Theoretical study on the reaction mechanism of “ligandless” Ni-catalyzed hydrodesulfurization of aryl sulfide†

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The reaction mechanism of Ni(COD)$_2$ catalyzed hydrodesulfurization of aryl sulfide PhSMe with HSiMe$_3$ as the reducing agent has been studied by using density functional theory methods. Both PhSMe-coordinated pathway and “ligandless” pathway have been identified and compared. It is found that these two reaction pathways are kinetically competitive and the σ-complex assisted metathesis (σ-CAM) transition state is the highest point on each energy profile for both pathways. Moreover, both the singlet and triplet reaction pathways of ligand substitutions have been compared and found that both singlet and triplet reaction mechanisms are competitive for the ligand substitution of COD with PhSMe on PhSMe-coordinated pathway while the triplet mechanism holds a distinct advantage over singlet one for that of COD with HSiMe$_3$ on “ligandless” pathway.

Introduction

Ni catalysts, which are less toxic and less expensive comparatively, have spurred considerable interest in synthetic organic chemistry, particularly in activating chemical bonds, such as C–H, C–C, C–O, C–N, C–S, and so on. Among all these bonds, the cleavage of C–S bonds has been less explored. Organosulfur compounds as electrophiles have been used in cross-coupling reactions to construct new C–C bonds. Moreover, the cleavage of C=S bonds in organosulfur compounds makes extensive use of removal of blocking groups and temporary directing groups. Hydrodesulfurization, i.e., cleaving the C=S bond to form C–H bond, plays an importance role in manufacturing nonpolluting fuel from natural resources. As early as 1940s, several Ni-mediated hydrodesulfurization reactions were reported with a large excess of Raney nickel as the reducing agent. The homogeneous Ni-catalyzed hydrodesulfurization was carried out first by Wenkert and co-workers with stoichiometric amounts of highly reactive Grignard reagents possessing β-hydrogens as the reducing agent. In 1999, Vicic and Jones found that the hydrodesulfurization of thiophene can be catalyzed by the nickel hydride dimer [[dippe]NiH$_2$] with H$_2$ as the reducing agent. Recently, silanes have been explored as the hydride source instead of H$_2$ in palladium, rhodium or nickel catalyzed hydrodesulfurization of aryl sulfides. The Ni(COD)$_2$ (COD = (Z,Z)-1,5-cyclooctadiene) catalyzed reactions of aryl methyl thiocarboxylates (ArSMe) with dimethylethylsilane (HSiMe$_2$Et) have been presented by Martin and co-workers (Scheme 1). It is found that the reaction gives excellent chemoselectivity under relatively mild reaction condition (90 °C), and especially the reaction can proceed under “ligandless” condition, i.e., the typical σ-donor ancillary ligands such as phosphines are not present.

By the experimental deuterium-labeling analysis, the authors ruled out the possibility of β-H elimination and proposed a possible reaction mechanism, which consists of oxidative addition, metathesis and reductive elimination steps. However, the details of the reaction mechanism were not studied and some fundamental issues remain to be answered. For example, although there are no σ-donor ancillary ligands under the reaction condition, the reactant ArSMe has the S atom, which can coordinate to the metal center to form σ-donor bond. As the bond dissociation energies of Ni ← C$_2$H$_4$ coordinate bonds (34.3–41.2 kcal mol$^{-1}$) have been calculated to be a little higher than these of Ni ← S coordinate bonds (25.2–37.0 kcal mol$^{-1}$), whether or not the reactant ArSMe replaces COD in Ni(COD)$_2$ acting as spectator ligand should be considered.

Scheme 1 Ni(COD)$_2$ catalyzed reaction of aryl methyl thiocarboxylates with dimethylethylsilane.
In this paper, the detailed reaction mechanism is investigated by using density functional theory (DFT) methods. To simplify the reaction, ArSMe and HSiMe₂Et are modeled by PhSMe and HSiMe₃, respectively. The reaction pathways with or without PhSMe (i.e., the “ligandless” one) as spectator ligand have been calculated and compared to figure out which one is preferred. As Ni(0)/Ni(II) and Ni(i)/Ni(III) catalytic cycles, which may include low spin and high spin species, are generally involved in nickel catalyzed reactions, the different oxidation states and spin states of Ni are also considered. Hoping this theoretical study will give an insight into understanding the reaction mechanism of the “ligandless” reaction in detail.

