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Mechanisms of Ni N-Heterocyclic Carbene Catalysts for C-O Bond Hydrogenolysis of Diphenyl Ether: A Density Functional Study

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Ni(SIPr)(η²-PhOPh) is the key active species for C-O bond hydrogenolysis of diphenyl ether.
ABSTRACT

Catalysts for aromatic C-O bond activation can potentially be used for the lignin degradation process. We investigated the mechanisms of C-O bond hydrogenolysis of diphenyl ether (PhOPh) by the nickel N-heterocyclic carbene (Ni-SIPr) complex to produce benzene and phenol as products. Our calculations revealed that diphenyl ether is not only a substrate, but also serves as a ligand to stabilize the Ni-SIPr complex. The Ni(SIPr)(η^6-PhOPh) complex is initially formed before rearranges to Ni(SIPr)(η^2-PhOPh), the active species for C-O bond activation. The catalytic reaction has three steps: (i) oxidative addition of Ni(SIPr)(η^2-PhOPh) to form [Ni(SIPr)(OPh)(Ph)]^0, (ii) σ-complex-assisted metathesis, in which H_2 binds to the nickel to form [Ni(SIPr)(OPh)(Ph)(H_2)]^0, then benzene (or phenol) is eliminated, and (iii) reductive elimination of phenol (or benzene) and the binding of PhOPh to regenerate Ni(SIPr)(η^2-PhOPh). As the rate determining step is at the oxidative addition step (+24 kcal/mol), we also calculated the free energy barriers for the oxidative addition of diaryl ether containing a trifluoromethyl electron withdrawing group (PhOC_6H_4CF_3) and found that C-O bond activation at the carbon adjacent to the aryl ring that contains the electron withdrawing substituent is preferred. This is in agreement with the experimental results, in that the major products are phenol and trifluoromethylbenzene. Moreover, the hydrogenation of benzene via Ni(SIPr)(η^2-C_6H_6) requires a high energy barrier (+39 kcal/mol); correspondingly, the hydrogenation products, e.g., cyclohexane and cyclohexadiene, were not observed in the experiment. Understanding the reaction mechanisms of the nickel catalysts for C-O bond hydrogenolysis of diphenyl ether will guide the development of catalytic systems for aromatic C-O bond activation to achieve the highest possible selectivity and efficiency.
INTRODUCTION

Catalysts for aromatic C-O bond activation are significant for the conversion of lignin biomass to arene feedstocks.¹,² Wenkert et al. first reported the cross-coupling reaction of aryl methyl ether and phenyl Grignard reagents using a NiCl₂(PPh₃)₂ catalyst.³ Apart from Grignard reagents,⁴,⁵ other carbon nucleophiles, e.g., organozinc⁶ and arylboronic reagents,⁷,⁹ have been used for C-O bond activation. Despite being less reactive, hydrogen attracted much attention for use as a substrate in place of the carbon nucleophile.

Hydrogenolysis of aromatic C-O bonds can be done by a heterogeneous Ni catalyst.¹⁰ However, its high reactivity results in further hydrogenation of the product, which leads to product mixtures of arenes and alcohols as well as cycloalkanes and cycloalkanols.¹,¹⁰ Recently, Sergeev and Hartwig² reported that the nickel N-heterocyclic carbene complex (Ni-SIPr) (Scheme 1) can catalyze hydrogenolysis of diaryl ethers² to produce arenes and alcohols as products. The reaction of the diaryl ether containing an electron withdrawing trifluoromethyl group can proceed at a lower temperature than the unsubstituted diphenyl ether and diaryl ethers with an electron donating group. In a competition experiment in which both diphenyl ether and 4-tert-butylphenyl methyl ether are present, C-O bond hydrogenolysis for the diphenyl ether was preferred (Scheme 1). As lignin contains aromatic C-O bonds, which are generally difficult to activate, this selective catalytic system could have promising applications in lignin degradation.

Density functional theory (DFT) can complement experimental studies to give insights into the reaction mechanisms of C-O bond activation by Ni complexes.¹¹,¹² Shi and coworkers⁷ reported that Ni(PCy₃)₂Cl₂ can selectively activate the aryl C-O bond (Ar-OAc) in the reaction of a series of aryl esters with arylboronic reagents to obtain biaryl products, although the acyl C-O bond (ArO-Ac) is weaker and normally perceived to be activated first. Liu and coworkers¹³ performed density functional study on the mechanisms and revealed that although the oxidative addition of ArO-Ac to the Ni⁰ complex is more facile than the oxidative addition of Ar-OAc, the subsequent transmetalation step for the former needs to overcome a higher energy barrier.
Scheme 1. Ni-SIPr reactions for C-O bond hydrogenolysis of diaryl ethers.

