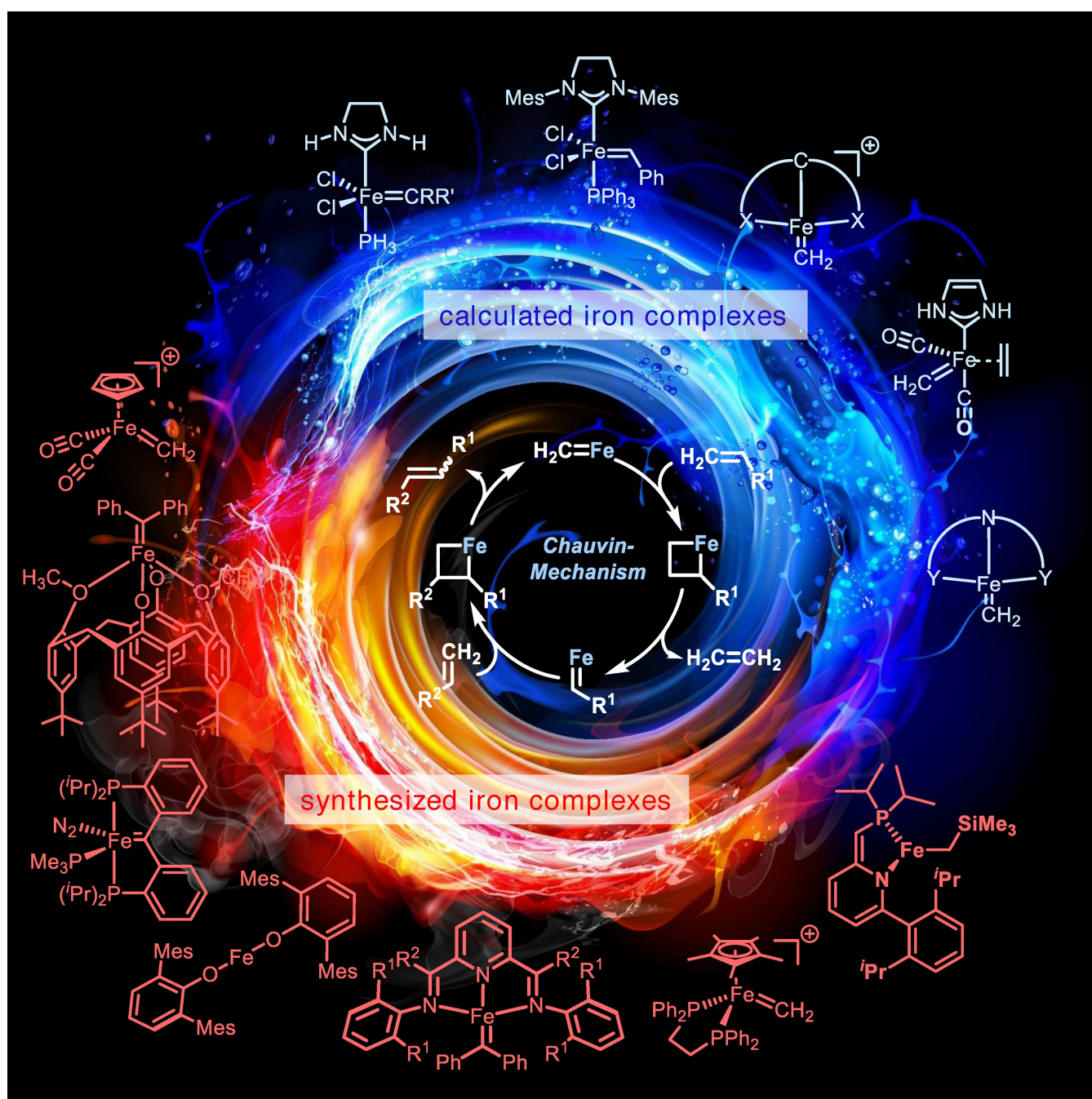


ECC **Iron-Catalyzed Olefin Metathesis: Recent Theoretical and Experimental Advances**Benedikt W. Grau,^[a] Alexander Neuhauser,^[a] Sadig Aghazada,^[b, c] Karsten Meyer,^{*,[b]} and Svetlana B. Tsogeva^{*,[a]}*Dedicated to the memory of Professor Robert H. Grubbs*

Abstract: The “metathesis reaction” is a straightforward and often metal-catalyzed chemical reaction that transforms two hydrocarbon molecules to two new hydrocarbons by exchange of molecular fragments. Alkane, alkene and alkyne metathesis have become an important tool in synthetic chemistry and have provided access to complex organic structures. Since the discovery of industrial olefin metathesis in the 1960s, many modifications have been reported; thus, increasing scope and improving reaction selectivity. Olefin metathesis catalysts based on high-valent group six elements

or Ru(IV) have been developed and improved through ligand modifications. In addition, significant effort was invested to realize olefin metathesis with a non-toxic, bio-compatible and one of the most abundant elements in the earth's crust; namely, iron. First evidences suggest that low-valent Fe(II) complexes are active in olefin metathesis. Although the latter has not been unambiguously established, this review summarizes the key advances in the field and aims to guide through the challenges.

Introduction

Convenient construction of carbon–carbon bonds is of utmost importance in synthetic chemistry.^[1] The olefin metathesis reaction is one of the most prominent and elegant tools to build double bonds. Its applicability is almost unlimited and even challenging syntheses can be handled with tailor-made catalysts.^[2] Olefin metathesis is used not only in the synthesis of simple polymers, such as polynorbornene, but also in synthetically challenging structures^[3] and pharmaceuticals,^[4] for example, Simeprevir.^[5] In 2005, Chauvin, Grubbs and Schrock were awarded with the Nobel prize in chemistry for their pioneering work on olefin metathesis.^[6] In addition to the olefin–olefin metathesis reaction, recently reported carbonyl–alkyne^[7] and carbonyl–olefin^[7b,8] metathesis reactions further expand the space of synthetically available structures. However, the latter do not follow the Chauvin mechanism and the use of different types of catalysts is required, for example, Lewis acids.

Olefin disproportionation was achieved with ill-defined heterogeneous tungsten or molybdenum catalysts.^[9] Two main

theories for olefin metathesis reaction were proposed: a pairwise mechanism (Scheme 1A) suggested by Calderon^[10] and a non-pairwise mechanism (Scheme 1B) proposed by Chauvin in 1971. The proof for the prevalence of the non-pairwise mechanism was accomplished by cross-metathesis experiments by Chauvin in 1971 and later by Katz (with cyclooctane, 2-butane and 4-octane)^[11] and by Grubbs in 1975 (depicted in Scheme 1).^[12] Deuterated and non-deuterated 1,7-octadiene were brought to reaction with the heterogeneous catalyst obtained from mixing of WCl_6 and *n*-butyl lithium and the non-heterogeneous catalyst $PhWCl_3-AlCl_3$. As the resulting cyclohexene was inactive towards metathesis, the obtained mixture of ethenes could be analyzed by gel permeation chromatography. Their ratios were found to be consistent with a non-pairwise mechanism; regardless of catalysts. It is important to mention that the individual reaction-steps are reversible, therefore, leading to the statistical yields of the desired olefins.^[6c]


In 1989, Schrock reported the structurally authenticated metallacyclobutane intermediate,^[13] a milestone in olefin metathesis catalysis, further supporting the non-pairwise mechanism (Scheme 2).^[6c,14]


Aiming at improving selectivity and achieving homogenous catalysis, Schrock reported the molybdenum-based metallocarbene **1** (Figure 1), proficient to perform metathesis as a

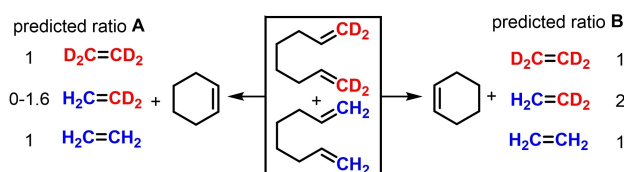
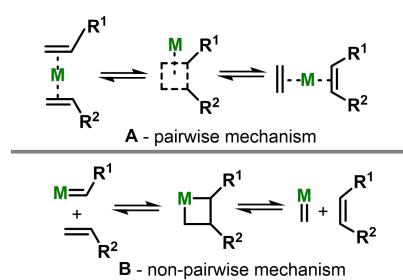
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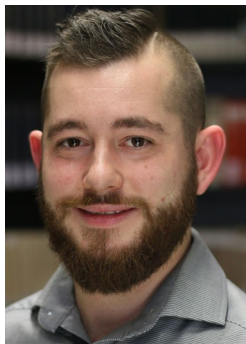
Scheme 1. Proposed alternative mechanisms for olefin metathesis reaction.

novel, well-defined catalyst.^[15] These highly active molybdenum catalysts are also highly air-sensitive. Consequently, Grubbs' more stable Ru-based catalyst (2), developed in 1992, was preferred in the organic chemistry community.^[16]

Grubbs' catalyst found a widespread application in synthesis, but the difficulty of catalyst recovery made further improvements necessary. Subsequently, in 1999, Hoveyda reported a conveniently recyclable variation of Grubbs' catalyst 4 (Figure 1).^[17]

Schrock-type catalysts, such as 1, show the highest activity towards olefin metathesis; thus, enabling metathesis with tri- or even tetra-substituted alkenes.^[6b,18] Regardless, in addition to low selectivity, these catalysts suffer from incompatibility with acids, alcohols and aldehydes. The advantages of bench-stable and functional group tolerant catalysts 2–5 comes with the lack of activity towards tri- or tetra-substituted olefines.^[19] The dissociation of one of the phosphine ligands leads to the highly reactive on-cycle 14-electron species. Consequently, second generation catalysts sporting an N-heterocyclic carbene ligand

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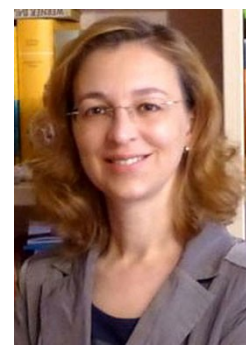
Sadig Aghazada was born in Astara (Azerbaijan) in 1990. After graduation from Lomonosov Moscow State University (Russia) in 2013 with specialist degree, he earned his Ph.D. from EPFL (Switzerland). From 2018 to 2021, he was working as a postdoctoral fellow in the Meyer lab at the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), focusing on transition metal carbene complexes. In 2021, he joined ETH Zurich as an SNSF postdoctoral fellow.