Computational details

All calculations were performed with Gaussian09 package. Molecular geometries of the model complexes were optimized without symmetry constraints via DFT calculations using B3LYP functional, which has been shown to be adequate for studies of many nickel catalyzed reactions. The Wachters-Hay basis set 6-311G was used for Ni with an additional set of d polarization function, while all other main group atoms were described with 6-31G(d) basis set (the combination of the two basis sets is named as BS1). The ultrafine integration grid (99 590) was employed for making such optimizations more reliable. Frequencies calculations were carried out at the same level of theory to check all the optimized geometries as minima or transition states and to obtain zero point energy and thermal correction to free energies at 298.15 K and 1 atm. Intrinsic reaction coordinates (IRC) using the local quadratic approximation (LQA) were calculated for each transition state to confirm the connecting of two relevant minima. To consider solvent effects, the single-point energy calculations for all the gas-phase optimized species were implemented at the level of ωB97XD functional combined with a larger basis set 6-31++G(d,p) using the SMD model in toluene. If not specifically pointed out, all energies during this article are based on the sum of Gibbs free energies of Ni(COD)₂ + 2PhSMe + HSiMe₃ in toluene solvent. Minimum energy crossing point (MECP) program was applied to locate the crossing point between singlet and triplet species if necessary.

Results and discussion

Complex Ni(COD)₂, 1, the precursor of catalyst in experiments, has been calculated firstly and compared with the X-ray crystal structure (Fig. 1). It is found that both the calculated bond distances of four coordination bonds and the two calculated bite angles of COD agree well with the experimentally measured parameters having the absolute differences within 0.013 Å and 0.4°, respectively, suggesting that the computational method is adequate to give the accurate molecular geometries.

To generate a vacant coordination site, one C=C double bond of a chelating COD ligand in 1 dissociates via transition state TS₁ to give complex 2 with the C=C double bond dangling free (Fig. 2). The conformation of the non-chelating COD in 2 is twist-boat, same as in the Ni(0) complex observed by Tauchert et al. in experiment. The coordination of thioether PhSMe and dissociation of non-chelating COD occur simultaneously through interchange mechanism via transition state TS₂ to form complex 3, in which PhSMe is coordinated to Ni with one double bond of benzene ring. TS₂ is 23.2 kcal mol⁻¹ higher than the reference point.

Oxidative addition of PhSMe to Ni(0) center proceeds via transition state TS₃ leading to phenyl-Ni(II) thiolate complex 4 (Fig. 3), followed by the dissociation of one C=C bond of chelating COD through transition state TS₄ to give complex 5A. In complex 5A, the Ph group is trans to the vacant site due to its relatively strong trans influence. The overall energy barrier of oxidative addition of PhSMe is 26.3 kcal mol⁻¹ relative to the reference point. In addition, replacing two COD ligands of 1 with two PhSMe molecules generating Ni(PhSMe)₂ 1T has also been considered, it is found that the corresponding oxidative addition of PhSMe to Ni(PhSMe)₂ 1T is not feasible kinetically (see Fig. S1 in ESI†).
The silane HSiMe₃ coordinates directly to complex 5A from the vacant site via TS₅A-6A giving complex 6A, followed by σ-CAM assisted metathesis (σ-CAM)³⁰ through TS₆A-7 to generate complex 7 in which the formed (methylthio)trime-thylsilane (Me₃SiSMe) is coordinated to Ni center (Fig. 4a). In Fig. 4b, isomerization of 5A generates complex 5B with the vacant site trans to the methylthio group (SMe). When HSiMe₃ coordinates to complex 5B from the vacant site occurs via TS₅B-6B giving complex 6B, from which the σ-CAM proceeds through TS₆B-8 to release one benzene and generate complex 8 simultaneously. In addition, two other σ-CAM transition states are given in Fig. S2. As these four corresponding σ-CAM transition states are higher than 35 kcal mol⁻¹, indicating that the σ-CAM process with COD coordinated to Ni is not kinetically feasible.