In this study, we used density functional theory to study the mechanism of the Ni-SIPr catalyst for the hydrogenolysis of the C-O bond of diphenyl ether (PhOPh). In the catalytic reaction between PhOPh and H₂ using Ni(COD)₂ and SIPr-HCl in the presence of tert-butoxide base, Ni(SIPr)(η⁶-PhOPh) can be formed and rearranged to Ni(SIPr)(η²-PhOPh), the active species. The reaction mechanisms and the key species were investigated (Scheme 2). The catalytic cycle has three steps: (i) oxidative addition of Ni(SIPr)(η²-PhOPh) to form [Ni(SIPr)(OPh)(Ph)]⁰, (ii) σ-complex-assisted metathesis (σ-CAM), in which H₂ binds to the nickel and benzene (or phenol) is eliminated, and (iii) reductive elimination of phenol (or benzene) and rebinding of PhOPh to recover Ni(SIPr)(η²-PhOPh). Understanding the reaction mechanisms of the nickel catalysts for C-O bond hydrogenolysis of diphenyl ether will guide the development of catalytic systems for aromatic C-O bond activation to achieve the highest possible selectivity and efficiency.
Scheme 2. Reaction mechanism for C-O bond hydrogenolysis of diphenyl ether by nickel N-heterocyclic carbene complex (L = SIPr). The catalytic cycle has three steps: (i) oxidative addition (OA), (ii) σ-complex-assisted metathesis (σ-CAM), and (iii) reductive elimination (RE).

COMPUTATIONAL DETAILS

All calculations were performed with Gaussian09 program. All structures were fully optimized with default convergence criteria and frequencies were calculated to ensure that there was no imaginary frequency for minima and only one imaginary frequency corresponding to the reaction coordinate for transition states. The intrinsic reaction coordinate (IRC) calculations were performed to confirm that the transition states lead to the expected intermediates. Zero-point energies and thermodynamic functions were calculated at default settings (298.15 K and 1 atm). B3LYP functional with basis set 1 (BS1) was used for all geometry optimizations and frequency calculations. In BS1, Stuttgart relativistic small core (RSC) 1997 ECP basis set was used for Ni; 6-31++G(d,p) was used for N, C, O, and H on the imidazole ring of SIPr (Scheme 1) and on the substrates, i.e., diphenyl ether and H2; 6-31G was used for all other atoms (the substituents on the imidazole ring.
of SIPr). As M06 functional has been successfully used for other Ni complex studies, we carried out single point energy and solvation free energy corrections by M06 with basis set 2 (BS2) on the gas-phase optimized structures using conductor-like polarizable continuum model (CPCM) with Bondi atomic radii and solvation parameters corresponding to m-xylene ($\varepsilon = 2.348$). BS2 is the same as BS1 except that 6-31G(d) is used for the substituents on the imidazole ring of SIPr. The standard states were corrected to 1 mol/L. Unless otherwise specified, the energies mentioned throughout the article refer to relative free energies with solvent correction in m-xylene calculated by M06/BS2//B3LYP/BS1.

RESULTS AND DISCUSSION

A. Formation of the Ni(SIPr)(η$_2$-PhOPh) active species

Under the experimental conditions that Sergeev et al. reported, tert-butoxide base was used to generate the free N-heterocyclic carbene ligand (SIPr) from SIPr.HCl. The cyclooctadiene (COD) in the Ni(COD)$_2$ precursor can easily undergo ligand substitution with SIPr to form Ni(SIPr)(COD) (-0.3 kcal/mol) (Fig. 1). From the X-ray crystal structure of (η$_2$;η$_2$-hexadiene)Ni(SIPr), two double bonds of hexadiene lie in the same coordination plane, similarly for (styrene)$_2$Ni(IPr). Due to the ring constraint, two double bonds of COD cannot bind to the Ni in the same fashion as (hexadiene)Ni(SIPr) and (styrene)$_2$Ni(IPr); only one of the double bonds of COD coordinates to the nickel in the calculated structure of Ni(SIPr)(COD) (Fig. S1).
Fig. 1 Formation of Ni(SIPr)(η^2-PhOPh). The unfavorable species are shown in grey. Solvent corrected free energies relative to Ni(COD)_2 in m-xylene are given in kcal/mol.

