of ammonium oxide **5** into hydroxylamine **7**.
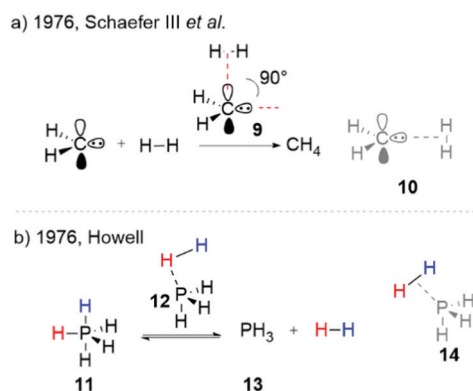
Scheme 2 (a) Insertion of methylene into H–H bond and (b) dehydrogenation of PH$_5$ **11** to PH$_3$ **13**.

place through a conformational ring inversion involving the planar carbocation **2** rather than a least-motion, suprafacial circumambulatory rearrangement *via* bicycles **3** and **4** (Scheme 1a).[7]

In an effort to further understand the stereochemical course of some common organic rearrangements, Trindle *et al.* revisited the conversion of ammonium oxides **5** to hydroxylamines **7**.

They found that they proceed by following a non-least-motion path involving a H-shift out of the symmetry plane (**6**). This chemical event is reminiscent of 1,3-sigmatropic rearrangements of alkenes since both processes present analogous nodal structures on the HOMO.[8] In contrast, the least-motion conversion of H$_3$NO to H$_2$NOH *via* **8** is forbidden in terms of the conservation of orbital symmetry (Scheme 1b).[9,10]

In 1976, Schaefer and coworkers analysed the insertion of methylene into the H$_2$ molecule. They found that the least-motion path **10** is unlikely, whereas no energy penalization was found for the non-least-motion pathway involving an initial C_s

approximation **9** (Scheme 2a).[11] Likewise, in the insertion of singlet methylene into a C–H bond of methane leading to ethane the non-least-motion concerted pathway was computed to be favourable with respect to the two-step abstraction–recombination process.[12] These results aligned well with the closely related previous report of Hoffmann, Gleiter and Mallory.[13]

Also in the 1970s, Howell reported that the dehydrogenation of phosphorane PH$_5$ (**11**) to phosphine PH$_3$ (**13**) follows a non-least-motion path consisting of a sequential departure of an axial (blue H) and an equatorial (red H) hydrogen atoms from phosphorus **12** rather than the concerted departure of both of them **14** (Scheme 2b).[14]
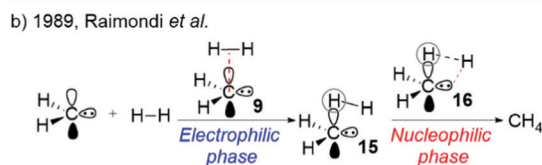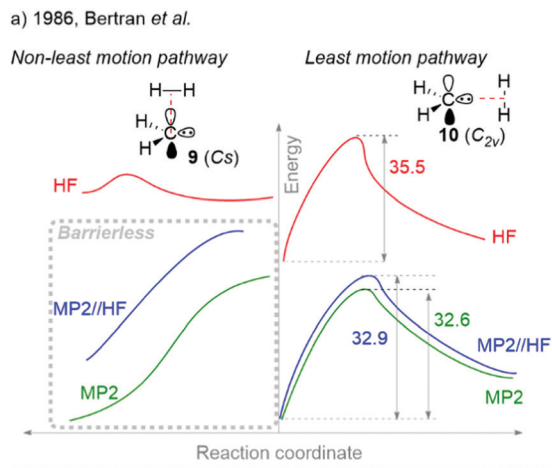
Since these early studies, the discussions concerning the NLMP have remained almost silent in the chemical literature, the reports devoted to this topic being rather scarce. In this review we next compile the reactions for which a non-least-motion path has been proposed. With this aim, the reactions are grouped by thematic blocks: (1) insertion reactions of carbenes into σ-bonds, (2) other insertions into single bonds such as O–H and D–D, (3) carbene and silylene additions to double bonds, (4) carbene, silylene and isocyanide dimerizations and (5) miscellaneous reactions.

1. Carbene insertion into H–H

The insertion of a carbene into H$_2$ is a prototypical process in which a symmetry forbidden least-motion and a symmetry-allowed non-least-motion path can compete.[11,15–20]

In 1987 Bertran *et al.*[21] revisited this reaction and specifically studied the effect of incorporating electron correlation (MP2 methods) on its energy landscape. For the non-least-motion approach (**9**), they found that electron correlation stabilizes the HF-energy landscape having a minor impact on the geometries. In fact the process becomes barrierless (Scheme 3a). These results are in agreement with those reported by Schlegel *et al.*[18] For the alternative least-motion path, represented by **10**, they computed that the incorporation of electron correlation has a minimal impact on either the energies or the geometries (Scheme 3b). In the least-motion path the maximum energies are obtained when the methylene angle (HCH) gets close to 180°. This linear arrangement of the singlet methylene was assigned by Bauschlier *et al.* to the minimization of the repulsion between the lone pair of the methylene and the σ-bond of the H$_2$ molecule.[20] Besides this maximum in energy coincides with a discontinuity on the electron configuration of the system, revealing that multiconfigurational calculations must be done in order to gain a reliable insight into the least-motion path.

In 1990, Raimondi *et al.*[22] revisited this system taking into consideration its multiconfigurational nature by using a multi-reference methodology. Specifically, they explored the reverse reaction *i.e.* the dissociation of CH$_4$ to CH$_2$ and H$_2$. They found an alternative barrierless non-least-motion pathway that accounts for the described transformation.[23] In this path, the H$_2$ approaches CH$_2$ with the H–H bond pointing along the direction of one of the non-bonding sp^3-like orbitals of

This journal is © the Owner Societies 2022

*Phys. Chem. Chem. Phys.*, 2022, **24**, 8064–8075 | **8065**

Scheme 3 (a) Energy profiles for the two modes of insertion of methylene into H_2 at different computational levels; and (b) the proposed multiconfigurational mechanistic description provided by Raimondi et al.[22] Energies are expressed in kcal mol^{-1}.

methylene (**9**) to form the first C–H bond at **15**. At the same time, the distal hydrogen can swing towards the second non-bonding-orbital of the methylene as shown in **16**. In this scenario, the formation of the first new C–H bond occurs directly while that of the second one is gradual and simultaneous with the weakening of the H–H bond (Scheme 3b).

Hence, both semiempirical and *ab initio* calculations indicate that the insertion of methylene into H_2 follows a non-least-motion process involving two discernible phases. First, there is an electrophilic step in which the empty p-orbital π^0 of methylene interacts with the σ-orbital of H_2, forming a three-centre bond. Second, there is a nucleophilic interaction between the σ^2 orbital of the methylene and the σ^* orbital of H_2. Calculations support the reaction taking place through the singlet state of methylene.[17,24,25]

In principle, one would expect this behaviour to be extensible to similar insertions of other carbenes. However, the respective investigations show that the electronic and structural nuances of each carbene determine its reactivity. We will describe next the shades found for the reactivity of different carbenes as result of that research.

