Keep it singlet – Towards in silico design of manganese catalysts for olefin metathesis

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Abstract

Olefin metathesis is one of the most significant transformations in organic chemistry and an excellent example for efficient homogeneous catalysis. Although most currently used catalysts are primarily based on 4d and 5d metals, cycloaddition and cycloreversion reactions can also be attributed to first-row transition metals, such as iron. Surprisingly, the potential of Mn(I) based catalysts for olefin metathesis has been unexplored, despite its prominence in homogeneous catalysis and its diagonal relationship to Ru(II). In the present paper, we have investigated the prospective capabilities of rationally designed Mn complexes for cycloaddition and reversion reactions, using density functional theory. To keep our model complexes as synthetically feasible as possible, we included CO as co-ligands and imposed octahedral coordination. Like iron systems, a singlet ground state is required for Mn based catalysts to facilitate olefin metathesis and to prevent undesired cyclopropanation. However, the stabilization of the singlet state requires a careful selection of σ-donor and π-acceptor properties. Our results show that bidentate ligands in conjunction with CO work best. Our findings support the isodiagonal relationship and show the viability of Mn(I) complexes as catalysts for olefin metathesis.

1 Introduction

Metathesis reactions are among the most important chemical processes in modern organic synthesis. They are used to efficiently break and rearrange carbon-carbon bonds obeying excellent atom economy, both in industrial-scale applications as well as in chemical and pharmaceutical research.[1] From a mechanisitc perspective, olefin metathesis (OM) is a [2+2]-cycloaddition that is catalyzed by proficient and well-defined metal-alkylidene complexes involving a metallacycle intermediate (Figure 1). For their pioneering work in this very field, Chauvin, Schrock and Grubbs were awarded the Nobel Prize in chemistry in 2005.[2,3]

Consequently, the most widely used types of catalysts for metathesis (of any type and flavor) are the Mo(NHC)(Imido) (NHC = N-heterocyclic carbene) based complexes developed by Schrock, the Ru(NHC) based systems later developed by Grubbs, as well as modifications of them as reported by Hoveyda[4] or Buchmeiser (see lower panel of Figure 1).[5,6] Even though the current catalysts provide high yields under mild conditions, the development of sustainable, base-metal catalysts is highly desirable.[7] One area of research, that is currently of significant interest, is the substitution of ruthenium with iron, the corresponding 3d transition metal of the first series of the periodic table. Numerous research groups have been working on the design of operational iron systems for OM both experimentally and theoretically.[8–17] Within this context, Milstein and

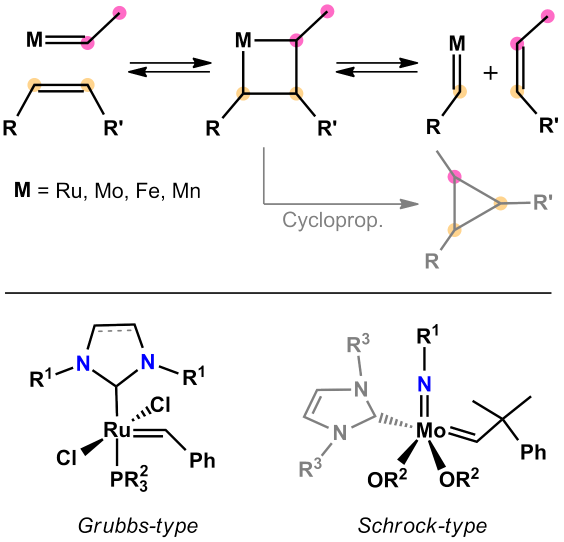

Figure 1: Olefin metathesis according to Chauvin's mechanism including cyclopropanation, the undesired side reaction encountered in first-row TM complexes (top). Prototypical operative metathesis catalysts with variable organic residues (R^i) influencing the reactivity and selectivity of the catalyst (bottom). One possible improvement of the Schrock-type system as devised by Buchmeiser is depicted in grey color (bottom, right).

coworkers recently reported on a new low-valent iron system supported by a bidentate PN ligand to be active in ring-opening metathesis polymerization.[18] While iron is well accepted as a surrogate to ruthenium in OM, it is somehow surprising not to find any investigations or at least considerations on the use of manganese for the same purpose. In recent years, several catalytic transformations involving Mn(I) complexes have been reported to exhibit similar structure, reactivity and stability as compared to the established Ru(II) and Fe(II) systems.[19–23] Alike the similar chemical properties between elements of the second and third period, it can be assumed that Ru(II) and isoelectronic Mn(I) comprise a diagonal relationship in the periodic table.[24,25] Unfortunately, the total number of currently known and stable manganese carbene complexes is low and mostly comprised of Fischer-type complexes that readily undergo cyclopropanation reactions.[26,27] Fischer-type carbenes are defined as M=CRX with X being a hetero atom and are thus electrophilic by nature in contrast to Schrock-type carbenes ($M{=}CR_2$). The only Mn system that resembles elements of OM was reported by Braunschweig and coworkers in 2013 and involves the formation of $[MnCp(CO)_2({=}CPh_2)]$ via cycloreversion of a Mn borylene metallacycle.[28] Consequently, manganese catalyzed olefin metathesis has (in contrast to iron) neither been theoretically studied nor experimentally attempted before.

