

Article

Mechanistic Investigations of the Hydrogenolysis of Diaryl Ethers Catalyzed by Nickel Complexes of N–Heterocyclic Carbene Ligands

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Ni(COD)₂ and SIPr under H₂.²⁰ They observed cleavage of the C_{aryl}–O bond and 90% deuterium incorporation in the newly formed arene (Scheme 1b), implying that reduction occurs by β -deuteride elimination from a methoxide ligand. Although revealing an important feature of the mechanism of the reaction of aryl methyl ethers, these studies did not reveal the mechanism of the reaction of diaryl ethers, which lack the requisite β -hydrogen. In addition, this study did not include the characterization of nickel complexes along the pathway for reaction of SIPr-ligated complexes, particularly the identity of the methoxide complex that would form.²²

Martin and coworkers reported silanolysis of the aromatic C–O bonds of aryl methyl ethers catalyzed by the combination of Ni(COD)₂ and PCy₃.²³ Detailed mechanistic experiments supported the initial formation of a phosphine-ligated, Ni¹-silyl complex (Scheme 1c).²¹ This species was proposed to undergo migratory insertion into the napthyl C=C bond and elimination of MeOSiR₃ to produce a Ni¹ aryl complex. Sigma-bond metathesis with silane was proposed then to produce the arene product and regenerate the active catalyst.

Scheme 2. Mechanistic Proposals from DFT Calculations on the Hydrogenolysis of Diaryl Ethers



Two studies have provided information on the mechanism of the hydrogenolysis of aryl ethers by DFT computations. These two studies led to two different mechanisms to be proposed for the hydrogenolysis of diaryl ethers by a complex formed from the combination of Ni(COD)₂ and an NHC ligand (Scheme 2). In 2014, Surawantanawong and coworkers proposed initial coordination of the diaryl ether to Ni⁰ to form SIPr–Ni(η^2 –Ph–OPh) (2),²⁴ followed by ratedetermining oxidative addition of the C–O bond to provide low-coordinate arylnickel phenoxide species **3**. Further reaction with H₂ was proposed to generate hydride **4**, which would undergo reductive elimination to form benzene and bind substrate to close the catalytic cycle.

More recently, Chung and coworkers proposed a mechanism that directly involved NaOt-Bu in the catalytic cycle for the hydrogenolysis of diaryl ethers.²⁵ They computed that the barrier to oxidative addition of the C–O bond to anionic Ni-alkoxide **5** to form the anionic Ni^{II} complex **6** would be lower than that for oxidative addition to a neutral complex, such as **2**. Dissociation of phenoxide from Ni-ate **6** would give the neutral Ni-t-butoxide **7**. Further reactions with H_2 would generate *t*-BuOH and the arene product. Thus, the mechanisms deduced by computation for hydrogenolysis involve Ni⁰ and Ni^{II} complexes, whereas the mechanism for silanolysis was concluded to involve Ni^I. The mechanisms deduced by computation for hydrogenolysis involve a neutral Ni complex in one case and an anionic Ni⁰ complex in another.

To gain firm experimental information on the mechanism of the hydrogenolysis of diaryl ethers, we have conducted a series of studies to prepare potential reaction intermediates, to obtain kinetic data on catalytic systems, and to study the rates and outcomes of individual steps in possible cycles.

Here, we describe the outcome of these studies on the mechanism of the hydrogenolysis of C-O bonds in diaryl ethers catalyzed by a SIPr-ligated Ni complex. Catalytic reactions and kinetic studies indicate that NaOt-Bu is not involved in the rate-determining portion of the catalytic cycle, even though it is necessary for the catalytic reactions to occur in high yield. Spectroscopic studies show that SIPr–Ni(η^6 –arene) is the resting state of the catalyst. Catalytically relevant SIPr-ligated Ni complexes with bound substrate and phenolic product have been synthesized independently, and a three-coordinate Ni metallacycle that is the formal product of oxidative addition of the C-O bond of dibenzofuran to Ni⁰ has been isolated and fully characterized. NaOt-Bu facilitates regeneration of the active catalytic species by deprotonation of the phenolic product to prevent the formation of inactive Ni^I phenoxide complexes lying off of the catalytic cycle.