While the ligand dissociation from Ni(SIPr)(COD) to form Ni(COD) and to form Ni(SIPr) is unfavorable (+25.1 and +27.7 kcal/mol, respectively) (Fig. 1), the ligand substitution of Ni(SIPr)(COD) with SIPr leads to the relatively stable Ni(SIPr)_2 complex (-9.6 kcal/mol). The calculated structure of Ni(SIPr)_2 is in good agreement with the X-ray crystal structure^{30} (Fig. S2).

Several studies on nickel phosphine^{13, 31} and N-heterocyclic carbene (NHC)^{32} complexes showed that for the sterically hindered monodentate ligands, the oxidative addition of the substrate preferably occurs on the monodentate complex rather than on the di-ligated complex. Here, we tried to locate [Ni(SIPr)_2(Ph)(OPh)]^0, the product of the oxidative addition of diphenyl ether on Ni(SIPr)_2, but all attempts were not successful. The oxidative addition of diphenyl ether on Ni(SIPr)_2 is unlikely due to the steric hindrance of SIPr.
Ogoshi and coworkers\textsuperscript{33} reported that a mixture of Ni(COD)\textsubscript{2} and NHC (SIPr and IPr) in an arene solution under H\textsubscript{2} at room temperature led to the formation of Ni(NHC)(\overset{\delta}{\eta}\textsubscript{6}-arene) complexes, as confirmed by X-ray crystal structures. According to their experiment,\textsuperscript{33} the presence of H\textsubscript{2} under the reaction conditions essentially led to hydrogenation of cyclooctadiene to form cyclooctane, which cannot coordinate with Ni. As Sergeev et al. used similar experimental conditions,\textsuperscript{2} the hydrogenation of cyclooctadiene is also expected. Although the COD substitution with diphenyl ether to form Ni(SIPr)(\overset{\delta}{\eta}\textsubscript{6}-PhOPh) is slightly endergonic (+5.1 kcal/mol) (Fig. 1), the hydrogenation of COD should favor the formation of Ni(SIPr)(\overset{\delta}{\eta}\textsubscript{6}-PhOPh). Moreover, Ni(SIPr)(\overset{\delta}{\eta}\textsubscript{6}-PhOPh) is more favorable than Ni(SIPr)(\overset{\delta}{\eta}\textsubscript{6}-m-xylene) by -7.2 kcal/mol (Fig. S3); thus, diphenyl ether can compete with \textit{m}-xylene solvent to form the active species for C-O bond activation.

Other coordination modes of diphenyl ether to Ni were explored. The O-bound Ni(SIPr)(OPh\textsubscript{2}) has a higher energy than \overset{\delta}{\eta}\textsubscript{6}-bound Ni(SIPr)(\overset{\delta}{\eta}\textsubscript{6}-PhOPh) (+9.2 kcal/mol) (Fig. 1), while Ni(SIPr)(\overset{\delta}{\eta}\textsubscript{2}-PhOPh) has a similar energy to Ni(SIPr)(\overset{\delta}{\eta}\textsubscript{6}-PhOPh) (-0.5 kcal/mol). Diphenyl ether in the \overset{\delta}{\eta} and \overset{\delta}{\eta} binding modes can accept a \pi-back donation from the electron rich Ni\textsuperscript{0}-SIPr. We propose that diphenyl ether is not only a substrate in the reaction but also serves as a ligand to stabilize the Ni-SIPr complex. Ni(SIPr)(\overset{\delta}{\eta}\textsubscript{6}-PhOPh) can easily rearrange to Ni(SIPr)(\overset{\delta}{\eta}\textsubscript{2}-PhOPh) (IN1), the active specie for C-O bond activation.

\textbf{B. C-O bond hydrogenolysis}

\textbf{a) The oxidative addition}

The Ni(SIPr)(\overset{\delta}{\eta}\textsubscript{2}-PhOPh) (IN1) complex undergoes oxidative addition to form transition state TS\textsubscript{1}, which has a three-centered interaction and an energy barrier of +24.0 kcal/mol, leading to formation of [Ni\textsuperscript{II}(SIPr)(Ph)(OPh)]\textsuperscript{0} (IN2) (Fig.2). The three-coordinate complex, IN2, with the phenyl group \textit{trans} to the vacant site, can rearrange to IN3 and IN4, with the phenolate and the SIPr \textit{trans} to the vacant site, respectively (Fig. S4). The phenolate in IN4 is actually in an \overset{\delta}{\eta}-coordination; the Ni-O bond distance is 1.93 Å, the Ni-C\textsuperscript{ipso} bond distance is 2.23 Å, and the Ni-C\textsuperscript{ortho} bond distance is 2.33 Å. These bond distances are similar to those in the crystal structure of the Ni \textit{a}-methylbenzyl
Accordingly, IN4 is the most stable structure. Note that there is no agostic or anagostic interaction in either IN2 or IN3; the distance between the isopropyl CH on the substituent of SIPr and the Ni is >3.0 Å (Fig. S4). As two strong *trans* influence ligands (phenyl and SIPr) are located in the opposite positions of the Ni, the Ni-C(SIPr) bond distance in IN3 is 2.03 Å, relatively weaker than the corresponding bond in IN2 (~1.88 Å). Thus, IN3 is less stable than IN2.