Vinylidene. In 1980 Li *et al.*[26] reported the study of the non-least-motion path for the insertion of singlet vinylidene into H_2 at the MINDO/3 computational level. In this contribution, they inferred that vinylidene and methylene react with H_2 following an analogous path. However, the stabilization *via* hyperconjugation that can take place with the vinylidene core but not with methylene marks a key distinction between both processes. This feature, combined with the different hybridization of the reacting centres (from sp^3 to sp^2) renders a lesser exergonicity
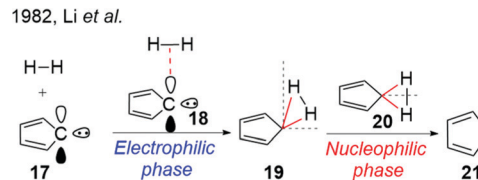
of the former compared to the latter: ($\Delta H_r^{MINDO/3}$(vinylidene insertion) = -85 kcal mol^{-1} *vs.* $\Delta H_r^{MINDO/3}$ (methylene insertion) = -107 kcal mol^{-1}).
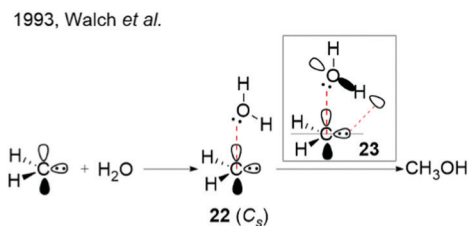
Cyclopentadienylidene, cyclopropenylidene and cyclopropylidene. The reaction of cyclopentadienylidene with H_2 were also described to follow a non-least-motion path featuring an electrophilic and a nucleophilic phase at a semiempirical level.[27] In this case, the lowest energy spin state of the cyclopentadienylidene is triplet. A general representation of the evolution of this reaction is depicted in Scheme 4. At long distances, the H_2 molecule rises above the plane of the carbene molecule to approach the empty p-orbital (π^0) of the carbenic carbon atom of cyclopentadiene (**17**), forming a three-centre bond at intermediate **19**. In the nucleophilic phase **20**, at *r* values lower than 1.44 Å, the σ-bond of H_2 is broken and the HCH plane rotates to yield finally cyclopentadiene (**21**). The activation energy of this reaction was calculated to be 2 kcal mol^{-1}. Note that the computed least-motion pathway *i.e.* the C_{2v} approximation of H_2 to cyclopentene involves a considerably higher activation energy (37 kcal mol^{-1}).

Almost simultaneously, Li *et al.*[28] studied the insertion of cyclopropenylidene and cyclopropylidene into H_2 at the same computational level. In both cases, the ground state for both carbenes is singlet and the non-least-motion path is preferred. They found that the insertion reactions follow a similar mechanism to that described for cyclopentadienylidene and methylene consisting in an electrophilic phase followed by a nucleophilic one. Nonetheless, there are some quantitative differences between the paths followed by both substrates. For instance, the higher electron density located at the carbene of cyclopropenylidene hinders more the flow of electrons from the H_2 to the carbene, resulting in a later transition state and therefore larger activation energy, compared to that of cyclopropylidene. Due to the repulsions between the lone pair at the carbenic carbon atom and the σ bond of H_2, the reaction following the least-motion path involves a much higher activation energy.

However, recent computational studies at CCSD(T) level point out that for the case of carbenes having a $\sigma^0\pi^2$ electron configuration for the singlet ground state, a least-motion reaction trajectory is preferred for σ-bond insertion and cycloaddition reactions.[29]

2. Other insertions into single bonds

Methylene (CH$_2$) insertion into the O–H bond. The potential energy surface for the reaction of $^1CH_2 + H_2O$ towards CH_3OH has been scrutinized by Walch *et al.*[30] at the CASSCF[6,6] level.

Scheme 4 Mechanistic description of the insertion of cyclopentadiene **17** into H_2.

8066 | *Phys. Chem. Chem. Phys.*, 2022, **24**, 8064–8075

This journal is © the Owner Societies 2022

1993, Walch *et al.*

**Scheme 5** Representation of the insertion of singlet methylene into water.

The reaction between $^1CH_2$ + H_2O was calculated barrierless and following a non-least-motion path (Scheme 5). Specifically, they described that at long distances the interactions between the substrates are mainly dipole–dipole thus leading to an initial approach of the dipoles antiparallel to each other. At shorter distances, a minimum is located on the potential energy surface (PES) described by the dative bonded structure **22** – with C_s symmetry – in which one lone pair at the O atom of H_2O donates into the π^0 orbital of the methylenic carbon atom. Later, the insertion of CH_2 into one of the O–H bonds requires rotating the water molecule until that bond is in the plane defined by O and the bisector of the HCH methylenic angle *via* **23**.

Methylidyne CH and BH insertion into H–H. Theoretical studies on the ground and excited states of diatomic carbenes have shown that they have a doublet ground state with a low lying quadruplet state as the lowest excited state,[31–37] except for C–Li where the situation is reversed.[38]

The first *ab initio* molecular orbital study of a methylidyne reaction was reported by Brooks and Schaefer III.[39] They studied the insertion of doublet methylidyne into molecular hydrogen and the abstraction of hydrogen by the quartet methylidene by using configurational interaction (CI) methods. Their calculations predicted an energy barrier of around 75 kcal mol^{-1} for the least-motion insertion pathway (**24**), where the CH insertion approach is perpendicular to the H–H bond at its center. However, when the C–H axis is parallel with the H–H axis (**25**) and the carbon atom approaches the center of the H–H bond, the energy barrier was only 4 kcal mol^{-1} (Scheme 6a). In this line, the temperature dependence of the rate coefficients for the insertion reaction of CH into D_2 was measured by Nelson *et al.*[40]

On the other hand, some boron-containing species are prone to insert into σ-bonds of diatomic molecules as D_2, H_2
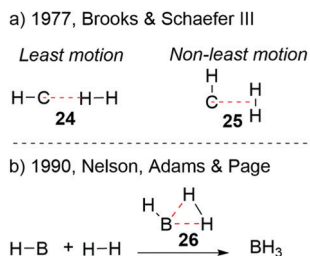
1996, Schlegel *et al.*

$$BH_{2-n}Cl_n + H_2 \longrightarrow BH_{4-n}Cl_n$$
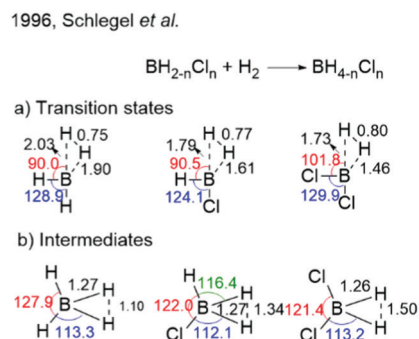
a) Transition states

b) Intermediates

Fig. 2 Computed chloroborane insertions into H_2 (a) transition states and (b) intermediates at the MP2(full)/6-31G(d) level. Distances are given in Angstroms (black) and angles in degrees (red, blue and green).

and HCl. The electronic structure principles governing the shape of the PES for the insertion of BH into H_2 are essentially the same as those reported for doublet and quartet methylidyne (CH).[39,41] Nelson *et al.*[42] investigated the mechanism ruling the BH + H_2/D_2 reactions by using CASSCF[6,7] and CI methods. They computed that the preferred approach of the reactants is one in which the B–H and the X_2 (X = H, D) molecules are nearly parallel to each other. The transition state **26** is computed to be planar with the H_2 internuclear axis nearly parallel to the B–H bond with an energy of 2.9 kcal mol^{-1} over the reactants (Scheme 6b).

Chloroboranes (BH_mCl_n) insertion into H_2 and HCl. The insertion reaction of boranes BH_mCl_n ($m + n = 0, 1, 2$) into the H_2 and HCl molecules was computationally studied by Schlegel *et al.*[43] They found that the energy barriers of these processes are highly affected by the degree of substitution at boron. They computed that monosubstituted boranes react slower with increasing halogen substitution. For instance, the computed energy barrier for BH + H_2 is 4.6 kcal mol^{-1} while for BCl + H_2 is 31.7 kcal mol^{-1}. The same trend is obtained by computing the insertion barriers of disubstituted borane derivatives (0.4, 6.7 and 12.0 kcal mol^{-1} for BH_2, $BHCl$ and BCl_2 + H_2 respectively). They also found that these latter insertion reactions feature two phases. An initial phase in which the hydrogen molecule interacts with the borane *via* its π^0 orbital at the transition state that connects with a tetracoordinate boron-intermediate. The computed geometrical parameters revealed that both transition structures and intermediates are highly distorted (Fig. 2). Similar structurally distorted transition state structures were computed for the insertion of smaller boranes into H_2 or HCl. Subsequently, in the second phase those intermediates can further progress *via* the H–H weakening towards the respective products $BH_{4-n}Cl_n$.