Karsten Meyer studied chemistry at the Ruhr-University of Bochum (Germany) and carried out his PhD thesis work under the direction of Professor Karl Wieghardt at the Max-Planck-Institute in Mülheim/Ruhr, receiving his Ph.D. (Dr. rer. nat., summa cum laude) in January 1998. With a DFG fellowship, Karsten proceeded to gain further research experience in the laboratory of Professor Christopher Cummins at the Massachusetts Institute of Technology (Cambridge, USA). In 2001, he was appointed to the faculty of the University of California, San Diego (UCSD) and was named an Alfred P. Sloan Fellow in 2004. In 2006, he accepted an offer (C4/W3) to be the Chair of Inorganic & General Chemistry at the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Germany. His research focuses on the synthesis of task-specific ligand architectures, their transition and actinide metal complexes for the conversion of small molecules of biological and industrial relevance as well as the development of (electro)catalysts in pre-organized materials, such as ionic liquids and ionic liquid crystals.



Svetlana B. Tsogoeva graduated with Distinction in 1995 from St. Petersburg State University, where she completed her doctoral thesis in 1998. Then, she moved to the Johann Wolfgang Goethe University, Frankfurt am Main, Germany, for postdoctoral research. In July 2000 she joined the Degussa AG Fine Chemicals Division as a research scientist. In January 2002 she was appointed a first junior professor in Germany at the Georg-August-University of Göttingen. Since February 2007, she has been professor of organic chemistry at the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Germany. Her research is currently focused on medicinal chemistry, multi-step domino processes, organocatalysis, autocatalytic transamination metathesis and Fe-catalyzed olefin metathesis.



(NHC) (3) were developed. The NHC ligand diminishes the re-association of the trans-coordinating ligand resulting in improved turnover numbers and catalytic activities even though it shows overall slower rates of activation compared to 2.^[20] Further improvements brought the introduction of an oxygen-chelate, which stabilizes the catalyst and prevents decomposition after reaction and during purification steps (see 4 and 5 in Figure 1).

As mentioned above, metathesis has many different applications, for example in polymerization processes, such as ring opening metathesis polymerization (A, *ROMP*) or acyclic diene metathesis (B, *ADMET*) (Scheme 3). Additionally, metathesis reactions are capable of yielding complex molecules by ring closing metathesis (C, *RCM*), cross metathesis (D, *CM*) and ring opening metathesis (E, *ROM*).^[4a] The cross Yne-Ene metathesis (F, *YNE-ENE*), the reaction between an alkyne and an alkene, can also be considered as a special case of cross metathesis.^[21]

Even though the current olefin metathesis catalysts provide high yields under mild conditions and short reaction times, development of a sustainable, cost efficient, non-toxic, abundant metal-based catalyst is highly desirable.^[22] One field of significant current interest relates to the substitution of ruthenium with its corresponding first-row transition metal congener. A possible candidate, bearing the features listed above, could be an iron-based catalyst, as metathesis is basically an olefin cycloaddition followed by a cycloreversion, and a multitude of iron-catalyzed cycloadditions have already been reported.^[23] While Lewis acid-catalyzed carbonyl-alkyne and carbonyl-olefin metathesis using iron compounds as catalyst already have been established, iron-catalyzed olefin-metathesis has not been realized so far^[24] and to the best of our knowledge only one review exists, where selected publications on iron catalyzed metathesis are mentioned amongst other first row transition metals.^[25] Therefore, an iron-derived carbene catalyst capable of performing olefin-olefin metathesis is highly desirable. As this field of research is still in its infancy, this review sums up the recent key developments and findings concerning iron-catalyzed metathesis. Herein, we summarize the reported attempts toward the iron-based olefin metathesis catalysis.

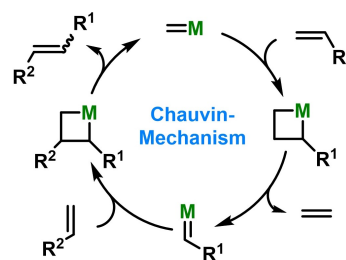
Theoretical Attempts on Iron-Catalysed Olefin Metathesis

As stated before, iron-catalyzed olefin metathesis has not been unambiguously realized yet. For the first-row transition metals, olefin cyclopropanation is preferred over metathesis. Also, due to lower bond-dissociation energies, in comparison to second and third-row transition metals, the first-row transition metal alkylidene complexes tend to transfer the alkylidene moiety.^[26] Regardless, the topic of iron-catalyzed metathesis was addressed in multiple computational studies.

In 2014, Dixon and co-workers reported a study on bond dissociation energies (BDEs) of different metal carbene complexes ($M = \text{Fe, Ru, Os}$; Carbene: $\text{CH}_2, \text{CHF}, \text{CF}_2$).^[27] This was done following their findings in olefin metathesis with Schrock-type catalysts ($M = \text{Cr, Mo, W}$), where CHF or CF_2 carbenes destabilized the triplet state of the carbene, leading to a complex unfit for catalyzing metathesis reactions.^[28] Their model system was based on the Grubbs II catalyst and five key intermediate structures were analyzed using high level CCSD(T) method with additional corrections to obtain near level accuracy (Scheme 4):

Whereas Ru and Os complexes unambiguously possess a singlet ground state, with large singlet-triplet and singlet-quintet gaps, the Fe complex features an open-shell ground state with a singlet state high in energy. Therefore, the ground states for iron complexes are mainly triplets or quintets, leading to cyclopropanation rather than the desired cycloreversion for this model structure.^[27]

The dissociation of one of the ancillary ligands is believed to lead to the 14-valence electron active species and, thus, $M\text{-PH}_3$ BDEs were computed to increase activity in the order $M = \text{Fe} <$



Scheme 2. Simplified reaction cycle of the Chauvin mechanism.

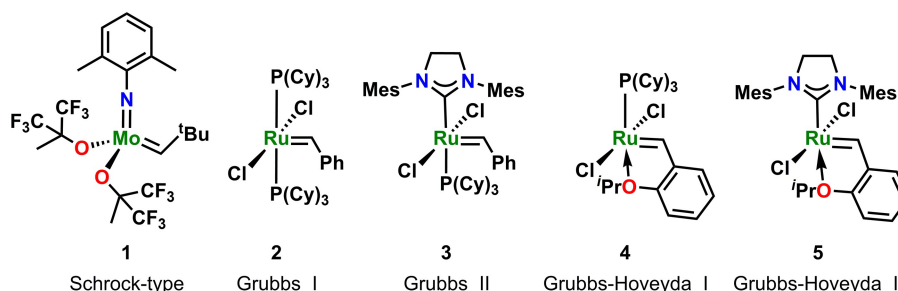
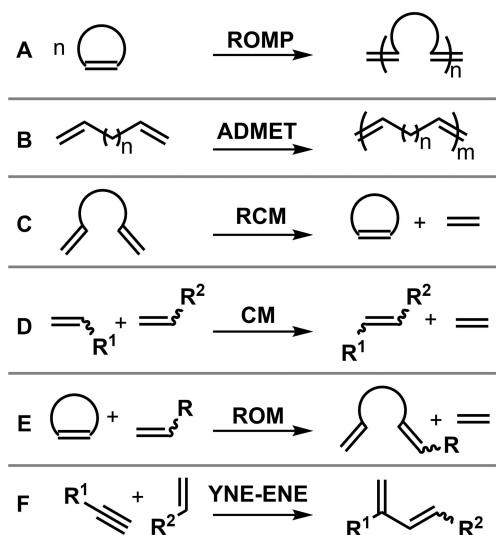


Figure 1. Overview of different catalysts employed in olefin metathesis.



Scheme 3. Summary of olefin metathesis variations.

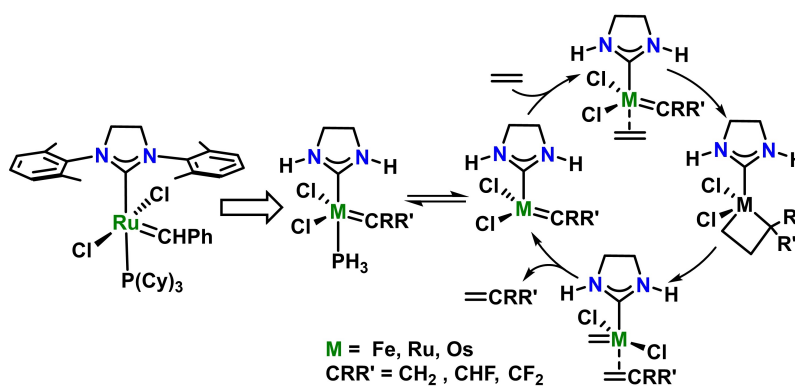
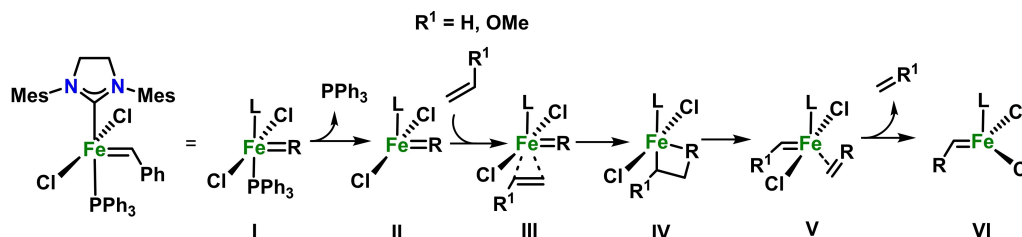
Ru < Os. For the iron methylene complex $[\text{FeCl}_2(\text{CH}_2)(\text{NHC})(\text{PH}_3)]$, PH_3 has the lowest BDE of 10.7 kcal/mol, followed by the NHC (42.9 kcal/mol) and the methylene (44.5 kcal/mol). Substitution of the methylene's one hydrogen with fluorine ($=\text{CHF}$) increases the BDEs of PH_3 (11.6 kcal/mol) and the NHC (43.9 kcal/mol) slightly, but decreases the BDE for the alkylidene to 38.5 kcal/mol. Difluoromethylene CF_2 leads to an overall decrease in BDEs but the order remains the same as with monofluoromethylene CHF ($\text{BDE}_{\text{PH}_3} = 6.2$ kcal/mol; $\text{BDE}_{\text{NHC}} =$