**Fig. 2** Relative free energy profiles for the overall mechanism for the C-O bond hydrogenolysis of diphenyl ether. Solvent corrected relative free energies in *m*-xylene are given in kcal/mol.

The binding of H2 to IN1 to form the H2-complex, Ni(SIPr)(η2-PhOPh)(H2) (Fig. S9) was also investigated. Generally, the dihydride mononuclear Ni complex is unstable, while the H2 adducts of Ni complexes are observable and can undergo heterolytic cleavage assisted by an amine base. The nickel hydride pathway should involve *tert*-butoxide in abstracting a proton from Ni(SIPr)(η2-PhOPh)(H2) to generate the nickel hydride species. Thus, we investigated the deprotonation of Ni(SIPr)(η2-PhOPh)(H2) by *tert*-butoxide base. However, steric hindrance from the ligands around the Ni atom prevented *tert*-butoxide access to abstract the proton. To the best of our knowledge, currently there is no experimental support for the formation of nickel hydride intermediates under these reaction conditions. Therefore, we exclude the nickel hydride pathway in this study.
b) The σ-Complex-Assisted Metathesis (σ-CAM)

As some Ni(II) complexes were found in the triplet state,\textsuperscript{39-41} we explored the triplet complex, [Ni\textsuperscript{II}(SIr)(Ph)(OPh)]\textsuperscript{0} (IN\textsubscript{2-T}) (Fig. S5). While the singlet complexes (IN\textsubscript{2}, IN\textsubscript{3}, and IN\textsubscript{4}) have T-shaped structures, the triplet IN\textsubscript{2-T} structure is a tetrahedron with a missing cap (Fig. S5).\textsuperscript{41} Two singly occupied molecular orbitals are Ni d\textsubscript{x2-y2}-based and Ni d\textsubscript{xy}-based orbitals with antibonding character (Fig. S6). Although the energy of IN\textsubscript{2-T} is only 2.8 kcal/mol higher than that of IN\textsubscript{2} (Fig. S5), the triplet Ni(II) H\textsubscript{2} complex could not be located. Upon geometry optimization, the H\textsubscript{2} simply dissociated away from the Ni. In the [NiFe] hydrogenase model study, Keith and Hall also reported that while the triplet state was possible for the Ni(II), H\textsubscript{2} binding to the high spin Ni was not found.\textsuperscript{42} Since the triplet complex is unlikely to bind H\textsubscript{2} and to undergo hydrogenolysis, only singlet complexes are discussed in this study.

For complexes IN\textsubscript{2}-IN\textsubscript{4}, the LUMO is a Ni d\textsubscript{x2-y2}-based orbital with σ-antibonding character (Fig. S7). As phenolate, the weak σ-donor ligand, is opposite to the vacant site, IN\textsubscript{3} has the lowest LUMO energy (Scheme 3). The HOMO of IN\textsubscript{3} is a Ni d\textsubscript{xy}-based orbital with π-antibonding to the oxygen p\textsubscript{y}-orbital of OPh (Fig. S7). In contrast, for the HOMO of IN\textsubscript{4}, not only does the Ni d\textsubscript{xy} orbital have a π-antibonding interaction with the π-orbital of phenyl, but it also has a bonding interaction with the π-orbital of OPh at one of the ortho carbons (Fig. S7). Thus, the HOMO energy of IN\textsubscript{4} is lower than that of IN\textsubscript{3}, making it more stable than IN\textsubscript{3}. Since the binding of H\textsubscript{2} at the vacant site of [Ni\textsuperscript{II}(SIr)(Ph)(OPh)]\textsuperscript{0} involves a charge transfer from the HOMO to the σ*-orbital of H\textsubscript{2} and a charge transfer from the σ-orbital of H\textsubscript{2} to the LUMO (Scheme 4), the highest HOMO energy and the lowest LUMO energy in IN\textsubscript{3} (Scheme 3) should facilitate the binding of H\textsubscript{2} to IN\textsubscript{3}. Correspondingly, IN\textsubscript{3} readily binds H\textsubscript{2} at the vacant site (~4.7 kcal/mol), while the binding of H\textsubscript{2} on IN\textsubscript{4} and IN\textsubscript{2} are unfavorable (~6.8 kcal/mol) (Fig. 2).
Scheme 3. Selected molecular orbital energies (in eV) for IN3, IN4 and IN2.