3. Carbene and silylene additions to double bonds

The reaction of carbenes with alkenes to form cyclopropanes has been studied for over 40 years. In 1956 Skell and Garner[44] postulated that the reaction would occur through the simultaneous bonding of a singlet carbene to the π bond of the alkene *via* a three-centre interaction of a π^0 orbital of the carbene with

a) 1977, Brooks & Schaefer III

Least motion   *Non-least motion*

b) 1990, Nelson, Adams & Page

Scheme 6 (a) Both modes of CH insertion into H_2 and (b) non-least-motion path for the insertion of BH into H_2.

a filled π^2 of the alkene. Such transition structure constitutes the first mention, in the chemical literature, to a non-least-motion pathway for the cyclopropanation reaction. Since then, this kind of transformation has been subjected to numerous theoretical studies.[45–50]

In such reactions the approximation of the reactants might happen, *a priori*, following either a σ or π approach (Fig. 3). In the first case, the σ-orbital of the methylene interacts with the π-bond of the alkene. In this approximation, the methylene hydrogens are oriented closely to their final disposition in the cyclopropane product. On contrary, in the second approach, the methylene lies in a plane parallel to the alkene. Calculations revealed that at a large separation between both reactants a π-approach is favoured. In fact, this approximation is off-centered likely due to the interaction of the hydrogens and the substituents of the alkene. At intermediate distances, the two molecules are already bonded and that is reflected in a decrease of the CCC angle and, consequently, there is an evolution from a π- to a σ-approach. The preference for the π-approach at long distances can be attributed to the formation of a 3-orbital, 2-electron interaction between the reagents that, however, becomes forbidden at shorter distances and thus forcing the reorientation to the σ-approach.[49]

Dichloromethylene (Cl₂C) addition to the C=C bond of substituted alkenes. The pathway behind the addition of halo-carbenes to alkenes was first explicitly discussed by Moore *et al.*[13] and has since been the subject of numerous theoretical studies.[51–55] For this transformation they proposed that a σ-approximation would be forbidden by the orbital symmetry, while a π-approximation involving a non-least-motion path would be allowed. Hence, based on theoretical evidence, they described that the attack of the carbene on the alkene is non linear with the forming bond at the non substituted carbon being more formed than that at the substituted one. In 1999, Singleton, Houk *et al.*[56] exploited the sensitivity of the kinetic isotopic effect (KIE) for the analysis of the transition state structures of these processes. By using a combined theoretical/experimental study they explored the quantitative isotopic effects for cyclopropanations of alkenes with dichlorocarbene. In the reaction between dichloromethylene and 1-butene yielding the cyclopropane **28** they described the existence of a significant difference between the KIEs at the two carbons of the alkene, thus suggesting a highly asymmetric transition state structure **27** – ruling out a distorted π-approximation – that would only be possible if a non-least-motion path is followed in this cycloaddition (Scheme 7).
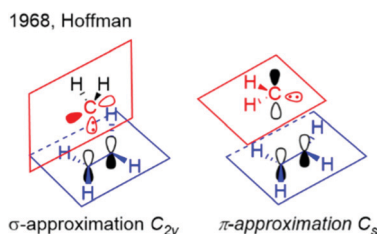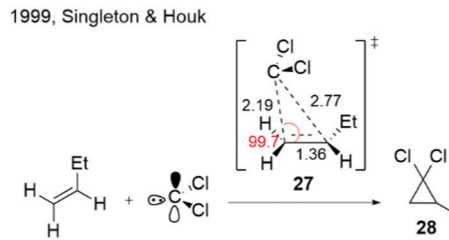

Scheme 7 Addition of dichloromethylene to 1-butene. Distances are given in Angstroms (black) and angles in degrees (red).

Dichloromethylene (Cl₂C) addition to the C=C bond of cyclopropenes. Only scarce studies are available on dihalocarbene insertions into small cyclic alkenes such as cyclopropene and cyclobutene leading towards the respective vicinal dihalocyclobu-tenes and cyclopentenes.[57–60] The results of an experimental study by Brinker *et al.* showed that the addition of dihalocarbenes to 1,2-diarylcyclopropanes **29** led not only to the expected vicinal dihalocyclobutenes **31** but also to the 1,1-dihalo-1,3-butadienes **33**.[61,62] Whereas the formation of the cyclobutenes is presumed to be a cationic cyclopropyl-allyl type of rearrangement of the bicyclic *gem*-dihalo adducts **30**, neither isolated nor spectroscopically observed, the butadienes **33** presumably derived from the zwitter-ionic species **32** (Scheme 8a).

In 2005, Merrer *et al.*[63] studied computationally the addition of dichloromethylene to a series of cyclopropenes. Similar to the previously described carbene insertions into other C=C bonds, this one also follows an asymmetric non-least-motion path. An interesting and differentiating feature of this reaction path is that it can lead to two different products: butadiene or cyclobutane. The dual reactive trajectory, along with the great exothermicity of the reaction (−75 and −100 kcal mol⁻¹ are released when forming bicyclobutane and butadiene, respectively) suggest that non-statistical dynamic effects might be of relevance. The computed PES features a flat region at the start of the reaction, followed by a bifurcation with a rapid decline to two minima, the bicyclobutene **34** and the butadiene **35**. From the bifurcation point, one reaction trajectory, that leads to the buta-diene, continues *via* a more steep-descend path than that leading to the cyclobutene.

Nevertheless, the cyclobutene is obtained in greater amount from the rearrangement of the primary [2+1] adduct, the bicyclobutane **34**. Although the butadienes are the global minima of these systems, its formation is possible only by a very abrupt change in the momentum of the system as the molecules traverse the PES. In contrast, the cyclobutenes are formed *via* a more direct reaction trajectory. In this case, a non-least-motion path is followed but, once reaching the bifurcation, the trajectory that favors the least distortion of the momentum of the system is preferred.

Carbyne (CH) addition to the C=C bond of ethylene. Detailed experimental/computational studies on carbyne additions to alkenes were carried out for the photochemical reactions of carbethoxymethylidyne,[64] showing that the doublet ground state of this carbyne undergoes concerted stereospecific [2+1]

Fig. 3 Orbital depiction of the two approaches of methylene to ethylene.
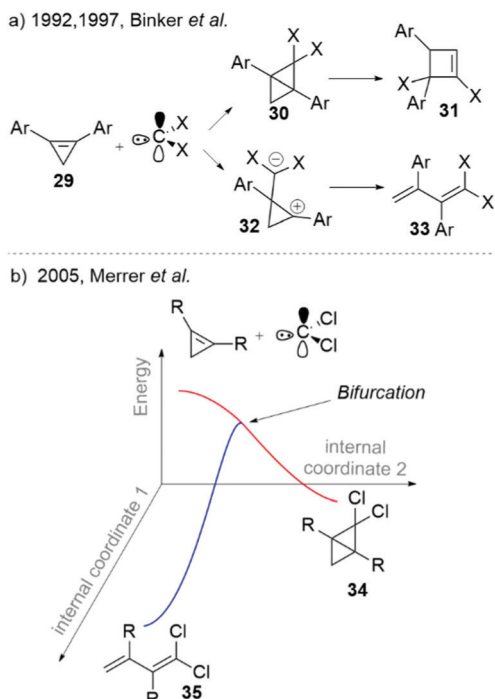
Scheme 8 Addition of dihalocarbenes to cyclopropenes.

cycloadditions to olefins and regioselective insertion into the C–H bonds of kinds of paraffin and olefins.

In 1985 Strausz *et al.* reported a high-quality *ab initio* molecular orbital study with limited configuration interaction on the PES of both the addition and insertion reactions of the ground state methylidyne radical to ethylene.[65] Their calculations predicted that the C–H insertion reaction, leading to the allyl radical, proceeds with higher activation energy (~ 15 kcal mol^{-1}) than the addition reaction *via* a non-least-motion pathway leading to the cyclopropyl radical.

