Hypothesis of Concerted Reactivity of Singlet Non-Covalent Radical Dimers

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Abstract

This article explores the intriguing domain of Frustrated Radical Pairs (FRPs) and their potential to form non-covalent dimers, termed Entangled Radical Pairs (ERPs), which exhibit unique singlet ground states and potential concerted reactivity, differing from traditional stepwise reactions. A few recent publications showed that in certain cases, when two radicals cannot form a covalent bond, they unexpectedly form a non-covalent dimer with a singlet ground state. This potentially opens a new elusive route of FRPs' reactivity, in which both radicals react simultaneously as one molecule. Here, we review a number of published articles, in which such reactivity probably took place, but was overlooked. The idea presented in this proposal suggests a path towards many interesting reactions, such as low temperature metal-free dehydrogenation of aliphatic hydrocarbons and others. Additionally, an alternative mechanism for the reactivity of Frustrated Lewis Pairs (FLPs) based on the ERP framework is proposed. Lastly, the implications of ERP model on the general theory of chemical bond formation are contemplated, suggesting a revision of the traditional views on hybridization and electron entanglement. The manuscript calls for further experimental and theoretical investigations to substantiate the presented hypotheses, aiming to unlock new pathways in radical chemistry and beyond.

Graphical abstract
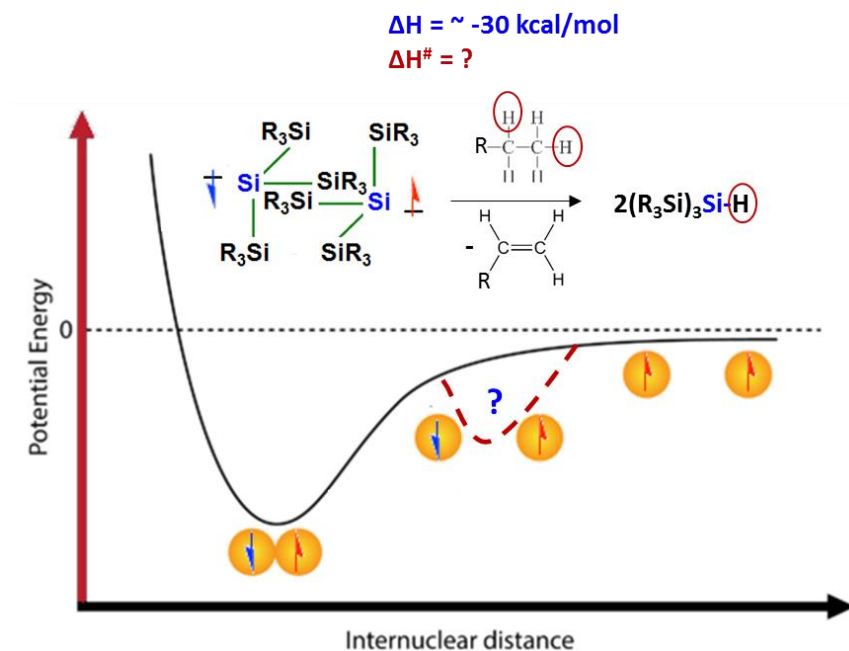
1. Introduction

Recent advances in the chemistry of Frustrated Radical Pairs (FRPs) suggest that two radicals, which cannot form a covalent bond between them, can yield products that are unachievable by alternative approaches.[1] The current knowledge postulate that the radicals in FRPs react in a stepwise manner; i.e., each radical in the pair reacts independently from another (unless they react with each other of course). For example, in a recent publication by Lin et al., the authors demonstrated the remarkable regioselective functionalization of aliphatic C–H bonds using FRPs generated from disilazide donors and an *N*-oxoammonium acceptor.[2] The radical generated from disilazide - abstracts the hydrogen and the *N*-oxoammonium radical reacts with the carbon centered radical. Such reactivity makes the FRPs substantially different from the Frustrated Lewis pairs (FLPs),[3] in which the bulky donor and acceptor form short-lived "encounter complex" and react simultaneously.[4,5] An interesting theoretical (and potentially practical) question is: can the two radicals in an FRP react simultaneously, and not in a stepwise manner? This question can be dissected into the following sub-questions: Can radicals form non-covalent dimers (short-lived or stable)? What can be the molecular and the electronic structure of such dimers? How the simultaneous reactivity of the radicals in FRP can be different from the consequent reactivity? If simultaneous reactivity is indeed possible, what interesting reactions can be done? All these and other related questions are discussed below.

