

## PAPER

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## Theoretical study on the reaction mechanism of "ligandless" Ni-catalyzed hydrodesulfurization of aryl sulfide†

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The reaction mechanism of Ni(COD)<sub>2</sub> catalyzed hydrodesulfurization of aryl sulfide PhSMe with HSiMe<sub>3</sub> 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  $\sigma$ -complex assisted metathesis ( $\sigma$ -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<sub>3</sub> on "ligandless" pathway.

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## 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,<sup>1</sup> C–C,<sup>2</sup> C–O,<sup>3</sup> C–N,<sup>4</sup> C–S,<sup>5–8</sup> 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.<sup>5</sup> Moreover, the cleavage of C–S bonds in organosulfur compounds makes extensive use of removal of blocking groups<sup>6</sup> and temporary directing groups.<sup>7</sup>

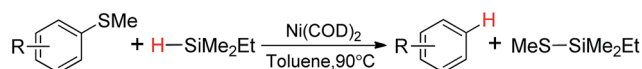
Hydrodesulfurization, *i.e.*, cleaving the C–S bond to form C–H bond, plays an importance role in manufacturing nonpolluting fuel from natural resources.<sup>8,9</sup> As early as 1940s, several Ni-mediated hydrodesulfurization reactions were reported with a large excess of Raney nickel as the reducing agent.<sup>10</sup> The homogeneous Ni-catalyzed hydrodesulfurization was carried out first by Wenkert and co-workers with stoichiometric amounts of highly reactive Grignard reagents possessing  $\beta$ -hydrogens as the reducing agent.<sup>11</sup> In 1999, Vicic and Jones found that the hydrodesulfurization of thiophene can be catalyzed by the nickel hydride dimer [(dippe)NiH]<sub>2</sub> with H<sub>2</sub> as the reducing agent.<sup>12</sup> Recently, silanes have been explored as the

hydride source instead of H<sub>2</sub> in palladium,<sup>13</sup> rhodium<sup>14</sup> or nickel<sup>15</sup> catalyzed hydrodesulfurization of aryl sulfides. The Ni(COD)<sub>2</sub> (COD = (Z,Z)-1,5-cyclooctadiene) catalyzed reactions of aryl methyl thioethers (ArSMe) with dimethylethylsilane (HSiMe<sub>2</sub>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  $\sigma$ -donor ancillary ligands such as phosphines are not present.<sup>15</sup>

By the experimental deuterium-labeling analysis,<sup>15</sup> the authors ruled out the possibility of  $\beta$ -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.<sup>15</sup> For example, although there are no  $\sigma$ -donor ancillary ligands under the reaction condition, the reactant ArSMe has the S atom, which can coordinate to the metal center to form  $\sigma$ -donor bond. As the bond dissociation energies of Ni  $\leftarrow$  C<sub>2</sub>H<sub>4</sub> coordinate bonds<sup>16</sup> (34.3–41.2 kcal mol<sup>−1</sup>) have been calculated to be a little higher than these of Ni  $\leftarrow$  S coordinate bonds<sup>17</sup> (25.2–37.0 kcal mol<sup>−1</sup>), whether or not the reactant ArSMe replaces COD in Ni(COD)<sub>2</sub> acting as spectator ligand should be considered.

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† Electronic supplementary information (ESI) available: Energy profiles of several secondary reaction pathways. Computation data of all transition states, minima and crossing points. Energy test of different post-HF and DFT methods. See DOI: 10.1039/c7ra10755b



Scheme 1 Ni(COD)<sub>2</sub> catalyzed reaction of aryl methyl thioethers with dimethylethylsilane.

In this paper, the detailed reaction mechanism is investigated by using density functional theory (DFT) methods. To simplify the reaction, ArSMe and HSiMe<sub>2</sub>Et are modeled by PhSMe and HSiMe<sub>3</sub>, 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,<sup>18</sup> 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.<sup>19</sup> Molecular geometries of the model complexes were optimized without symmetry constraints *via* DFT calculations using B3LYP functional,<sup>20</sup> which has been shown to be adequate for studies of many nickel catalyzed reactions.<sup>21</sup> The Wachters-Hay basis set 6-311G<sup>22</sup> 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 BSI). 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)<sup>23</sup> 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<sup>24</sup> combined with a larger basis set 6-311++G(d,p) using the SMD model<sup>25</sup> in toluene. If not specifically pointed out, all energies during this article are based on the sum of Gibbs free energies of Ni(COD)<sub>2</sub> + 2PhSMe + HSiMe<sub>3</sub> in toluene solvent. Minimum energy crossing point (MECP) program<sup>26</sup> was applied to locate the crossing point between singlet and triplet species if necessary.

## Results and discussion

Complex Ni(COD)<sub>2</sub> **1**, the precursor of catalyst in experiments,<sup>15</sup> has been calculated firstly and compared with the X-ray crystal structure (Fig. 1).<sup>28</sup> 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 TS<sub>1-2</sub> generating 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

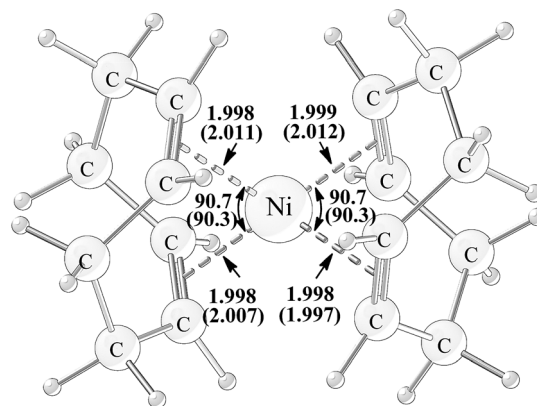


Fig. 1 Geometry structure of Ni(COD)<sub>2</sub> with the calculated and experimentally measured (in parentheses) bond distances (in unit of angstrom) and bite angles (in unit of degree).

by Tauchert *et al.* in experiment.<sup>29</sup> The coordination of thioether PhSMe and dissociation of non-chelating COD occur simultaneously through interchange mechanism *via* transition state TS<sub>2-3</sub> to form complex **3**, in which PhSMe is coordinated to Ni with one double bond of benzene ring. TS<sub>2-3</sub> is 23.2 kcal mol<sup>-1</sup> higher than the reference point.