37.6 kcal and $\text{BDE}_{\text{CF}_2} = 17.2$ kcal/mol). It is important to mention that the low BDEs for the bonding of C_2H_4 to iron indicate that ethylene would be only weakly coordinated to the metal center. Figure 2 illustrates the reaction profile for the olefin cycloaddition to the aforementioned complexes:

All of the calculated Ru and Os complexes exhibit singlet ground states. For the iron complexes, the identification of the exact ground spin state was challenging due to the small energy differences between singlet, triplet and quintet states.^[29] For the calculations concerning different substituted methylene derivatives, the cycloaddition step was shown to be highly endothermic, which is another indication for the low performance of the iron-based catalyst. However, this could also mean that – instead of electron withdrawing groups – electron releasing groups on the alkylidene moiety are needed to render the cycloaddition less endothermic.

In contrast to the reaction profile calculated for the Ru and Os model complexes, which not only form an energetically more stable olefin complex, but also show only a slight increase in energy when going from structure III to IV (Figure 2, top), the metallacyclobutane formation is a highly endothermic process for the Fe model complex. Additionally problematic, the step from the π - to cis-complex (Figure 2, bottom III to IV) becomes endothermic; hence, rendering the iron system un-fit for olefin metathesis.

Also in 2014, Poater and co-workers reported static DFT calculations for Grubbs-type iron complexes.^[22a] For this study, less simplified model structures, analogous to those addressed by Dixon and co-workers, were calculated (Scheme 5), including their corresponding transition states.

Scheme 4. Calculated reaction steps and intermediates by Dixon.^[27]Scheme 5. Metathesis reaction steps as calculated by Poater and co-workers.^[22a]

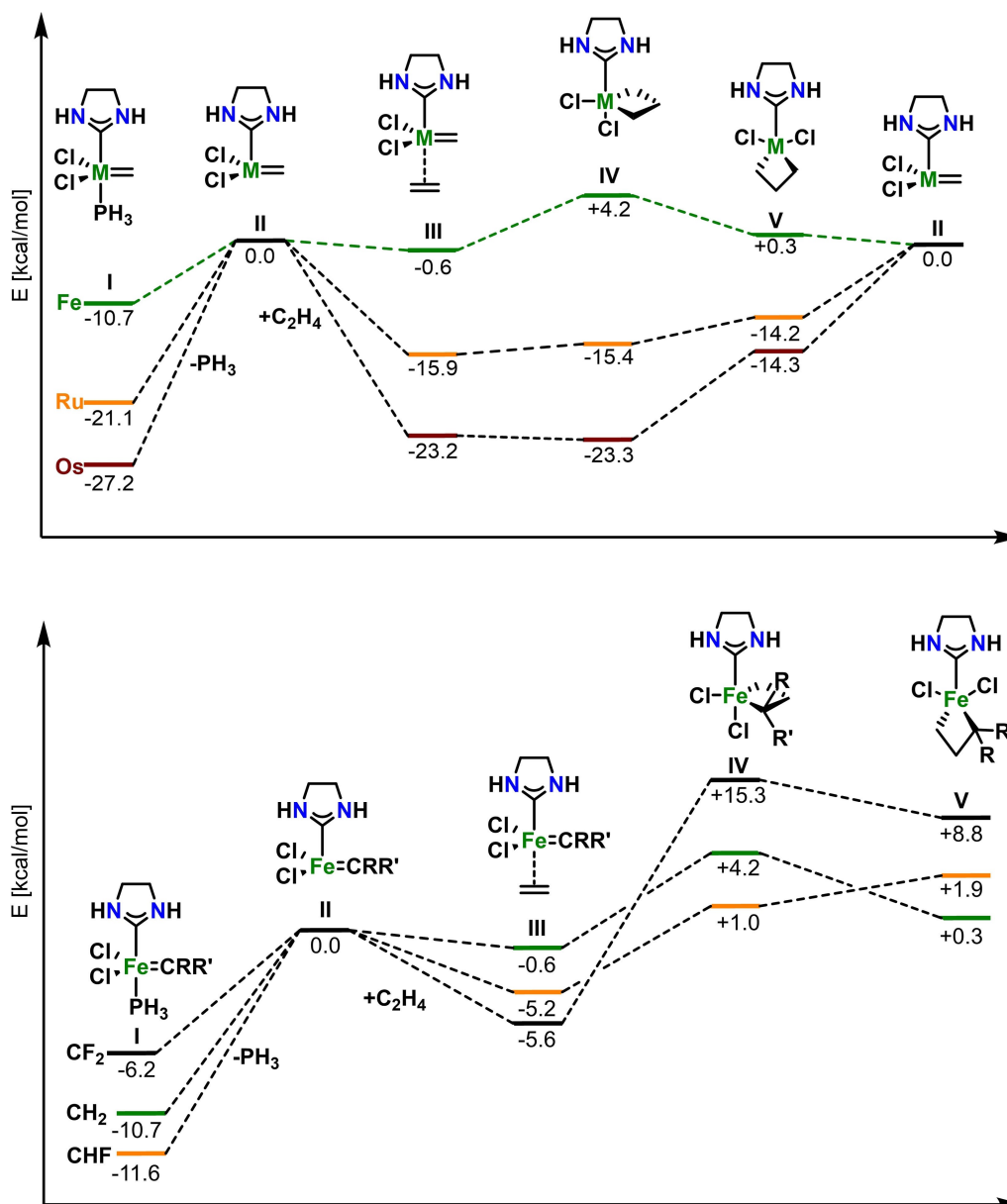


Figure 2. Energy profile of formation of Grubbs-type complexes with different metal centers, calculated at the CCSD(T)/aD level of theory with ΔE_{ZPE} (BLYP/aD) (top), and different carbenes, calculated with CCSD(T)/aD level with energies at 0 K (bottom).^[27]

The reaction profile illustrated in Figure 3 summarizes the obtained results. In the ground state, all calculated structures were found to have a singlet electronic state, except the two 14-valence electron species II and IV which have a quintet multiplicity.

The structure of species III (Scheme 5) was not stable, collapsing directly to trans-metallacycle IV. Additionally, ring opening did not lead to the expected π -coordinated complex V, but directly to VI. As the reaction profile does not contain stable intermediates, nor high energy barriers, the calculated profile could be consistent with an active catalyst, even though it is slightly endothermic.

In a subsequent work, the first part of the catalytic cycle with methoxyethene was investigated.^[30] The calculated reac-

tion mechanism with its intermediates is the same as the one depicted in Figure 3. By calculating the geometries of the optimized structures I–VI and their respective transition states, another reaction energy profile was obtained, which is shown in Figure 4:

Poater and co-workers concluded that not only the activation mechanism of the iron catalyst is similar to the Ru-based mechanism, starting with the initial dissociation of PPh₃, but that these two systems perform through similar reaction profiles as well.

Solans-Monfort and co-workers studied the influence of various ligands on the metathesis reaction and the most common side reaction for transition metals, namely the cyclo-

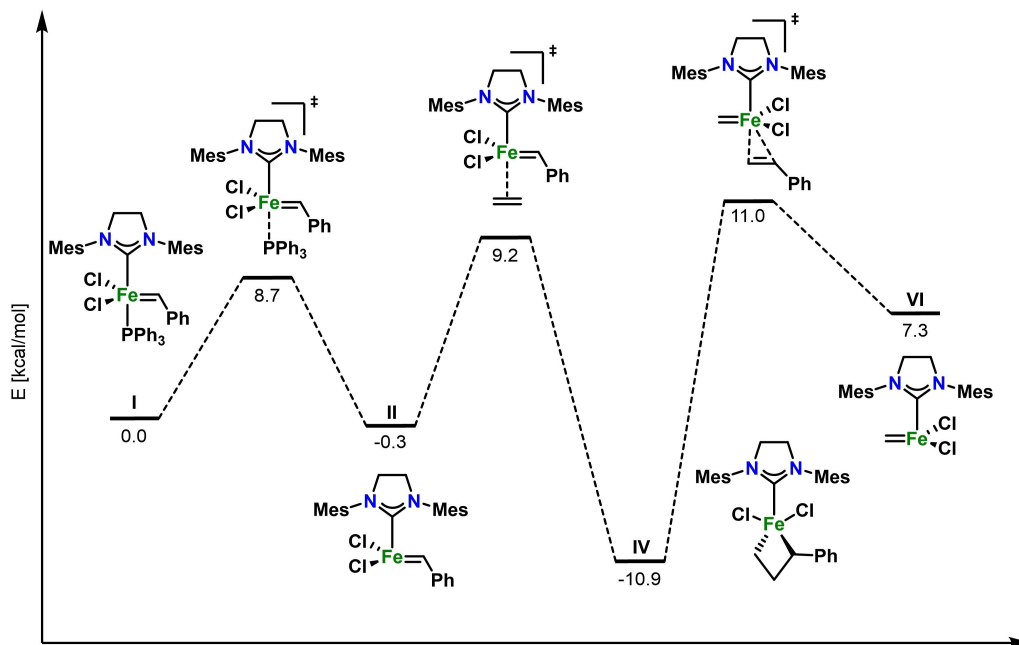


Figure 3. Reaction pathway computed by Poater and co-workers.^[22a]