2. Can radicals form non-covalent dimers?

There were several recent publications of non-covalent radical dimers stable at room temperature with a singlet ground state and/or a very small singlet-triplet (S-T) energy gap (ΔE_{S-T}) (Figure 1). In 2020 Sun et al. reported the syntheses of two air-stable olympicenyl radical derivatives (**1a** and **1b**).[6] X-ray crystallographic analysis revealed unique 20-center–2-electron head-to-tail π-dimer structures with intermolecular distances in the range of 3.2 - 3.4Å. Remarkably, the ground state of the π-dimers was found to be a singlet, with an S-T energy gaps estimated to be −2.34 kcal/mol and −3.28 kcal/mol for **1a** and **1b**, respectively. The monomeric doublet radical species were in equilibrium with the singlet π-dimer in solution. In 2023 Wang et al. reported two aromatic ion-radical pairs **2a** and **2b** with very small S-T energy gaps of −1.3E-3 and −0.58 kcal/mol, respectively.[7] Both ion-radical dimers were isolated and characterized by X-ray crystallography. The radicals in both pairs are held together by electrostatic attraction, while in **2b** the radicals also have π-π interactions between them. These examples clearly demonstrate that non-covalent radical dimers can form and that at certain configuration they will acquire a singlet ground state. In 2021 Li and Zhao et al. reported a polychlorinated bis(triarylmethyl) diradical metallacage (**3**) with singlet ground state at room temperature (ΔE_{S-T} = −0.53 kcal/mol).[8] The distance between the radical centers in this cage, which were shown to interact through space, exceeded 15Å. This shows, that even at the very high distance between the radical centers the complex can acquire the singlet ground state upon interaction through space.
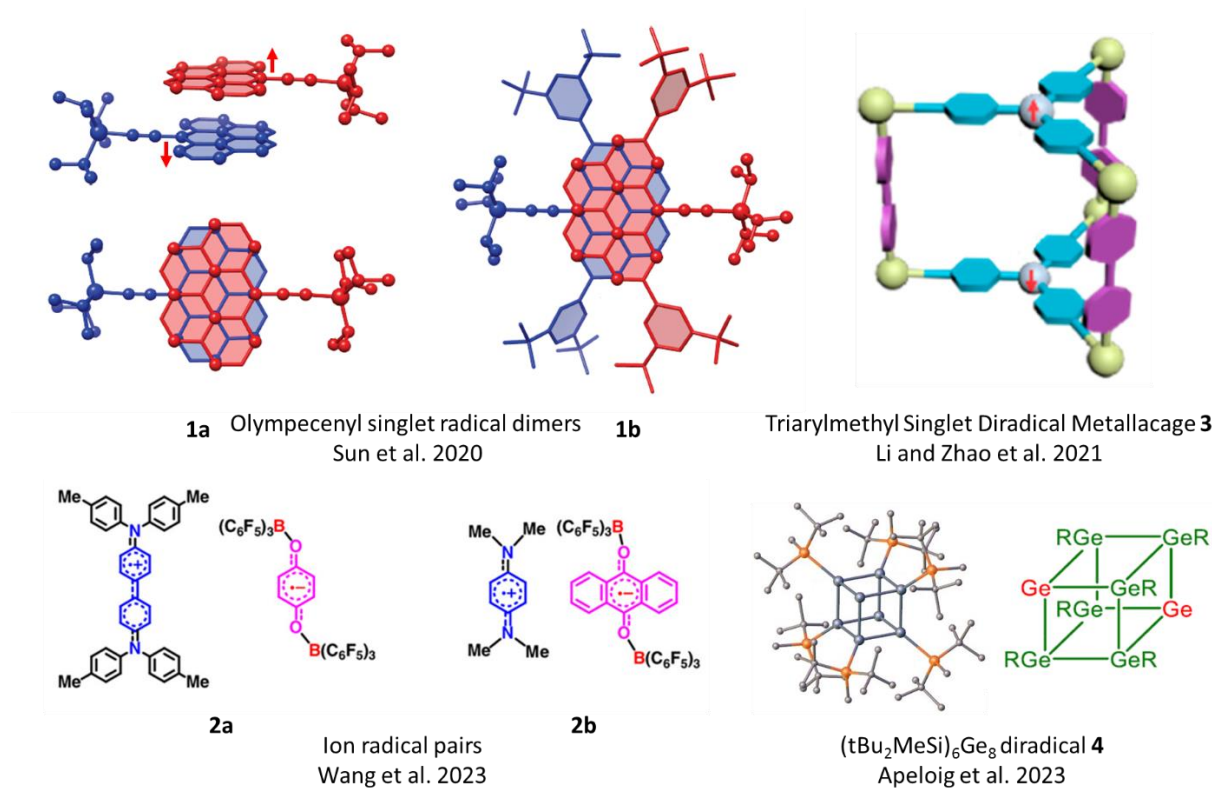
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1a   Olympecenyl singlet radical dimers   1b   Triarylmethyl Singlet Diradical Metallacage **3**
      Sun et al. 2020   Li and Zhao et al. 2021