Oxidative addition of PhSMe to Ni(0) center proceeds *via* transition state TS<sub>3-4</sub> 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 TS<sub>4-5A</sub> 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<sup>-1</sup> relative to the reference point. In addition, replacing two COD ligands of **1** with two PhSMe molecules generating Ni(PhSMe)<sub>2</sub> **1T** has also been considered, it is found that the corresponding oxidative addition of PhSMe to Ni(PhSMe)<sub>2</sub> **1T** is not feasible kinetically (see Fig. S1 in ESI†).

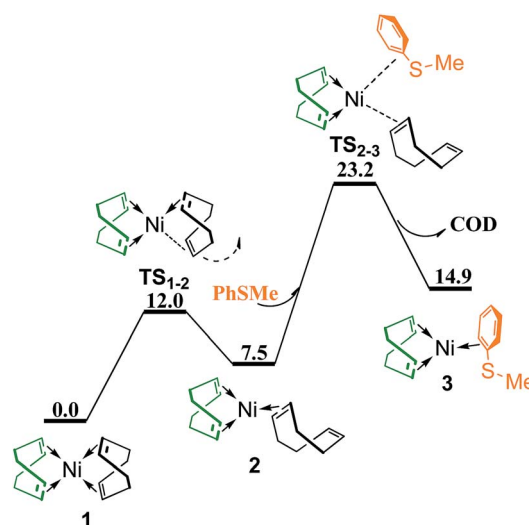


Fig. 2 Energy profile of ligand substitution of COD with PhSMe to give complex **3** (values are given in kcal mol<sup>-1</sup>).



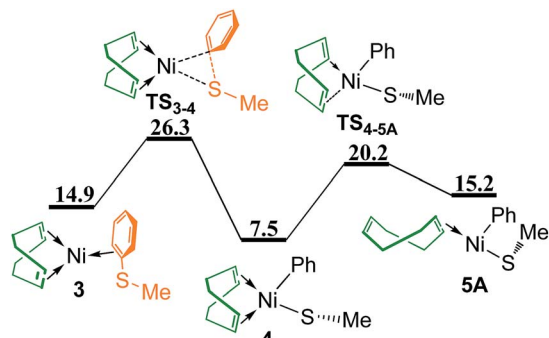


Fig. 3 Energy profile of oxidative addition and ligand dissociation to give complex 5A (values are given in kcal mol<sup>-1</sup>).

The silane HSiMe<sub>3</sub> coordinates directly to complex 5A from the vacant site *via* TS<sub>5A-6A</sub> giving complex 6A, followed by  $\sigma$ -complex assisted metathesis ( $\sigma$ -CAM)<sup>30</sup> through TS<sub>6A-7</sub> to generate complex 7 in which the formed (methylthio)trimethylsilane (Me<sub>3</sub>SiSMe) 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 HSiMe<sub>3</sub> coordinates to complex 5B from the vacant site occurs *via* TS<sub>5B-6B</sub> giving complex 6B, from which the  $\sigma$ -CAM proceeds through TS<sub>6B-8</sub> to release one benzene and generate complex 8 simultaneously. In addition, two other  $\sigma$ -CAM transition states are given in Fig. S2.<sup>†</sup> As these four corresponding  $\sigma$ -CAM transition states are higher than 35 kcal mol<sup>-1</sup>, indicating that the  $\sigma$ -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  $\sigma$ -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* TS<sub>5A-9A</sub> generating complex 9A, followed by the dissociation of COD *via* TS<sub>9A-10A</sub> giving complex 10A. The isomerization of 5A forms complex 5C, from which the coordination of PhSMe and dissociation of COD can occur simultaneously through TS<sub>5C-10B</sub> to generate complex 10B, which is the isomer of 10A (Fig. 5a). In Fig. 5b, the dissociation of COD from 5A first proceeds *via* TS<sub>5A-11</sub> forming complex 11, then coordination of PhSMe occurs *via* TS<sub>11-10A</sub> 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* TS<sub>5A-9B</sub> to give complex 9B, the dissociation of COD proceeds *via* TS<sub>9B-10A</sub> forming complex 10A. Among the four pathways of replacing COD ligand with PhSMe, the last one, *i.e.*, 5A  $\rightarrow$  TS<sub>5A-9B</sub>  $\rightarrow$  9B  $\rightarrow$  TS<sub>9B-10A</sub>  $\rightarrow$  10A, is most favorable as transition state TS<sub>5A-9B</sub> is the lowest one.

From complex 10A or 10B, there are four reaction pathways involving  $\sigma$ -CAM processes to generate Me<sub>3</sub>SiSMe or benzene (Fig. 6). The silane HSiMe<sub>3</sub> coordinates directly to complex 10B from the vacant site *via* TS<sub>10B-12A</sub> giving complex 12A, followed by  $\sigma$ -CAM through TS<sub>12A-13A</sub> to generate complex 13A in which the formed Me<sub>3</sub>SiSMe is coordinated to Ni center. Releasing Me<sub>3</sub>SiSMe or PhSMe from metal center generates three-coordinated complex 14 or 15. As 14 and 15 are higher than 35 kcal mol<sup>-1</sup> in energy, indicating that the reaction pathways