Silylene addition to the C=C bond of alkenes. According to the frontier orbital theory, the addition of a singlet silylene to an olefin leading to a silirane, *e.g.* **37**, is a transformation in which the evolution from reactants to products follows a non-least-motion pathway *via* transition structures like **36** (Scheme 9).
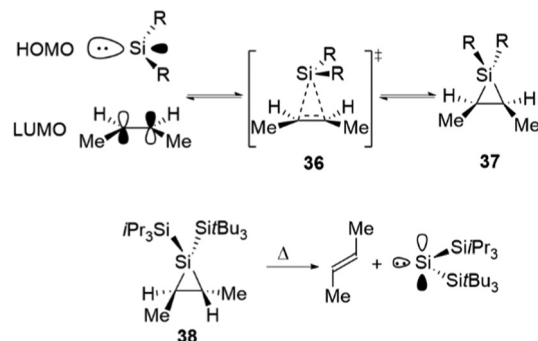
Scheme 9 Predicted insertion of silylene into *cis*-2-butene and thermolysis of silirane **38**.

Houk *et al.* proposed that the energy barriers of these kinds of reactions are mainly entropic dominated.[66] Therefore, an analysis based on the maximization of orbital interactions might lead to wrong predictions for the characterization of transition structures. In 2003, Gaspar *et al.* analyzed the kinetics of an inverse process, the thermal retroaddition of *trans*-2,3-dimethyl-1-tri-*tert*-butylsilyl-1-triisoproylsilylsilirane **38** towards the corresponding silylene and olefin, assuming that a non-least-motion path should lead to a lower entropy activation than the alternative least-motion approach.[67] By analyzing the activation parameters the authors confirmed that they agree with a non-least-motion pathway and that the nature of the substituents at Si affects the rate of its thermolysis by influencing the entropy of the reaction but not the enthalpy. These results align with those disclosed by Walsh *et al.* as result of their studies on the insertion of H$_2$Si and Me$_2$Si to different alkenes.[68,69] A non-least-motion pathway was also proposed for the addition of phosphinidene chalcogenides Ar–P = Z (Z = O, S) to olefins.[70]

4. Carbene, silylene and isocyanide dimerizations

As previously discussed, the dimerization of carbenes was initially described as a process in which the way the monomers interact is dependent on the spin state of the reactants.[5,6] Thus, when two singlet carbenes interact with each other they follow a non-least-motion pathway, the high electronic repulsion between the two lone pairs of the reactants being the determining factor of this interaction. However, when the reaction between two triplet carbenes is explored, the least-motion coupling is the preferred path.

In 1985, Morokuma *et al.* revisited the homodimerization of methylene and silylene by using multiconfigurational methodologies.[71] They obtained that triplet methylene is more stable than its singlet state and that the former dimerizes with no activation energy when following either a least or a non-least-motion path towards ethylene in its ground state. In contrast, the dimerization of two singlet methylenes renders ethylene in a Rydberg excited state independently of the path followed (see Fig. 1).[72] On the other hand, in the dimerization of SiH$_2$ towards the ground-state of disilylene, the non-least-motion trajectory is always energetically favoured regardless of the spin state of silylene. Furthermore, they investigated the heterodimerization between methylene and silylene. They observed that the reactant complex in which both units are in singlet state is more stable than the triplet analogous and also that in that favoured case the reactants interact following a barrierless non-least-motion pathway. The analysis of the reaction coordinate along such reaction path indicates that SiH$_2$ is acting as the electron acceptor and CH$_2$ as the electron donor, where the early stage of the reaction is governed by electrostatic interaction.

Other carbenes have been also the subject of theoretical studies. For instance, aminocarbenes are prone to dimerize under special reaction conditions and not all of them can couple as Alder *et al.* pointed out in their review.[73] Perhaps, the most important and indisputable experimental evidence concerning the dimerization of carbenes following a non-least-

This journal is © the Owner Societies 2022

Phys. Chem. Chem. Phys., 2022, **24**, 8064–8075 | **8069**

motion pathway was provided by Arduengo *et al.* who were able to crystallize the carbene-germanium adduct **40** resulting from the reaction between 1,3-dimesitylimidazol-2-ylidene **39** and germanium diiodide.[74] The pyramidalization of the Ge atom, the geometry around the Ge–C bond and the relative orientation of the GeI$_2$ and the carbene fragments of **40** are evidence of the non-least-motion approximation trajectory followed by both reactants (Scheme 10a).

In the latest 1990s, Oliva *et al.* published two papers reporting computational studies on the dimerization of diaminocarbene using DFT and QCISD(T)/MP2 methods. They concluded that a non-least-motion pathway operates for the homodimerization of the singlet ground-state of diaminocarbene **41** towards **42**. In this path the substituents at the N atom of the diaminocarbene have a notorious effect on the relative orientation of the reactants. While the transition state structure (**43**) for the non-substituted diaminocarbenes features a C_2-symmetry axis, there is no symmetry when methyl groups are attached to the N atoms. The broken symmetry stems from the steric repulsion of the methyl groups.[75] This repulsion provokes a charge transfer between the two reactive carbon atoms at the transition state structure, in other words, due to this repulsion one carbon atom acts as nucleophile whereas the other acts as the electrophilic centre (Scheme 10b).[76] Related transition structures were computed for the exothermic dimerization of cyclic diaminocarbenes such as imidazole-2-ylidines and imidazoline-2-ylidines.[77,78]

A thorough computational study, at DFT level, on the dimerization mechanisms of heterocyclic carbenes **44** has been reported by Yates *et al.*[79,80] (Scheme 10c). The analysis of the transition structures of ten examples revealed that the dimerization proceeds following a non-least-motion pathway where the two monomers side-on approach to each other (**46**) rather than in a perpendicular trajectory, as in the case of methylene
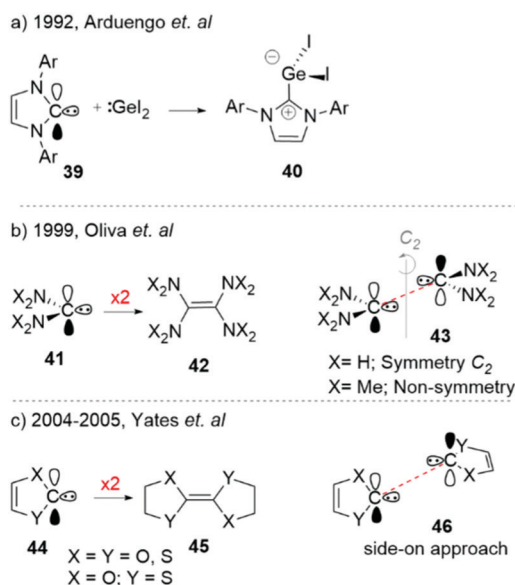
Scheme 10 (a) Formation of the carbene-GeI$_2$ adduct **40** and homo-dimerization of (b) acyclic diaminocarbenes **41** and (c) heterocyclic carbenes **44**.
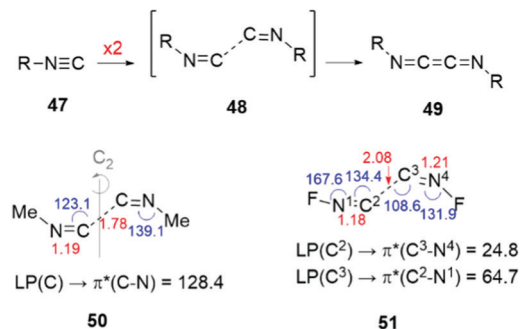
Scheme 11 Homodimerization of isocyanides **47** towards 1,4-diazabutatrienes **49** *via* transition state **48**. Transition structures **50** and **51** corresponding to the respective homodimerizations of Me–NC and F–NC. Distances are given in Angstroms (black), angles in degrees (blue) and E(2) values in kcal mol^{-1}.

dimerization (see Fig. 1). Curiously, those carbenes combining OO, SS, and SO atoms in the five-membered ring dimerizes involving a highly symmetric transition structure, whereas the rest of the analysed transition structures try to minimize the electronic repulsion between the two reacting carbon atoms *via* a non-symmetric transition state structure.