As mentioned in Introduction that the reactant thioether PhSMe may coordinate to Ni center to form σ-donor bond, the process involving thioether PhSMe substitution of COD are calculated and presented in Fig. 5. The coordination of PhSMe to complex 5A proceeds via TS₅A-9A giving complex 9A, followed by the dissociation of COD via TS₉A-10A giving complex 10A. The isomerization of 5A forms complex 5C, from which the coordination of PhSMe and dissociation of COD can occur simultaneously through TS₅C-10B to generate complex 10B, which is the isomer of 10A (Fig. 5a). In Fig. 5b, the dissociation of COD from 5A first proceeds via TS₅A-11 forming complex 11, then coordination of PhSMe occurs via TS₁₁-10A giving complex 10A. Fig. 5c shows another reaction pathway to generate complex 10A. Following the coordination of PhSMe from the site between Ph and COD via TS₅A-9B to give complex 9B, the dissociation of COD proceeds via TS₉B-10A forming complex 10A. Among the four pathways of replacing COD ligand with PhSMe, the last one, i.e., 5A → TS₅A-9B → 9B → TS₉B-10A → 10A, is most favorable as transition state TS₅A-9B is the lowest one.

From complex 10A or 10B, there are four reaction pathways involving σ-CAM processes to generate Me₃SiSMe or benzene (Fig. 6). The silane HSiMe₃ coordinates directly to complex 10B from the vacant site via TS₁₀B-12A giving complex 12A, followed by σ-CAM through TS₁₂A-13A to generate complex 13A in which the formed Me₃SiSMe is coordinated to Ni center. Releasing Me₃SiSMe or PhSMe from metal center generates three-coordinated complex 14 or 15. As 14 and 15 are higher than 35 kcal mol⁻¹ in energy, indicating that the reaction pathways involving TS₁₂A-13A is not feasible thermodynamically (Fig. 6a). In Fig. 6b, HSiMe₃ coordination to complex 10A from the site between PhSMe and Ph occurs via TS₁₀A-12B giving complex 12B, from which the σ-CAM proceeds through TS₁₂B-16A to generate complex 16A with benzene coordinated to Ni center. When HSiMe₃ coordinates to complex 10A from the site between Ph and SMe, the reaction involves TS₁₀A-12C to give complex 12C, followed by two σ-CAM via TS₁₂C-13B and TS₁₂C-16B, respectively, to generate complexes 13B and 16B, with the formed Me₃SiSMe and benzene coordinated to Ni center (Fig. 6c). Since TS₁₂C-16B (Fig. 6c) is lower than TS₁₂C-13B (Fig. 6c) and TS₁₂B-16A (Fig. 6b) by 3.0 and 4.1 kcal mol⁻¹, respectively, the pathway involving TS₁₂C-16B to generate complex 16B is most favorable.

Releasing benzene or PhSMe from complex 16B occurs via TS₁₆B-17 or TS₁₆B-18A forming three-coordinated complex 17 or 18A (Fig. 7), followed by the corresponding reductive elimination through TS₁₇-19 or TS₁₈A-20 to generate complex 19 or 20. The ligand substitution of PhSMe in 19 or benzene in 20 with

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**Fig. 3** Energy profile of oxidative addition and ligand dissociation to give complex 5A (values are given in kcal mol⁻¹).

