Tuning catalytic activity of dimolybdenum paddlewheel complexes by ligands: mechanism study on the radical addition reaction of CCl₄ to 1-hexene

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Abstract
The detailed catalytic mechanism of a series of paddlewheel complexes [Mo₂L₄] featuring Mo-Mo quadruply-bond on radical addition of CCl₄ to 1-hexene was studied using density functional theory. Different ligands of Mo-Mo bond are investigated to illustrate the ligand effect on the catalytic activity. The results show that the Mo-Mo quadruply-bond paddlewheel complexes have high catalytic activities on the title reaction. The whole reaction involves 4 steps. Firstly, the C-Cl bond of first CCl₄ is activated by [Mo₂L₄] catalyst, and [Mo₂L₃Cl] and CH₃COOCCl₃ are obtained. Then the second CCl₄ adds to [Mo₂L₃Cl] to produce [Mo₂L₃Cl₂] and ·CCl₃ radical; ·CCl₃ radical interacts with 1-hexene to get an addition, the addition product which reacts with one Cl atom of [Mo₂L₃Cl₂] to give the last product tBuCHClCH₂CCl₃ and regenerate [Mo₂L₃Cl]. The addition of the first CCl₄ to [Mo₂L₄] catalyst is the rate-determining step of the whole reaction. Because this step is not in the catalytic cycle, the reaction would speed up after a certain period of time. The catalytic activity of dimolybdenum paddlewheel complex is depended on the natural population analysis (NPA) charge of Mo and the redox potential E(Mo²⁴⁺/Mo²⁵⁺). The higher NPA of Mo atom and higher E(Mo²⁴⁺/Mo²⁵⁺) of the catalyst, the higher catalytic activity it has. Our results provide an explanation for experimental observations and useful insights for further development of bimetallic catalysts in radical addition reactions.

Keywords Dimolybdenum paddlewheel complex · Metal-metal quadruply-bond · Radical addition · Catalytic activity · Ligand effect

Introduction
Since the first dimolybdenum complex (molybdenum(II) acetate) containing Mo-Mo multiple bond was isolated and characterized [1], a large number of polymetal-metal bonding complexes have been synthesized [2–8]. In particular, the metal-metal bonded compounds with unique paddlewheel structures have played a major role in development of coordination chemistry [9] and continued to be of interest for their catalytic [10], photophysical [11], electronic [12], and structural properties[13] as well as reactivity [14, 15]. Among these paddlewheel compounds, dimolybdenum compounds, Mo₂L₄, have attracted much more attention due to their unique configuration and catalytic applications [16–21]. The Mo₂L₄ paddlewheel compounds possess a quadruple metal-metal bond (σ²π⁴δ²) supported by four bridging ligands, such as carboxylates, amides, and pyrrolidinates [2, 22–24]. These compounds exhibit one-electron redox property in radical transformation processes, which can result in reductively cleaving a carbon-halogen bond in organic halides to generate organic radicals [2, 4, 18, 24–26].

The study of K. Mashima et al. showed that Mo₂(OCOAr)₄ (Ar=2,4,6-iPr₃C₆H₂) was used for a catalytic radical addition reaction of CCl₄ to 1-hexene in THF-d₈ at 80°C to give 1,1,1,3-tetrachlorohexane regioselectively in 84% yield. They also found that the redox properties of [Mo₂⁻] complexes are changed by replacing the ligands, and the catalytic activity for the radical addition reaction strongly depends on the redox potential of the [Mo₂⁻] complexes [4]. N. J. Patmore found that
the electronic structure of Mo-Mo quadruple bonds can be tuned through O/S substitution of N by lowering the HOMO energy of Mo$_2$ and reducing the Mo$_2$$^{4+}$/$^{5+}$ oxidation potential [27].