RESULTS AND DISCUSSION

To gain experimental data on the mechanism of the hydrogenolysis of diaryl ethers catalyzed by an NHC-ligated Ni complex, we analyzed in more depth the effect of base, monitored the nickel species present in these reactions, obtained kinetic data, and obtained information on the reactivity of isolated, potential intermediates by single-turnover studies. Studies on catalytic hydrogenolyses in the absence and presence of NaOt-Bu revealed that NaOt-Bu is necessary to achieve high yields in this reaction, and NMR and UV-Vis spectroscopy revealed the resting state of the Ni catalyst. Kinetic studies showed the order in which the individual steps of the catalytic cycle occur, and isolation of discrete Ni⁰, Ni^I, and Ni^{II} complexes enabled each elementary step to be studied directly, including the step involving hydrogen and a process that can lead to catalyst decomposition.

Dependence of Yield on NaOt-Bu: The published nickel-catalyzed cleavage of diaryl ethers was conducted with added NaOt-Bu.¹⁸ NaOt-Bu was initially added to the system to deprotonate the carbene precursor SIPr•HCl (1) to generate the free carbene SIPr.²⁶ However, the role of NaOt-Bu is more extensive than simply generating the free carbene from the hydrochloride salt.

As initially reported,¹⁸ the hydrogenolysis of diaryl ether **8** catalyzed by the combination of Ni(COD)₂ and SIPr•HCl (1) with an excess of NaOt-Bu formed arene 10 in 81% yield and fully converted diaryl ether **8** (Table 1, Entry 1).¹⁸ To bypass the role of NaOt-Bu in generating the free carbene, we conducted reactions catalyzed by the combination

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Table 1. Effect of Base on the Hydrogenolysis of DiarylEther 8^a

\langle	>° ⁄	CF3	20 mol % [Ni] X equiv NaOt-Bu H ₂ (1 atm) toluene, 100 °C		+ CF ₃				
	8		18 h	9	10				
	Ũ			5	10				
		NHC or NHC	2						
_	Entry	Precursor	Base	Conversion (%) b	Yield of 10 (%) ^b				
	1	SIPr•HCI	NaOt-Bu	100	81				
	2	SIPr	-	19	19				
	3	SIPr	NaOt-Bu	100	82				
	4	SIPr	NaOPh	28	25				

^{*a*}Reactions were conducted on a 0.15 mmol scale in a sealed Schlenk tube under H_2 atmosphere. See the Supporting Information for further experimental details ^{*b*}Conversions and yields were determined by ¹⁹F-NMR spectroscopy against an internal standard.

of Ni(COD)₂ and the free carbene SIPr in the presence and absence of NaOt-Bu. The reaction catalyzed by 20 mol% Ni(COD)₂ and 40 mol% carbene without added NaOt-Bu gave only 19% yield of arene **10** (Table 1, Entry 2). In contrast, the reaction catalyzed by these components in the presence of NaOt-Bu gave full conversion of ether **8** and 82% yield of arene **10** (Table 1, Entry 3). If NaOt-Bu were simply forming the free carbene from SIPr•HCl, then the reaction of ether **8** catalyzed by the combination of Ni(COD)₂ and free SIPr as ligand in the absence of NaOt-Bu should have occurred to full conversion and formed arene and phenol in high yield. Thus, NaOt-Bu participates

Table 2. Catalytic Reactivity of Ni complexes 11, 14, 16and 18 in the Hydrogenolysis of Diaryl Ether 8^a

