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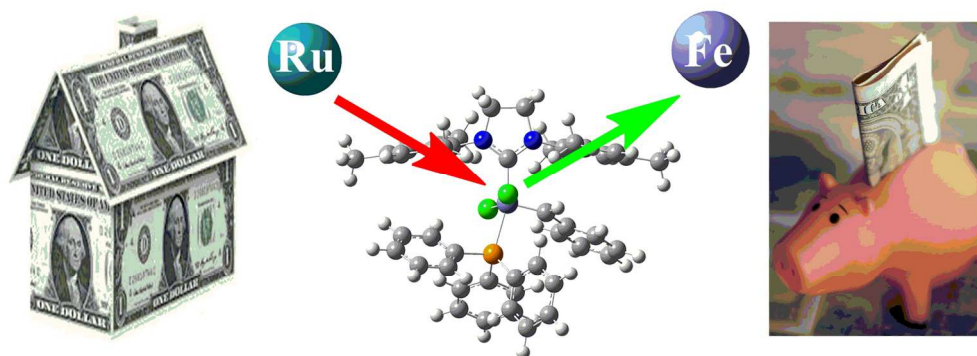


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To replace Ru by Fe in olefin metathesis, a dream?
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ARTICLE TYPE

Comparing Ru and Fe-Catalyzed Olefin Metathesis

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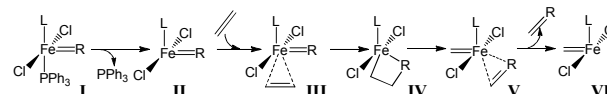
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Density functional theory calculations have been used to explore the potential of Fe-based complexes with a N-heterocyclic carbene ligand, as olefin metathesis catalysts. Apart from a less endothermic reaction energy profile, a small reduction in the predicted upper energy barriers (≈ 2 kcal/mol) is calculated in the Fe catalyzed profile with respect to the Ru catalysed profile. Overall, this study indicates that Fe-based catalysts have the potential to be very effective olefin metathesis catalysts.

Olefin metathesis is a powerful method for the formation of carbon-carbon double bonds in synthetic chemistry.¹ As a testimony to its importance, metathesis reactions are now employed to access fine chemicals,² asymmetric synthesis (biologically active compounds),³ new functionalized materials and various polymers.⁴ According to the Chauvin mechanism, the principal steps of olefin metathesis involve the transformation of a metal-alkylidene complex and a coordinated olefin into a four-membered metallacycle, whose opening in the forward direction leads to the formation of the observed products.⁵ The clarification of the reaction mechanism and the development of highly efficient Mo and Ru catalysts were awarded with the 2005 Nobel prize for Chemistry to Chauvin, Schrock and Grubbs.⁶ Focusing on Ru-catalysts, the activity of the “first-generation” phosphane-based catalysts was significantly improved with the discovery of “second-generation” catalysts, where an N-heterocyclic carbene (NHC) replaces one phosphane group.^{7,8} In the last decade, the development of many variants of Ru-based catalysts paved the way for widespread applications of olefin metathesis in the synthesis of complex organic molecules,⁹ as well in the polymer industry and has a potential even in the petrochemical industry. While highly efficient, these metals are relatively expensive and limited in supply.

Indeed, one of the principal keywords of modern chemistry is sustainability, which means reducing the environmental impact of processes and products, optimizing the use of finite resources and minimizing waste. In the case of processes, this also implies the replacement of expensive, toxic and less abundant metals in catalysts with large scale applications, with cheaper, less toxic and more abundant metals. In the context of olefin metathesis, replacing ruthenium with its lighter congener, iron, as the active