2a   2b
      Ion radical pairs   (tBu₂MeSi)₆Ge₈ diradical **4**
      Wang et al. 2023   Apeloig et al. 2023

Figure 1. Ground state singlet diradicals / radical pairs which isolation was recently reported

3. Can a radical without significant spin delocalization form a non-covalent dimer with the singlet ground state?

In the abovementioned radicals **1**-**3**, the unpaired electrons were delocalized over the aromatic rings. Radicals without such delocalization are more reactive and therefore are more interesting for potential applications. What can be the molecular structure of a non-covalent radical dimer without conjugation with π-bonds? Such dimers were not yet reported in the literature, but a hint for the answer can be found in a recent publication by Apeloig et al. They reported the synthesis of octagermacubane **4** (Ge_8R_6) with two Ge radical centers, which was isolated in high yield and characterized by X-ray crystallography (Figure 1).[9] Pan and Frenking performed theoretical analysis and showed that **4** is a singlet diradical, in which the radical centers ("Ge0" atoms) interact with each other, despite the long distance of 4.25 Å between them.[10] The singlet state of **4** was calculated to be 15.2 kcal/mol lower in energy than the triplet state. It was shown that there is a direct charge flow between the Ge radical centers in the molecule which likely causes the entanglement of the unpaired electrones. In 1990 Michl et al. reported C_8H_6 cubane diradical, which was also a ground state singlet with calculated ΔE_{S-T} of 10.5 kcal/mol.[11] Upon

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closer look, such molecules (E_8R_6) can be seen as two ER_3 ($Ge(GeR_3)_3$ or CR_2H) radicals, which oriented "back-to-back" and covalently bound in a cube (Figure 2). But what will happen if such two radicals are not bound covalently? And what type of interaction can non-covalently connect two pyramidal radicals of ER_3 type?
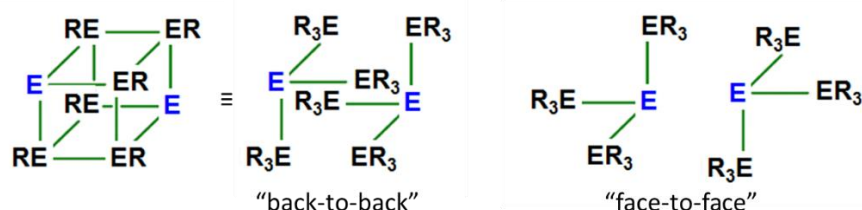

Figure 2. "Back-to-back" vs. "face-to-face" radical dimers orientation.

In 2023 Schreiner et al. published a review article showing that London forces (dispersion energy) must be taken into consideration in structures and dynamics of chemical reactions.[12] Can London forces lead to formation of short-lived singlet radical dimers? In 2022 Schreiner's group reported a study that showed that silyl groups are strong dispersion energy donors.[13] Thus, we looked at the reactivity of branched organosilicon centred radicals of tris(silyl)silyl type. There were many reports about fine tuning of the silyl side groups' size on such radicals that yield different reactivity as described below.

4 Can silyl radicals form a singlet radical pair (non-covalent dimer) via London forces with a through-space interaction between the radical centers?

In 2002, Sekiguchi et al. synthesized the first isolable silyl radical ($tBu_2MeSi)_3Si\cdot$ (5) lacking conjugation with π-bonds (Figure 3).[14] In this radical, the bulky tBu_2MeSi substituents provided significant kinetic stability and the radical could be stored for months in inert conditions both in solid state and in solution. In 2009 Apeloig et al. reported an FRP-type reactivity of such bulky silyl radicals, by showing that under irradiation one radical molecule abstracts hydrogen from another.[15] The possibility of non-covalent dimerization was not discussed in this publication.

In 2005, Apeloig et al. reported their study of the covalent dimerization of silyl radicals with substituents of varying sizes in *n*-hexane at 290K (Figure 3).[16] The study was conducted, among others, on ($Me_3Si)_3Si\cdot$ (6), ($Me_3SiMe_2Si)_3Si\cdot$ (7), and ($tBuMe_2Si)_3Si\cdot$ (8), which were generated by irradiation from the corresponding bissilylmercury compounds. Second order decay of the electron paramagnetic resonance (EPR) signal of the radicals was recorded for all studied molecules after the irradiation was turned off. However, while 6 (k_{dim} = 1×10^8 M^{-1}sec^{-1}) and 7 (k_{dim} = 5×10^3 M^{-1}sec^{-1}) formed dimers, which were isolated and fully characterized, for 8 (k_{dim} = 2×10^2

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M^{-1}sec^{-1}) stable dimer did not form and the sole product with ^{29}Si NMR signals was the product of hydrogen abstraction, hydrosilane (tBuMe$_2$Si)$_3$SiH (**9**).