Recently, we published a theoretical study dealing with the homodimerization of isocyanides **47** towards 1,4-diazabutatrienes **49** (Scheme 11).[81–83] As in the dimerization of carbenes we observed that the habitually chameleonic[84] isocyanides follow a non-least-motion pathway along the reaction coordinate *via* the transition state **48**. Although in most of the cases both monomers behave equally along the non-least-motion reaction coordinate, in a few cases the independent monomers differ each other not only at the transition state structure but also at the early stages of the reaction, as is the case of the dimerization of F–NC, MeO–NC and SMe–NC. This fact motivated us to coin the term superchameleons as a qualifier for such isocyanides since, when reacting with itself, one unit acts as electron acceptor and the other as donor. For instance, whereas the computed transition state structure for the dimerization of Me–NC **50** is planar and show C_2 symmetry with all the geometrical parameters and orbital charge transfer E(2) values [LP(C) → π*CN] equals in both units, the exotic behaviour of F–NC is observed in its non-symmetric transition structure **51** with quite different geometric and electronic features at its two subunits (Scheme 11). This peculiar behaviour was reasoned attending to an initial stabilizing intermolecular electrostatic interaction between the lone pair of the C atom of the first isocyanide unit and the deficient density area of the F–N bond of the second monomer.

5. Others

Different chemical transformations as the formation of euph-7-ene by the *Tetrahymena* cyclase[85] or the methylene transfer from CH$_2$N$_2$ to ruthenium/osmium complexes[86] were postulated to evolve *via* a non-least motion pathway. In the following lines we highlight some examples in which the preference of the non-least path over the least-motion path has been analysed in detail:

a) 1985, Jemmis *et al.*

b) 1989, Pranata & Dougherty
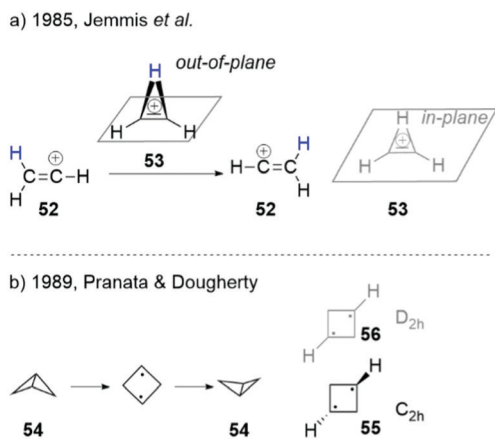
Scheme 12 (a) 1,2-H shifts of vinyl cation **52** and (b) ring-flipping of bicyclobutane **54**.
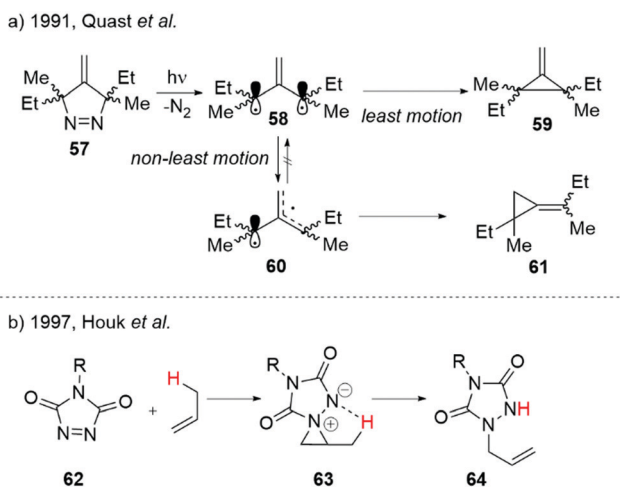
1,2-H shifts. Vinyl cations, like the parent **52**, are known to undergo facile 1,2-H shifts. For a long time, these migrations were presumed to proceed through planar 2-electrons 3-centers cations like **53**, that is, *via* least-motion pathways. However, semiempirical and *ab initio* SCF molecular orbital calculations on the degenerate rearrangement of the parent **52** suggest that the transition state structure **51** in which the migrating group bends out-of-the plane containing the resting HC≡CH moiety, presents lower energy than the planar one **53**. The lower energy of **51** is caused by the maximization of the bonding of the migrating hydrogen with the initial and terminal carbon atoms (Scheme 12a).[87] Other haptotropic shifts have been also proposed to occur preferentially by following non-least-motion pathways across polycyclic carbynes.[88]

Cyclobutanediyl conformational exchange. In 1989, Pranata and Dougherty reported a theoretical study on the triplet and singlet potential energy surfaces of cyclobutanediyl **54**. Using the valence bond and HF methods they found that the ring-flipping conformational exchange of bicyclobutane occurs by

following a non-least-motion pathway.[89] They computed that the inversion of the ring involves a non-planar intermediate with symmetry C_{2h} **55** instead of the intuitive D_{2h} species **56** as previously suggested by Gassman *et al.*[90] (Scheme 12b).

Photoextrusion of N$_2$ from pyrazoline derivatives. Quast and Jacobi reported that the photoextrusion of molecular dinitrogen from diastereomeric 3-methylene-1-pyrazolines **57** yielded mixtures of methylenecyclopropanes **59** and alkylidenecyclopropanes **61** in different ratios.[91] They ascribed the formation of both products **59** and **61** to the least and non-least-motion pathways, respectively. Curiously, both mechanistic channels would share the bis-orthogonal trimethylenemethane **58** as the key intermediate. The experimental ratio of the products is closely related, on the one hand, to the propensity for its cyclization leading to the least-motion product (**59**) and, on the other hand, to the C–C bond rotation in the structure **60** therefore conducting to the non-least-motion product **61** (Scheme 13a).

Ene reaction. The precise course of the ene-reaction of 1,2,4-triazoline-2,4-diones (TADs) **62** with propene towards **64** remained unclear for a long time. In 1997 Houk *et al.* revisited this reaction and analysed in detail its mechanism by using semiempirical and DFT methods.[92] The computed stepwise mechanism involves a rate-determining initial step that occurs by a non-least-motion pathway leading to the peculiar spiro-cyclic and zwitterionic intermediates **63**. The transition state of this first step accounts not only for the formation of the two new C–N bonds but also for the rotation of the methyl group so that one of its H atoms is brought close to the second nitrogen atom of the original TAD azo fragment. In such transition state, the tilt angle of the TAD ring with respect to the propene plane is 45°. This value does not only ensure that the stabilizing N–H interaction, of electrostatical and secondary orbital nature, is maximized, but it also reveals the nucleophilic and electrophilic interactions between both fragments at this transition state structure (TAD-LUMO with propene-HOMO and TAD-HOMO with propene-LUMO) (Scheme 13b).

Conclusions

In this review we have revised a group of reactions that were proven to violate the principle of least motion. As shown, the violations are mainly to ensure that the reacting molecules preserve the orbital symmetry and maximize their mutual interaction. Most of the examples here discussed are devoted to the reactions of carbenes, boranes and silylenes, such as insertion and addition processes on σ and π bonds, respectively, and even (homo)dimerizations. In all these cases the preference for the non-least-motion path is related to the minimization of the orbital interactions involving the σ^2 orbital of the carbene species. Other processes as H-shifts, conformational exchanges or ene-reactions have been also characterised as non-least-motion reactions.

The advances in the development of computational methods, not only the accessibility to multireference methods but also to

a) 1991, Quast *et al.*

b) 1997, Houk *et al.*

Scheme 13 (a) Photolysis of methylenepyrazolines **57** and (b) ene-reaction of triazolinedione **62**.