**Fig. 4** Energy profiles of σ-CAM process from complex 5A or 5B with HSiMe₃: (a) coordination of HSiMe₃ directly to the vacant site; (b) coordination of HSiMe₃ from the site between COD and Ph (values are given in kcal mol⁻¹).
COD ligand gives complex 21, and subsequently ligand substitution of Me3SiSMe with another COD regenerates complex Ni(COD)2 1. Since the energy difference between TS16B–17 and TS16B–18A is only 0.5 kcal mol\(^{-1}\), in order to give more accurate comparison, the single-point energies for these two transition states were re-calculated at the \(\omega\)B97XD/def2-QZVPPD level. It is found that TS16B–17 is only 0.1 kcal mol\(^{-1}\) lower than TS16B–18A. These results indicate that the dissociation of PhSMe or benzene ligand from 16B occurs randomly.

Fig. 5  Energy profiles of ligand substitution of COD with PhSMe: (a) coordination of PhSMe followed by dissociation of COD or simultaneously; (b) coordination of PhSMe following dissociation of COD; (c) coordination of PhSMe from the site between Ph and COD followed by dissociation of COD (values are given in kcal mol\(^{-1}\)).

COD ligand gives complex 21, and subsequently ligand substitution of Me3SiSMe with another COD regenerates complex Ni(COD)2 1. Since the energy difference between TS16B–17 and TS16B–18A is only 0.5 kcal mol\(^{-1}\), in order to give more accurate comparison, the single-point energies for these two transition states were re-calculated at the \(\omega\)B97XD/def2-QZVPPD level. It is found that TS16B–17 is only 0.1 kcal mol\(^{-1}\) lower than TS16B–18A. These results indicate that the dissociation of PhSMe or benzene ligand from 16B occurs randomly.

Fig. 6  Energy profiles of \(\sigma\)-CAM process from complex 10A or 10B with HSiMe3: (a) coordination of HSiMe3 directly to the vacant site; (b) coordination of HSiMe3 from the site between PhSMe and Ph; (c) coordination of HSiMe3 from the site between Ph and SMe (values are given in kcal mol\(^{-1}\)).
The mechanism without COD ligand or PhSMe spectator ligand has also been considered. In Fig. 8, following the coordination of HSiMe₃ to the vacant site of three-coordinated complex 5A via TS₅₆-2₂, the release of COD proceeds via TS₂₂₋₂₃ₐ giving complex 2₃ₐ, in which an agostic interaction is formed. Isomerization of 2₃ₐ generates complex 2₃ₐ with the vacant site trans to Ph ligand. TS₂₂₋₂₃ₐ (35.1 kcal mol⁻¹) is relatively high in energy, showing that this associated mechanism of ligand substitution is not favorable to form the complex without coordinated COD. Another reaction pathway to generate complex 2₃ₐ was found and presented in Fig. 9 involving several triplet transition states and intermediates. Complex 5ₐ first isomerizes to 5ₐ and then overcomes a crossing point CP₁ to form a triplet 5ₐ which gives complex 2₃ₐ in which HSiMe₃ is weakly coordinated to Ni with relatively long Ni–H and Ni–Si bond distances of 2.28 and 3.58 Å, respectively, and COD is strongly coordinated to Ni with two relatively short Ni–C bond distances of 2.21 and 2.37 Å, respectively. Complex 2₂₋₂₃ₐ isomerizes via TS₂₃₋₂₃ₐ to form complex 2₂₋₂₃ₐ, which has relatively short Ni–H and Ni–Si bond distances of 1.86 and 3.19 Å, as well as two relatively long Ni–C bond distances of 2.63 and 2.64 Å. Release of COD proceeds via TS₃₋₂₃ₐ giving complex 2₃ₐ (Fig. 9b). There is another pathway from 5ₐ to form complex 2₃ₐ (Fig. 9c). The dissociation of COD first proceeds via TS₃₋₄ₐ giving complex 4ₐ, then coordination of PhSMe occurs via TS₃₋₄ₐ giving complex 2₃ₐ. Isomerization of 2₃ₐ takes place to form complex 2₃ₐ, which goes through a crossing point CP₂ to generate the singlet complex 2₃ₐ mentioned in Fig. 8. TS₃₋₄ₐ, the most high point on this triplet reaction pathway 5ₐ → 5ₐ → CP₁ → 5ₐ → 5ₐ → TS₅₆₋₂₃ₐ → 2₃ₐ → TS₂₂₋₂₃ₐ → 2₂₋₂₃ₐ → 2₃ₐ → TS₂₃₋₂₃ₐ → 2₃ₐ in Fig. 9, is 25.5 kcal mol⁻¹ lower than TS₂₂₋₂₃ₐ on the corresponding singlet reaction pathway (Fig. 8), indicating that this reaction pathway involving a double spin-flip singlet → triplet → singlet is preferred kinetically. Similar double spin-flip course has been
reported by Schlangen and Schwarz in computational study of NiH⁺ + CH₄ → Ni(CH₃)⁺ + H₂ reaction.⁵¹