The difference in reactivity between **7** (with M$_3$Si group in β position) and **8** (with Me$_3$C group in β position) was explained by the difference in flexibility between the side groups. Both **7** and **8** were shown to acquire "back-folded" conformation of the side groups with either "discus" or "umbrella" shape (Figure 1, bottom). Me$_3$Si-Me$_2$Si-Si fragment in **7** was shown to be more flexible than M$_3$C-Me$_2$Si-Si fragment in **8**, and therefore was capable to form the "discus" conformation, which allowed covalent dimerization, while for M$_3$C-Me$_2$Si-Si moiety the "umbrella" conformation was much more stable, and it hindered the ability of the molecules of radical **8** to approach each other and form a Si-Si bond.
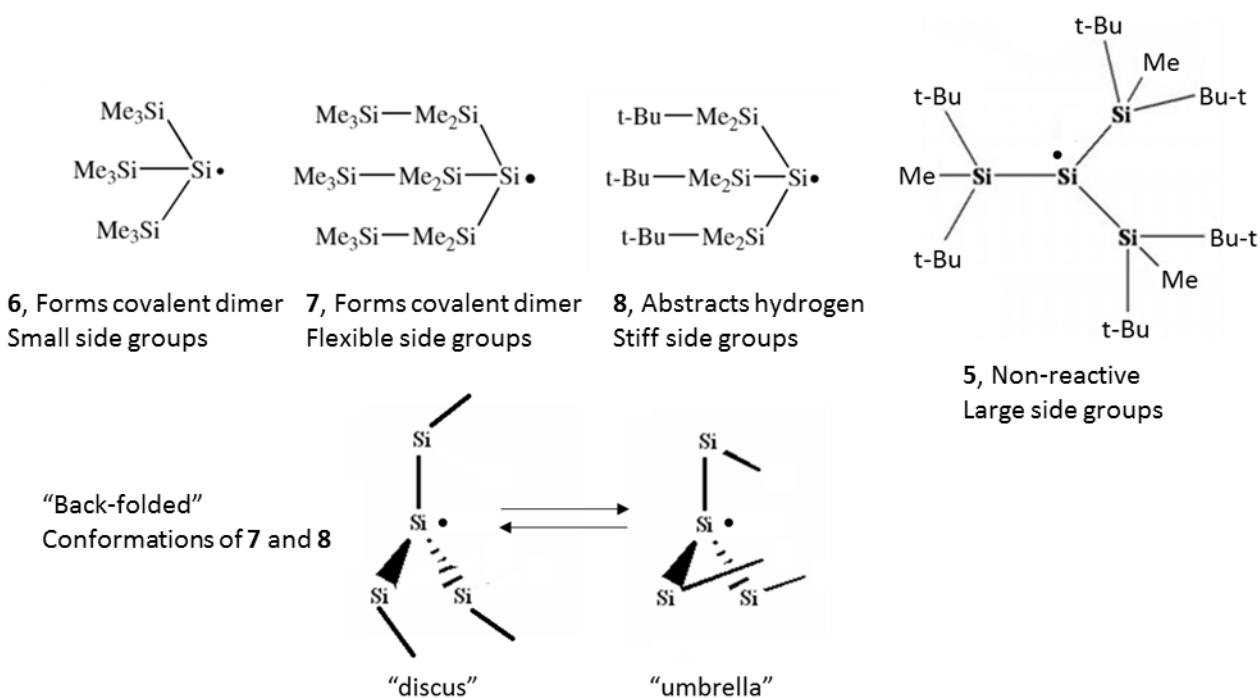

Figure 3. Top: tris(silyl)silyl radicals mentioned in this paper and their reactivity when dissolved in hexane. Bottom: conformations of the side groups in radicals **7** and **8**. While **7** is capable to adopt both, in **8** the umbrella conformation is dominant (see ref. 16 for details).

If radical **8** decayed via a hydrogen abstraction from external source, first order decay is expected and not the second, but this phenomenon was not explained in the publication. The source of the hydrogen in the hydrosilane product **9** also remained unexplained. It was not a result of abstraction from the side groups, since no other silicon containing products were observed in the reaction mixture.