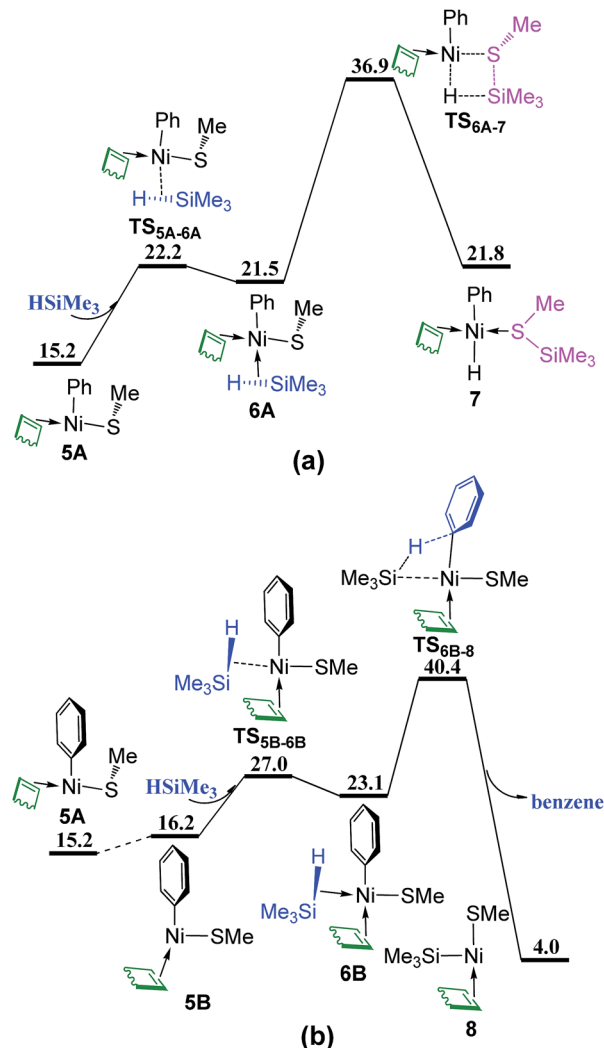


Fig. 4 Energy profiles of  $\sigma$ -CAM process from complex 5A or 5B with HSiMe<sub>3</sub>: (a) coordination of HSiMe<sub>3</sub> directly to the vacant site; (b) coordination of HSiMe<sub>3</sub> from the site between COD and Ph (values are given in kcal mol<sup>-1</sup>).

involving TS<sub>12A-13A</sub> is not feasible thermodynamically (Fig. 6a). In Fig. 6b, HSiMe<sub>3</sub> coordination to complex 10A from the site between PhSMe and Ph occurs *via* TS<sub>10A-12B</sub> giving complex 12B, from which the  $\sigma$ -CAM proceeds through TS<sub>12B-16A</sub> to generate complex 16A with benzene coordinated to Ni center. When HSiMe<sub>3</sub> coordinates to complex 10A from the site between Ph and SMe, the reaction involves TS<sub>10A-12C</sub> to give complex 12C, followed by two  $\sigma$ -CAM *via* TS<sub>12C-13B</sub> and TS<sub>12C-16B</sub>, respectively, to generate complexes 13B and 16B, with the formed Me<sub>3</sub>SiSMe and benzene coordinated to Ni center (Fig. 6c). Since TS<sub>12C-16B</sub> (Fig. 6c) is lower than TS<sub>12C-13B</sub> (Fig. 6c) and TS<sub>12B-16A</sub> (Fig. 6b) by 3.0 and 4.1 kcal mol<sup>-1</sup>, respectively, the pathway involving TS<sub>12C-16B</sub> to generate complex 16B is most favorable.

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



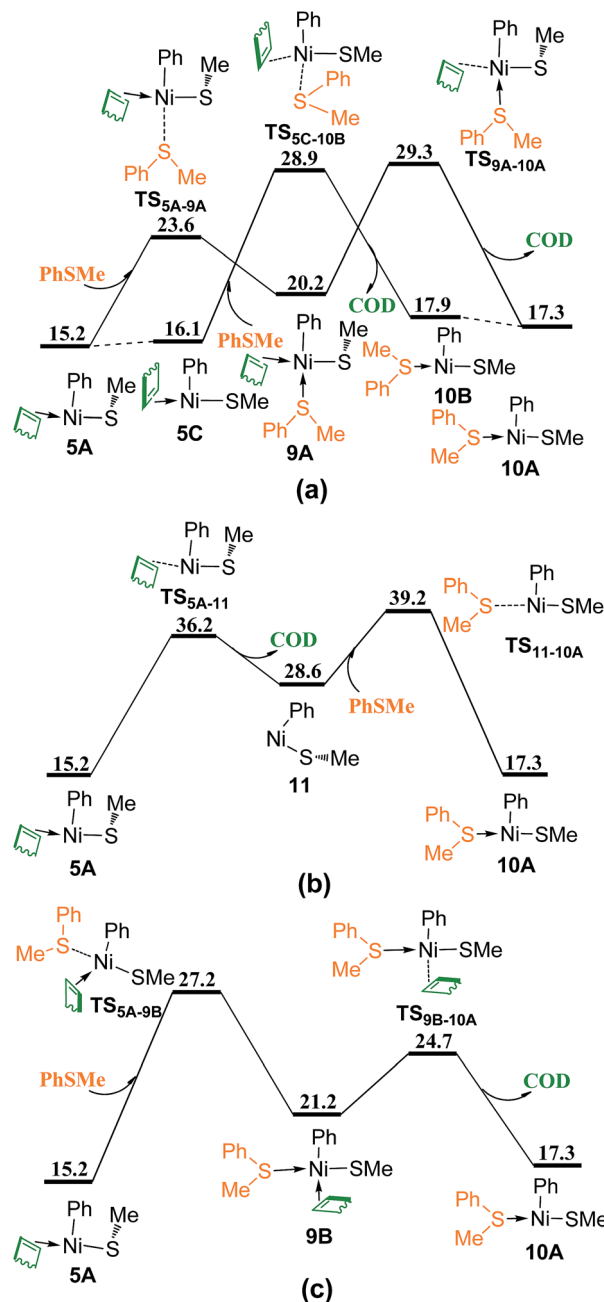


Fig. 5 Energy profiles of ligand substitution of COD with PhSMe: (a) coordination of PhSMe followed by dissociation of COD or simultaneously; (b) coordination of PhSMe following dissociation of COD; (c) coordination of PhSMe from the site between Ph and COD followed by dissociation of COD (values are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

COD ligand gives complex **21**, and subsequently ligand substitution of Me<sub>3</sub>SiSMe with another COD regenerates complex Ni(COD)<sub>2</sub> **1**. Since the energy difference between TS<sub>16B-17</sub> and TS<sub>16B-18A</sub> is only 0.5 kcal mol<sup>-1</sup>, in order to give more accurate comparison, the single-point energies for these two transition states were re-calculated at the ωB97XD/def2-QZVPPD level. It is found that TS<sub>16B-17</sub> is only 0.1 kcal mol<sup>-1</sup> lower than TS<sub>16B-18A</sub>. These results indicate that the dissociation of PhSMe or benzene ligand from **16B** occurs randomly.