From complex 23B (Fig. 10), the σ-CAM proceeds via TS₂₃B–18B and TS₂₃B–24 to give complex 18B and 24 with the formed benzene and Me₃SiSMe as ligand, respectively. TS₂₃B–18B is 6.2 kcal mol⁻¹ lower than TS₂₃B–24, showing that the σ-CAM process giving the benzene coordinated complex 18B is preferred. Isomerization of 18B generates complex 18A, which has been mentioned in Fig. 7.

Since the reaction pathway involving the triplet species has been found to be preferred for ligand substitution of COD in complex 5A with HSiMe₃ to generate complex 23B (Fig. 8 and 9), the corresponding triplet mechanism should be considered for ligand substitution of COD in complex 5A with reactant PhSMe to give complex 10A, the singlet pathway of which has been discussed in Fig. 5c. Isomerization of the triplet complex 5B⁴ generated from the singlet complex 5A through a crossing point CP1 (Fig. 9a) forms complex 5C⁴ (Fig. 11). Coordination of PhSMe proceeds via TS₅C–9A forming complex 9A⁴, subsequently isomerization of 9A⁴ gives complex 9B⁴, in which PhSMe is weakly coordinated with relatively long Ni–S bond distance of 2.577 Å, and COD is strongly coordinated with two relatively short Ni–C bonds of 2.265 and 2.425 Å, respectively. Complex 9B⁴ isomerizes via TS₅C–9A, giving complex 9C⁴ which has relatively short Ni–S bond of 2.438 Å, and two relatively long Ni–C bonds of 2.651 and 2.641 Å. Release of COD proceeds via TS₅C–9A, giving complex 10³ which can overcome a crossing point CP3 (Fig. 12) to generate the singlet complex 10A which has emerged in Fig. 5. Comparing the most favored singlet (Fig. 5c) and triplet (Fig. 9a, 11 and 12) reaction pathways, it is found that the highest singlet transition state TS₅5A–9B (27.2 kcal mol⁻¹ in Fig. 5c) is only 0.8 kcal mol⁻¹ higher than the triplet one TS₅C–9A (26.4 kcal mol⁻¹ in Fig. 11). In order to give more accurate comparison, the single-point energies for TS₅A–9B and TS₅C–9A were re-calculated at the ωB97XD/def2-QZVPDP level. It is found that TS₅A–9B is only 0.5 kcal mol⁻¹ higher than TS₅C–9A. These results indicate that the two reaction pathways are competitive with the triplet one slightly favored.

Besides the reactant PhSMe (Fig. 2), another reactant HSiMe₃ may also react first with complex 2 (Fig. 13). Oxidative addition of HSiMe₃ and dissociation of the dangling COD ligand from complex 2 proceed simultaneously via transition state TS₂₅ giving complex 25, from which one C=C bond of chelating COD dissociates through transition state TS₂₅–26 forming complex 26. The energy barrier of TS₂₅–26 is 28.5 kcal mol⁻¹, still lower.
Fig. 11  Energy profile of triplet mechanism of ligand substitutions of COD with PhSMe (values are given in kcal mol\(^{-1}\)).

Fig. 12  Energy profile of spin cross process from triplet state to singlet state (values are given in kcal mol\(^{-1}\)).