All approaches to use elements of the first transition metal series for olefin metathesis face certain intrinsic challenges that need to be addressed in order to devise an active catalyst: (i) The metal-carbene ($M{=}CR_2$) bond tends to be weaker in 3d metal systems than in 4d/5d transition metal systems.[12,29] This fact leads to cyclopropanation being the preferred reaction in first row transition metal (carbene) complexes.[30] (ii) While heavier metals such as Ru and Mo favour low-spin closed shell configurations, first row metals usually exhibit a wide range of possible spin-states, which are close in energy. (iii) Surface crossings between single and triplet states are likely to take place.[31] (iv) Open shell systems hamper the coordination of an olefin and could very likely also undergo other radical reactions. However, in the absence of experimental data, theoretical studies can aid to guide experimental synthesis, predict trends and patterns and exclude unsuitable systems. Due to the complex electronic structure and the multitude of accessible spin states in Mn (and Fe) systems, the computational chemist faces the problem of accurately describing these states and their relative energies.[32] For this reason, it is not surprising that the first Fe systems to show activity in OM were discovered years after their computational exploration. In this contribution, we explore the feasibility of low-valent manganese alkylidene complexes supported by rationally designed mono-, bi- and tridentate ligand-systems for potential use in OM by means of density functional theory. The focus was on the conception of systems that are feasible to make in a laboratory rather than direct analogues of known Ru/Mo catalysts.

2 Computational Methods

All computations in the present study were performed with the ORCA 5.0 program package[33] utilizing the Vienna Scientific Cluster (VSC 4) in part. Electronic ground state calculations, including geometry optimizations, frequencies and transition-state searches were carried out with density functional theory (DFT) using the TPSSh meta-hybrid functional[34] together with Grimme's D3 dispersion correction[35] and Ahlrichs' def2-SVP basis set.[36] The resolution of identity (RI) approximation was used along with the corresponding auxiliary basis sets to accelerate the calculations. Free energies at 298 K were calculated using the rigid-rotor harmonic oscillator (RRHO) approximation as implemented in ORCA and real frequencies below 100 cm^{-1} were raised to 100 cm^{-1} to improve accuracy.[37] Final single-point energies were calculated with TPSSh/def2-TZVP/D3 on already obtained geometries, while Gibbs energies were obtained by adding zero point energies, thermal and entropic corrections at 298 K. For geometry optimizations and single-point calculations implicit solvation was included via the CPCM model and dichloromethane as solvent.[38] Transition states were localized with the help of the nudged elastic band (NEB) method as implemented in ORCA and confirmed to be first-order saddle points by analysis of the Hessian. Intrinsic reaction coordinate (IRC) calculations have been employed to verify the correct assignment of transition states by following the eigenvector of the corresponding imaginary frequency, starting from the TS structures and connecting with reactants and products. Minimum Energy Crossing Points (MECP) were calculated using the algorithm implemented in ORCA and the SurfCrossOpt keyword.[39] DLPNO-CCSD(T) calculation were performed on previously obtained geometries, using the def2-TZVP basis set and a converged BP86[40] UKS reference wave function.[41] Orbital plots and graphics were visualized and generated with ChemCraft.[42] Following literature, we further define the parameter δ as $\Delta\Delta G^{\ddagger} = \Delta G(\mathrm{TS}_{\mathrm{cycloprop}}) - \Delta G(\mathrm{TS}_{\mathrm{cyclorevers}})$ to describe the likeliness of metathesis over cyclopropanation if the singlet spin state is maintained.[11]

3 Results and Discussion

In pursuit of an in silico operational manganese system for olefin metathesis, we first developed a series of suitable model complexes that allow for a comparison with already known and investigated (Fe or Ru) complexes regarding spin state splittings and thermodynamic parameters. Figure 2 displays a compilation of Mn complexes supported by mono-, bi- and tridentate ligands considered in this work and represents the starting point of our study. Despite the lack of knowledge on the synthetic realisation, these molecules are presented as olefin adducts, being the necessary first step of a cycloaddition in OM with ethylene as the test substrate. For direct comparison with a literature known Fe system, we initially adopted the simple, but effective model catalyst **1** reported by Mauksch and Tsogoeva[16] and substituted the putative Fe(II) center with formally isoelectronic Mn(I). For simplicity reasons, only one topological isomer was considered, bearing the coordinated olefin, a CO ligand and the carbene fragment in the equatorial plane. Since these simple trigonal bipyramidal model systems are very challenging (if not impossible) to realize experimentally, we have chosen models that are closer to molecules already known in the literature. The preparation of low-spin Mn(I) complexes is commonly based on the reaction of a suitable carbonyl precursor such as $Mn(CO)_5Br$ or $Mn_2(CO)_{10}$ with bidentate or tridentate ligands and subsequent chemical modifications. Bidentate ligands and more so pincer ligands allow for easy modifications of steric and electronic parameters and could stabilize the obtained Mn complexes.[43] Moreover, chemical experience dictates that the presence of carbon monoxide is an inherent component of most low-spin manganese complexes and that a coordination number of five or more likely six is usually encountered in these molecules.[44–46] These factors and the need for strongly σ-donating ligands seem highly relevant for stabilizing singlet states throughout the metathesis process. A consequent improvement over **1** in terms of experimental and structural feasibility, as well as donor strength could be the introduction of a bidentate ligand and carbon monoxide (see Fig. 2, complex **2**).

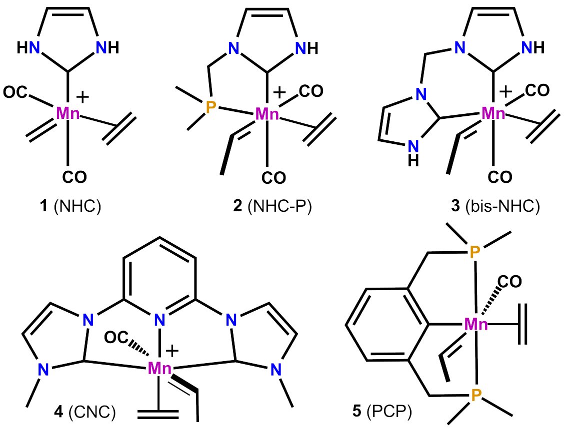

Figure 2: Manganese model systems for olefin metathesis investigated in this work.