		X equiv Na H _a (1 ati		+
~ 8	~ CF3	toluene, 10 18 h	0° ℃ 9	 ✓ CF₃ 10
Entry	[Ni]	х	Conversion (%) ^b	Yield of 10 (%) ^b
10	11	2.5	100	69
2	11	0	14	12
3	14	2.5	98	79
4	14	0	16	16
5	16	2.5	< 5	0
6 ^{<i>d</i>}	16	2.5	91	62
7 ^e	18	2.5	94	63
8	18	0	8	0
SIPr	SIPr		>N_N<	SIPr
Ni SIPr			Ni	
11	14		16	18

^{*a*}Reactions were conducted on a 0.15 mmol scale in a sealed Schlenk tube under H₂ atmosphere. See the Supporting Information for further experimental details. ^{*b*}Conversions and yields were determined by ¹⁹F-NMR spectroscopy against an internal standard. ^{*c*}Reaction was heated for 6 h. ^{*d*}SIPr•HCl (1, 40 mol%) was added as ligand. ^{*e*}The reaction mixture was allowed to stir at room temperature for 10 min prior to heating.

in the catalytic system after generation of the active cata-

lyst. Under the basic conditions of our hydrogenolysis of C–O bonds, the product phenol **9** would be converted to the corresponding phenoxide salt. Thus, we tested whether the effect of NaOt-Bu resulted from forming NaOAr salts that would react at some point of the catalytic process. To do so, we conducted the reaction of ether **8** with H₂ catalyzed by the combination of Ni(COD)₂ and free SIPr with NaOPh in place of NaOt-Bu. This reaction occurred to only 28% conversion after 18 hours (Table 1, Entry 4).

The same effect of NaOt-Bu on the conversion of diaryl ethers was observed when the reactions were initiated with the preformed Ni⁰ complex Ni(SIPr)₂ (11).²⁷ The reaction catalyzed by di-ligated complex 11 with 2.5 equivalents of NaOt-Bu formed arene 10 in 69% yield, but the reaction catalyzed by di-ligated complex 11 without added base occurred in only 12% yield (Table 2, Entry 1–2). This body of results on the reactions with free carbene as ligand or the pre-formed, NHC-ligated Ni⁰ complex 11 as catalyst demonstrate that NaOt-Bu is necessary for the hydrogenolysis catalyzed by a Ni complex ligated by SIPr.

Identification of the Resting State of the Catalyst: To gain further insight into the mechanism of the Ni-catalyzed hydrogenolysis of diaryl ethers we identified the catalyst resting state by spectroscopic techniques. Catalytic reactions containing Ni(SIPr)₂ changed color from purple to red when heated to 100 °C. This color change indicated that the active Ni species in solution was not the bis-NHC complex 11. Instead, the major species is SIPr-Ni(η^6 -C₆D₆) (12) or an analogous η^6 -arene complex, depending on the arene solvent. In non-aromatic solvents, SIPr-Ni⁰ binds diaryl ether substrates to generate η^6 bound Ni complexes (vide infra). Complex 12 was prepared in this manner by heating 11 in C₆D₆ (Figure 1, top) at 100 °C for 1 hour. This reaction gave a mixture that consisted of an approximately 1:1 mixture of C₆D₆-ligated 12 and free ligand 13 (Figure 1, bottom). Mononuclear Ni-NHC complexes of the general structure NHC–Ni(η^6 –arene) have been reported previously by Ogoshi in 2014.²⁸ The complete conversion of **11** to **12** in C₆D₆ at 100 °C shows that ligand dissociation from bis-NHC complex 11 and association of the aromatic solvent occurs under conditions analogous to those we reported for hydrogenolysis of diaryl ethers.¹⁸