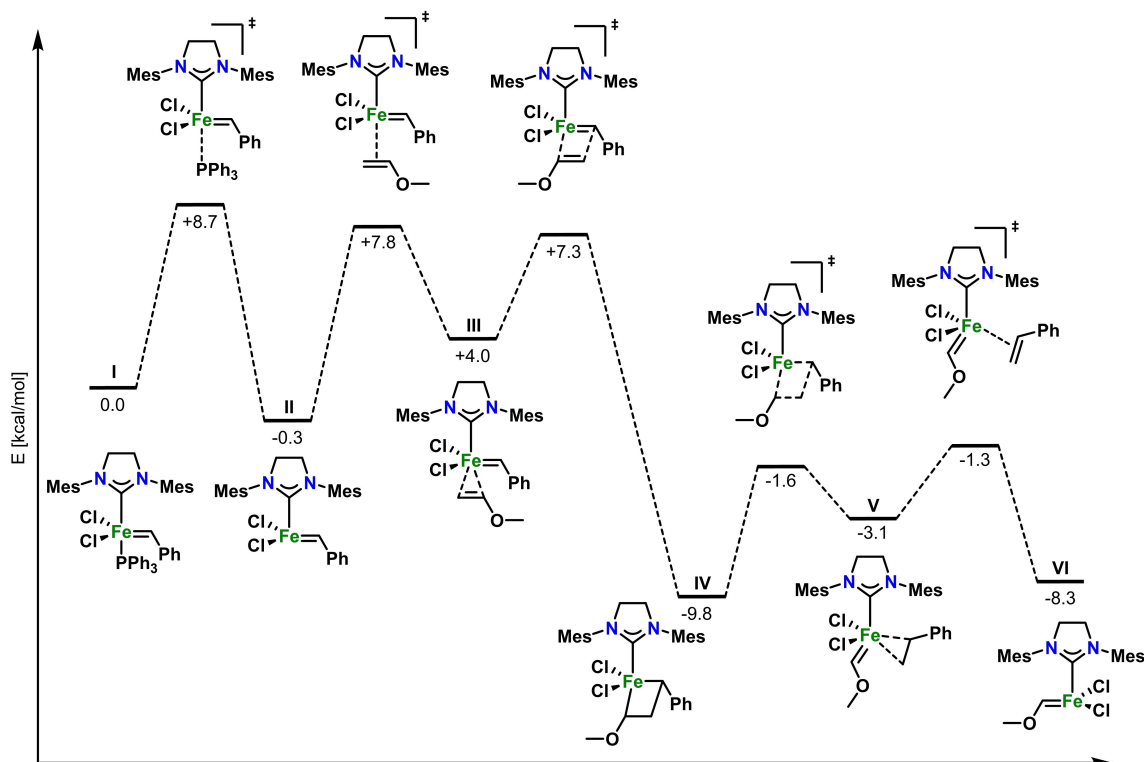
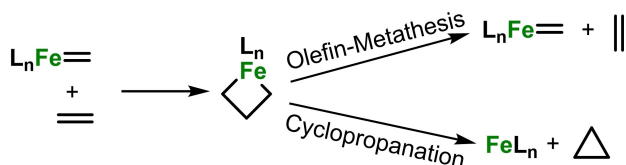


Figure 4. Reaction pathway including transition states as calculated by Poater and co-workers.^[30]

propanation reaction (Scheme 6),^[31] using DFT(OPBE)-D2 level of theory.^[26]

Several model iron complexes, some with known ligands, were compared to the reference system consisting of the second-generation Grubbs catalyst. Calculation of the reaction

energy profile for the reference Ru catalyst showed that cyclopropanation is endergonic and disfavored, if there is no spin-crossing to the triplet state (Figure 5). For the iron analogs, significant structural differences between the singlet state (trigonal bipyramidal (TBP) geometry) and the triplet state



Scheme 6. Metathesis vs. the cyclopropanation side reaction for $n=3$.^[26]

(disordered square pyramidal (SP) geometry) of the metallacyclobutane intermediate were computed. Therefore, tetra-coordinated iron (IV) complexes with different ligands (Figure 6) were designed and their reaction energy profiles were studied *in silico*. Rigid tridentate chelating ligands with strong σ -donating groups were found to be the most promising in destabilizing the triplet state and favoring the singlet ground state.

The two main benefits are, first, the stabilization of the singlet state accompanied by a strengthening of the $M=CH_2$ bond, thus disfavoring the cyclopropanation reaction. Calculations for **6** revealed a similar reaction energy profile as found for the Grubbs catalyst, which may provide access to iron-catalyzed olefin metathesis if spin crossing to the triplet-state is avoided (Figure 5b). Secondly, the importance of σ -donors and the geometry of ligands are stressed, which might be key to a successful design of Fe catalysts active in olefin metathesis.

Inspired by reports of low-valent Fe-catalyzed [2+2] cycloadditions,^[23b] a 2017 theoretical study by Mauksch and Tsogoeva indicated that low oxidation state Fe(II), rather than Fe(IV) complexes, with the general structure $L_3Fe=CR_2$, may favor energetically the singlet over the triplet state in both carbene and metallacyclobutane complexes, therefore enabling facile olefin metathesis.^[32] To stabilize the implied singlet state of iron, ligands bearing both strong σ -donating as well as π -accepting abilities, for example, CO (as well as Fischer-type and N-heterocyclic carbenes), were employed, as in the trigonal-bipyramidal Fe(II) complex **10**, depicted in Figure 7. In structures of this type, the closed-shell singlet ($S=0$) ground state is responsible for the suppression of the undesired cyclopropanation side reaction. Please note, that the carbene is always considered a dianionic ligand herein.

As the methylidene carbon must still be nucleophilic enough, as in Schrock-type carbenes, to allow metallacyclobutane formation (as this involves formation of a carbon-carbon bond), the resulting complexes assume an intermediate position between the extremes of Fischer and Schrock carbenes.

Electron exchange correlation generally favors triplet over singlet species,^[33] but this is true in particular for B3LYP, which contains the hybrid B3 exchange functional.^[34] Nevertheless, singlet and triplet state metallacyclobutane species are already very close in energy at B3LYP (Figure 8) and a singlet with pseudo-octahedral geometry was found being even lower in energy than the triplet.^[32] Moreover, calculations employing the BP86 density functional with a different (B88) exchange term, or with the OLYP functional, containing the OPTX exchange,^[35] also applied by Solans-Montfort and co-workers and by Truhlar

and co-workers (see below), resulted in a sizable energetic preference of all investigated ($S=0$) and closed-shell singlet with respect to high-spin ($S=1$) triplet state complexes and for all reaction steps.^[32] Cyclopropanation also possesses high calculated energy barriers on the singlet potential energy surface and, consequently, [2+2] cycloreversion and therefore metathesis, is kinetically preferred. In conclusion, low-valent and low-spin (especially closed-shell) Fe(II)-complexes could provide an alternative to the previously investigated Fe(IV) complexes, which are often charged complexes and are difficult to prepare. The low barrier to cycloreversion has been linked by the authors to the (Craig-Möbius) aromaticity of the respective closed-shell (orbital symmetry allowed) transition state structure.^[32]

A more recent report from Solans-Monfort and co-workers summarized the *in silico* study of selected penta- (rather than tetra-) coordinated iron complexes with regards to their proficiency in olefin metathesis (Figure 9).^[36]

First, model complexes with previously established ligands were examined for their ability to catalyze metathesis:

Ligands in complexes **11** and **12** were used to stabilize high-valent oxo-complexes by Costas and co-workers.^[37] The ligand of complex **13** is a simplified version of the TIMEN ligand system used to stabilize an Fe(IV) nitride complex by Meyer and co-workers.^[38] A Ni(II/III) complex of the ligand depicted in complex **14** was used for C–O bond formation in aryl hydroxylation and methoxylations.^[39] Unfavorably, the methylidene complexes illustrated in Figure 9 and their metallacyclobutane intermediates were computed to have high-spin ground states, thus favoring cyclopropanation over olefin metathesis. Therefore, the authors decided to explore how the reactivity of Fe(IV) complexes is influenced by ligand flexibility, by σ -donating abilities of the ligands and by the oxidation state of the iron center. Concerning the ligand flexibility, the authors suggested, despite their own observation that modifications influencing ligand flexibility are not favorable, that rigid chelating ligands may stabilize the carbene singlet state and might therefore partly suppress alkene cyclopropanation. Furthermore, the authors showed that high σ -donating abilities of the supporting chelates results in the stabilization of the singlet state, which is understood as a significant destabilization of an iron d-orbital pointing towards the C_β of the metallacycle, hinting at a potentially general strategy for achieving such a singlet ground state. Additionally, neutral oxygen ligands *trans* to the carbene moiety, such as a furan, are proposed to disfavor alkene cyclopropanation, without destabilizing the singlet ground state. Based on this study, the most promising candidates are depicted in Figure 10:

Especially, 5-coordinate Fe(IV) complex **17** was mentioned as the most promising candidate, possessing a reaction energy profile reminiscent of that of a second generation Grubbs catalyst. Unfortunately, all of the selected complexes do appear to prefer cyclopropanation over olefin metathesis kinetically. For the square-pyramidal Fe(II) complexes, this was attributed to their „closed-shell“ 18 valence electron nature, which impairs olefin coordination, resulting in a high activation barrier for