Experimentally, such a compound could be obtained from a carbonyl precursor [Mn(NHC-P)$(CO)_3$R] (R = Alkyl, Aryl, OAc) or even a putative dinuclear pre-catalyst.[23,47] To further increase the donor strength of the ligand, a bis-NHC system could be employed, which is also well established in literature (see Figure 2, complex **3**).[48] For both systems with the general formula [(L-

L)Mn(=CHCH$_3$)(CO)$_2$(C$_2$H$_4$)] for the initial olefin adduct, various isomeric structures can be drawn, having either a trans-CO or a cis-CO configuration. Depending on the synthetic approaches and possible isomerisation reactions, all of them could be accessible. For simplicity reasons, only one isomer was considered in the following. In accordance with the suggestions by Truhlar and Solans-Monfort, we have additionally chosen tridentate pincer ligands of the type CNC[49] and (anionic) PCP[50] (see **4** and **5** in Figure 2) as the scaffolds for our Mn systems to be investigated.

For a selection of these model systems, relevant stationary points along the OM reaction path were calculated including the initial olefin adduct, and the corresponding metallacyclobutane structure, as well as the transition states (TS) for [2+2] cycloaddition, cycloreversion and cyclopropanation – both, for the singlet and triplet spin-state. Since all model complexes exhibit a d^6 electron configuration, a low-spin (S = 0) singlet state, a triplet state (S = 1) and a quintet high-spin (S = 2) state can be relevant. As mentioned initially (see Computational Methods), we adopted the meta-hybrid exchange-correlation functional TPSSh (with 10% HF exchange), as it was found to accurately predict spin state splittings of manganese and iron based spin cross-over compounds.[51,52] Table 1 summarizes the relative Gibbs energies of all considered species with respect to the initial olefin adduct and also provides literature values for the active Grubbs system [Ru(IMesH$_2$)(Cl$_2$)(=CH$_2$)] (IMesH$_2$ = 1,3-dimesityl-imidazol-4,5-dihydro-2-ylidene) (**Ru**). According to the literature, OM with this well known Ru catalyst displays a barrier of 12.7 kcal/mol for cycloaddition of ethylene and is characterized by a high δ value of 18.2 kcal/mol.[10]

Table 1: Relative Gibbs free energies (kcal/mol) of relevant species involved in OM and cyclopropanation reactions with respect to the initial singlet olefin adduct.

Model system	Olefin Adduct		Metallacycle		Cyclopropanation	
	S = 0	S = 1	S = 0	S = 1	S = 0	S = 1
Ru [ref. 10]	0.0	19.5	–6.8	8.2	8.6	–7.4
1	0.0	8.6	5.1	–0.6	–4.4	–15.0
2	0.0	22.1	–8.1	4.2	–16.1	–10.6
3	0.0	18.5	–7.5	0.7	–18.0	–12.9
4	0.0	20.8	–8.4	–15.9	–23.9	–25.7
5	0.0	12.7	1.3	–5.3	–11.9	–11.9

The reaction energy profile for the simple model catalyst **1** with a Grubbs-type N-heterocyclic carbene (NHC) moiety is depicted in Figure 3. The starting point for the olefin metathesis cycle is the formation of a stable olefin adduct as first intermediate. As opposed to the reported Fe system, it can be observed that the Mn=CH$_2$ unit in the optimized closed-shell olefin adduct is rotated by almost 90° and results in a non-collinear arrangement with the coordinated olefin (see Supporting Information, S1). This small change in geometry resembles the reported Fe triplet geometry instead of the anticipated singlet state. Additionally, it was found that the calculated M-C$_\alpha$ bond lengths in the optimized singlet Mn metallacycle are 0.10 Å shorter than for the Fe case. The singlet metallacycle displays a trigonal bipyramidal geometry, while the triplet geometry resembles a distorted square pyramid. In contrast to the iron system, the metallacyclobutane formation is also slightly endergonic with 5.1 kcal/mol, but the metathesis process is feasible and clearly preferred over cyclopropanation as indicated by a difference (δ) of $\Delta G(\mathrm{TS}_{\mathrm{cycloprop}})$ and $\Delta G(\mathrm{TS}_{\mathrm{cyclorevers}})$ of 16.7 kcal/mol. Furthermore, the initially mentioned rotation of the $\mathrm{Mn{=}CH_2}$ unit is likely responsible for the slight increase in the energy of the consecutive transition state for [2+2]-cycloaddition as compared to the iron congener.