To probe the identity of the resting state of the Ni catalyst directly by NMR spectroscopy, aliquots from the reaction of Ph₂O with H₂ catalyzed by the combination of Ni(COD)₂ and NHC 1 with excess NaOt-Bu at room temperature and 100 °C were monitored by NMR spectroscopy (see the Supporting Information for further experimental details). The only NHC-ligated Ni species observed in the catalytic hydrogenolysis of diphenyl ether by NMR spectroscopy was SIPr-Ni(η^6 -C₆D₆) (12). This complex accounted for 96% of the initially added nickel complex, as determined by integration of Ni complex 12 vs diphenyl ether. The ¹³C-NMR spectrum of C_6D_6 -ligated 12 is particularly diagnostic of its structure, containing a 1:1:1 triplet at 89.3 ppm $(J^{I}_{C-D} = 25.4 \text{ Hz})$ that corresponds to the carbons of coordinated C₆D₆; this ¹³C-NMR signal is observed clearly in the ¹³C NMR spectrum of an aliquot of the reaction mixture for the catalytic hydrogenolysis of diphenyl ether.

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Figure 1. ¹H-NMR spectra of Ni(SIPr)₂ (**11**, top) and the thermolysis of Ni(SIPr)₂ (**11**) in C₆D₆ at 100 °C (bottom). Ni complex **11** undergoes ligand exchange with C₆D₆ to provide SIPr–Ni(η^6 –C₆D₆) (**12**, \blacklozenge) and free SIPr (**13**, \blacklozenge).

Because NMR silent Ni complexes could be formed in the catalytic reaction mixture, we also monitored these reactions by UV-vis spectroscopy. We compared these spectra of the catalytic reaction to those of discrete isolated nickel complexes. The UV-Vis spectrum of a solution of $Ni(SIPr)_2$ (11) in toluene contains three distinctive bands (Figure 2, purple trace). In contrast, the UV-Vis spectrum of a catalytic hydrogenolysis reaction mixture (Figure 2, black trace) lacked these signals. Instead, the major absorbance of the catalytic reaction mixture was at 365 nm, and this absorption is identical to that of independently prepared SIPr-Ni(η^6 -C₆H₆) (14) (red trace, Figure 2). This result shows the absence of large amounts of NMR silent Ni complexes in the catalytic reaction mixture and is consistent with the high conversion of the nickel catalyst precursor to SIPr-Ni(η^6 -arene), as determined by NMR spectroscopy.

Catalytic Competence of the Catalyst Resting State: The catalytic competence of SIPr–Ni(η° –C₆H₆) (14) was assessed by running the hydrogenolysis of diaryl ether 8 with 14 as catalyst in a sealed Schlenk tube under 1 atm of H₂. The reaction of ether 8 with H₂ catalyzed by SIPr- $Ni(\eta^{6}-C_{6}H_{6})$ (14) with added NaOt-Bu occurred to 98% conversion and gave 79% yield of arene 10 (Table 2, Entry 3). The yield of arene 10 from the reaction catalyzed by SIPr–Ni(η° –C₆H₆) (14) with added NaOt-Bu is comparable to the yield of arene 10 from the hydrogenolysis of ether 8 catalyzed by the combination of Ni(COD)₂, ligand, and NaOt-Bu (Table 1, Entries 1,3). In addition, the hydrogenolysis of ether 8 catalyzed by the combination of Ni(COD)₂, ligand, and NaOt-Bu proceeds at approximately the same rate as the hydrogenolysis catalyzed by SIPr- $Ni(\eta^6-C_6H_6)$ (14) with added NaOt-Bu. After 2 hours, these reactions occurred with 71% and 74% conversion of ether 8 respectively (see the Supporting Information for full reaction profiles).



Figure 2. UV–Vis spectrum (toluene, 298K) of Ni(SIPr)₂ (**11**, 0.13 μ M, purple trace), an aliquot from a typical hydrogenolysis reaction mixture under H₂ prior to heating ([Ni] = 0.17 μ M, black trace, see the Supporting Information for further experimental details), and of SIPr–Ni(η^6 –C₆H₆) (**14**, 0.17 μ M, red trace).