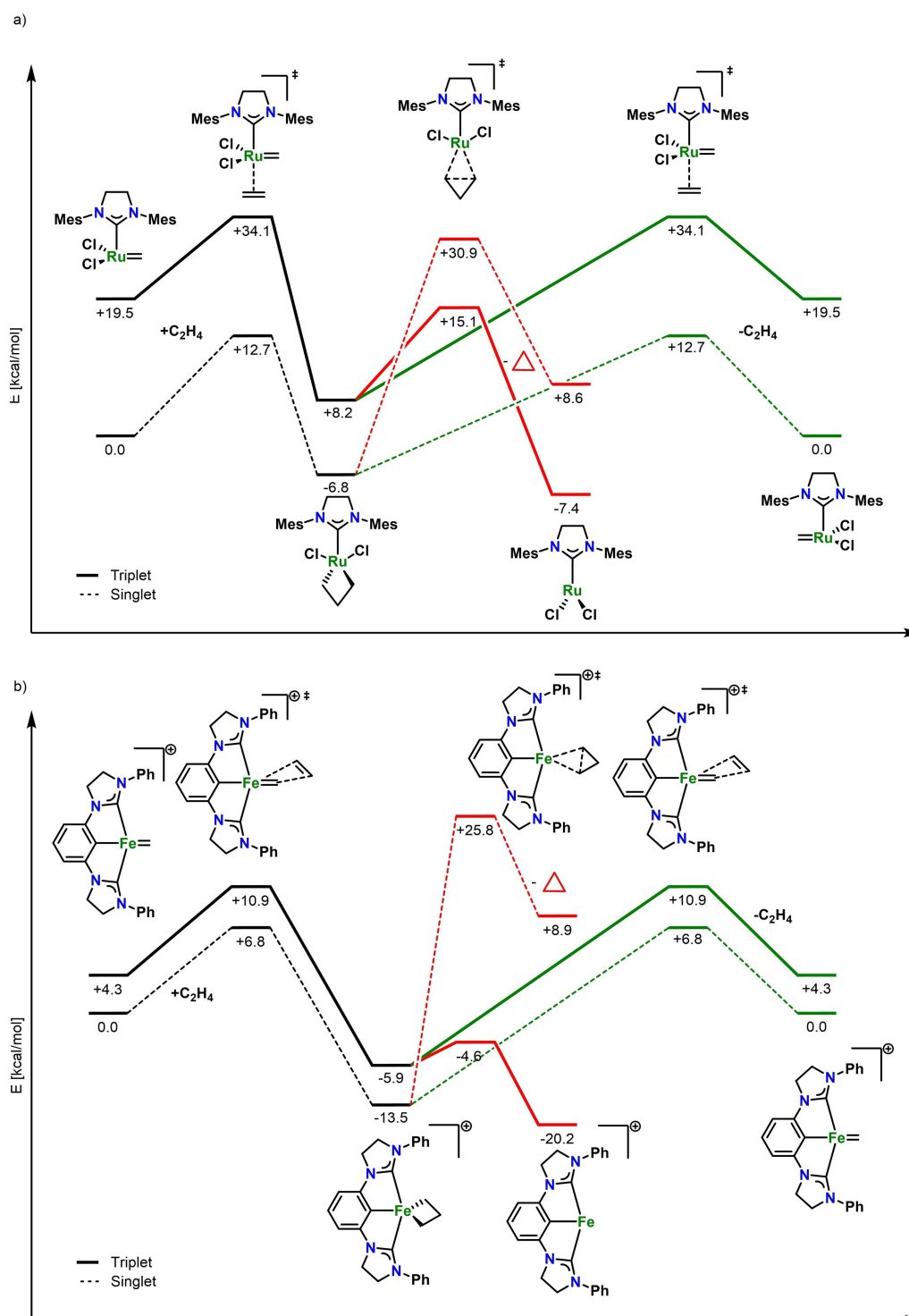


Figure 5. Overview of charged and neutral iron (IV) complexes investigated by Solans-Monfort and co-workers.^[26]

cycloreversion, while the Fe(IV) metallacyclobutane complexes do not possess singlet ground states.

Following the works by Solans-Monfort and co-workers as well as that by Mauksch and Tsogoeva, Yang and Truhlar further addressed different types of chelating pincer ligands, calculating the electron density and formal negative charge on the iron

center in low-valent iron complexes.^[40] To predict whether the singlet or the triplet state is preferred, they defined a δ -value, expressing the difference in the free energies of activation for the cyclopropanation minus the cycloreversion. The results suggest that higher δ -values imply a higher probability for the cycloreversion and lower, more negative δ -values indicate a

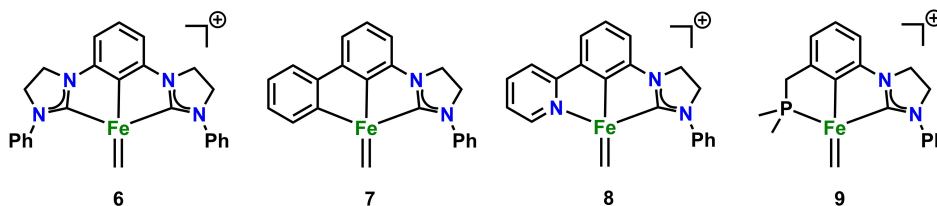


Figure 6. Reaction energy profiles computed by Solans-Monfort and co-workers:^[26] a) with reference Grubbs-type Ru(IV) catalyst; b) with tridentate σ -donating ligand Fe(IV) catalyst.

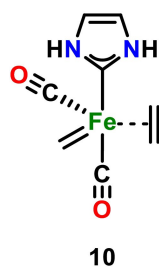


Figure 7. Structure of a TBP Fe(II) low spin closed-shell model metathesis catalyst as proposed by Mauksch and Tsogoeva.^[32]

higher probability for the cyclopropanation. A linear correlation between a higher probability for cyclopropanation and a more positive partial charge on the Fe-center of the metallacyclobutane complex was observed. The most promising ligands, according to these calculations, are Kirchner's PNP- (18) or CNC-type ligands (19), as used in the groups of Danopoulos^[41] and Crabtree.^[42] PDI (bis(imido)pyridine)-type ligands (20), however, exhibited a negative δ -value, making the cyclopropanation more likely to occur (Figure 11).

A full catalytic cycle with all relevant intermediates and transition states was calculated with the (unrestricted) OPBE

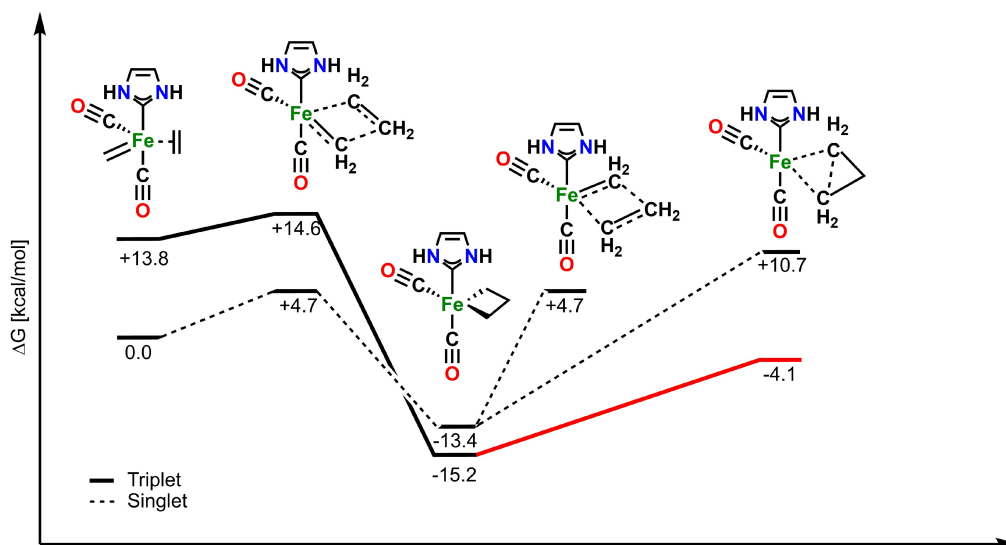


Figure 8. Reaction energy profile for metathesis vs. cyclopropanation pathways for TBP model complex 10, computed on singlet and triplet potential energy surface by Mauksch and Tsogoeva.^[32] At OLYP/6-31G* level, metallacyclobutane triplet is 8.7 kcal/mol (12.1 kcal/mol at BP86) higher in energy than closed-shell singlet.

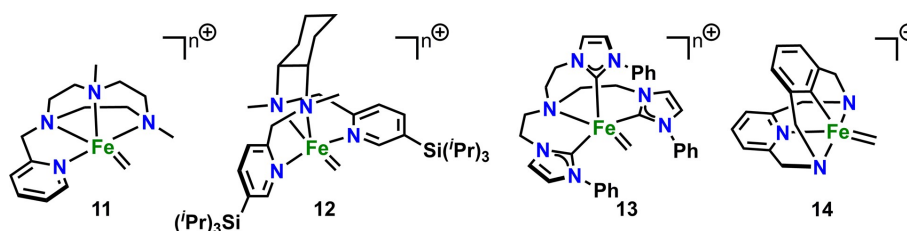


Figure 9. Examples of iron (IV) ($n=2$) and iron (II) ($n=0$) complexes studied by Solans-Monfort and co-workers.^[36]

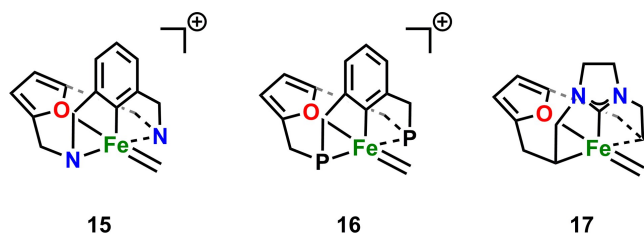


Figure 10. Furan-derived Fe(IV) complexes as proposed by Solans-Monfort and co-workers.^[36]

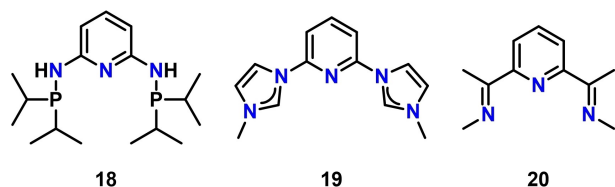


Figure 11. Examples of ligands studied computationally by Yang and Truhlar to be employed in their low-spin Fe(II) complexes.^[40]

functional, containing OPTX exchange, which was shown to give promising results for high-spin iron complexes^[43] and for the CNC-type ligand 19, indeed showing that the singlet state is lower in energy for all relevant steps for the tetra-coordinated Fe(II) catalyst and that the transition state for the cyclopropanation has a higher Gibbs free energy than that for the desired cycloreversion (Figure 12). Even though computations were carried out without spin-restriction, spin contamination was found to be below 5% for all investigated singlet species, which are therefore effectively closed-shell systems.