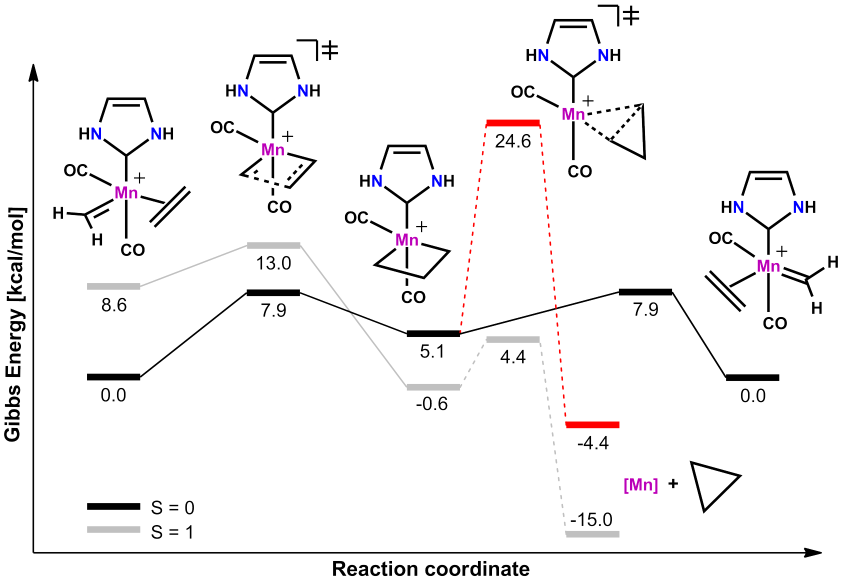

Figure 3: Reaction energy profile for OM with model catalyst **1**. The reaction paths describing cyclopropanation are depicted with dotted lines and red color. The transition states for cycloaddition and cycloreversion are identical for symmetry reasons. All energies are given in kcal/mol obtained using TPSSh/def2-TZVP/D3//TPSSh/def2-SVP/D3 in dichloromethane.

The singlet-triplet energy splitting for the metallacyclobutane intermediate is one of the most crucial parameters in first-row TM metathesis and was calculated to be $\Delta G_{\mathrm{ST}} = -5.7$ kcal/mol with TPSSh and $\Delta G_{\mathrm{ST}} = -5.4$ kcal/mol employing DLPNO-CCSD(T) in favor of the triplet state. A survey on the performance of various exchange-correlation functionals on the singlet-triplet splitting for metallacycle **1** can be found in the electronic Supporting Information (see Table S1). The quintet state of the metallacyclobutane is located just 0.4 kcal/mol above the triplet state and could also play a role in surface crossing events and deactivation processes. Similar to the reported iron system, the transition state for the [2+2]-cycloaddition in the singlet state also exhibits aromatic character with a NICS(1) value (NICS = Nucleus Independent Chemical Shift) of −18.7 ppm (cf. −19.4 ppm) which further supports our initial assumption on the isodiagonal relationship between Ru(II)/Fe(II) and Mn(I) (vide supra).[53]

The implementation of bidentate ligands in complexes **2** and **3**, as well as sixfold coordination to increase the degree of synthetic viability has significant impact. As an example, the reaction energy profile for olefin metathesis with the NHC-P complex **2** is depicted in Figure 4.

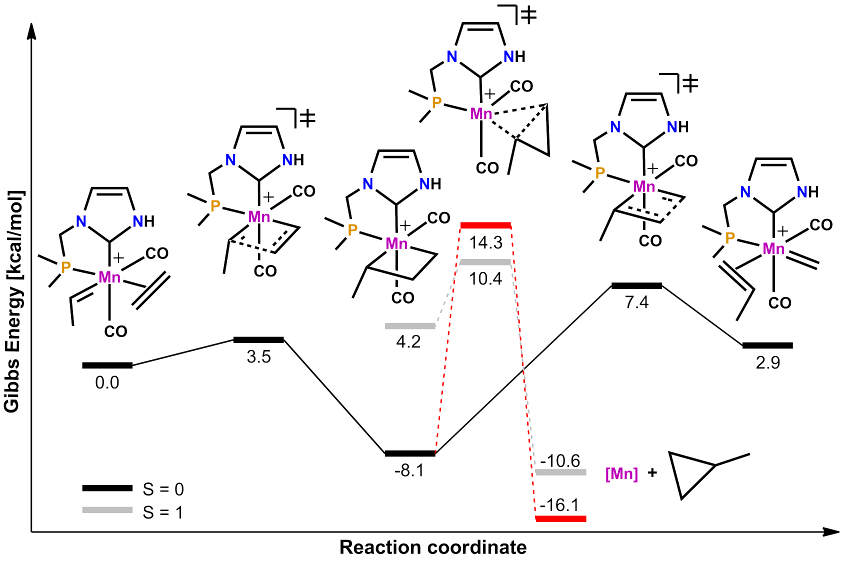

Figure 4: Reaction energy profile for OM with model catalyst **2**. The reaction path describing cyclopropanation is depicted with dotted lines and red color. All energies are given in kcal/mol obtained using TPSSh/def2-TZVP/D3//TPSSh/def2-SVP/D3 in dichloromethane.

The energetic barrier for the initial [2+2]-cycloaddition of the simple test substrate ethylene is low ($\Delta G^{\ddagger} = 3.5$ kcal/mol) and quickly leads to formation of a stable singlet metallacycle. In the absence of surface crossings (vide infra) and isomerisation reactions, the most important side reaction is cyclopropanation and formation of methylcyclopropane. The barrier for this process was calculated to be 22.4 kcal/mol in the singlet state. The cycloreversion process forming the propene adduct at 2.9 kcal/mol displays a barrier of $\Delta G^{\ddagger} = 15.5$ kcal/mol and therefore an overall δ value of 6.9 kcal/mol is obtained. Under the same conditions, complex **3** behaves similar with a barrier for cyclopropanation of 20.0 kcal/mol and $\delta = 6.0$ kcal/mol (see Supporting Information). Most importantly, the observed inversion of the spin state ordering ($\Delta G_{\mathrm{ST}} > 0$, see Table 1) and the preference for the singlet state of the metallacycles can be primarily attributed to the presence of the strong π-acceptor ligand CO as an additional ligand, but also to the changes in electronic structure induced by altering the (ligand field) symmetry. The ligand systems in use can be easily varied in the precursor molecules or precatalysts in order to tune ΔG_{ST} and the reactivity in OM. Analyzing the reaction energy profiles for **2** and **3** (see also Table 1) shows that the reactivity on the S = 0 potential energy surface is initially similar and rather independent of the bidentate ligands used. Consequently, both complexes, if generated (in-situ), could have the necessary prerequisites to act as catalysts in OM, likely using a more appropriate and reactive substrate.