Kinetic Data and Experimental Rate Law: To gain quantitative kinetic data on the hydrogenolysis reaction catalyzed by the isolated arene complex, we measured the rate dependence of each component of the hydrogenolysis of ether 8 in the presence of NaOt-Bu catalyzed by SIPr– Ni(η^6 –C₆H₆) (14) (Scheme 3). The data were acquired by the method of initial rates by ¹⁹F-NMR spectroscopy in toluene under an atmosphere of H₂ at 100 °C in sealed tubes. The kinetic data on this reaction were obtained by the method of initial rates, rather than a full kinetic profile, to ensure sufficient mass transport of H₂, to avoid kinetic effects of the consumption of H₂ as the reaction proceeds, and to circumvent the long reaction times needed to achieve high conversions of starting material.

Scheme 3. Kinetic Reaction Orders of the Hydrogenolysis of Ether 8.



The dependence of the initial rate on the concentration of ether **8** and the concentration of Ni complex **14** was first order, and the dependence on the concentration of NaO*t*-Bu and the pressure of H_2 was zero order (see the Supporting Information for further experimental details). These kinetic data for the hydrogenolysis are consistent with a mechanism by which cleavage of the C–O bond in the diaryl ether by a Ni⁰ complex is rate determining, and the product of this step reacts with hydrogen and base in steps with transition-state energies that are lower than that for the reaction of the Ni⁰ species with the diaryl ether. This evidence for rate-limiting cleavage of the C–O bond is also consistent with the observed Ni⁰ resting state.



for separate reactions

By measuring the rate of the reaction under an atmosphere of D₂, rather than H₂, the kinetic isotope effect of the hydrogenolysis of ether **8** was found to be 1.0 ± 0.1 (Scheme 4). This value agrees with the lack of dependence of rate on the pressure of H₂ and indicates that cleavage of the H–H bond is not involved during the rate–limiting step.

Substrate Binding: Prior to oxidative addition of the C– O bond in the substrate to a SIPr-ligated Ni⁰ complex, the substrate would likely replace the coordinated arene solvent in the resting state. The reaction of Ni complex 14 with excess Ph₂O in C₆D₁₂ formed a mixture of the starting complex 14 and SIPr–Ni(η^6 –Ph–OPh) (15). The ¹H-NMR spectrum of 15 contains resonances that are shifted significantly upfield (~ 4.8-5.3 ppm) of typical aromatic signals, consistent with coordination of one of the phenyl rings in Ph₂O to Ni. The peaks in the ¹H-NMR spectrum corresponding to the second aromatic ring are not shifted from the aromatic region, indicating that the nickel is bound to only one of the two aryl rings of the ether.

Scheme 5. Isolation of Substrate Bound Ni Complex 15



 η^6 -Diaryl ether **15** was isolated from the reaction of Ni complex **14** and excess Ph₂O in hexamethyldisiloxane solvent (Scheme 5). Complex **15** was characterized by single-crystal X-ray diffraction and by multi-dimensional NMR spectroscopy (see the Supporting Information for detailed assignment). Although the quality of the crystallographic data was not suitable for deducing detailed information on the bond lengths and angles, the data did confirm the assigned connectivity as η^6 -arene complex **15**. The bound and unbound aryl rings in complex **15** exchange rapidly at room temperature, as deduced by 2D exchange spectroscopy (EXSY), with a rate constant of 0.35 s⁻¹.

The isolated material contained a less abundant Ni complex 15* containing a bound diaryl ether (3.2:1 ratio of 15 to 15* in the isolated material at room temperature in C_6D_{12} ; see the Supporting Information for further discussion and spectral data). Although we have not determined its precise structure, 15* clearly contains an η^6 -bound and an unbound aryl unit of the diaryl ether, like 15, and compounds 15 and 15* rapidly equilibrate at room temperature, as deduced by 2D EXSY, with an exchange rate constant of 0.11 s⁻¹. The bound and unbound aryl ring in 15* also exchange rapidly at room temperature, as deduced by 2D EXSY, with a rate constant of 0.45 s⁻¹. The characterization and isolation of complex 15 is strong evidence that the solvent-bound Ni⁰ resting state binds diaryl ether prior to the next step of the reaction. Computations by Surawantanawong support this ligand exchange but suggest further isomerization of η^6 -diaryl ether 15 to η^2 -diaryl ether 2 precedes oxidative addition.²⁹ Although this mechanism could be occurring, our observation of chemical shifts characteristic of an η^6 -arene interaction imply that neither the major observed species 15 nor the minor species 15* are this η^2 -adduct.