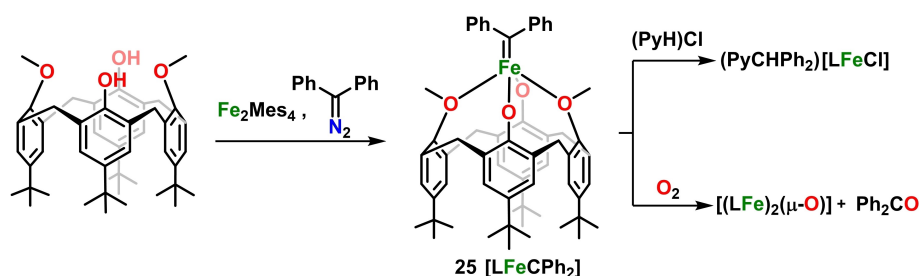
The authors even propose a route to the iron alkylidene complex starting from the $[\text{Fe}(\text{CNC})(\text{N}_2)_2]$ precursor, which can react with an alkyne to the respective alkylidene target via tautomerization. Unfortunately, the formation of this alkylidene complex from an alkyne is not supported experimentally and, so far, there are no reports showing the successful synthesis of the $\text{Fe}(\text{CNC})(=\text{CHR})$ complex (Figure 13).

Synthetic Attempts on Iron-Catalyzed Olefin Metathesis

In 1966, Pettit and Jolly reported that upon protonolysis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CH}_2\text{OMe})]$, the iron methylene $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CH}_2)]^+$ (21) intermediate effects the cyclopropanation of olefines.^[44] Later, low temperature synthesis and low-temperature NMR studies by Brookhart further suggested the formation of complexes 22 and 23 thus, supporting Pettit's initial proposition.^[45] Brookhart also showed that the parent methylene can be stabilized at cryogenic conditions using a more electron-releasing ligand – 1,2-bis(diphenylphosphino)ethane (dppe) instead of carbonyls, while Lapinte reported a room temperature stable iron methylene complex sporting the methylated Cp^* (Cp^* = pentamethylcyclopentadienyl) and dppe ancillary ligands.^[46,47] Only recently, Meyer and co-workers presented an unambiguous proof of the formation of a diamagnetic iron methylene complex, namely $[(\text{Cp}^*)(\text{dppe})\text{Fe}=\text{CH}_2]$ (24, see Figure 14).^[48] The thorough XRD structural analysis, together with a ^{57}Fe Mössbauer and computational study, suggest an iron methylene complex exhibiting a Fischer-type electronic structure; yet, with considerable alkylidene character. Both σ - and π -bonds between the iron center and the methylene ligand are highly covalent. This results in substantial oxidation of the iron center and, therefore, a low ^{57}Fe Mössbauer isomer shift value. Yet, no olefin metathesis was reported with any of Pettit-type iron alkylidene complexes.

In 1997, Floriani et al. reported the synthesis of the Fe(II)-diphenylmethylene complex 25, stabilized by a calix[4]arene ligand.^[49] This complex exhibits a high spin state, a high thermal stability and is resistant toward hydrolysis. Regardless, strong iron-carbene bonding, cleavage of which can only be achieved by acids or O_2 , makes 25 not suitable for olefin metathesis (Scheme 7).

Grubbs, following the discovery of the first generation of Ru-based catalysts for metathesis, reported the attempts to synthesize the Fe-based analogue by reacting $\text{FeCl}_2(\text{PMe}_2\text{Ph})_2$ with ethyl diazoacetate or diphenyldiazomethane.^[50] These reactions do not lead to the desired iron carbene complexes but, instead, the diazoalkanes insert into the Fe–P bond without the release of N_2 ; thus, forming the respective phosphazine complex (26, 27, 28, see Figure 15).



Scheme 7. Structure, synthesis and reactivity of Floriani's iron carbene complex.^[49]

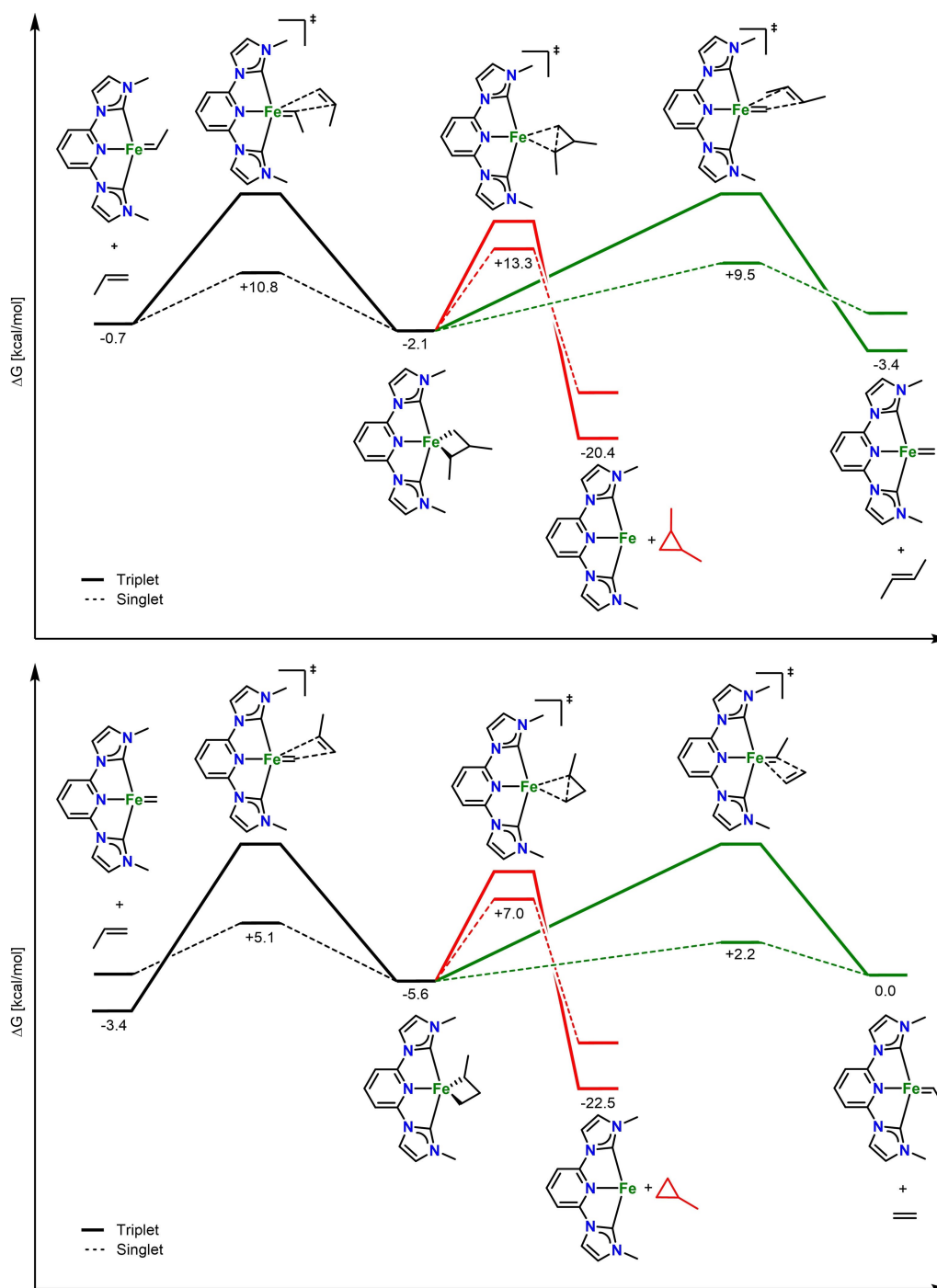


Figure 12. Reaction energy profile of a tetra-coordinated Fe(II) complex with CNC ligand as calculated by Yang and Truhlar.^[40]

More recently, Chirik^[51] and co-workers reported the synthesis of the iron diphenylmethylene complex $[(^R\text{PDI})\text{Fe}(\text{CPh}_2)]$ (**32**) starting from the dimer $[(^R\text{PDI})\text{Fe}(\text{N}_2)]_2(\mu_2\text{-N}_2)$ (**31**) and diphenyldiazomethane. Complex **32** was described to have a high-spin Fe(II) center antiferromagnetically coupled to two radicals on the bis(imino)pyridine and carbene ligands, which results in an $S=1$ ground state. Probing the reactivity of complex **32** towards various olefins at room temperature did not result in any reaction, neither metathesis nor cyclopropana-

tion and heating these reactions mixtures to 85 °C resulted in its decomposition (Scheme 8).