Regarding the geometries of the olefin adducts **2** and **3** in the triplet state, we observed that the obtained minima are higher in energy. However, small displacements and applying tight optimization criteria leads to significant structural rearrangements and a CO ligand migrating to the alkylidene carbon forming a very stable Mn-C(H)(CH_3)(C=O) motif (see Figure 5). A similar optimization behavior was also found using other exchange-correlation functionals, including BP86. Hence, it is not an artefact of the approximated exchange-correlation functional. The quintet states for the adducts and the metallacycles showed dissociative character with respect to ethylene or CO, and thus could not be fully converged. We assume that both observed behaviors, the migratory insertion-like reactivity of the nucleophilic alkylidene in the triplet state and dissociation of CO or olefin in higher spin states could lead to early deactivation of the catalyst or precatalyst. It should not go unmentioned that migratory insertion of highly nucleophilic ligands such as alkyl groups is also a well-known concept in manganese carbonyl chemistry in the ground state.[47]

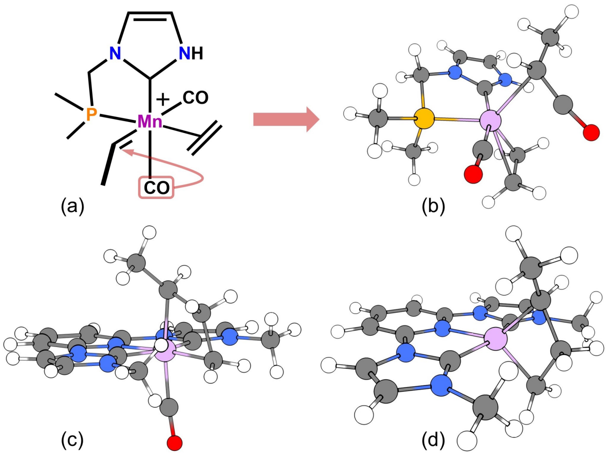

Figure 5: Rearrangement reaction of carbonyl complex **2** (a) in the triplet state to a ketene-like system (b). Singlet metallacycle of **4** in octahedral geometry (c) and relaxation to a trigonal bipyramidal structure after (hypothetical) removal of a CO ligand (d).

In order to stabilize metallacyclobutane intermediates in the singlet state and disfavor alkene cyclopropanation, various authors advocated for the use of strongly donating pincer ligands.[10,11] Whereas the pincer ligands in the model systems **4** and **5** do show a trend to stabilize the presented olefin adducts (see Figure 2) in the singlet state, surprisingly, stronger donation destabilizes the metallacycles. Consequently, for system **4** a singlet-triplet splitting of −7.5 kcal/mol was obtained and for system **5** a value of −6.5 kcal/mol, respectively, making the triplet state energetically favored. These finding are further supported by single-point BP86/def2-TZVP/D3 calculations – with BP86 being a pure GGA functional – yielding ΔG_{ST} values of −4.4 kcal/mol and −1.5 kcal/mol, respectively. This observation is somehow surprising, as the CNC and related pincer ligand systems are known to be strong donors and were found to be excellent candidates in computational studies on Fe catalysts for OM. However, in the majority of these studies on iron catalysts, five-fold coordinated systems were investigated, and CO is rarely utilized as a co-ligand.[8] If a CO ligand molecule is removed from designated the catalyst **4**, and the metallacycle structures reoptimized again for the S = 0 and S = 1 state, a singlet-triplet splitting of −19.2 kcal/mol is obtained (see Supporting Information). It can be seen that the magnitude of the splitting increases and the triplet state still remains the more favorable one. If the Mn atom is additionally replaced by Fe in complex **4** and the CO ligand removed, a singlet-triplet splitting of −0.5 kcal/mol is obtained, a value close to as reported by Yang and Truhlar for a similar but promising Fe(CNC) system.[11] It is noteworthy that for the Fe species the deviation from $<S^2>$ in the triplet state is with 0.10 very low, but in the Mn species it increases to 0.72 – pointing towards a more complex electronic structure of the Mn systems. The distinct behavior of Mn vs. Fe illustrates the striking difference between manganese and iron based isostructural complexes regarding the stability of spin states. The sole use of strongly σ-donating polydentate ligands is therefore not sufficient for developing an operative manganese based catalyst for metathesis.

It is well known in literature that metallacycles in five-fold coordinated Fe and Ru complexes (such as **Ru**) usually display a trigonal bipyramidal geometry in the singlet state and a square pyramidal geometry in the triplet state.[10] Indeed, this behavior is also observed in the simple five-fold coordinated complex **1**. In contrast, a six-fold octahedral coordination (see complexes **2**-**6**) imposes geometrical constraints on the metallacycle and forces the metallacycle to adopt a square pyramidal geometry rather than a trigonal bipyramidal coordination. As a consequence, the singlet state is destabilized in comparison to the triplet state. While for complexes with bidentate ligands (**2** and **3**) the singlet state remains to be the ground state, for complexes with tridentate ligands (**4** and **5**) the triplet state is now energetically favored. To alleviate the unfavorable geometrical constraints, we investigated how a hypothetical removal of a CO molecule from complex **4** impacted the metallacycle geometry. We observed that re-optimization of the metallacycle geometry on the singlet surface led to relaxation and a change towards the desired trigonal bipyramidal geometry (see Figure 5, lower panel). While we anticipated a stabilization of the singlet state, in sharp contrast, we found that the triplet state was even more favorable. This seemingly contradicting behavior can be explained by the nature of the removed CO ligand: As a strong field ligand, CO has a significant impact on the electronic structure of the metal, aiding the relative stabilization of the singlet state. Consequently, this effect over-compensates the structural relaxation of the metallacycle in a five-fold coordinated environment. To achieve the desired stabilization of the singlet state an intricate balance of ligands and geometry is required. Hence, it would be of interest to examine the influence of various polydentate ligands in more detail, but this is beyond the scope of this current article.