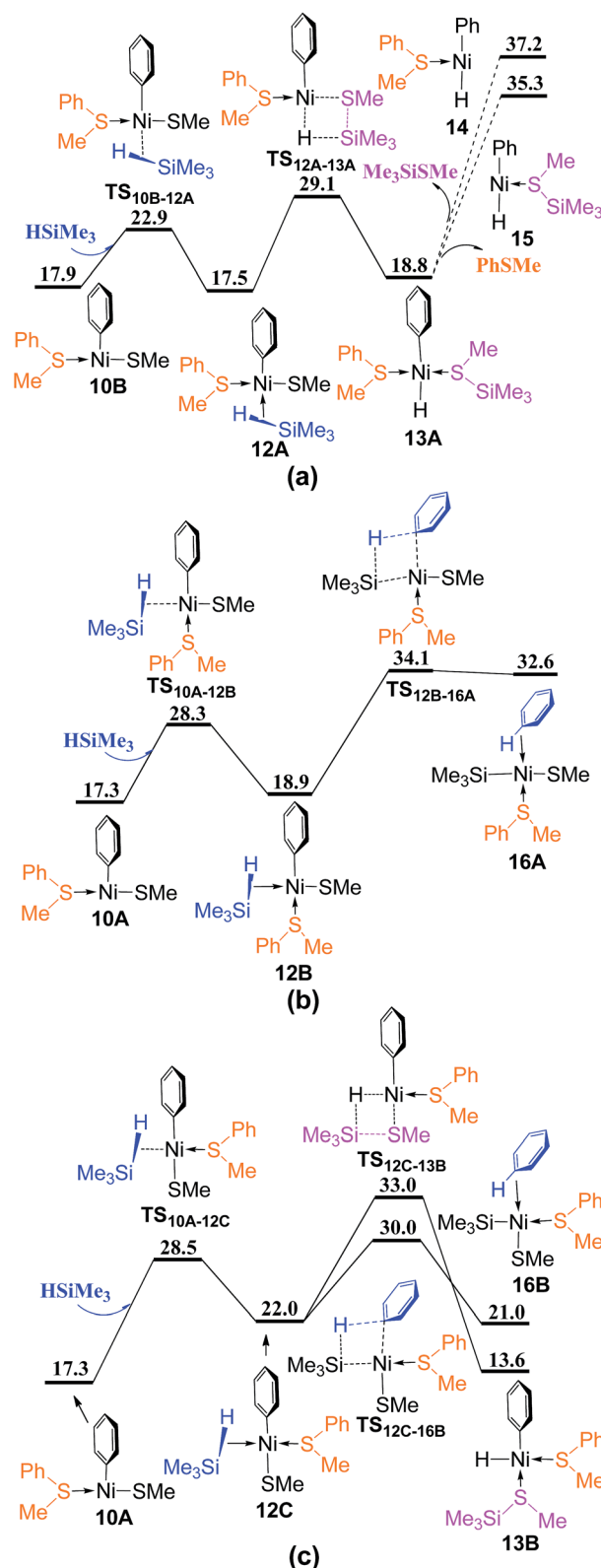


Fig. 6 Energy profiles of σ-CAM process from complex 10A or 10B with HSiMe<sub>3</sub>: (a) coordination of HSiMe<sub>3</sub> directly to the vacant site; (b) coordination of HSiMe<sub>3</sub> from the site between PhSMe and Ph; (c) coordination of HSiMe<sub>3</sub> from the site between Ph and SMe (values are given in kcal mol<sup>-1</sup>).





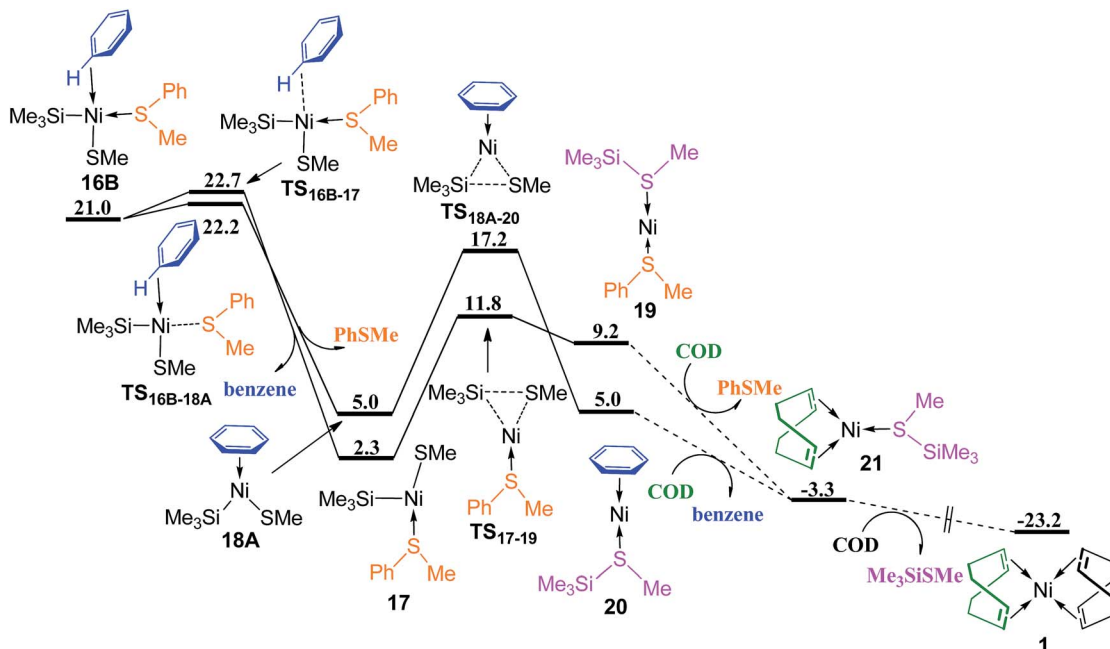


Fig. 7 Energy profiles of ligand substitution and reductive elimination to regenerate  $\text{Ni}(\text{COD})_2$  (values are given in  $\text{kcal mol}^{-1}$ ).