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Based on the discussion above, it is reasonable to hypothesize that the second order decay of **8** can be explained by a singlet dimer formation as shown in Figure 4. The stiff "umbrella" conformation of the radical **8**'s side groups makes "back-to-back" non-covalent dimerization plausible since this way the radical centers can be closer to each other and this resembles the cubane diradical structure which is a singlet in the abovementioned germanium (**4**) and carbon analogues. Interestingly, also in the diradical metallacage **3** the radical centers are oriented "back-to-back" to each other,[8] so one may assume that this orientation is actually required for the pyramidal radicals to have the singlet ground state. This requires further theoretical investigations. I suggest to denote the radical pairs (non-covalent dimers) with ground state singlet as Entangled Radical Pairs (ERPs).
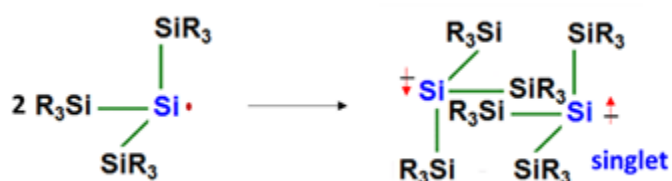

Figure 4. Hypothetical dimerization of $(R_3Si)_3Si\cdot$ to form the ERP (a singlet "back-to-back" pair). Density functional theory (DFT) calculations of this reaction should be conducted to support the hypothesis.

5. How the simultaneous reactivity of ERP can be different from the consequent reactivity of "standard" FRP?

In general, the concerted reaction leading to the same products may in theory require smaller activation energy (Figure 5). Below a few published reactions are discussed, in which a simultaneous reaction could occur, but may have been overlooked.
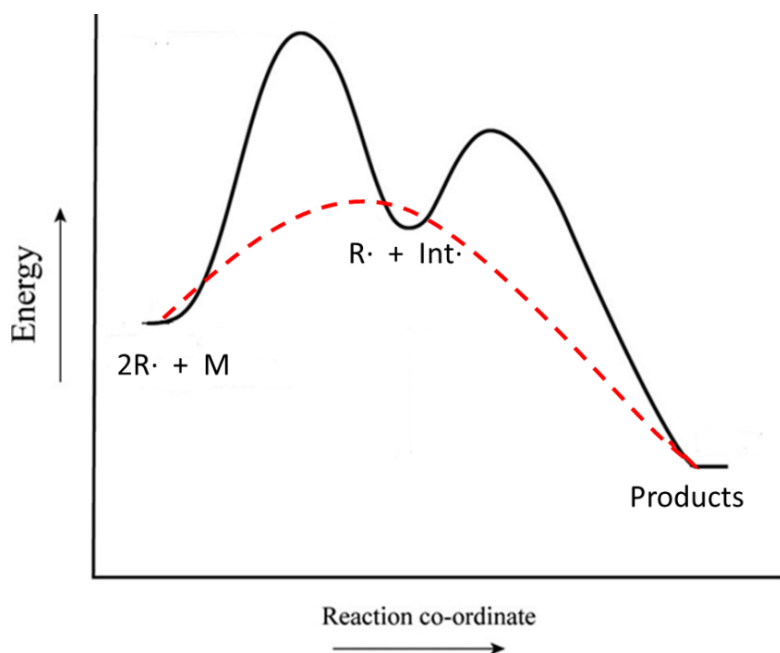
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Figure 5. Theoretical comparison of reaction profiles of stepwise (solid black line) and simultaneous (dashed red line) reactions of an FRP (2R·) with a molecule (M). Int· stands for radical intermediate.

5a. Hypothesis: double hydrogen abstraction from hydrocarbons

Anyone who worked with persistent radicals in hydrocarbon solvents knows that a very common side process is their reactions is the hydrogen abstraction. The exact source of the hydrogen is rarely studied, while it is often assumed that it comes either from a side group of another radical or from the solvent.[17] If the hydrogen is abstracted from the side group, additional byproducts should form, but this assumption cannot be correct if the hydrogen abstraction product is the only byproduct in the reaction mixture. Moreover, the abstraction of hydrogen by a persistent radical from either a side group or an aliphatic hydrocarbon solvent is unlikely to happen, since it will lead to much less stable species via an endothermic process.

On the other hand, if two radicals could react simultaneously, yielding the hydrogen abstraction product and an alkene (Equation 1), this would be a highly exothermic process. In the publication by Lin et al., the authors demonstrated the functionalization of aliphatic C–H bonds using FRPs.[2] But can an FRP cleave two C-H bonds simultaneously like shown in Equation 1 with relatively low activation energy?

$$2R\cdot \ + \ R_2HC\text{-}CHR_2 \ \rightarrow \ 2RH \ + \ R_2C{=}CR_2 \qquad\qquad (1)$$

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In the previous section the possible non-covalent dimerization of radical **8** was discussed.[16] **8** decayed in *n*-hexane via a hydrogen abstraction from external source, but the source of the hydrogen in the hydrosilane product **9** remained unexplained. It was not a result of abstraction from the side groups, since no other silicon containing products were observed in the reaction mixture.[18] Can the reactivity of **8** be explained by simultaneous abstraction of two hydrogen atoms from the *n*-hexane solvent by an ERP of **8**? Thermodynamically, a dehydrogenation of an aliphatic hydrocarbon (Eq. 1) by a tris(silyl)silyl radical pair would be exothermic by ca. 30 kcal/mol (according to standard enthalpy tables).[17] Such reaction will produce hexene, which will either evaporate with the solvent or, since there are free radicals in the solution, polymerize and precipitate. In both scenarios it could have been overlooked.