Lastly, degradation reactions caused by surface crossings between singlet and triplet surfaces require closer inspection. A well known concept in this regard is the use of minimum energy crossing points (MECP) to approximate the adiabatic transition between two spin states. Such processes are formally spin-forbidden in the absence of spin-orbit coupling. As suggested by Harvey, these points can be calculated using an optimization algorithm utilizing combined gradients for the singlet and triplet PES to eventually yield a geometry where $\Delta E_{\mathrm{ST,SCF}} = 0$.[54] As mentioned before, our simple test system **1** displays a metallacyclobutane intermediate with the triplet state being 5.7 kcal/mol more stable than the singlet state. The question arises, how easy such a crossing to the high-spin state and consequently decomposition via cyclopropanation would be. We could localize a MECP at $\Delta G_{\mathrm{MECP}} \approx 2.3$ kcal/mol above the singlet state, low enough to be of relevance and allow thermal deactivation of the catalyst. Similarly, for the PCP complex **5** a MECP could be localized at $\Delta G_{\mathrm{MECP}} \approx 2.9$ kcal/mol above the singlet state. These surface crossing points are well-accessible at reaction conditions and can compete with cycloreversion.

4 Conclusions

The present work investigated the potential of olefin metathesis with a series of Mn based catalysts by exploring thermodynamics and energetics of homo metathesis with DFT. Our study highlights challenges that have to be addressed in the design of functional catalysts. Based on our findings we conclude: (i) The overall thermodynamics and free energy profiles for the metathesis cycle with Mn based systems are feasible and comparable to literature known Fe systems. (ii) Cyclopropanation is a viable side reaction in iron and manganese based systems with the associated barriers being lower in the triplet state than in the singlet state. The cyclopropanation products are very stable with respect to educts. (iii) Similar to iron, control of spin states plays a crucial role in the conception of manganese catalyst for metathesis. (iv) Surface crossings are likely to take place if the triplet state is lower in energy. Together, this supports our assumptions on the isodiagonal relationship and the suitability of low-valent manganese. The focus of our investigation was on designing systems that could be prepared in a laboratory and are feasible from a synthetic point of view. Therefore, we have established the requirement of an octahedral geometry, six-fold coordination and the inclusion of carbon monoxide as a co-ligand. As cyclopropanation is the major side reaction, the structure and spin state splittings of the involved metallacycles are of paramount importance. Consequently, any attempt to design Mn catalysts needs to obey the principle "Keep it singlet" and focus on the stabilization of the singlet metallacycle intermediate.

Our preliminary results show that the mere use of polydentate ligands is not sufficient to stabilize the singlet states of these Mn species and that a sensible screening and selection needs to take place. In this context, bidentate ligands were shown to be potentially interesting. A major drawback of the mandated octahedral geometry is the increase in spacial demand leading to easier migratory insertion-like reactivity and the destabilization of the singlet metallacycle. Consequently, five-fold coordination to prevent the destabilization of the trigonal bipyramidal singlet metallacycle could be necessary or a delicate balance between a constrained geometry due to polydentate ligand and strong donors/acceptors has to be achieved. Despite these yet to be tackled issues, the high abundance of first-row transition metals provides an opportunity to develop inexpensive and non-toxic catalysts. Our contribution may serve as a first guideline for the experimental chemist to pave the way for the design of novel manganese based catalysts for olefin metathesis.

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Notes

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References

[1] Fürstner, A. Olefin Metathesis and Beyond. *Angewandte Chemie International Edition* **2000**, *39*, 3012–3043.

[2] Grubbs, R. H. Olefin-Metathesis Catalysts for the Preparation of Molecules and Materials (Nobel Lecture). *Angewandte Chemie International Edition* **2006**, *45*, 3760–3765.

[3] Schrock, R. R. Multiple Metal–Carbon Bonds for Catalytic Metathesis Reactions (Nobel Lecture). *Angewandte Chemie International Edition* **2006**, *45*, 3748–3759.

[4] Hoveyda, A. H. Evolution of Catalytic Stereoselective Olefin Metathesis: From Ancillary Transformation to Purveyor of Stereochemical Identity. *The Journal of Organic Chemistry* **2014**, *79*, 4763–4792.

[5] Buchmeiser, M. R. Homogeneous Metathesis Polymerization by Well-Defined Group VI and Group VIII Transition-Metal Alkylidenes: Fundamentals and Applications in the Preparation of Advanced Materials. *Chemical Reviews* **2000**, *100*, 1565–1604.

[6] Benedikter, M. J.; Musso, J. V.; Frey, W.; Schowner, R.; Buchmeiser, M. R. Cationic Group VI Metal Imido Alkylidene N-Heterocyclic Carbene Nitrile Complexes: Bench-Stable, Functional-Group-Tolerant Olefin Metathesis Catalysts. *Angewandte Chemie International Edition* **2021**, *60*, 1374–1382.

[7] Bullock, R. *Catalysis without Precious Metals*; Wiley-VCH: Weinheim, Germany, 2010.