metal, is a desirable solution. This has prompted the scientific community to look for metathesis catalysts containing iron.¹⁰ However, this new strategy is still in its infancy.¹¹ To this end, experimental exploration of the catalysts chemical space to find new catalysts is a tedious task, which is often driven by trial and error. This explains the popular usage of computational techniques as a tool to screen more rapidly novel catalyst architectures to explore their potential as efficient catalysts for the reaction of interest. In the present study, we use density functional theory (DFT) calculations to investigate the potential catalytic behavior of Fe-based olefin metathesis catalysts.¹² DFT based prediction of promising new compounds is not a new approach and it has been also used to suggest a new class of olefin metathesis catalysts.^{13,14} The goal of the present study was to understand the effect of replacing Ru by Fe, on the catalytic behavior of N-heterocyclic carbene (NHC) based catalysts. Our computational results show that Fe-based catalysts are indeed able to promote a reaction pathway perfectly consistent with a well performing olefin metathesis catalyst. For this study we computed the free energy surface for the reaction promoted by $\text{Fe}(\text{SiMe}_3)_2(\text{=CHPh})\text{PPh}_3$ when ethylene is the substrate, according to the mechanism shown in Scheme 1. To understand the effectiveness of the Fe-based catalyst, we compared it to the corresponding Ru $\text{Ru}(\text{SiMe}_3)_2(\text{=CHPh})\text{PPh}_3$ catalyst.¹⁵



Scheme 1. Olefin metathesis reaction pathway studied in this study.

Figure 1 gives the most stable species and the free energy for the $\text{Fe}(\text{SiMe}_3)_2(\text{=CHPh})\text{PPh}_3$ mediated olefin metathesis reaction with ethylene as a substrate. Going into details, the simplest dissociative pathway starts with the initial loss of PPh_3 ligand in **I**, forming the catalytically active 14e species **II**, which is predicted to be almost isoenergetic with **I**. This step requires the overcoming of a barrier of 8.7 kcal/mol.

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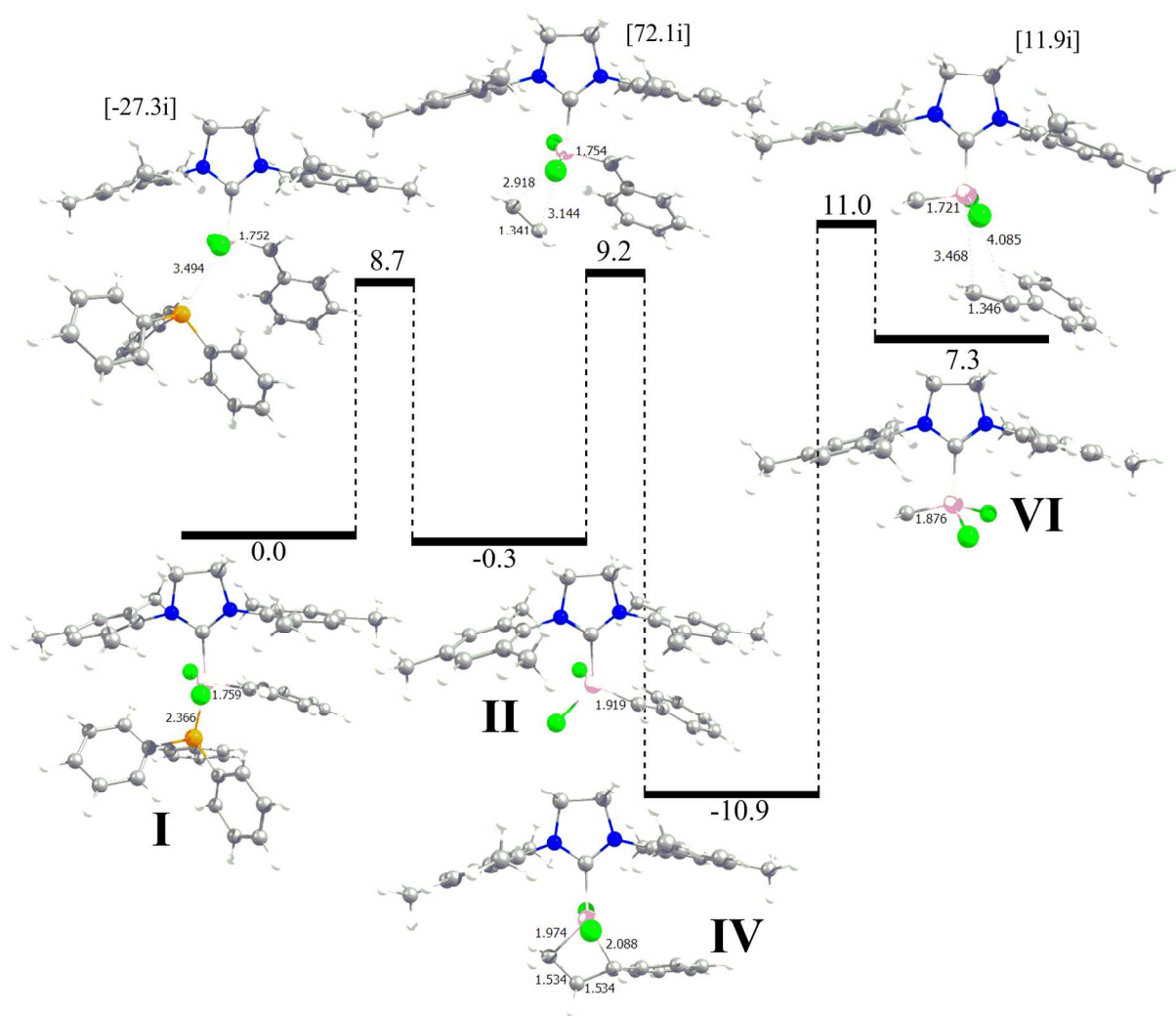