This journal is © the Owner Societies 2022

Phys. Chem. Chem. Phys., 2022, **24**, 8064–8075 | **8071**

techniques that allow for a detailed understanding of the pathway from reactants to products, have been of utmost relevance for the rationalization of mechanisms initially envisioned as following least-motion paths. The use of high computational levels allowed detailed analyses of such reaction steps, apparently simple on the basis of the transition state theory, showing its hidden complexity. Thus, if someone come across reaction steps with peculiar IRCs showing motions larger than that intuitively expected, with rare changes in the direction and/or curvature of the computed reaction path (something that has been compared to a molecular dance),[93] she or he should not be surprised, most probably is facing a non-least-motion step. Similar cases are well-known and a good collection of them is compiled herein. Some have been then rationalized by analysing in detail the respective reaction coordinates and partitioning the apparently unique reaction step (from the reaction complex to the product) into various reaction phases by using recent methodologies as URVA. Such methodology revealed a sequence of several chemical events, as well as new, originally "hidden" transition states as Kraka and Cremer discussed.[94] Moreover, those studies suggest that in the scrutiny of any reaction by computational methods, a detailed analysis of some individual reaction step could allow its disaggregation into reaction phases by showing relevant "hidden" stationary points. Such analysis might thus contribute to the discovery of novel and interesting processes, as it has been proved with the characterization of the so-called "interrupted" and "aborted" pericyclic reactions.[95]

Author contributions

M. C. R – investigation, writing; M. A.: conceptualization, investigation, supervision, writing; M. M.-L.: investigation, project administration, supervision, writing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 F. O. Rice and E. Teller, The role of free radicals in elementary organic reactions, *J. Chem. Phys.*, 1938, **6**, 489–496.

2 S. I. Miller, Stereoselection in the elementary steps of organic reactions, *Adv. Phys. Org. Chem.*, 1968, **6**, 185–332.

3 J. Hine, The principle of least nuclear motion, *Adv. Phys. Org. Chem.*, 1977, **15**, 1–61.

4 M. L. Sinnott, The principle of least nuclear motion and the theory of stereoelectronic control, *Adv. Phys. Org. Chem.*, 1988, **24**, 113–204.

5 R. Hoffmann, R. Gleiter and F. B. Mallory, Non-least-motion potential surfaces. The dimerization of methylenes and nitroso compounds, *J. Am. Chem. Soc.*, 1970, **92**, 1460–1466.

6 H. Basch, Dimerization of methylenes by their least motion, coplanar approach: A multiconfiguration self-consistent field study, *J. Chem. Phys.*, 1971, **55**, 1700–1708.

7 J. A. Berson and J. A. Jenkins, Homotropylium-4-d ion. Energy barrier to a non-least-motion circumambulatory rearrangement, *J. Am. Chem. Soc.*, 1972, **94**, 8907–8908.

8 C. Trindle and D. D. Shillady, *Ab initio* Gaussian lobe self-consistent field computations on the interconversion of ammonium oxide with hydroxylamine, and implications for the rearrangements of substituted hydroxylamines, *J. Am. Chem. Soc.*, 1973, **95**, 703–707.

9 R. B. Woodward and R. Hoffmann, Stereochemistry of electrocyclic reactions, *J. Am. Chem. Soc.*, 1965, **87**, 395–397.

10 R. Hoffmann and R. Woodward, *The Conservation of Orbital Symmetry*, Elsevier, 1971.

11 C. W. Bauschlicher, K. Haber, H. F. Schaefer and C. F. Bender, Concerted non-least-motion pathway for the singlet methylene insertion reaction $CH_2(^1A_1) + H_2 \rightarrow CH_4$, *J. Am. Chem. Soc.*, 1977, **99**, 3610–3614.

12 R. C. Dobson, D. M. Hayes and R. Hoffmann, A potential surface for the insertion of singlet methylene into a carbon–hydrogen bond, *J. Am. Chem. Soc.*, 1971, **93**, 6188–6192.

13 R. Hoffmann, R. Gleiter and F. B. Mallory, Non-least-motion potential surfaces. Dimerization of methylenes and nitroso compounds, *J. Am. Chem. Soc.*, 2002, **92**, 1460–1466.

14 J. M. Howell, An *ab initio* potential surface for phosphorane fragmentation, PR5 ⇌ PR3 + R2, *J. Am. Chem. Soc.*, 1977, **99**, 7447–7452.

15 P. Cremaschi and M. Simonetta, *Ab initio* calculations for the reactions $CH_2 + H_2$ and $CH_2 + CH_2$, *J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 1801–1809.

16 H. Kollmar, MO calculations on electrophilic reactions-II. The addition of hydrogen to methylene, a carbene insertion process, *Tetrahedron*, 1972, **28**, 5893–5901.

17 J. N. Murrell, J. B. Pedley and S. Durmaz, Potential energy surfaces for the reaction $CH_2 + H_2 \rightarrow CH_4$, *J. Chem. Soc., Faraday Trans. 2*, 1973, **69**, 1370–1380.

18 C. Sosa and H. B. Schlegel, Carbene and silylene insertion reactions. *Ab initio* calculations on the effects of fluorine substitution, *J. Am. Chem. Soc.*, 1984, **106**, 5847–5852.

19 H. Kollmar and V. Staemmler, *Ab initio* calculations of the potential energy surface of the reaction of singlet methylene with the hydrogen molecule, *Theor. Chim. Acta*, 1979, **51**, 207–217.

20 C. W. Bauschlicher, H. F. Schaefer and C. F. Benderlc, The least-motion insertion reaction $CH_2(^1A_1) + H_2 \rightarrow CH_4$. Theoretical study of a process forbidden by orbital symmetry, *J. Am. Chem. Soc.*, 1976, **98**, 1653–1658.

8072 | *Phys. Chem. Chem. Phys.*, 2022, **24**, 8064–8075

This journal is © the Owner Societies 2022

21 M. Ortega, J. M. Lluch, A. Oliva and J. Bertran, A theoretical insight into the insertion reaction of singlet methylene to the hydrogen molecule, *Can. J. Chem.*, 1987, **65**, 1995–1999.

22 M. Sironi, M. Raimondi, D. L. Cooper and J. Gerratt, *Ab initio* spin-coupled description of the reactions $CH_2(^1A_1)$ + $H_2 \rightarrow CH_4$ and $CH_4 \rightarrow CH_3(^2A_1')$ + H, *J. Am. Chem. Soc.*, 1990, **112**, 5054–5060.

23 W. Kirmse, *Carbene Chemistry*, Elsevier, 1971.

24 P. S. T. Lee, R. L. Russell and F. S. Rowland, The reactions of triplet methylene with alkyl radicals in ordinary photolysis systems, *J. Chem. Soc. D*, 1970, 18–19.

25 H. M. Frey, Kinetic evidence for a large separation between singlet and triplet methylene, *J. Chem. Soc., Chem. Commun.*, 1972, 1024–1025.

26 S. W. Chiu and W. K. Li, Mindo/3 study of the addition of hydrogen to vinylidene, *J. Mol. Struct.*, 1980, **66**, 221–226.

27 W.-K. Li and H.-T. Tsang, MIND0/3 study of cyclopentadienylidene and its insertion into molecular hydrogen, *Croat. Chem. Acta*, 1983, **56**, 103–112.

28 H. T. Tsang and W. K. Li, MINDO/3 study of the hydrogen insertions of cyclopropenylidene and cyclopropylidene, *THEOCHEM*, 1983, **104**, 95–104.

29 S. F. Clewing and J. P. Wagner, $\sigma_0\pi_2$ Singlet ground state carbenes undergo least-motion reactions with H_2 and alkenes, *J. Org. Chem.*, 2021, 5–10.

30 S. P. Walch, Theoretical characterization of the reaction CH_3 + OH $\rightarrow$ CH_3OH $\rightarrow$ products: The $^1CH_2 + H_2O$, $H_2 + HCOH$, and $H_2 + H_2CO$ channels, *J. Chem. Phys.*, 1993, **98**, 3163–3167.

31 G. C. Lie, J. Hinze and B. Liu, Calculated a4$\Sigma-$, A2Δ, B2$\Sigma-$ states of CH, *J. Chem. Phys.*, 2003, **57**, 625.

32 G. C. Lie, J. Hinze and B. Liu, Valence excited states of CH. I. Potential curves, *J. Chem. Phys.*, 2003, **59**, 1872.