The mechanism without COD ligand or PhSMe spectator ligand has also been considered. In Fig. 8, following the coordination of  $\text{HSiMe}_3$  to the vacant site of three-coordinated complex **5A** via  $\text{TS}_{5\text{A}-22}$ , the release of COD proceeds via  $\text{TS}_{22-23\text{A}}$  giving complex **23A**, in which an agostic interaction is formed. Isomerization of **23A** generates complex **23B** with the vacant site *trans* to Ph ligand.  $\text{TS}_{22-23\text{A}}$  ( $35.1 \text{ kcal mol}^{-1}$ ) 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 **23B** was found and presented in Fig. 9 involving several triplet

transition states and intermediates. Complex **5A** first isomerizes to **5C** and then overcomes a crossing point **CP1** to form a triplet complex **5B<sup>3</sup>** (Fig. 9a). The density functional  $\omega\text{B97XD}$  has been proved to be appropriate to evaluate the energy of triplet species (see Table S1 in ESI†). **CP1** is  $10.5 \text{ kcal mol}^{-1}$  lower than  $\text{TS}_{22-23\text{A}}$  (Fig. 8), suggesting that the reaction prefers to involve the triplet species. Isomerization of **5B<sup>3</sup>** gives **5A<sup>3</sup>**. Silane  $\text{HSiMe}_3$  coordinates to **5A<sup>3</sup>** via  $\text{TS}_{5\text{A}-22\text{A}}$  giving complex **22A<sup>3</sup>** in which  $\text{HSiMe}_3$  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 **22A<sup>3</sup>** isomerizes via  $\text{TS}_{22\text{A}-22\text{B}}$  to form complex **22B<sup>3</sup>**, 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  $\text{TS}_{22\text{B}-23\text{A}}$  giving complex **23A<sup>3</sup>** (Fig. 9b). There is another pathway from **5A<sup>3</sup>** to form complex **23A<sup>3</sup>** (Fig. 9c). The dissociation of COD first proceeds via  $\text{TS}_{5\text{A}-11}$  forming complex **11<sup>3</sup>**, quasi-linear same as in  $\text{NiSar}_2$  ( $\text{Ar} = \text{C}_6\text{H}_3-2,6-(\text{C}_6\text{H}_2-2,4,6-i\text{Pr}_3)_2$ ) observed by Nguyen *et al.* in experiments,<sup>30</sup> then coordination of PhSMe occurs via  $\text{TS}_{11-23\text{A}}$  giving complex **23A<sup>3</sup>**. Isomerization of **23A<sup>3</sup>** takes place to form complex **23B<sup>3</sup>**, which goes through a crossing point **CP2** to generate the singlet complex **23B** mentioned in Fig. 8.  $\text{TS}_{5\text{A}-22\text{A}}$ , the most high point on this triplet reaction pathway  $5\text{A} \rightarrow 5\text{C} \rightarrow \text{CP1} \rightarrow 5\text{B}^3 \rightarrow 5\text{A}^3 \rightarrow \text{TS}_{5\text{A}-22\text{A}}^3 \rightarrow 22\text{A}^3 \rightarrow \text{TS}_{22\text{A}-22\text{B}}^3 \rightarrow 22\text{B}^3 \rightarrow \text{TS}_{22\text{B}-23\text{A}}^3 \rightarrow 23\text{A}^3 \rightarrow 23\text{B}^3 \rightarrow \text{CP2} \rightarrow 23\text{B}$  in Fig. 9, is  $25.5 \text{ kcal mol}^{-1}$  in energy,  $9.6 \text{ kcal mol}^{-1}$  lower than  $\text{TS}_{22-23\text{A}}$  on the corresponding singlet reaction pathway (Fig. 8), indicating that this reaction pathway involving a double spin-flip singlet  $\rightarrow$  triplet  $\rightarrow$  singlet is preferred kinetically. Similar double spin-flip course has been

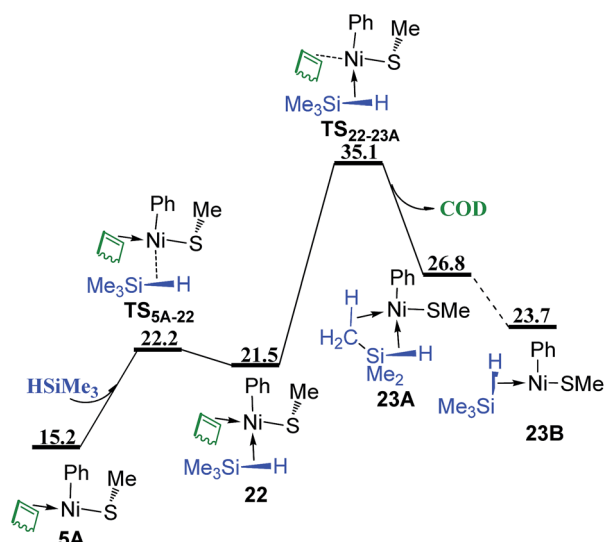


Fig. 8 Energy profile of ligand substitution of COD with  $\text{HSiMe}_3$  (values are given in  $\text{kcal mol}^{-1}$ ).