Figure 1. Computed stationary points for the olefin metathesis reaction pathway for $\text{Fe}(\text{SiMe}_3)_2(\text{=CHPh})\text{PPh}_3$ with ethylene as a substrate (free energies in kcal/mol, selected distances in Å, the imaginary frequencies characterizing the transition states structures are given in brackets).

The next step corresponds to the coordination of the olefin substrate to the metal in **II** to give the intermediate **III**, which lies 9.5 kcal/mol above **II**. However due to the low size of the entering olefin the system collapses to the more stable metallacycle intermediate **IV**, which lies 10.6 kcal/mol below **II** or 10.9 kcal/mol below **I**. The followed ring opening of metallacycle **IV** might result in the formation of another coordination intermediate **V**, but instead of the unstable intermediate **V** the alkene releases, leading to the formation of second 14e species **VI**, overcoming a barrier 1.8 kcal/mol higher in energy with respect to the **II**→**III** step. This complex **VI** is 7.3 kcal/mol higher in energy with respect to precatalyst **I**, suggesting that the overall reaction pathway is somewhat endothermic, but neither too much stable intermediates nor too high energy barrier are observed, which means that the calculated profile would be

consistent with an active catalyst. On the other hand, the analysis with a bigger olefin like methoxy-ethene revealed an exothermicity of 8.3 kcal/mol, and species **III** and **V** could be located, however being highly unstable, being 3.7 and 5.2 kcal/mol less stable than the species **II** and **VI**, respectively. It is worth mentioning that all complexes in the above studied reaction pathway exhibited singlet ground state except for the two 14e species, **II** and **VI**, which displayed a quintuplet ground state. And the metallacycle **IV** displays a triplet ground state, which might be one of the problems for the reactivity for these Fe catalysts. However, the energy window between singlet and quintuplet ground states spans only about 4.0 kcal/mol. Additionally, the septuplet spin state is predicted to be at least 17.9 kcal/mol above the singlet ground state.