33 M. Larsson, M. R. A. Blomberg and P. E. M. Siegbahn, Theoretical and experimental studies of a new predissociation in the A2Δ state of CC1, *Mol. Phys.*, 1982, **46**, 365–382.

34 M. Bialski and F. Grein, Theoretical studies on low-lying valence states of NS, SiF, and CCl, *J. Mol. Spectrosc.*, 1976, **61**, 321–331.

35 W. P. White, R. M. Pitzer, C. Weldon Mathews and T. H. Dunning, The electronic states of carbon monofluoride: Rydberg states, *J. Mol. Spectrosc.*, 1979, **75**, 318–326.

36 T. H. Dunning, W. P. White, R. M. Pitzer and C. W. Mathews, The electronic states of carbon monofluoride: Low-lying valence states, *J. Mol. Spectrosc.*, 1979, **75**, 297–317.

37 J. A. Hall and W. G. Richards, A theoretical study of the spectroscopic states of the CF molecule, *Mol. Phys.*, 1972, **23**, 331–343.

38 A. Mavridis and J. F. Harrison, Electronic structure of the carbyne C–Li and the carbene Li_2C, *J. Am. Chem. Soc.*, 2002, **104**, 3827–3833.

39 B. R. Brooks and H. F. Schaefer, Reactions of carbynes. Potential energy surfaces for the doublet and quartet methylidyne (CH) reactions with molecular hydrogen, *J. Chem. Phys.*, 1977, **67**, 5146–5151.

40 C. T. Stanton, N. L. Garland and H. H. Nelson, Temperature dependence of CH(CD) + D2 reaction kinetics, *J. Phys. Chem.*, 1991, **95**, 1277–1282.

41 L. L. Lohr and R. C. Boehm, Temperature dependence of CH(CD) + D2 reaction kinetics, *J. Phys. Chem.*, 1991, **95**, 3203.

42 N. J. Caldwell, J. K. Rice, H. H. Nelson, G. F. Adams and M. Page, Theoretical and experimental investigation of the reaction BH + D2 $\rightarrow$ BHD2, *J. Chem. Phys.*, 1990, **93**, 479–488.

43 H. B. Schlegel, A. G. Baboul and S. J. Harris, Potential surfaces for unimolecular and bimolecular gas phase reactions of BHmCln calculated at the G2 level of theory, *J. Phys. Chem.*, 1996, **100**, 9774–9779.

44 P. S. Skell and A. Y. Garner, Reactions of bivalent carbon compounds. Reactivities in olefin-dibromocarbene reactions, *J. Am. Chem. Soc.*, 1956, **78**, 5430–5433.

45 J. F. Blake, S. G. Wierschke and W. L. Jorgensen, Variational transition state for the reaction of Cl2C: With ethylene and the thermodynamics of carbene additions, *J. Am. Chem. Soc.*, 2002, **111**, 1919–1920.

46 W. R. Moore, W. R. Moser and J. E. LaPrade, Reactions of the dibromocarbene adducts of bicyclo[2.2.1]heptene and bicyclo[2.2.1]heptadiene, *J. Org. Chem.*, 2002, **28**, 2200–2205.

47 N. G. Rondan, K. N. Houk and R. A. Moss, Transition states and selectivities of singlet carbene cycloadditions, *J. Am. Chem. Soc.*, 1980, **102**, 1770–1776.

48 B. Zurawski and W. Kutzelnigg, Ab initio calculation of the reaction path for the addition of singlet (1a1) methylene to ethylene, *J. Am. Chem. Soc.*, 1978, **100**, 2654–2659.

49 R. Hoffmann, Trimethylene and the addition of methylene to ethylene, *J. Am. Chem. Soc.*, 1968, **90**, 1475–1485.

50 R. Hoffmann, D. M. Hayes and P. S. Skell, Potential Surfaces for the Addition of CH2 and CF2 to Ethylene and Isobutene, *J. Phys. Chem.*, 1972, **76**, 664–669.

51 A. E. Keating, M. A. Garcia-Garibay and K. N. Houk, Origins of stereoselective carbene 1,2-shifts and cycloadditions of 1,2-dichloroethylidene: A theoretical model based on CBS-Q and B3LYP calculations, *J. Am. Chem. Soc.*, 1997, **119**, 10805–10809.

52 K. N. Houk, N. G. Rondan and J. Mareda, Are π-complexes intermediates in halocarbene cycloadditions?, *J. Am. Chem. Soc.*, 1984, **106**, 4291–4293.

53 R. Hoffmann, H. W. Heine, R. Peavy, T. Letters, A. J. Durbetaki, J. Org Chem, D. EMcGreer, N. W. K. Chiu, M. G. Vinje, K. C. K. Wong, C. J. Chem, N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, F. F. Wesley and J. Amer, Organic and biological chemistry trimethylene and the addition of methylene to ethylene, *Angew. Chem., Int. Ed. Engl.*, 1965, **87**, 633.

54 L. Xu, C. E. Doubleday and K. N. Houk, Dynamics of carbene cycloadditions, *J. Am. Chem. Soc.*, 2011, **133**, 17848–17854.

55 K. N. Sedenkova, E. B. Averina, Y. K. Grishin, J. V. Kolodyazhnaya, V. B. Rybakov, T. S. Kuznetsova, A. Hughes, G. D. P. Gomes, I. V. Alabugin and N. S. Zefirov, Substituent effects on stereoselectivity of dihalocarbene reactions with cyclohexadiene and on the reactivity of bis-dihalocyclopropanes in electrophilic

This journal is © the Owner Societies 2022

Phys. Chem. Chem. Phys., 2022, **24**, 8064–8075 | **8073**

nitrations en route to pyrimidine: *N*-Oxides, *Org. Biomol. Chem.*, 2017, **15**, 9433–9441.

56 A. E. Keating, S. R. Merrigan, D. A. Singleton and K. N. Houk, Experimental proof of the non-least-motion cycloadditions of dichlorocarbene to alkenes: Kinetic isotope effects and quantum mechanical transition states, *J. Am. Chem. Soc.*, 1999, **121**, 3933–3938.

57 W. Mahler, Double addition of a carbene to an acetylene, *J. Am. Chem. Soc.*, 1962, **84**, 4600–4601.

58 H. Hart and M. Nitta, The structures of the dichlorocarbene adducts of hexamethyldewarbenzene, *Tetrahedron Lett.*, 1974, **15**, 2109–2112.

59 E. V. Dehmlow, Ein spiro[cyclopropan-bicyclobutan] als zwischenprodukt einer ungewöhnlichen dichlohcarbenaddition, *Tetrahedron Lett.*, 1975, **16**, 203–206.

60 B. M. Trost and R. C. Atkins, The reaction of dichlorocarbene with trimethylcyclopropene, *J. Chem. Soc. D*, 1971, 1254.

61 J. Weber, L. Xu and U. H. Brinker, First formation of 1,1-dihalo-1,3-butadienes from reactions of dichloro- and dibromocarbenes with cyclopropenes via new addition-rearrangements, *Tetrahedron Lett.*, 1992, **33**, 4537–4540.

62 J. Weber and U. H. Brinker, Evidence for a stepwise addition of carbenes to strained double bonds: Reactions of dihalocarbenes with cyclopropenes, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1623–1626.

63 D. C. Merrer and P. R. Rablen, Dichlorocarbene addition to cyclopropenes: A computational study, *J. Org. Chem.*, 2005, **70**, 1630–1635.

64 O. P. Strausz, G. J. A. Kennepohl, F. X. Garneau, T. DoMinh, B. Kim, S. Valenty and P. S. Skell, Formation and reactions of monovalent carbon intermediates. III. The reaction of carbethoxymethyne with olefins, *J. Am. Chem. Soc.*, 1974, **96**, 5723–5732.

65 R. K. Gosavi, I. Safarik and O. P. Strausz, Molecular orbital studies of carbyne reactions: Addition and insertion reaction paths for the reaction, *Can. J. Chem.*, 1985, **63**, 1689–1693.