How the hypothesis of concerted dehydrogenation of hydrocarbons by ERP can be further experimentally and theoretically supported? The fastest path is to repeat the generation of radical **8** in hexane and to characterize the solution and the precipitate. This can be done by reacting the hydrosilane (tBuMe$_2$Si)$_3$SiH with a radical initiator (tBu$_2$Hg or AIBN). As well, DFT calculations on a model system, e.g., of reaction of (Me$_3$Si)$_3$Si· with ethane, should be performed (Figure 6). Other radicals that are known to decay via hydrogen abstraction in hydrocarbon solvents can also be studied.
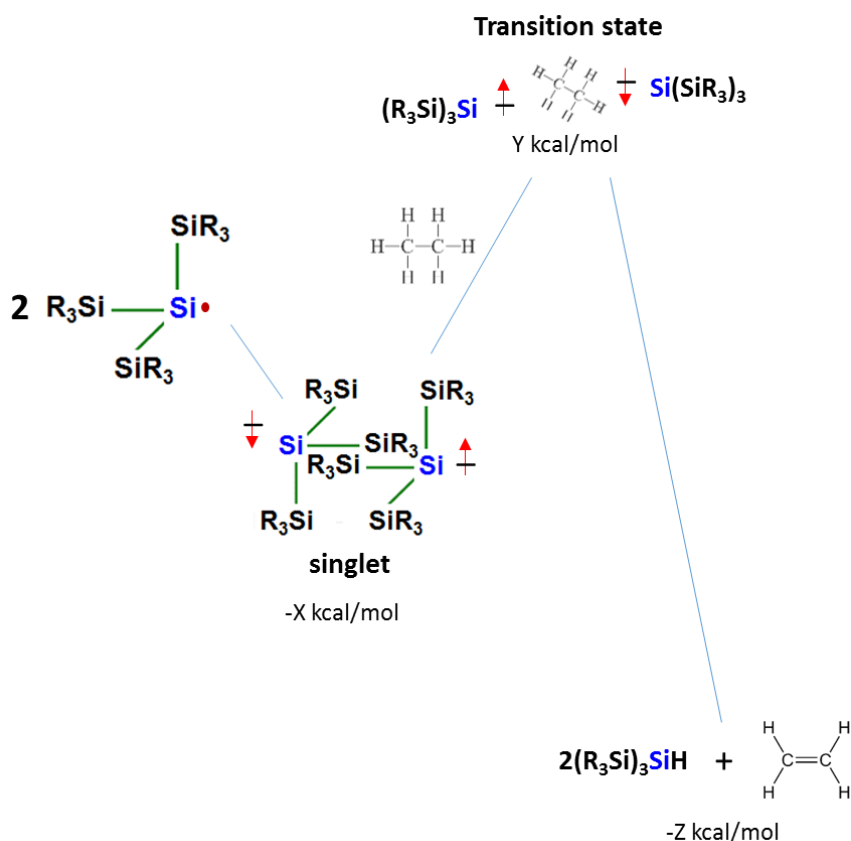

Figure 6. Concerted dehydrogenation of ethane by a silyl ERP (R$_3$Si = Me$_3$Si) − hypothetical reaction profile to be calculated.

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If the hypothesis is correct, such dehydrogenation of alkanes may find application in many areas from hydrocarbons cracking to synthesis of fine organic chemicals. Being highly endothermic, such reactions usually rely on transition metal catalysts, high temperatures, and/or complex stepwise processes.[19] With more research, one can gain more control over the dehydrogenation of hydrocarbons by ERPs at moderate temperatures and without use of expensive transition metals.