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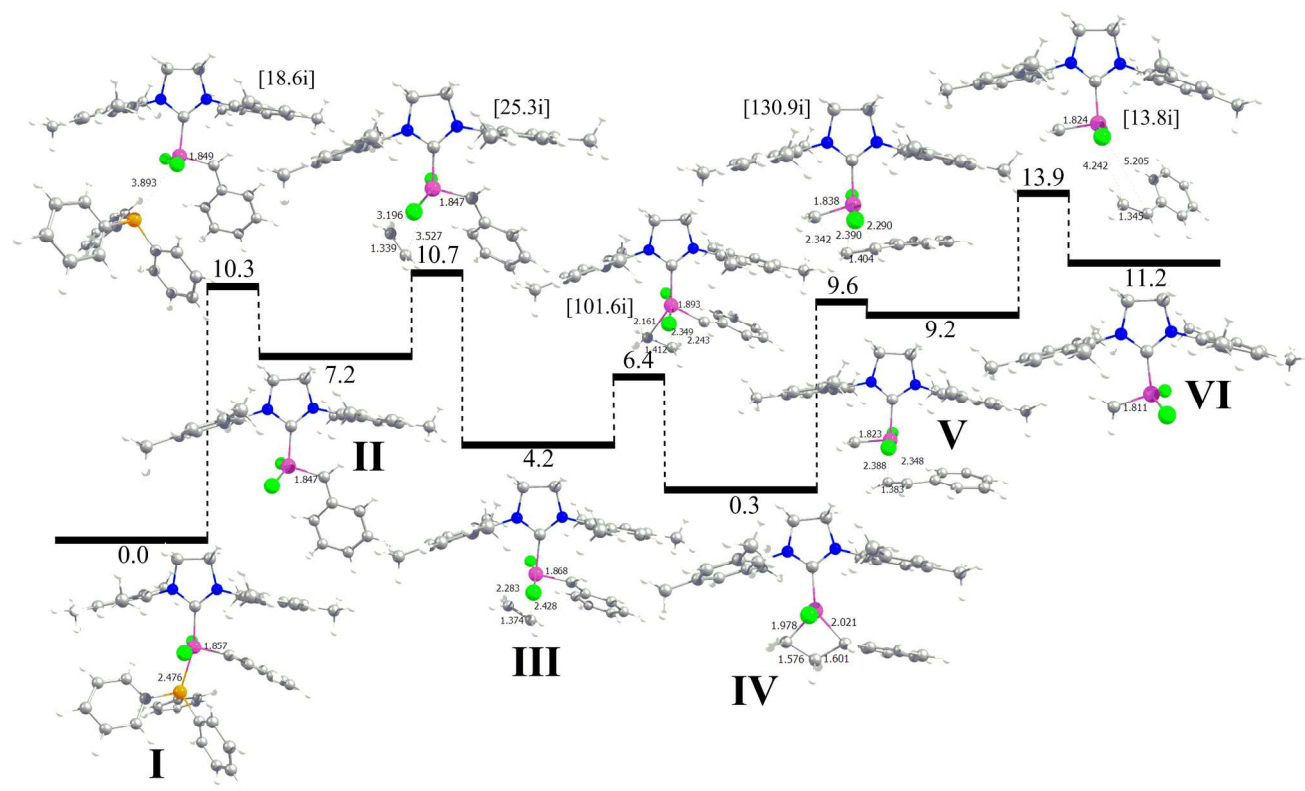


Figure 2. Computed stationary points for the olefin metathesis reaction pathway for $\text{Ru}(\text{SiMes})\text{Cl}_2(=\text{CHPh})\text{PPh}_3$ with ethylene (energies in kcal/mol, selected distances in Å, the imaginary frequencies characterizing the transition states structures are given in brackets).