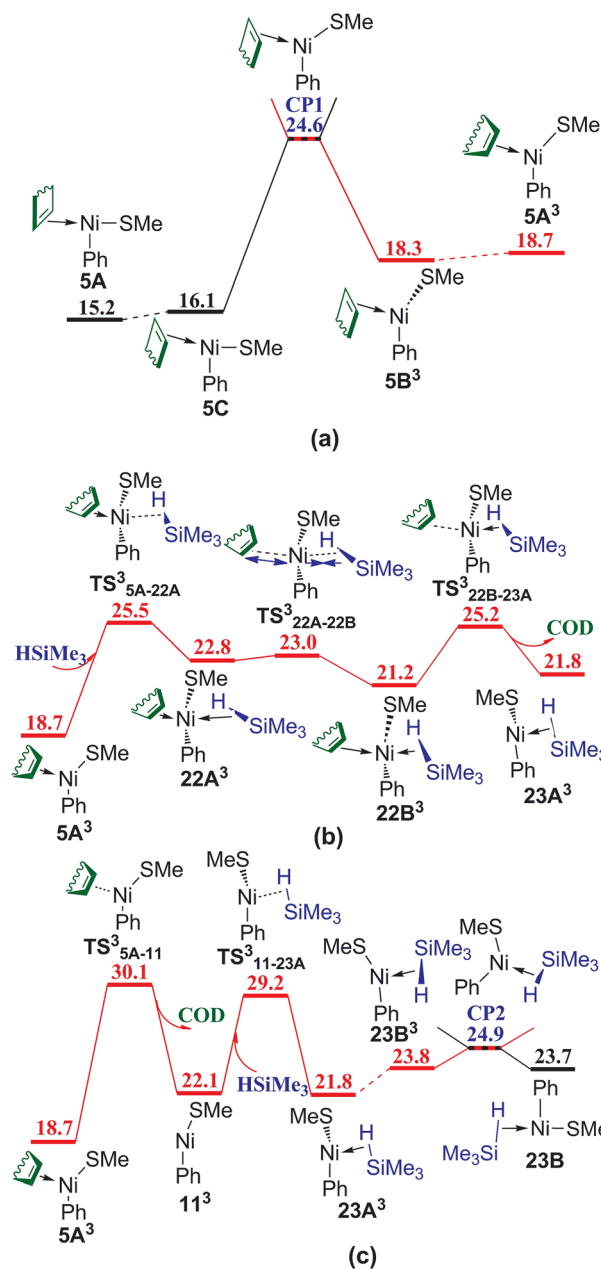


Fig. 9 Energy profiles of ligand substitution of COD with HSiMe<sub>3</sub> involving triplet species: (a) spin cross process from singlet state to triplet state; (b) triplet mechanism of ligand substitution of COD with HSiMe<sub>3</sub>; (c) spin cross process from triplet state to singlet state (values are given in kcal mol<sup>-1</sup>).

reported by Schlagen and Schwarz in computational study of  $\text{NiH}^+ + \text{CH}_4 \rightarrow \text{Ni}(\text{CH}_3)^+ + \text{H}_2$  reaction.<sup>31</sup>

From complex **23B** (Fig. 10), the  $\sigma$ -CAM proceeds *via*  $\text{TS}_{23\text{B}-18\text{B}}$  and  $\text{TS}_{23\text{B}-24}$  to give complex **18B** and **24** with the formed benzene and Me<sub>3</sub>SiSMe as ligand, respectively.  $\text{TS}_{23\text{B}-18\text{B}}$  is 6.2 kcal mol<sup>-1</sup> lower than  $\text{TS}_{23\text{B}-24}$ , showing that the  $\sigma$ -CAM process giving the benzene coordinated complex **18B** is preferred. Isomerization of **18B** generates complex **18A**, which has been mentioned in Fig. 7.

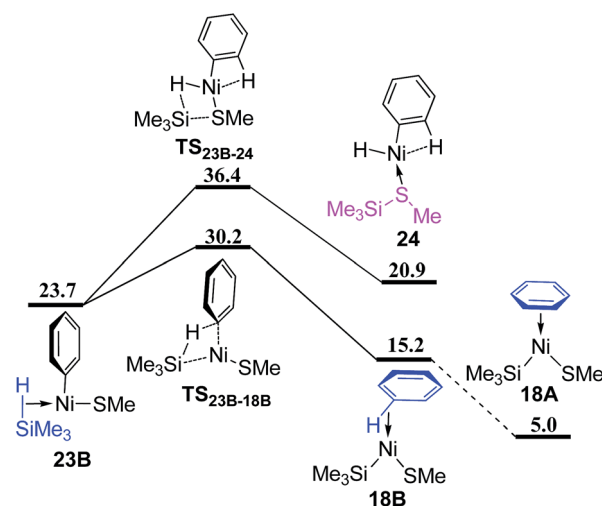


Fig. 10 Energy profiles of  $\sigma$ -CAM process from complex **23B** (values are given in kcal mol<sup>-1</sup>).

Since the reaction pathway involving the triplet species has been found to be preferred for ligand substitution of COD in complex **5A** with HSiMe<sub>3</sub> 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 **5B**<sup>3</sup> generated from the singlet complex **5A** through a crossing point **CP1** (Fig. 9a) forms complex **5C**<sup>3</sup> (Fig. 11). Coordination of PhSMe proceeds *via*  $\text{TS}_{5\text{C}-9\text{A}}$  forming complex **9A**<sup>3</sup>, subsequently isomerization of **9A**<sup>3</sup> gives complex **9B**<sup>3</sup>, 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 **9B**<sup>3</sup> isomerizes *via*  $\text{TS}_{9\text{B}-9\text{C}}$  giving complex **9C**<sup>3</sup> 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*  $\text{TS}_{9\text{C}-10}$  giving complex **10**<sup>3</sup>, 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  $\text{TS}_{5\text{A}-9\text{B}}$  (27.2 kcal mol<sup>-1</sup> in Fig. 5c) is only 0.8 kcal mol<sup>-1</sup> higher than the triplet one  $\text{TS}_{5\text{C}-9\text{A}}$  (26.4 kcal mol<sup>-1</sup> in Fig. 11). In order to give more accurate comparison, the single-point energies for  $\text{TS}_{5\text{A}-9\text{B}}$  and  $\text{TS}_{5\text{C}-9\text{A}}$  were re-calculated at the  $\omega\text{B97XD}/\text{def2-QZVPPD}$  level. It is found that  $\text{TS}_{5\text{A}-9\text{B}}$  is only 0.5 kcal mol<sup>-1</sup> higher than  $\text{TS}_{5\text{C}-9\text{A}}$ . These results indicate that the two reaction pathways are competitive with the triplet one slightly favored.