[8] Grau, B. W.; Neuhauser, A.; Aghazada, S.; Meyer, K.; Tsogoeva, S. B. Iron-Catalyzed Olefin Metathesis: Recent Theoretical and Experimental Advances. *Chemistry – A European Journal* **2022**, *28*, e202201414.

[9] Belov, D. S.; Tejeda, G.; Bukhryakov, K. V. Olefin Metathesis by First-Row Transition Metals. *ChemPlusChem* **2021**, *86*, 924–937.

[10] de Brito Sa, E.; Rodriguez-Santiago, L.; Sodupe, M.; Solans-Monfort, X. Toward Olefin Metathesis with Iron Carbene Complexes: Benefits of Tridentate σ-Donating Ligands. *Organometallics* **2016**, *35*, 3914–3923.

[11] Yang, B.; Truhlar, D. G. Computational Design of an Iron Catalyst for Olefin Metathesis. *Organometallics* **2018**, *37*, 3917–3927.

[12] de Brito Sa, E.; Rimola, A.; Rodriguez-Santiago, L.; Sodupe, M.; Solans-Monfort, X. Reactivity of Metal Carbenes with Olefins: Theoretical Insights on the Carbene Electronic Structure and Cyclopropanation Reaction Mechanism. *The Journal of Physical Chemistry A* **2018**, *122*, 1702–1712.

[13] de Brito Sa, E.; Rodriguez-Santiago, L.; Sodupe, M.; Solans-Monfort, X. Influence of Ligands and Oxidation State on the Reactivity of Pentacoordinated Iron Carbenes with Olefins: Metathesis versus Cyclopropanation. *Organometallics* **2018**, *37*, 1229–1241.

[14] Poater, A.; Chaitanya Vummaleti, S. V.; Pump, E.; Cavallo, L. Comparing Ru and Fe-catalyzed olefin metathesis. *Dalton Trans.* **2014**, *43*, 11216–11220.

[15] Luque-Urrutia, J. A.; Gimferrer, M.; Casals-Cruanas, E.; Poater, A. In Silico Switch from Second- to First-Row Transition Metals in Olefin Metathesis: From Ru to Fe and from Rh to Co. *Catalysts* **2017**, *7*.

[16] Mauksch, M.; Tsogoeva, S. B. Iron-Catalyzed Olefin Metathesis with Low-Valent Iron Alkylidenes. *Chemistry – A European Journal* **2017**, *23*, 10264–10269.

[17] Eisenstein, O.; Hoffmann, R.; Rossi, A. R. Some geometrical and electronic features of the intermediate stages of olefin metathesis. *Journal of the American Chemical Society* **1981**, *103*, 5582–5584.

[18] Takebayashi, M. A., Satoshi Iron; Feller, M.; Rivada-Wheelaghan, O.; Leitus, G.; Diskin-Posner, Y.; Shimon, L. J. W.; Avram, L.; Carmieli, R.; Wolf, S. G.; Cohen-Ofri, I.; Sanguramath, R. A.; Shenhar, R.; Eisen, M.; Milstein, D. Iron-catalysed ring-opening metathesis polymerization of olefins and mechanistic studies. *Nature Catalysis* **2022**, *5*, 494–502.

[19] Zell, T.; Langer, R. From Ruthenium to Iron and Manganese—A Mechanistic View on Challenges and Design Principles of Base-Metal Hydrogenation Catalysts. *ChemCatChem* **2018**, *10*, 1930–1940.

[20] Gorgas, N.; Kirchner, K. Isoelectronic Manganese and Iron Hydrogenation/Dehydrogenation Catalysts: Similarities and Divergences. *Accounts of Chemical Research* **2018**, *51*, 1558–1569.

[21] Kallmeier, F.; Kempe, R. Manganese Complexes for (De)Hydrogenation Catalysis: A Comparison to Cobalt and Iron Catalysts. *Angewandte Chemie International Edition* **2018**, *57*, 46–60.

[22] Mukherjee, A.; Milstein, D. Homogeneous Catalysis by Cobalt and Manganese Pincer Complexes. *ACS Catalysis* **2018**, *8*, 11435–11469.

[23] Buhaibeh, R.; Filippov, O. A.; Bruneau-Voisine, A.; Willot, J.; Duhayon, C.; Valyaev, D. A.; Lugan, N.; Canac, Y.; Sortais, J.-B. Phosphine-NHC Manganese Hydrogenation Catalyst Exhibiting a Non-Classical Metal-Ligand Cooperative H2 Activation Mode. *Angewandte Chemie International Edition* **2019**, *58*, 6727–6731.

[24] Rayner-Canham, G. Isodiagonality in the periodic table. *Foundations of Chemistry* **2011**, *13*, 121–129.

[25] Mashima, K. Diagonal Relationship among Organometallic Transition-Metal Complexes. *Organometallics* **2021**, *40*, 3497–3505.

[26] Hoye, T. R.; Rehberg, G. M. Manganese Fischer carbene chemistry: reactions of Cp'(CO)2Mn:C(OMe/OLi)R with enynes, 1-hexyne, and acrylates. *Organometallics* **1990**, *9*, 3014–3015.

[27] Dutta, P. K.; Chauhan, J.; Ravva, M. K.; Sen, S. Directing-Group-Assisted Manganese-Catalyzed Cyclopropanation of Indoles. *Organic Letters* **2019**, *21*, 2025–2028.