In 2016, K. Mashima et al. synthesized a series of mixed ligated tris(amidinate) dimolybdenum complexes as catalysts for radical addition of CCl$_4$ to 1-hexene [24]. Their experimental investigation showed that the nature of the ligands was a crucial factor for initiating the catalytic reaction. Rational catalytic cycle of radical addition reaction catalysed by [Mo$_2$(DAniF)$_3$(OCO(CH$_3$))] (DAniF = CH$_3$NCHNCH$_3$) is proposed (Scheme 1). The catalytic activities of series of mixed-ligated dimolybdenum complexes are higher than those of homoleptic Mo$_2$ complexes [24].

In this work, the addition reaction between CCl$_4$ and 1-hexene catalysed by a series of quadruple-bonded dimolybdenum complexes are investigated based on density functional theory calculations. The aims of this work are (1) to illustrate the addition reaction mechanism of CCl$_4$ and 1-hexene catalysed by the quadruple-bonded dimolybdenum complexes, (2) to determine how the ligand tunes the catalytic activity of Mo$_2$L$_4$, and (3) to screen out the ligands of Mo$_2$L$_4$ with high activity. We seek to provide theoretical prediction for the catalytic activity of quadruple-bonded dimolybdenum paddlewheel complexes on radical addition reaction and to inspire the future applications in organic syntheses.

### Computational details

All of the calculations were performed at PBEPBE-D3 [28, 29]/Def2-SVP [30, 31] level using Gaussian 09 package [32]. A functional, including dispersion correction [33, 34], has been proven that it can provide accurate energies for transition metals [35]. The vibrational frequency calculations were calculated at the same level to confirm the stable structure has no and the transition state has only one imaginary frequency. Intrinsic reaction coordinate (IRC) [36, 37] was calculated to confirm the linkage relationship between the transition states and stable points. In order to characterize the chemical bond changes in the reaction pathway, the Wiberg bond index and natural population charge were also obtained at the PBEPBE/Def2-SVP level using NBO 3.1 programme [38].

### Results and discussion

#### Catalytic mechanism of Mo$_2$(CH$_3$NCHNCH$_3$)$_3$(OCOCH$_3$) (denoted as CAT) on title reaction

Based on the catalytic cycle for addition reaction of CCl$_4$ to 1-hexene catalysed by CAT (Scheme 1), the catalytic mechanism has been calculated and determined. This transformation involves 4 steps. Firstly, the C-Cl bond of first CCl$_4$ is activated by CAT, and [Mo$_2$L$_3$Cl](L=CH$_3$NCHNCH$_3$) and CH$_3$COOCCl$_3$ are obtained. Then the second CCl$_4$ adds to Mo$_2$L$_3$Cl to produce [Mo$_2$L$_3$Cl$_2$] and CCl$_3$ radical; CCl$_3$ radical interacts with 1-hexene to carry out another addition reaction, and Cl atom migrates from [Mo$_2$L$_3$Cl$_2$] to CCl$_3$ radical; CCl$_3$ radical interacts with 1-hexene to carry out another addition reaction, and Cl atom migrates from [Mo$_2$L$_2$Cl$_2$], and products 1,1,1,3-tetrachlorohexane $^6$BuCHClCH$_2$CCl$_3$ and [Mo$_2$L$_3$Cl] are regenerated. The optimized geometries of the catalyst, reactants, complexes (COM), transition states (TS), and products are shown in Fig. 1, with the main parameters labelled on the geometries. The optimized xyz coordinates for the stationary points are given in Table S1-S22 (Supporting Information). The potential energy surfaces of the C-Cl bond activation are shown in Fig. 2 and those of the addition reactions in Fig. 3. For convenience, the total energy of the reactants of each step is taken as the reference zero of energy.