In 2015, Wolczanski, Meyer and co-workers introduced a series of formally Fe(IV) complexes^[52] (**33**, **34** and **35**, Figure 16).^[52]

The low Mössbauer isomer shift value obtained for complex **34** initially suggests a high oxidation state iron center. However, the authors advocate that the low isomer shift could also originate from the short and notably covalent Fe–carbene

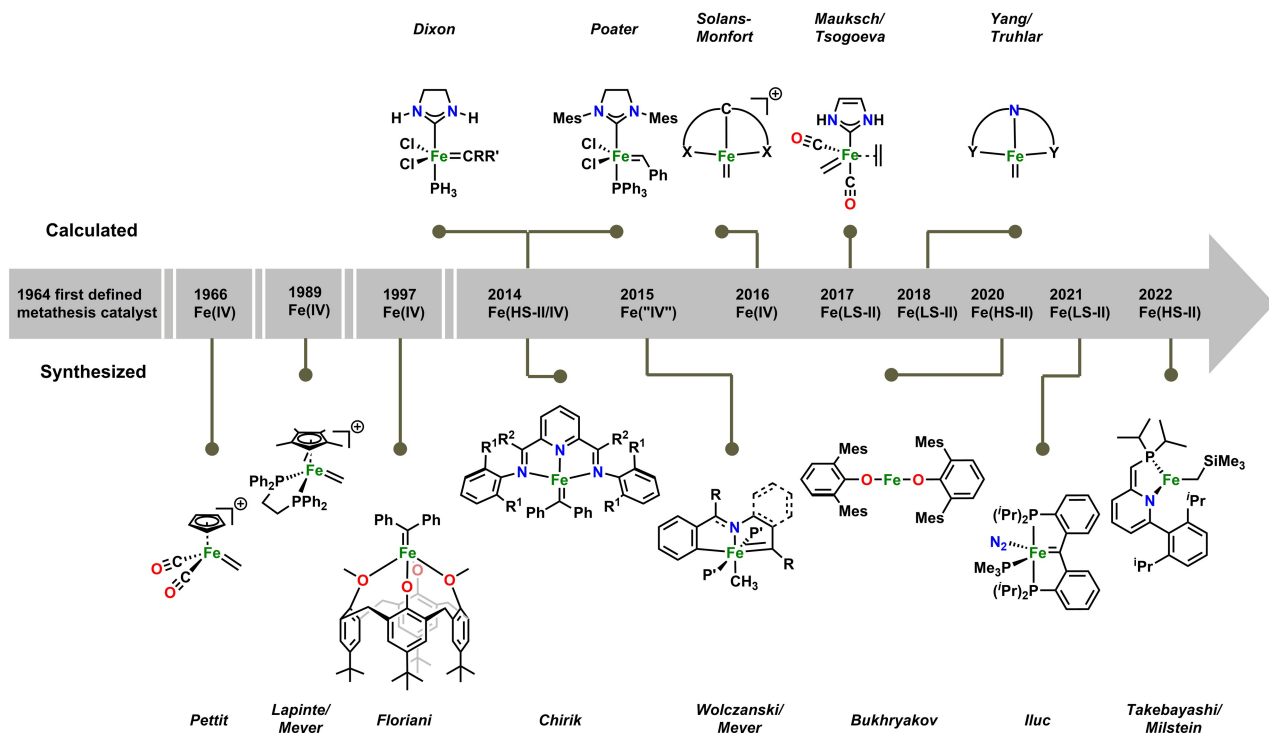


Figure 13. Overview of the most promising calculated and synthesized iron complexes as olefin metathesis catalysts over the years (HS = high spin, LS = low spin).

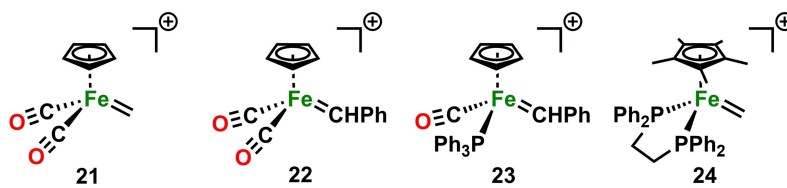


Figure 14. Proposed complex 21 of Pettit and Jolly, Brookhart's complexes 22 and 23 and Lapinte's complex 24.

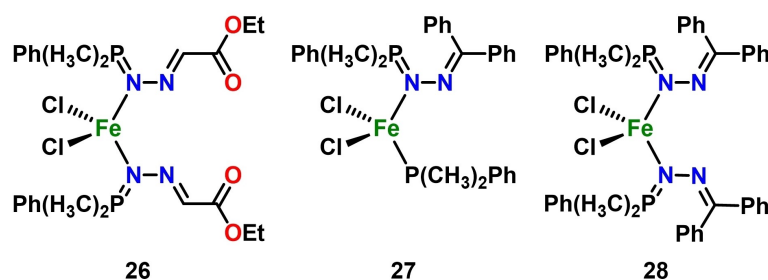
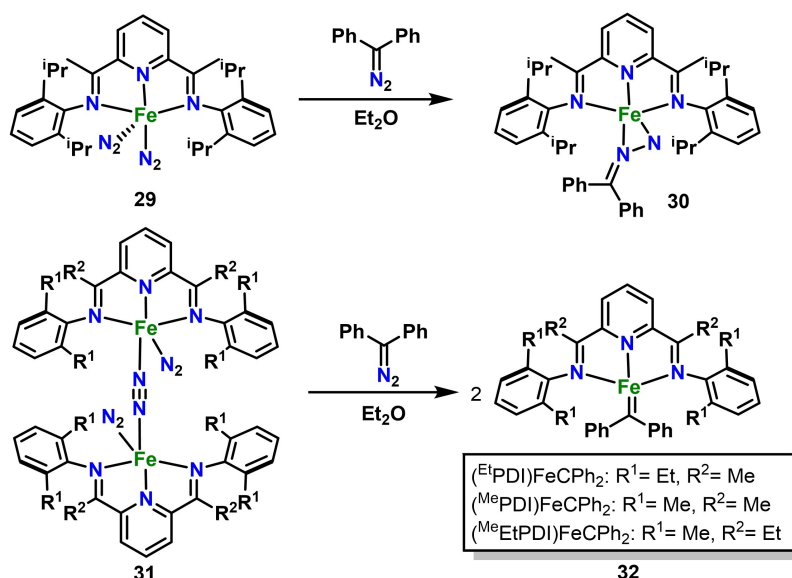


Figure 15. Phosphazine complexes 26, 27 and 28 reported by Grubbs.^[50]

bond. The positive charge of the complex could cause the contraction of *d* orbitals, which, in turn, may inhibit metathesis reactivity. Subsequently, Wolczanski and co-workers introduced a series of uncharged "Fe(IV)" alkylidenes by treating **34** (depicted in Figure 16) with different nucleophiles and converting the coordinated imine to the amide.^[52d,e]

Unfortunately, charge neutral complexes (Figure 17) are also inactive in olefin metathesis. Arguably, strong Fe–PMe₃ bonding in complexes **37**, **38** and **39** prevents ligand dissociation and formation of the active species. Even complex **36**, bearing a dinitrogen molecule as a possibly labile ligand, was reportedly inactive. While complexes **36–39** have, computationally, Fe(II) character and, hence, the corresponding orbital for olefin



Scheme 8. Unsuccessful (top) and successful (bottom) synthesis of Chirik's Fe(II) carbene.^[51]

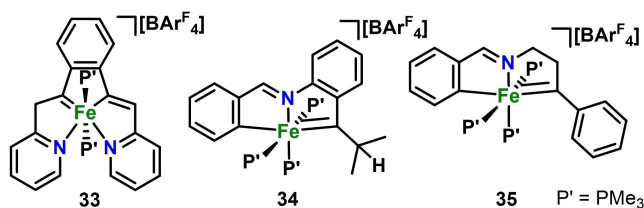


Figure 16. Iron complexes synthesized by Wolczanski, Meyer and co-workers.^[52]

coordination and metallacyclobutane formation is principally available, the isopropyl group seems to thwart the catalytic activity as it hinders the olefins' approach.

With these results in hand, a complex bearing a hydrogen instead of an isopropyl group, yielding the corresponding Fe(II)=CHR species, was further investigated (Figure 18, top). Calculations presented in this work also underline that

previously synthesized complexes by Wolczanski and co-workers have mainly Fe(II) character due to resonance stabilization (Figure 18, bottom). Yet again, the new Fe=CHR complex was inactive in olefin metathesis reaction. The resulting complex could be considered an Fe(II) vinyl complex with a cationic iron center and an anionic chelate with highly delocalized charge.

In conclusion, the synthesized compounds possess mainly a d^6 electron configuration at the central iron ion and no activity towards olefin metathesis.

The first successful iron-catalyzed polymerization of norbornene, starting from a well-defined precatalyst complex, was achieved in 2021 by the group of Bukhryakov.^[53] With a high spin iron complex **40** (Scheme 9), featuring two bulky, monodentate alkoxide ligands, norbornene ROMP with 16% conversion was achieved. Surprisingly, after addition of various alkylidene precursors known to catalyze ROMP with transition metals, such as Ru, W or Au, the conversion of the monomer

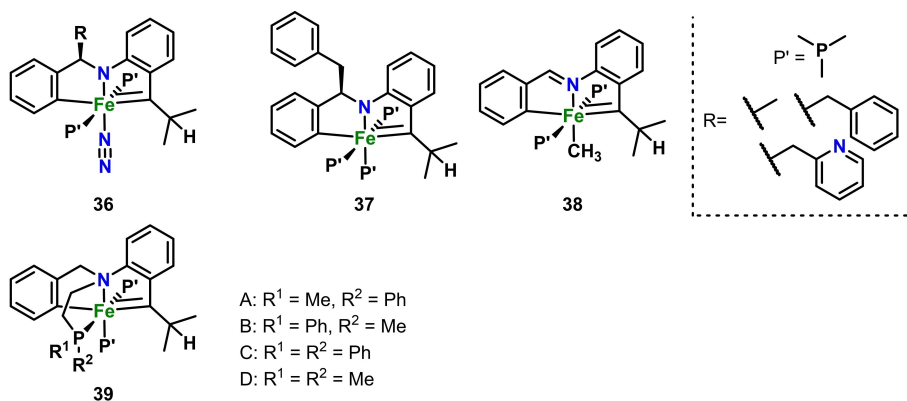


Figure 17. Neutral "Fe(IV)"-complexes synthesized by Wolczanski and co-workers.^[52d,e]