5b. Hypothesis: reaction of ERP with benzene

It is highly likely that some reported persistent or stable radicals in fact form ERPs and that can explain their unusual reactivity. For example, Andrada et al. recently reported the generation of the first Al(II) radical, which reacts at room temperature in benzene solution to form a non-aromatic adduct of two radicals to one benzene molecule (Figure 7).[20] The authors propose stepwise mechanism, for which they calculate the activation energy (ΔG) of 23.5 kcal/mol. According to the author's proposal, in the first step, one radical reacts to yield mono-adduct, which later reacts with another radical. While this mechanism possible, simultaneous addition of two radicals to one benzene molecule will most likely require significantly smaller activation energy. Also, since the reaction happens in benzene solution, it is easier to imagine that a radical pair reacts with one benzene molecule at ambient temperature, rather than two independent radicals. This idea requires of course additional theoretical (DFT) and experimental (e.g., kinetic) investigations.
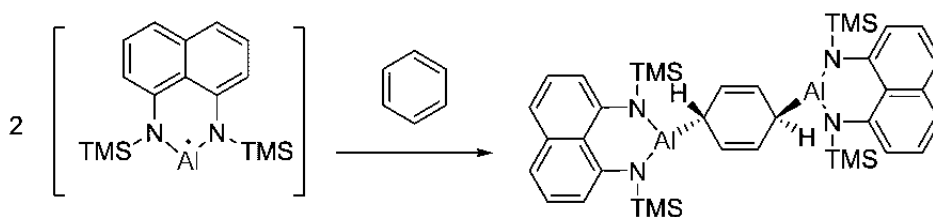

Figure 7. Reaction of Al(II) radical pair with benzene.

6. Possible implications on the mechanism of Frustrated Lewis Pairs (FLPs) reactions

FLP is a combination of a Lewis acid acceptor (A) and a Lewis base donor (D) that cannot bond to form a coordinative complex due to steric hindrance. FLPs exhibit very interesting and often unusual chemistry.[3] The mechanism of FLPs reactivity was studied intensively by several groups. In the latest publication on this topic by Pinter et al., the dihydrogen splitting by several different FLPs was investigated.[5] Mechanisms of Electron Transfer (ET) to the σ^* orbital of H_2 and an Electric Field (EF) driven charge separation of the H-H bond were discussed (Figure 8, top). The

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conclusion was that the latter is more plausible since electron transfer to the σ^* orbital of H_2 would require significantly higher activation energy.

I propose an alternative model, which do not contradict the previous findings, and which is based on the ERP hypothesis. Thus, I suggest to look at the FLP not as two separate molecules, but as a single molecule ("Encounter Complex"[3]). Such complex will have its own "HOMiO" (Highest Occupied "interMolecular" Orbital), which can be described as a superposition of resonance structures (RS). One of the RS can be the ERP, as shown in Figure 8 (bottom). In such ERP a small portion of electron density will be on the acceptor already when the encounter complex forms. Next, upon interaction with dihydrogen, the wave function would collapse towards the ERP and the dihydrogen would split via radical mechanism. In specific cases the whole electron transfer may occur from donor to the base even before interaction with the reactant, and such reaction indeed was recently reported by Müller and coworkers.[21]
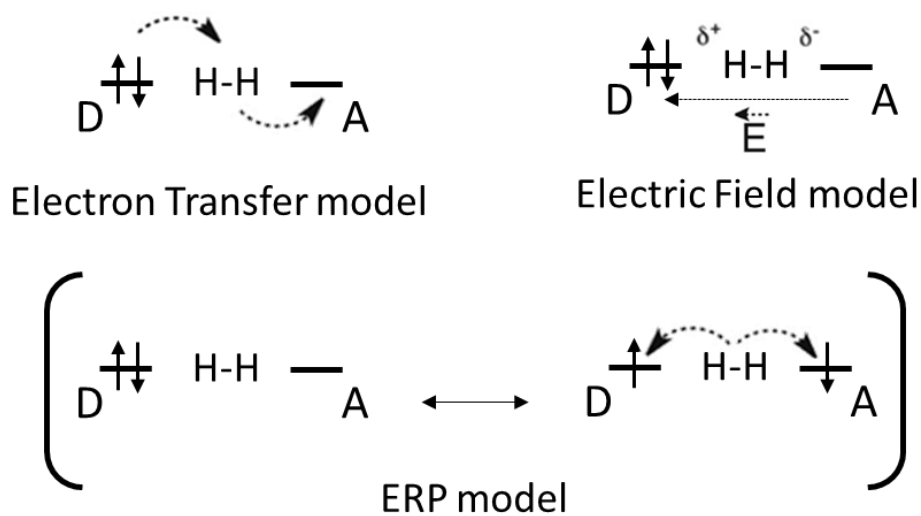

Figure 8. Top: proposed mechanisms for dihydrogen splitting by an FLP discussed in ref. 4. Bottom: hypothetical ERP model that can explain the FLP reactivity

To support this mechanism the following studies can be conducted:

(a) Analysis of the RS of the fully optimized Encounter Complexes using NRT[22] calculations.