#### First C-Cl bond activation

At the beginning of the reaction between CAT and CCl$_4$, the Cl of CCl$_4$ firstly interacts with one of the Mo atom of CAT to form COM1. In COM1, the two Mo atoms and two O atoms are in the same plane (D$_{Mo-Mo-O-O}=0^\circ$), and the bond length of Mo-O bond near the CCl$_4$
As the reaction happens, the Cl atom goes near to the Mo atom. At the same time, the O atom of OCOCH₃ ligand is pushed to leave away the Mo atom. In TS1, the distance between Mo and Cl decreases from 3.506 Å to 2.618 Å, and the Mo-O bond length increases to 3.128 Å, which means that Mo-O bond is broken. After TS1, the C-Cl bond of CCl₄ elongates gradually and the OCOCH₃ ligand leaves away the Mo atom, the D<sub>Mo-Mo-O-O</sub>−73.8° in COM2. Through TS2, the CCl₃ and OCOCH₃ leave away the [Mo₂] group and interact with each other to form CH₃OOCCl₃ and [Mo₂(CH₃NCHNCH₃)₃Cl] (PCI). In PCI, the Cl atom is above the Mo-Mo bond, and the two Mo-Cl bonds are just the equal.

The potential energy surface of this reaction step is shown in Fig. 2(1). The energy barrier (ΔG°) of TS1 is 21.5 kcal/mol and that of TS2 is 21.7 kcal/mol, and the energy barriers are not high; thus, this step could happen at mild conditions. Our calculated ΔG° is slightly smaller than that determined by kinetic experimental results, 26.0 kcal/mol at 303K [24]. The experimental
value is larger because it is determined in the presence of excess CCl₄ and pyridine; the coordination of pyridine suppresses the reaction, which has been found in former studies [2, 8]. In this step, the changes of Mo-Mo bond are slight. In CAT, the bond length of Mo-Mo bond is 2.098 Å, and the Wiberg bond order is 3.18. As the reaction happens, the Mo-Mo bond length increases a little. In PCl, the Wiberg bond order of Mo-Mo bond (3.23) is slightly larger than that in CAT.

**Second C-Cl bond activation** The second step also begins at the Cl atom of CCl₄ attacking the Mo atom of PCl to form the COM4. Then, this Cl atom links to Mo atom and pushes the Cl atom in PCl to another Mo atom through TS3 to form [Mo₂(CH₃NCHNCH₃)₃Cl₂] (PCl₂) and CCl₃ radical. As shown in Fig. 2(2), the $\Delta G^\#$ of TS3 is only 1.6 kcal/mol, and the energy of TS3 is lower than the sum energy of separated reactants PCl and CCl₄, meaning this step can occur easily. In PCl₂, the bond order of Mo-Mo decreases to 2.69.

**CCl₃ addition to 1-hexene** The dissociated CCl₃ radical attacks the C1 atom of 1-hexene with an energy barrier of 9.0 kcal/mol (Fig. 3). In this reaction process, the spin electron density migrates from the C atom of CCl₃ radical to the C2 atom of 1-hexene, COM7 forms. This step has been discussed in our former work [8].

**Cl atom migration and [Mo₂L₃Cl] regeneration** The last step of the reaction is the C2 atom of COM7 interacts with one Cl atom of PCl₂, and the Cl atom migrates from Mo atom to C2 atom via TS5. After TS5, COM9 forms, and then it separates to Product (Pro) 1,1,1,3-tetrachloroheptane and PCl. The $\Delta G^\#$ of this step is 16.2 kcal/mol.
In summary, the whole reaction pathway contains four steps. Among them, the first C-Cl bond activation process is the rate-determining step and it is not in the catalytic cycle. The catalytic cycle contains the second C-Cl bond activation, CCl₃ radical addition to 1-hexene, Cl atom migration, and [Mo₂L₃Cl] regeneration processes. The ΔGᵣ of the first step are about 22.0 kcal/mol; those of other three steps are within 20.0 kcal/mol. Therefore, increasing the reaction temperature could accelerate the first C-Cl bond activation process, and the whole reaction would speed up after a certain period of time and not need the heating.