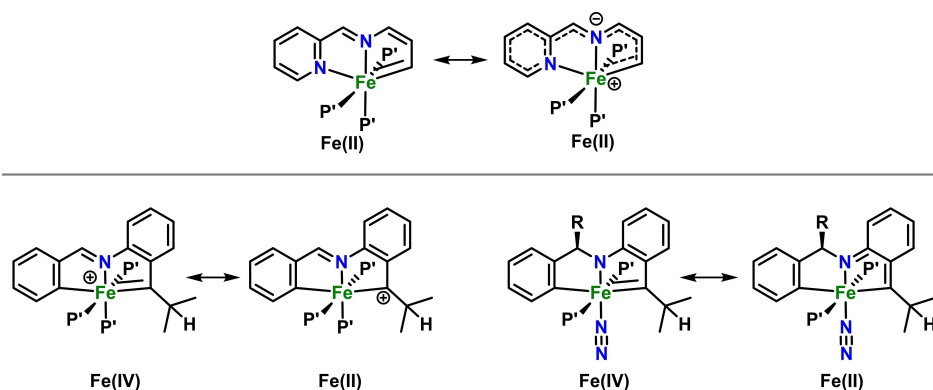
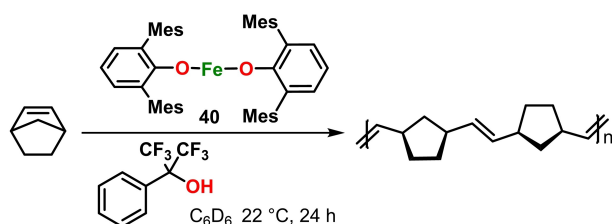


Figure 18. Fe(II) resonance structures of formal Fe(IV) complexes investigated by Wolczanski and co-workers.



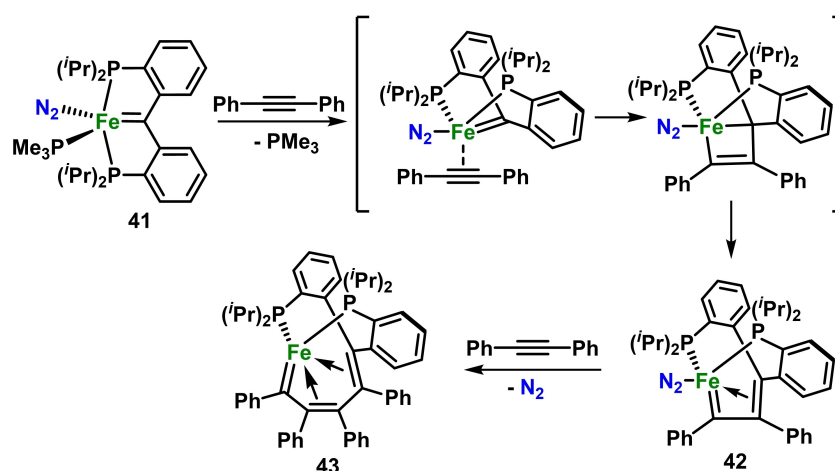
Scheme 9. Polymerization of norbornene to syndiotactic polynorbornene by Bukhryakov and co-workers.^[53]

decreased. This led to the conclusion that no active iron alkylidene species takes part in this reaction. The authors' conclusion was further substantiated by the fact that the addition of other alkenes, such as cyclooctene or cycloocta-1,7-diene, to the operating reaction did not yield polymers with those fragments incorporated. Regardless, addition of fluorinated alkoxides as an additive led to an improved conversion of up to 84% after 24 h, resulting in highly stereoregular *cis*, syndiotactic polynorbornene (Scheme 9). Presumably, the syn-

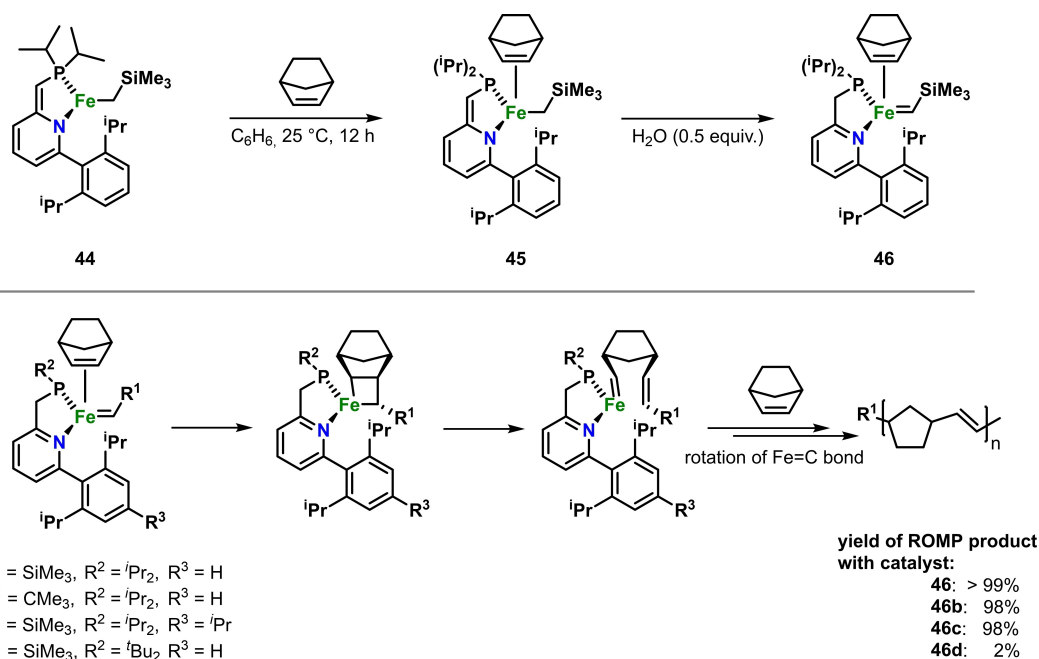
diotacticity of the polymer stems from the active polynuclear iron clusters, which could form in the reaction mixture.

Having studied late transition metal carbenes, the group of Iluc successfully synthesized the (distorted) trigonal-bipyramidal iron (II) carbene complex **41**, capable of [2 + 2] cycloaddition of diphenylacetylene, resulting in a conjugated iron alkylidene **42** after rearrangement from the metallacyclobutene structure.^[54] Upon treatment with another equivalent of diphenylacetylene, extension of the ring system to an η^3 -vinyl carbene with elimination of the N₂ yields the stable 18-valence electron complex **43**. Conceptually, this work emphasizes the possibility of alkyne-olefin metathesis with a well-defined iron complex (Scheme 10).

Very recently Takebayashi, Milstein and co-workers reported the successful ROMP of cyclic olefins (e.g., norbornene and its derivatives and of substituted cyclopropene) catalyzed by a three-coordinate iron(II) catalyst **44** (Scheme 11).^[55] The catalyst features a bidentate pyridine-based ligand and (trimethylsilyl)methylene, resulting in a trigonal planar high spin Fe(II) complex. In contrast to all other catalysts, the formation of the carbene takes place after the coordination of norbornene by



Scheme 10. Reaction of Iluc's TBP iron (II) carbene complex with diphenylacetylene.^[54]

Scheme 11. Formation of Takebayashi/Milstein's Fe(II) alkylidene and ROMP of norbornene.^[55]

elimination of the alkyl ligands' H_α and aromatization of pyridine (45–46), which is proposed to be the rate determining step. To facilitate this step, 0.5 equivalents of water were added, which resulted in a higher activity of the catalyst. After this, the reaction follows the Chauvin mechanism with formation of a metallacyclobutane intermediate (which the authors proposed to be in a triplet state) and subsequent topomerisation of the complex (internal rotation of Fe=C bond from apical to equatorial position), resulting in pure trans, isotactic polynorbornene product with high molecular weight.

Conclusion

Iron, one of the most abundant elements in the earth's crust, is in focus of extensive research in catalysis. In spite of numerous attempts over the decades to replace toxic, rare and expensive Ru in homogenous catalysts for olefin metathesis by well-defined iron catalysts, it turned out a major obstacle to replace Ru(IV) catalysts by Fe(IV) catalysts. Hence, focus in theoretical investigations and synthetic work turned, since recently, on low-valent Fe(II) catalysts.^[32,40,53,55] To date, only two examples of iron-catalyzed metathesis with such (high-spin) Fe(II) catalysts have been demonstrated.^[53,55] A major problem, identified as undesired competing alkene cyclopropanation, is linked to the often-preferred high spin ground state of iron-derived complexes. To overcome this issue, the role of the ligand environment and the iron ion's formal oxidation and spin state appears crucial and warrants further mechanistic investigations. In particular, while in recent theoretical work therefore a closed shell involved Chauvin intermediate is proposed (as is also the case for Ru),^[32,40] preliminary results of DFT calculations

suggested a triplet ground state of the involved metallacyclobutane.^[55] Hence, to proceed towards broad scope iron-catalyzed olefin metathesis, further elucidation of mechanistic details appears essential.

Summarizing, and as the preparation of actual Fe(IV) carbenes, previously considered to be necessary in order to fulfil the "d⁴-rule",^[52a] still remains challenging, recent theoretical and synthetic work suggests that Fe(II) carbenes may instead offer a more promising route towards successful iron-based metathesis catalysis. By combining such low oxidation state iron centers with strong ligands and by combining the strengths of both in silico design and concurrent synthetic work, realization of broadly applicable iron-catalyzed olefin metathesis could be within reach in the near future.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: iron catalysis · ligands · metathesis catalysts · olefin metathesis · olefins

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