Scheme 2  Transition states of metathesis or quasi-metathesis processes from various Ni-hydride species with PhSMe. \(^a\)Quasi-metathesis with two or more steps. \(^b\)Standard \(\sigma\)-metathesis. \(^c\)Oxidative addition of HSiMe\(_3\) occurs simultaneously. \(^d\)H atom of the Ni-hydride has to migrate to the COD ligand or the phenyl ring before this transition state (values are given in kcal mol\(^{-1}\)).
necessary to consider the following metathesis steps. The corresponding transition states of metathesis or quasi-metathesis to generate Me$_3$SiSMe or benzene are listed in Scheme 2. Three situations of ligand ($L_n$) and the corresponding four topological orientations have been considered. It is found that all the transition states are higher than 60 kcal mol$^{-1}$ in energy, indicating that all the reaction pathways following the reaction of HSiMe$_3$ with complex 2 are not feasible kinetically (see Fig. S3–S5† for details of these reactions).

In addition, since the formation of dimeric Ni(i) complex and Ni(i) radical (Scheme 3) has been demonstrated theoretically to be favored by using the phosphine ligand, but not by using the NHC ligand, we also calculated the reaction free energies for the formation of Ni(i) species with COD ligand. However, the reaction is 52.1 kcal mol$^{-1}$ endergonic, showing that the Ni(i) species are thermodynamically unstable.

The overall catalytic cycles are presented in Fig. 14. The reaction mainly involves oxidative addition, ligand substitution, σ-CAM, reductive elimination and ligand substitution steps. For the first ligand substitution and σ-CAM steps, two reaction pathways, i.e., the PhSMe-coordinated pathway and the “ligandless” pathway are involved having very small energy difference, only 0.2 kcal mol$^{-1}$ between the rate-determining σ-CAM transition state $TS_{12C-16B}$ (30.0 kcal mol$^{-1}$ in Fig. 6c) in the former pathway and $TS_{23B-18B}$ (30.2 kcal mol$^{-1}$ in Fig. 10) in the latter one, indicating the two reaction pathways are competitive. The single-point energies of $TS_{12C-16B}$ and $TS_{23B-18B}$ were re-calculation at the ωB97XD/def2-QZVPPD level, and it is found that $TS_{12C-16B}$ becomes slightly higher than $TS_{23B-18B}$ by

Scheme 3 The comparison of reaction free energies ($\Delta G^\circ$, in kcal mol$^{-1}$) of the formation of dimeric Ni(i) complexes and Ni(i) radicals with two previous works.

Fig. 14 The overall catalytic cycles (values of energy are given in kcal mol$^{-1}$).
The reaction rate of PhSMe-coordinated pathway slows down when the PhSMe concentration becomes so low that there are no enough PhSMe spectator ligands.

Conclusions
The detailed reaction mechanism of Ni(COD)₂ catalyzed reaction of PhSMe with HSiMe₃ has been investigated by using density functional theory methods. The reaction mainly involves oxidative addition, ligand substitution, metathesis, reductive elimination and ligand substitution steps. For the first ligand substitution and σ-CAM, both PhSMe-coordinated pathway and “ligandless” pathway have been presented. It is found that the singlet and triplet pathways are competitive for ligand substitution of COD with PhSMe on PhSMe-coordinated pathway and that of COD with HSiMe₃ on “ligandless” pathway prefers the triplet mechanism. The σ-CAM transition states of these two pathways are the rate-determining TSs for the whole reaction process, with an energy difference of 0.2 (±0.3) kcal mol⁻¹ at the ωB97XD/6-311+G(d,p)//B3LYP/BSI (ωB97XD/def2-QZVPFPD//B3LYP/BSI) level, indicating both pathways are competitive. The competition of both pathways combined with the experimental 99% yield points out that the reaction should proceed on two pathways in early stage, as the concentration of reactant PhSMe decreases, the reaction would go on the “ligandless” reaction pathway.

Conflicts of interest
There are no conflicts to declare.

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Notes and references