Scheme 4. H2 orbital interaction with the d_{x^2-y^2}-based and the d_{xy}-based orbitals of the three-coordinate Ni(II) complex.

The binding of H2 at the vacant site of [Ni(SIPr)(Ph)(OPh)]0 (IN2, IN3, and IN4) leads to the formation of the H2-complex [Ni(H2)(SIPr)(Ph)(OPh)]0 (IN5, IN6, and IN7, respectively) (Fig.2). Generally, dihydride complexes can be formed on the electron rich transition metal, which can
provide a \( \pi \)-backbonding to the binding \( \text{H}_2 \).\textsuperscript{43-45} Here the dihydride complex, \([\text{Ni}(\text{H})(\text{SIPr})(\text{Ph})(\text{OPh})]^0\), the product from the oxidative addition of \( \text{H}_2 \) on \([\text{Ni}^{II}(\text{SIPr})(\text{Ph})(\text{OPh})]^0\) was not found. Therefore, the \( \text{H}_2 \)-complex \([\text{Ni}(\text{H}_2)(\text{SIPr})(\text{Ph})(\text{OPh})]^0\) undergoes O-H bond and C-H bond formation through \( \sigma \)-bond metathesis.

\textbf{IN5} can proceed to the \( \sigma \)-bond metathesis \textit{via} the transition state \textbf{TS2}, which involves a four-centered interaction (Fig.3). Although the \( \text{H}_2 \) is perpendicular to the coordination plane of \textbf{IN5} (Fig.3), the rotational barrier for \( \text{H}_2 \) is rather small (1-2 kcal/mol).\textsuperscript{46} The geometry of \textbf{TS2} has the transferred \( \text{H} \) close to \( \text{Ni} \) (1.72 Å); this can be classified as \( \sigma \)-complex-assisted metathesis (\( \sigma \)-CAM) as suggested for late transition metal complexes.\textsuperscript{47, 48} The O-H bond is formed and the H-H bond is weakened. The T-shaped nickel complex \([\text{Ni}(\text{SIPr})(\text{Ph})(\text{H})]^0\) with the hydride \textit{trans} to the empty site (\textbf{IN8}) is then obtained, and phenol is eliminated. The overall energy barrier is +19.3 kcal/mol (Fig. 2). Similarly, \textbf{IN7} can undergo \( \sigma \)-complex-assisted metathesis \textit{via} \textbf{TS4} to form the O-H bond (Fig. 3), leading to \textbf{IN8} formation and phenol elimination. The overall energy barrier (+22.0 kcal/mol) is slightly higher than that \textit{via} \textbf{TS2} (Fig. 2).

On the other hand, \( \sigma \)-CAM \textit{via} \textbf{IN6} and transition state \textbf{TS3} is facile (Fig. 2). The electronic energy of \textbf{TS3} is slightly higher than that of \textbf{IN6} (Table S1). After the solvent correction, the free energy of \textbf{TS3} becomes slightly lower than \textbf{IN6} (< 1 kcal/mol) (Fig. 2). The intrinsic reaction coordinate (IRC) calculations indicated that \textbf{TS3} really is the transition state for the \( \sigma \)-CAM of \textbf{IN6}. The nickel assists with the H-H bond cleavage and the C-H bond formation; the T-shaped nickel complex \([\text{Ni}(\text{SIPr})(\text{OPh})(\text{H})]^0\) with the hydride \textit{trans} to the empty site (\textbf{IN9}) and benzene are obtained as products. The benzene elimination is more favorable than the phenol elimination by -17.4 kcal/mol (Fig. 2), corresponding to the stronger C-H bond in comparison to the O-H bond.\textsuperscript{49}
Fig. 3 Optimized geometries of $\sigma$-CAM intermediates $[\text{Ni}(\text{H}_2)(\text{SIPr})(\text{Ph})(\text{OPh})]^0$ (IN5, IN6, and IN7) and transition states (TS2, TS3, and TS4). Calculated bond distances are shown in Å. All H atoms are omitted for clarity except for those of H$_2$. Ni atoms are shown in green, C atoms in grey, O atoms in red, N atoms in blue, and H atoms in white.