Besides the reactant PhSMe (Fig. 2), another reactant HSiMe<sub>3</sub> may also react first with complex **2** (Fig. 13). Oxidative addition of HSiMe<sub>3</sub> and dissociation of the dangling COD ligand from complex **2** proceed simultaneously *via* transition state  $\text{TS}_{2-25}$  giving complex **25**, from which one C=C bond of chelating COD dissociates through transition state  $\text{TS}_{25-26}$  forming complex **26**. The energy barrier of  $\text{TS}_{25-26}$  is 28.5 kcal mol<sup>-1</sup>, still lower

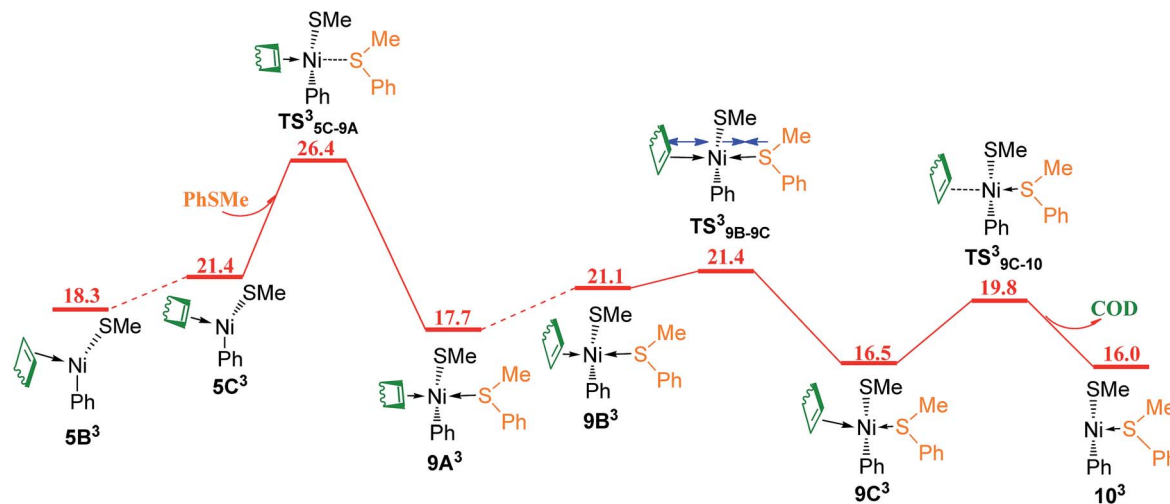


Fig. 11 Energy profile of triplet mechanism of ligand substitutions of COD with PhSMe (values are given in kcal mol<sup>-1</sup>).

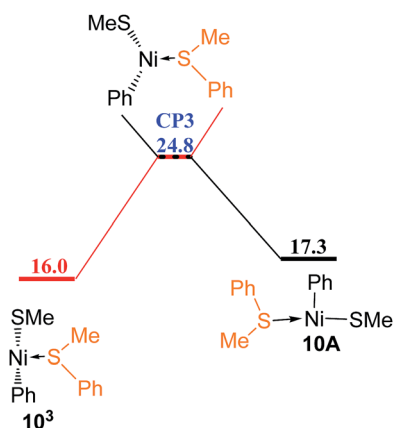


Fig. 12 Energy profile of spin cross process from triplet state to singlet state (values are given in kcal mol<sup>-1</sup>).

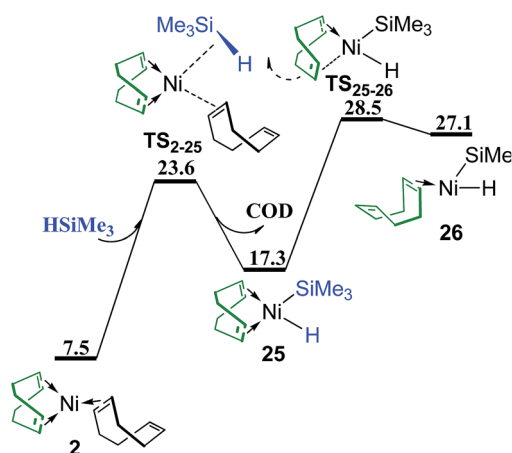


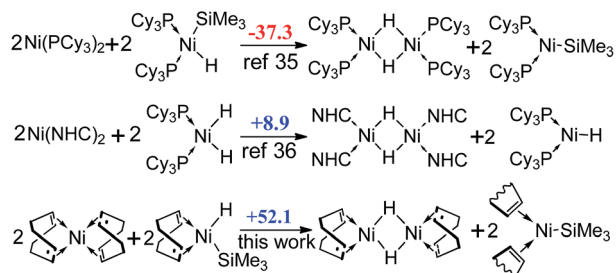
Fig. 13 Energy profile of ligand substitution of COD with HSiMe<sub>3</sub> and the oxidative addition of HSiMe<sub>3</sub> to give complex 26 (values are given in kcal mol<sup>-1</sup>).

than TS<sub>23B-18B</sub> (30.2 kcal mol<sup>-1</sup> in Fig. 10) and TS<sub>12C-16B</sub> (30.0 kcal mol<sup>-1</sup> in Fig. 6c) which are involved in the reaction pathways when PhSMe reacts first with complex 2. Thus, it is

	L <sub>n</sub> =COD	L <sub>n</sub> =none	L <sub>n</sub> =PhSMe
 L <sub>n</sub> -Ni-H Ph-SMe SiMe <sub>3</sub>	 TS <sub>C1a</sub> <sup>α,δ</sup> 74.4	 TS <sub>N1</sub> <sup>β</sup> 80.4	 TS <sub>T1</sub> <sup>γ</sup> 73.5
to generate MeSSiMe <sub>3</sub>			
 Ph-SMe SiMe <sub>3</sub>	 TS <sub>C2a</sub> <sup>α</sup> 97.5		 TS <sub>T2</sub> <sup>δ</sup> 97.0
to generate benzene			
 MeS-Ph SiMe <sub>3</sub>	 TS <sub>C3</sub> <sup>δ</sup> 76.8	 TS <sub>N2b</sub> <sup>α,δ</sup> 61.8	 TS <sub>T3</sub> <sup>β</sup> 73.7
 MeS-Ph SiMe <sub>3</sub>	 TS <sub>C4</sub> <sup>γ</sup> 72.5		 TS <sub>T4</sub> <sup>γ</sup> 76.5

Scheme 2 Transition states of metathesis or quasi-metathesis processes from various Ni-hydride species with PhSMe. <sup>α</sup>Quasi-metathesis with two or more steps. <sup>β</sup>Standard σ-metathesis. <sup>γ</sup>Oxidative addition of HSiMe<sub>3</sub> occurs simultaneously. <sup>δ</sup>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<sup>-1</sup>).