66 K. N. Houk, N. G. Rondan and J. Mareda, Theoretical studies of halocarbene cycloaddition selectivities. A new interpretation of negative activation energies and entropy control of selectivity, *Tetrahedron*, 1985, **41**, 1555–1563.

67 P. Jiang, D. Trieber and P. P. Gaspar, Kinetic studies on the thermal decomposition of trans-2,3-dimethyl-1-tri-*tert*-butylsilyl-1-triisopropylsilylsilirane and the mechanism of silylene generation, *Organometallics*, 2003, **22**, 2233–2239.

68 N. Al-Rubaiey, I. W. Carpenter, R. Walsh, R. Becerra and M. S. Gordon, Direct gas-phase kinetic studies of silylene addition reactions: $SiH_2 + C_3H_6$, $SiH_2 + i-C_4H_8$, and $SiMe_2 + C_2H_4$. The effects of methyl substitution on strain energies in siliranes, *J. Phys. Chem. A*, 1998, **102**, 8564–8572.

69 N. Al-Rubaiey and R. Walsh, Gas-phase kinetic study of the prototype silylene addition reaction $SiH_2 + C_2H_4$ over the temperature range 298-595 K. An example of a third-body mediated association, *J. Phys. Chem.*, 1994, **98**, 5303–5309.

70 P. P. Gaspar, H. Qian, A. M. Beatty, D. André D'Avignon, J. L. F. Kao, J. C. Watt and N. P. Rath, *Tetrahedron*, Pergamon, 2000, vol. 56, pp. 105–119.

71 K. Ohta, K. Morokuma and E. R. Davidson, Dimerization paths of CH_2 and SiH_2 fragments to ethylene, disilene, and silaethylene: MCSCF and MRCI study of least-and non-least-motion paths, *J. Am. Chem. Soc.*, 1985, **107**, 3466–3471.

72 D. Feller and E. R. Davidson, A multiconfigurational self-consistent field study of the D_2h dissociation of excited-state ethylene, *J. Phys. Chem.*, 1983, **87**, 2721–2722.

73 R. W. Alder, M. E. Blake, L. Chaker, J. N. Harvey, F. Paolini and J. Schütz, When and how do diaminocarbenes dimerize?, *Angew. Chem., Int. Ed.*, 2004, **43**, 5896–5911.

74 A. J. Arduengo, H. V. R. Dias, J. C. Calabrese and F. Davidson, A Carbene-GeI₂ adduct: Model of the non-least-motion pathway for dimerization of singlet carbenes, *Inorg. Chem.*, 1993, **32**, 1541–1542.

75 J. M. Oliva, Rate constant calculations in the dimerization of diaminocarbene: A direct dynamics study, *Chem. Phys. Lett.*, 1999, **302**, 35–42.

76 R. W. Alder, M. E. Blake and J. M. Oliva, Diaminocarbenes; calculation of barriers to rotation about carbene–N bonds, barriers to dimerization, proton affinities, and ¹³C NMR shifts, *J. Phys. Chem. A*, 1999, **103**, 11200–11211.

77 M. J. Cheng and C. H. Hu, A computational study on the stability of diaminocarbenes, *Chem. Phys. Lett.*, 2000, **322**, 83–90.

78 M. J. Cheng and C. H. Hu, Computational study on the stability of imidazol-2-ylidenes and imidazolin-2-ylidenes, *Chem. Phys. Lett.*, 2001, **349**, 477–482.

79 D. C. Graham, K. J. Cavell and B. F. Yates, Dimerization mechanisms of heterocyclic carbenes, *J. Phys. Org. Chem.*, 2005, **18**, 298–309.

80 D. C. Graham and B. F. Yates, Increased stability of NO and NS heterocyclic carbenes?, *Aust. J. Chem.*, 2004, **57**, 359–364.

81 M. Marin-Luna and M. Alajarin, Unraveling the computed non-least motion pathway for the homodimerization of superchameleonic isocyanides: the peculiar nonsymmetrical (F–NC)₂ reactant complex, *Phys. Chem. Chem. Phys.*, 2021, **23**, 16973–16980.

82 M. Marin-Luna and M. Alajarin, In search of 1,4-diazabutatrienes, the elusive isocyanide homodimers: The superchameleonic F–NC, *J. Org. Chem.*, 2020, **85**, 11975–11979.

83 M. Alajarin and M. Marin-Luna, Unmasking the elusive 1,4-diazabutatrienes: The stabilizing role of the N-substituents, *Phys. Chem. Chem. Phys.*, 2021, **23**, 6091–6097.

84 G. dos P. Gomes, Y. Loginova, S. Z. Vatsadze and I. V. Alabugin, Isonitriles as stereoelectronic chameleons: The donor–acceptor dichotomy in radical additions, *J. Am. Chem. Soc.*, 2018, **140**, 14272–14288.

85 J.-L. Giner and J. Feng, Stereochemical investigations of the *Tetrahymena cyclase*, a model system for euphane/tirucallane biosynthesis, *Org. Biomol. Chem.*, 2017, **15**, 2823–2830.

86 D. Huang, G. J. Spivak and K. G. Caulton, Mechanistic and thermodynamic aspects of methylene transfer from CH_2N_2 to $MHCl(CO)L_2$ (M = Ru, Os; L = tertiary phosphine): Non-least motion behavior and extreme dependence on phosphine identity, *New J. Chem.*, 1998, **22**, 1023–1025.

8074 | *Phys. Chem. Chem. Phys.*, 2022, **24**, 8064–8075

This journal is © the Owner Societies 2022

87 E. D. Jemmis, K. S. Sarma and P. N. V. Pavankumar, A non-least motion pathway for 1,2-shift in cyclic vinyl cations, *THEOCHEM*, 1985, **22**, 305–311.

88 S. Brydges, N. Reginato, L. P. Cuffe, C. M. Seward and M. J. McGlinchey, High and low barriers to haptotropic shifts across polycyclic surfaces: The relevance of aromatic character during the migration process, *C. R. Chim.*, 2005, **8**, 1497–1505.

89 J. Pranata and D. A. Dougherty, Theoretical studies of the singlet and triplet potential energy surfaces of cyclobutane-diyl, *J. Phys. Org. Chem.*, 1989, **2**, 161–176.

90 P. G. Gassman, M. L. Greenlee, D. A. Dixon, S. Richtsmeier and J. Z. Gougoutas, X-ray and theoretical analysis of the relationship between substituent steric effects and the structure of bicyclo[1.1.0]butane. The unexpected flexibility of the bicyclo[1.1.0]butane skeleton, *J. Am. Chem. Soc.*, 1983, **105**, 5865–5874.

91 H. Quast and H. Jakobi, Retention of configuration and *E/Z* stereoselectivity in the photolysis of *cis*- and *trans*-tetraalkyl-4-methylene-1-pyrazolines, *Chem. Ber.*, 1991, **124**, 1619–1626.

92 J. S. Chen, K. N. Houk and C. S. Foote, The nature of the transition structures of triazolinedione ene reactions, *J. Am. Chem. Soc.*, 1997, **119**, 9852–9855.

93 I. V. Alabugin, *Stereoelectronic Effects: A Bridge Between Structure and Reactivity*, John Wiley & Sons, Ltd, Chichester, UK, 2016.

94 E. Kraka and D. Cremer, Computational analysis of the mechanism of chemical reactions in terms of reaction phases: Hidden intermediates and hidden transition states, *Acc. Chem. Res.*, 2010, **43**, 591–601.

95 D. V. Vidhani, M. E. Krafft and I. V. Alabugin, Gold(I)-catalyzed allenyl cope rearrangement: Evolution from asynchronicity to trappable intermediates assisted by stereoelectronic switching, *J. Am. Chem. Soc.*, 2016, **138**, 2769–2779.

This journal is © the Owner Societies 2022

Phys. Chem. Chem. Phys., 2022, **24**, 8064–8075 | **8075**