Note that the energy barrier for the H$_2$ addition across the Ni-Ph bond via IN6 is lower than that across the Ni-OPh bond via IN5 and IN7. This can be related to the structural change upon $\sigma$-CAM. With H$_2$ opposite to the weak *trans* ligand, IN6 has stronger Ni-H bonds (~1.6 Å) than those on IN5 and IN7 (~1.8 Å) (Fig. 3). The H-H bond on IN6 (0.82 Å) is also weaker than those on IN5 and IN7 (0.77-0.78 Å). These should facilitate the H-H bond cleavage in IN6. Moreover, the geometry of TS3 is only slightly changed from that of IN6; the H-H distance is lengthened by ~0.1 Å and the Ni-Ph distance is slightly lengthened (0.05 Å) (Fig. 3). On the other hand, the changes in geometries from IN5 to TS2 and from IN7 to TS4 are more pronounced; the H-H distances and the Ni-OPh distances...
are lengthened by ~0.2 Å. Thus, the energy barrier for the O-H bond formation is higher than that for the C-H bond formation (Fig. 2).

c) **The Reductive Elimination**

**IN8** readily proceeds to reductive elimination of benzene *via* a three-centered transition state, **TS5** (Fig. 2). Diphenyl ether then binds to the Ni to regenerate Ni(SiPr)(η²-PhOPh). The C-H distance in **IN8** is shortened by -0.65 Å to form a bond in **TS5** (Fig. 4). On the other hand, **IN9** undergoes reductive elimination *via** TS6 to generate phenol with a high energy barrier of +19.4 kcal/mol. The O-H distance in **IN9** is shortened by -1.27 Å to form a bond in **TS6**. Corresponding to the energy barriers, the structure of **TS5** represents the “earlier” transition state compared to that of **TS6** (Fig. 4).

![Fig. 4 Optimized geometries of reductive elimination intermediates (IN8 and IN9) and transition states (TS5 and TS6). Calculated bond distances are shown in Å. All H atoms are omitted for clarity except for the one on Ni. Ni atoms are shown in green, C atoms in grey, O atoms in red, N atoms in blue, and H atoms in white.](image-url)
The possibility of four-coordinate intermediates for the reductive elimination was also investigated. The binding of diphenyl ether to IN9 was calculated. The O-bound square planar complex, Ni(SIPr)(H)(OPh)(OPh₂), can be formed with an increase in energy of 3.5 kcal/mol (Fig. S8) while the η²⁻ and η⁶⁻-bound complexes were not found. The Ni-OPh₂ distance in Ni(SIPr)(H)(OPh)(OPh₂) is rather long (2.44 Å). Moreover, the transition state for the reductive elimination of phenol cannot be located; diphenyl ether dissociated away and the structure became TS6 during the transition state optimization. Thus, it is unlikely that the diphenyl ether coordinates to Ni²⁺(SIPr)(H)(OPh), IN9, before the reductive elimination of phenol.

d) The Overall Mechanism

In the mixture of SIPr, diphenyl ether, and H₂, the Ni(COD)₂ precursor can form Ni(SIPr)(η⁶⁻-PhOPh), which can readily rearrange to Ni(SIPr)(η²⁻-PhOPh) (IN1). The Ni(SIPr)(η²⁻-PhOPh) complex undergoes oxidative addition to form [Ni(SIPr)(Ph)(OPh)]⁺ with an energy barrier of +24.0 kcal/mol (Fig.2). Considering the overall catalytic reaction, this is the rate determining step. Then, IN2, the [Ni(SIPr)(Ph)(OPh)]⁺ complex with the phenyl trans to the vacant site is formed. IN2 can rearrange to IN3, the [Ni(SIPr)(Ph)(OPh)]⁻ complex with the phenolate trans to the vacant site. IN3 can then bind H₂, proceed to σ-complex-assisted metathesis to generate benzene, and reductively eliminate phenol with the highest energy barrier at the reductive elimination step (+19.4 kcal/mol). Alternatively, IN2 can bind H₂, proceed to σ-complex-assisted metathesis to generate phenol, and reductively eliminate benzene with the highest energy barrier at the σ-CAM step (+19.3 kcal/mol). The energy barriers for the pathway via IN3 and via IN2 are comparable; thus, both pathways are possible. Notably, for both pathways, C-H bond formation is facile, while O-H bond formation requires more structural changes and needs to overcome a high energy barrier (~19 kcal/mol).