For comparison, the dissociative mechanism (Figure 1) for the Ru-based analogue ($\text{Ru}(\text{SiMes})\text{Cl}_2(=\text{CHPh})\text{PPh}_3$) and the corresponding energy profile is shown in Figure 3. The main results can be summarized as follows: in case of Ru, the first three barriers are predicted to be roughly 2 kcal/mol higher in energy when compared to the respective barriers for Fe; additionally, the 14e Ru-species, **II** and **VI**, are thermodynamically less stable with respect to precatalyst **I**, while for Fe these 14e species are nearly isoenergetic (**II**) with respect to the precatalyst **I**. Overall, the inspection of Figure 2 indicates that the Ru catalyzed ethylene metathesis reaction is less exothermic in nature when compared to Fe. Of course, this can be related to the higher electrophilicity of the Fe-based precatalyst **I**, with a calculated Parr electrophilicity index $\omega = 239.4$, relative to the Ru, with $\omega = 221.4$. Accordingly, the chemical hardness of precatalyst **I**, 13.5 for Fe with respect to 12.1 for Ru, implies that the Fe-based **I** is more reactive. These theoretical findings suggest that the nature of the metal plays an important role, and that Fe-based catalysts have the potential to be more efficient than Ru-based ones. To further investigate this point, we focused on the structural details of precatalyst **I**.

The relative lower stability of species **I** for Fe with respect to Ru,

was further studied replacing the PPh_3 by Py, PMe_3 and PCy_3 ligands, being Py 8.0 and PMe_3 11.8 kcal/mol below **II**, and PCy_3 3.3 kcal/mol less stable.¹⁶ On the other hand, in case of Fe, the metal-NHC bond in precatalyst **I** is 0.09 Å shorter than in Ru. This might influence the sterics of the SiMes NHC ligand. Indeed, the analysis of the buried volume, $\%V_{\text{Bur}}$,¹⁷ of the NHC ligand gives a value of 30.5 in the Ru complex, and the slightly lower value of 30.0 in the Fe complex. Consequently, the short bond distance of Fe with the NHC pushes the mesityl aromatic rings up, promoting the interaction of an entering olefin substrate with the metal. Going further into structural details, a Mayer Bond Order (MBO) analysis^{18,19} of the Fe- and Ru-based precatalyst **I** reveals a weaker metal-P bond for Fe (0.701 for Fe vs 0.885 for Ru), a similarly strong SiMes-metal bond (0.925 for Fe vs 0.905 for Ru) and a stronger M-alkylidene bond in the case of Fe (1.793 for Fe vs 1.729 for Ru). Thus, the main structural difference is that the metal-P interaction for Fe is more labile. Consequently, the phosphine is more prone to dissociate from the iron centre in comparison to ruthenium. Finally, the last difference to point out is the higher stability of the Fe-metalacycle **IV** with respect to the corresponding Ru one, which could make its opening more difficult with Fe-catalysts.

Conclusions

In summary, we have reported the first theoretical study describing the mechanism for the Fe-based olefin metathesis reaction using DFT calculations. Differently from Ru, Fe-based catalysts display a less endothermic reaction energy profile. The differences in the thermodynamics of the metathesis reaction between Fe and Ru can be attributed to the high electrophilicity (and less chemical hardness) of the Fe-based precatalysts. Finally, our computational results substantially offer a detailed geometrical and energetic understanding of the Fe-based olefin metathesis reactions. The main message of this work is that Fe-based catalysts have a metathesis reaction profile consistent with that of a good performing catalyst, indicating that experimental efforts in this area could indeed result in a new generation of Fe-based olefin metathesis catalysts.

Computational Details

All DFT static calculations were performed at the GGA level with the Gaussian09 set of programs,²⁰ using the BP86 functional of Becke and Perdew.²¹ The electronic configuration of the molecular systems was described with the standard triple- ζ valence plus polarization basis set for H, C, N, P, and Cl (TZVP keyword in Gaussian).²² For Fe and Ru we used the small-core, quasi-relativistic Stuttgart–Dresden effective core potential, with an associated valence basis set contracted (standard SDD keywords in Gaussian09).²³ The geometry optimizations were performed without symmetry constraints, and the characterization of the located stationary points was performed by analytical frequency calculations. The reported energies include solvent effects estimated with the polarizable continuous solvation model PCM, using CH₂Cl₂ as a solvent.²⁴

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† Electronic Supplementary Information (ESI) available: Cartesian coordinates. See DOI: 10.1039/b000000x/

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