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

necessary to consider the following metathesis steps. The corresponding transition states of metathesis or quasi-metathesis to generate  $\text{Me}_3\text{SiSMe}$  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  $60 \text{ kcal mol}^{-1}$  in energy, indicating that all the reaction pathways following the reaction

of  $\text{HSiMe}_3$  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,<sup>32</sup> but not by using the NHC ligand,<sup>33</sup> we also calculated the reaction free energies for the formation of Ni(I) species with COD ligand. However, the reaction is  $52.1 \text{ kcal mol}^{-1}$  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,  $\sigma$ -CAM, reductive elimination and ligand substitution steps. For the first ligand substitution and  $\sigma$ -CAM steps, two reaction pathways, *i.e.*, the  $\text{PhSMe}$ -coordinated pathway and the “ligandless” pathway are involved having very small energy difference, only  $0.2 \text{ kcal mol}^{-1}$  between the rate-determining  $\sigma$ -CAM transition state  $\text{TS}_{12\text{C}-16\text{B}}$  ( $30.0 \text{ kcal mol}^{-1}$  in Fig. 6c) in the former pathway and  $\text{TS}_{23\text{B}-18\text{B}}$  ( $30.2 \text{ kcal mol}^{-1}$  in Fig. 10) in the latter one, indicating the two reaction pathways are competitive. The single-point energies of  $\text{TS}_{12\text{C}-16\text{B}}$  and  $\text{TS}_{23\text{B}-18\text{B}}$  were recalculated at the  $\omega\text{B97XD/def2-QZVPPD}$  level, and it is found that  $\text{TS}_{12\text{C}-16\text{B}}$  becomes slightly higher than  $\text{TS}_{23\text{B}-18\text{B}}$  by

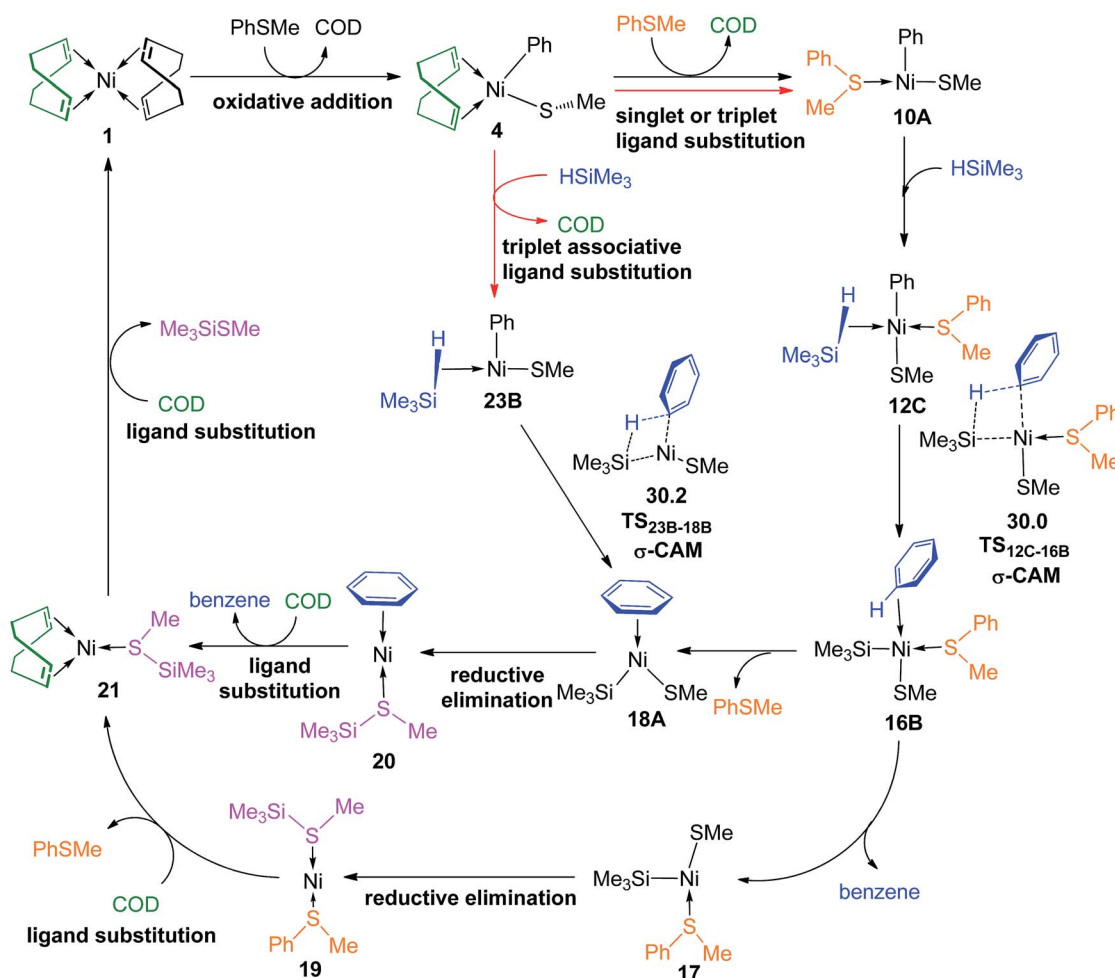


Fig. 14 The overall catalytic cycles (values of energy are given in  $\text{kcal mol}^{-1}$ ).





0.3 kcal mol<sup>-1</sup>. The results suggest that the PhSMe-coordinated and “ligandless” pathways are competitive. Considering the 99% yield in experiments,<sup>15</sup> it may be concluded that the two pathways are feasible at the early and most stages, but the “ligandless” one dominates the late stage of the reaction, as 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)<sub>2</sub> catalyzed reaction of PhSMe with HSiMe<sub>3</sub> 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  $\sigma$ -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 HSiMe<sub>3</sub> on “ligandless” pathway prefers the triplet mechanism. The  $\sigma$ -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<sup>-1</sup> at the  $\omega$ B97XD/6–311++G(d,p)//B3LYP/BSI ( $\omega$ B97XD/def2-QZVPPD//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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