From the experiment by Sergeev and Hartwig,² a large amount of Ni(COD)₂ precursor and SIPr ligand (10-20%) was used to complete the reaction at 100-120 °C. This supports the formation and accumulation of Ni(SIPr)₂, which is not the key species for C-O bond activation. Although the formation of Ni(SIPr)(η²⁻-PhOPh), the active species, is feasible, the Ni(SIPr)(η²⁻-PhOPh) is less stable than Ni(SIPr)₂ (~14 kcal/mol) (Fig. 1). In place of the formation of the catalyst in situ from Ni(COD)₂,
SIPrHCl, and ‘BuO base, Ni(SIPr)(η6-arene) could be worth exploring as a starting catalyst. Since the Ni:SIPr ratio is kept at 1:1, the redistribution of Ni(SIPr)(η6-arene) to Ni(SIPr)2 should be minimal. According to our study, the Ni(SIPr)(η6-arene) can readily rearrange to Ni(SIPr)(η2-PhOPh), the active species for the C-O bond activation. The synthesis of Ni(SIPr)(η6-arene) is known as recently reported by Ogoshi and coworkers.33

C. C-O Bond Activation Selectivity

Since the oxidative addition step was found to be the rate determining step, we also investigated the oxidative addition of diaryl ethers, which contain the electron withdrawing trifluoromethyl group. The Ni(SIPr)(η2-C6H4CF3OPh) complex with η2-coordination at the aryl ring, in which the trifluoromethyl group is located (IN1-Fa), is slightly more stable than the complex with η1-coordination at the phenyl ring (IN1-Fb) (-1.04 kcal/mol) (Fig. 5); correspondingly, the Ni-C(aryl) bond distances on IN1-Fa are slightly shorter than those on IN1-Fb and IN1 (Fig. 6).

C-O bond activation preferably occurs at the carbon on the aryl ring with the trifluoromethyl group via TS1-Fa (+21.6 kcal/mol) rather than on the unsubstituted aryl ring via TS1-Fb (+25.3 kcal/mol); the Ni-Cipso bond distance on TS1-Fa is lengthened from that on IN1-Fa by 0.03 Å while that on TS1-Fb is lengthened by 0.04 Å (Fig. 6). Thus, the former reaction, which leads to phenol and C6H5CF3 as products, is more favorable, in agreement with the products observed experimentally.2 The free energy barrier for the oxidative addition of Ni(SIPr)(η2-C6H4CF3OPh) via TS1-Fa is also lower than that of Ni(SIPr)(η2-PhOPh) via TS1 (+24.0 kcal/mol); correspondingly, Sergeev et al. showed that the reaction of the diaryl ether containing a trifluoromethyl substituent can proceed at a lower temperature than that of diphenyl ether.2 Similar to the study on the oxidative addition of substituted aryl halide on palladium50 and rhodium51 complexes, the electron withdrawing group on the aryl ring accelerates the oxidative addition reaction.
Fig. 5 Free energy profiles for the oxidative addition of diaryl ether. Solvent corrected relative free energies in m-xylene are given in kcal/mol.

![Free energy profile](image)

**Fig. 5**

Fig. 6 Optimized geometries in the oxidative addition of Ni(SIPr)(\(\eta^2\)-PhOPh) and the oxidative addition of Ni(SIPr)(\(\eta^2\)-C\(_6\)H\(_4\)CF\(_3\)OPh).

![Optimized geometries](image)

**Fig. 6**
D. Hydrogenation

Unlike for the heterogeneous Ni catalysts, the hydrogenation products, e.g., cyclohexadiene and cyclohexane, were not observed for the Ni-SIPr catalytic system. As the structure of Ni(NHC)(benzene) is known, the formation of Ni(SIPr)(η⁶-C₆H₆) is expected. Our calculation also shows that the ligand exchange of diphenyl ether with benzene in Ni(SIPr)(η⁶-PhOPh) is favorable; the Ni(SIPr)(η⁶-C₆H₆) is slightly more stable than Ni(SIPr)(η⁶-PhOPh) (-1.2 kcal/mol) (Fig. S3). While the Ni(SIPr)(η⁶-PhOPh) can readily transform to Ni(SIPr)(η²-PhOPh) (Fig. 1), the same occurs for Ni(SIPr)(η⁶-C₆H₆) to Ni(SIPr)(η²-C₆H₆) (Fig. 7). Thus, we investigated the hydrogenation of Ni(SIPr)(η²-C₆H₆).