[28] Bauer, J.; Braunschweig, H.; Damme, A.; Jimenez-Halla, J. O. C.; Kramer, T.; Radacki, K.; Shang, R.; Siedler, E.; Ye, Q. Metathesis Reactions of a Manganese Borylene Complex with Polar Heteroatom–Carbon Double Bonds: A Pathway to Previously Inaccessible Carbene Complexes. *Journal of the American Chemical Society* **2013**, *135*, 8726–8734.

[29] Vasiliu, M.; Arduengo, A. J. I.; Dixon, D. A. Role of Electronegative Substituents on the Bond Energies in the Grubbs Metathesis Catalysts for M = Fe, Ru, Os. *The Journal of Physical Chemistry C* **2014**, *118*, 13563–13577.

[30] Hamaker, C. G.; Mirafzal, G. A.; Woo, L. K. Catalytic Cyclopropanation with Iron(II) Complexes. *Organometallics* **2001**, *20*, 5171–5176.

[31] Schröder, D.; Shaik, S.; Schwarz, H. Two-State Reactivity as a New Concept in Organometallic Chemistry. *Accounts of Chemical Research* **2000**, *33*, 139–145.

[32] Ye, S.; Neese, F. Accurate Modeling of Spin-State Energetics in Spin-Crossover Systems with Modern Density Functional Theory. *Inorganic Chemistry* **2010**, *49*, 772–774.

[33] Neese, F. Software update: The ORCA program system—Version 5.0. *WIREs Computational Molecular Science* **2022**, *12*, e1606.

[34] Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. Comparative assessment of a new nonempirical density functional: Molecules and hydrogen-bonded complexes. *The Journal of Chemical Physics* **2003**, *119*, 12129–12137.

[35] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *The Journal of Chemical Physics* **2010**, *132*.

[36] Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[37] Luchini, G.; Alegre-Requena, J. V.; Funes-Ardoiz, I.; Paton, R. S. GoodVibes: Automated Thermochemistry for Heterogeneous Computational Chemistry Data. *F1000Research* **2020**, *9*, 291.

[38] Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *The Journal of Physical Chemistry A* **1998**, *102*, 1995–2001.

[39] Harvey, J. N.; Aschi, M.; Schwarz, H.; Koch, W. The singlet and triplet states of phenyl cation. A hybrid approach for locating minimum energy crossing points between non-interacting potential energy surfaces. *Theoretical Chemistry Accounts* **1998**, *99*, 95–99.

[40] Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A* **1988**, *38*, 3098–3100.

[41] Drosou, M.; Mitsopoulou, C. A.; Pantazis, D. A. Spin-state energetics of manganese spin crossover complexes: Comparison of single-reference and multi-reference ab initio approaches. *Polyhedron* **2021**, *208*, 115399.

[42] Chemcraft version 1.8 - https://www.chemcraftprog.com (May 2023).

[43] Peris, E.; Crabtree, R. H. Key factors in pincer ligand design. *Chem. Soc. Rev.* **2018**, *47*, 1959–1968.

[44] Garbe, M.; Junge, K.; Beller, M. Homogeneous Catalysis by Manganese-Based Pincer Complexes. *European Journal of Organic Chemistry* **2017**, *2017*, 4344–4362.

[45] Kaim, V.; Kaur-Ghumaan, S. Manganese Complexes: Hydrogen Generation and Oxidation. *European Journal of Inorganic Chemistry* **2019**, *2019*, 5041–5051.

[46] Vanden Broeck, S. M.; Cazin, C. S. Manganese-N-heterocyclic carbene (NHC) complexes - An overview. *Polyhedron* **2021**, *205*, 115204.

[47] Weber, S.; Stöger, B.; Veiros, L. F.; Kirchner, K. Rethinking Basic Concepts - Hydrogenation of Alkenes Catalyzed by Bench-Stable Alkyl Mn(I) Complexes. *ACS Catalysis* **2019**, *9*, 9715–9720.

[48] Franco, F.; Pinto, M. F.; Royo, B.; Lloret-Fillol, J. A Highly Active N-Heterocyclic Carbene Manganese(I) Complex for Selective Electrocatalytic CO2 Reduction to CO. *Angewandte Chemie International Edition* **2018**, *57*, 4603–4606.

[49] Myren, T. H. T.; Lilio, A. M.; Huntzinger, C. G.; Horstman, J. W.; Stinson, T. A.; Franklin, T.; Moore, C.; Lama, B.; Funke, H. H.; Luca, O. R. Manganese N-Heterocyclic Carbene Pincers for the Electrocatalytic Reduction of Carbon Dioxide. *Organometallics* **2019**, *38*, 1248–1253.

[50] Himmelbauer, D.; Stöger, B.; Veiros, L. F.; Kirchner, K. Reversible Ligand Protonation of a Mn(I) PCP Pincer Complex To Afford a Complex with an η^2-Caryl–H Agostic Bond. *Organometallics* **2018**, *37*, 3475–3479.

[51] Amabilino, S.; Deeth, R. J. DFT Analysis of Spin Crossover in Mn(III) Complexes: Is a Two-Electron S = 2 to S = 0 Spin Transition Feasible? *Inorganic Chemistry* **2017**, *56*, 2602–2613.

[52] Jensen, K. P.; Cirera, J. Accurate Computed Enthalpies of Spin Crossover in Iron and Cobalt Complexes. *The Journal of Physical Chemistry A* **2009**, *113*, 10033–10039.

[53] Schleyer, P. v. R.; Wu, J. I.; Cossío, F. P.; Fernández, I. Aromaticity in transition structures. *Chem. Soc. Rev.* **2014**, *43*, 4909–4921.

[54] Poli, R.; Harvey, J. N. Spin forbidden chemical reactions of transition metal compounds. New ideas and new computational challenges. *Chem. Soc. Rev.* **2003**, *32*, 1–8.