**Influences of ligands on the catalytic activity**

Based on the mechanism study, the first step is the rate-determining step, and the experimental results show that the catalytic activity is correlated to the redox potential of Mo₂⁴⁺/Mo₂⁵⁺ [4, 27]. In order to screen out the high activity catalyst, the electronic structures of [Mo₂] complexes with different ligands are calculated. The relationship between the electronic structure and the ΔGᵣ of the first step is found to determine how the ligand tunes the catalytic activity of Mo₂L₄. The following catalysts are considered (Scheme 2).

The Gibbs energy barriers (ΔGᵣ), redox potentials (E(Mo₂⁴⁺/Mo₂⁵⁺)), and natural population analysis charges of Mo atom of different catalysts are listed in Table 1. In general, the Gibbs free energy change in solution (ΔGₘ) during the reduction is defined as the sum of the electron affinity (EA) and solvation energy (ΔΔGₘ) [39, 40]. The EA equals to the Gibbs free energy change in gas (ΔGₘ) and ΔΔGₘ is the Gibbs
energy changes from the neutral state to anionic state in the solvent states. That is, \( \Delta G_{\text{soln}} = E_A (\Delta G_{\text{gas}}) + \Delta \Delta G_{\text{solv}} \).

In this work, the calculation of redox potential is performed using a slightly modified procedure following an established method [41]. It is calculated as follows: Geometries were optimized in gas phase followed by single-point energy calculations in solvent CHCl₃. Solvation was modelled by the polarized continuum model (PCM). The Gibbs free energies of the redox reaction in CHCl₃ were calculated as follows:

\[
\Delta G_{\text{solv}} = G_{\text{solv}} (\text{Mo}^{4+}_2) - G_{\text{solv}} (\text{Mo}^{5+}_2) 
\]

Then the calculated Gibbs free energies were converted to absolute electron redox potential according to Nernst equation:

\[
\Delta G_{\text{solv}} = -F E (\text{Mo}^{4+}_2/\text{Mo}^{5+}_2) 
\]

where F is the Faraday constant, 96500 C·mol⁻¹.

Comparing the redox potential of Mo₂(CH₃NCHNCH₃)₄ with those of mixed-ligated [Mo₂] catalysts, it can be seen that the E(Mo₂⁴⁺/Mo₂⁵⁺) of Mo₂(CH₃NCHNCH₃)₄ is the lowest. As one CH₃NCHNCH₃ ligand is substituted by OCO(R) (R=CH₃, 3-py, 4-py, ph, Furan), the redox potential of E(Mo₂⁴⁺/Mo₂⁵⁺) increases distinctly. Moreover, the NPA charges of Mo atoms are also increased. The more positive charge of Mo atom will facilitate the attacking of Mo to Cl of CCl₄ with negative charge. Thus, the catalytic activities of mixed-ligated [Mo₂] catalysts are higher than those of homoleptic. The R in the ligands has little influence on the activity.

In total, the catalytic activity is correlated to the redox potential of E(Mo₂⁴⁺/Mo₂⁵⁺) and NPA charge of Mo. The higher E(Mo₂⁴⁺/Mo₂⁵⁺) and NPA charge of the catalyst, the higher activity it has.

### Conclusions

The detailed catalytic mechanisms of a series of paddlewheel complexes [Mo₂L₄] featuring Mo-Mo quadruply-bond with different ligands on the radical addition of CCl₄ to 1-hexene were investigated. The following conclusions can be drawn:

1. The Mo-Mo quadruply-bond paddlewheel complexes are good catalysts on the radical addition reaction of CCl₄ to 1-hexene.
2. The whole reaction involves 4 steps. The addition of the first CCl₄ is the rate-determining step of the whole reaction, and the reaction would speed up after a certain period of time.
3. The catalytic activity of dimolybdenum paddlewheel complex is depended on the natural population analysis (NPA) charge of Mo and the redox potential E(Mo²⁴⁺/
Mo$^{5+}$. The higher E(Mo$_2^{4+}$/Mo$_2^{5+}$) and NPA charge of the catalyst, the higher activity it has.

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Declarations

Conflict of interest The authors declare no competing interests.

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