The binding of H₂ to Ni(SIPr)(η²-C₆H₆) (IN10) leads to the formation of the H₂-complex, [Ni⁰(SIPr)(H₂)(η²-C₆H₆)] (IN11) with a H-H distance of 0.83 Å (Fig. 8); the reaction is unfavorable with a change in the free energy of +6.5 kcal/mol (Fig.7). The H-transfer from the Ni to the adjacent carbon on the benzene then occurs via the transition state TS7 with an overall energy barrier of +25.1 kcal/mol. On TS7, the breaking H-H bond distance is lengthened by +0.84 Å and the forming C-H bond distance is shortened by -0.92 Å from those on IN11. The C-H bond is completely formed in IN12 (1.25 Å) (Fig. 8). There is a C-H agostic interaction in IN12 (with the Ni-H distance of 1.58 Å), similar to Spencer’s β-agostic nickel ethyl cations (with the Ni-H distance of 1.64 Å). IN12 is almost isoenergetic (< 1 kcal/mol) to TS7.

The reductive elimination of cyclohexadiene from IN12 involves the three-centered transition state, TS8 with a rather high overall energy barrier of +39.0 kcal/mol, leading to the formation of [Ni⁰(SIPr)(η²-C₆H₆)] (IN13). Moreover, the overall process is endergonic (+7.2 kcal/mol) (Fig. 7). Therefore, the formation of cyclohexadiene and other hydrogenation products are unlikely to occur. This corresponds to the experimental results that reported only benzene and phenol as products.
Fig. 7 Free energy profiles for the hydrogenation of benzene. Solvent corrected relative free energies in *m*-xylene are given in kcal/mol.

Fig. 8 Optimized structures for the hydrogenation of benzene on Ni-SIPr. Calculated bond distances are shown in Å.
CONCLUSIONS

We investigated the mechanisms for the C-O bond hydrogenolysis of diphenyl ether by the nickel N-heterocyclic carbene (Ni-SIPr) complex to obtain benzene and phenol as products. According to the calculations, the Ni(COD)$_2$ precursor can undergo ligand substitutions with SIPr and with diphenyl ether to form Ni(SIPr)(η$^6$-PhOPh). The Ni(SIPr)(η$^6$-PhOPh) complex can readily rearrange to Ni(SIPr)(η$^2$-PhOPh), the active species for C-O bond activation. Thus, diphenyl ether is not only a substrate, but also serves as a ligand to stabilize the Ni-SIPr complex. Although the formation of Ni(SIPr)(η$^2$-PhOPh), the active species, is feasible, the Ni(SIPr)(η$^2$-PhOPh) complex is less stable than Ni(SIPr)$_2$, the catalytically inactive species. To minimize the formation and accumulation of Ni(SIPr)$_2$, we suggest that Ni(SIPr)(η$^6$-arene) should be explored as a starting catalyst. The synthesis of Ni(SIPr)(η$^6$-arene) is known and Ni(SIPr)(η$^6$-arene) can easily undergo ligand exchange with diphenyl ether to form Ni(SIPr)(η$^2$-PhOPh).

The catalytic reaction has three steps: (i) oxidative addition of Ni(SIPr)(η$^2$-PhOPh) to form [Ni(SIPr)(OPh)(Ph)]$^0$, (ii) σ-complex-assisted metathesis (σ-CAM), in which H$_2$ binds to Ni to form [Ni(SIPr)(OPh)(Ph)(H$_2$)]$^0$, then benzene (or phenol) is eliminated, and (iii) reductive elimination of phenol (or benzene) and rebinding of diphenyl ether to regenerate Ni(SIPr)(η$^2$-PhOPh). The rate determining step was found to be the oxidative addition step (+24 kcal/mol), in agreement with the experimental results which showed that the substrate with an electron withdrawing substituent on the aryl ring can undergo the catalytic reaction for C-O bond hydrogenolysis at a lower temperature than the unsubstituted aryl ether. We also revealed that the hydrogenation of benzene via Ni(SIPr)(η$^2$-C$_6$H$_6$) requires a high energy barrier (+39.0 kcal/mol), corresponding to the experimental results in that the hydrogenation products, e.g., cyclohexane, cyclohexadiene, were not observed. Understanding the reaction mechanisms of the nickel catalysts for C-O bond hydrogenolysis of diphenyl ether will provide useful guidance for the development of catalytic systems to achieve the highest possible selectivity and efficiency in aromatic C-O bond activation. The selectivity towards the C-O bond activation at the aromatic C-O bond over the aliphatic C-O bond is under investigation.
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NOTES AND REFERENCES

Electronic Supplementary Information (ESI) available: Fig.s (energies and graphical representations) and xyz coordinates. See DOI: 10.1039/b000000x/