(b) Review of the published dihydrogen splitting reactions with FLPs: if the proposed mechanism is correct, the radical stabilizing substituents on the base and acid will promote the splitting. Note: delocalization may weaken the dihydrogen splitting ability, so stabilization without delocalization (e.g., with silyl or bulky alkyl substituents) may be preferred.

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7. Implications on the chemical bond formation theory.

The ERP idea provides an interesting insight into the process of chemical bond formation after collision of two radicals. When a chemical bond forms after the collision, two processes take place (a) hybridisation of two orbitals into one molecular orbital, and (b) entanglement (acquisition of the superposition of opposite spins according to Pauli principle). Currently, it is believed that both processes happen simultaneously upon collision. However, if the radicals cannot reach each other – the two processes in fact happen independently. I.e., if the collision is prevented and the radicals are stopped at a certain distance - the electrons interact to acquire the superposition of opposite spins without bond formation. Perhaps, the standard chart of the chemical bond formation energy, which is shown in all textbooks, should be modified as shown in Figure 9. This view may have further interesting implications beyond organic chemistry.
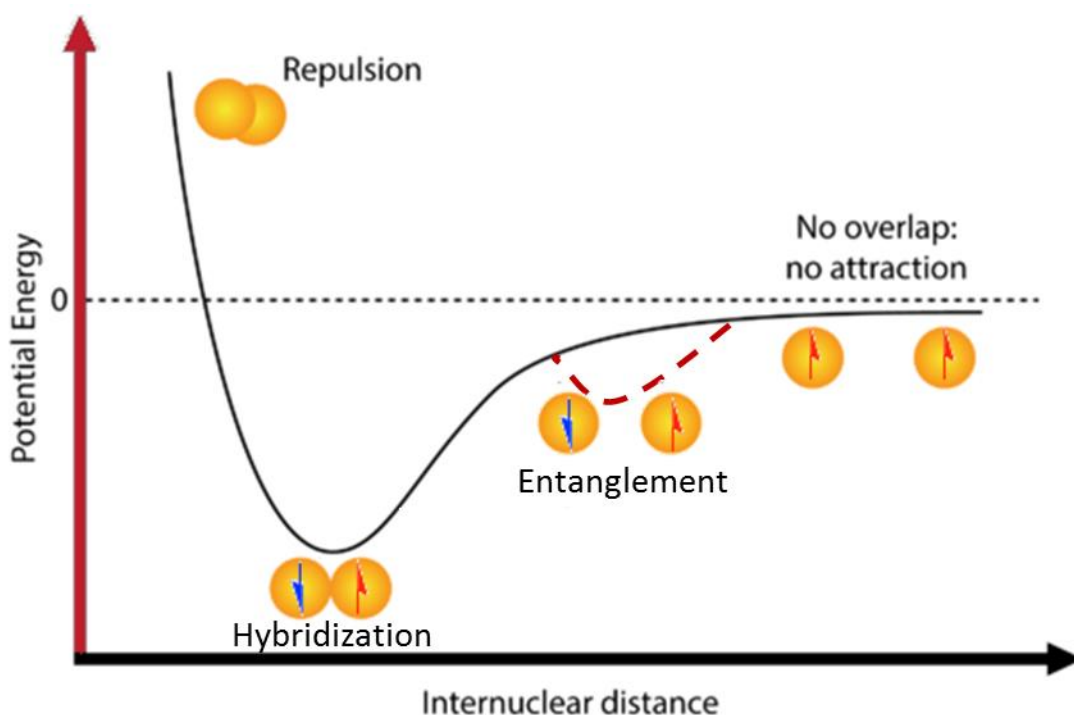

Figure 9. Hypothetical chart of the chemical bond formation energy between two radicals with separated entanglement and hybridization events. The dashed red line represent an energy minimum that exists when radicals cannot freely approach each other to form a covalent bond.

8. Conclusions

It was demonstrated that non-covalent radical dimers can form via π-π interactions, electrostatic attraction, and probably also via London forces. At certain configurations, the dimers will acquire a singlet ground state via interaction between the unpaired electrons through space. These

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dimers were denoted Entangled Radical Pairs (ERPs). Such ERPs can in theory react simultaneously and likely such reactions were observed and reported but the path of simultaneous reaction was overlooked. E.g., a hydrogen abstraction by silyl and other radicals that often occurs as a side process in radical reactions conducted in hydrocarbon solvents can be a result of concerted abstraction of two hydrogen atoms from the solvent by an ERP. As well, ERP idea can shed light on the mechanisms of reactions of FLPs, FRPs, and on the chemical bond formation in general. To confirm the ideas presented in this article further experimental and theoretical investigations are required, some of which are proposed above.

Acknowledgements

Supporting information

https://youtu.be/Myuq1Kfswd8?si=T9VW9TsBoIfghDJZ

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