Independent Generation of NHC-Ligated Arylnickel Phenoxide Complexes: Few three-coordinate T-shaped Ni^{II} species have been reported. All of them possess a metallacyclic core and, with one exception,³⁰ are stabilized by a sterically hindered NHC ligand.³⁰⁻³³ Although one could imagine that the direct synthesis or observation of three-coordinate SIPr-Ni(Ar)(OAr) could be accomplished by the salt metathesis of SIPr-Ni(Ar)(X) and phenoxide, Matsubara reported that the products from the direct oxidative addition of aryl halides to NHC-ligated Ni⁰ are dinuclear Ni¹ complexes containing bridging halides or aryl groups.³⁴ To our knowledge, monomeric NHC-Ni(Ar)(X) complexes containing a single NHC ligand have not been reported previously. A similar Ni^{II} species was isolated as a cationic arylnickel complex stabilized by solvent with an outer sphere iodide.³⁵ This adduct was proposed to exist in equilibrium with NHC-Ni(Ar)(X). Stable, four-coordinate Ni complexes of the general form (NHC)₂Ni(Ar)(X) bearing less sterically demanding NHC ligands than SIPr have been reported.³⁶⁻⁴⁰

Scheme 6. Synthesis of Ni^{II} Aryl Phenoxide 16



Considering the lack of NHC–Ni(Ar)(X) complexes, we prepared TMEDA–Ni(o–Tolyl)(OPh) (16) in which the TMEDA ligand might be displaced by an NHC to form the formal product of oxidative addition of the C–O bond in a diaryl ether to Ni⁰. In addition, we prepared a metallacyclic aryl Ni^{II} phenoxide complex ligated by SIPr.

TMEDA-ligated **16** was prepared by the reaction of TMEDA-Ni(o-Tolyl)Cl⁴¹ with NaOPh. Complex **16** was isolated from this reaction in 71% yield, and its structure was confirmed by X-ray crystallography (Scheme 6). The hydrogenolysis of ether **8** catalyzed by Ni complex **16** in the absence of external carbene provided <5% conversion (Table 2, Entry 5). However, the reaction of ether **8** with H₂ catalyzed by complex **16** in the presence of SIPr•HCl (**1**) and NaOt-Bu gave arene **10** in 62% yield (Table 2, Entry 6). We hypothesize that displacement of the TMEDA in complex **16** by SIPr generates the catalytically active, transient SIPr-Ni(o-Tolyl)(OPh). Treatment of **16** with SIPr **13**

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to form observable quantities of SIPr–Ni(*o*–Tolyl)(OPh) led to no reaction at lower temperatures and to decomposition at elevated temperatures. To prepare a stable arylnickel phenoxide complex ligated by SIPr, we targeted the product of oxidative addition of a cyclic diaryl ether, such as dibenzofuran. We envisioned that metallacycle **18** could be formed independently by initial oxidative addition of aryl bromide **17** containing a pendant phenoxide to Ni⁰ to form the Ni^{II} bromide **19**. Rapid intramolecular cyclization of the pendant phenoxide in bromide **19** would provide complex **18**. The rapid intramolecular displacement of bromide would avoid the need to isolate an unstable arylnickel halide complex.

As designed, the three-coordinate complex 18 that would result from oxidative addition of a dibenzofuran C-O bond was synthesized independently by the reaction of phenoxide 17 with SIPr–Ni(η^6 –C₆H₆) (Scheme 7). The deep purple Ni complex 18 was isolated in 79% yield. The structure of 18 was suggested to be a three-coordinate metallacycle from multi-dimensional ¹H and ¹³C-NMR spectroscopy experiments and was confirmed by single crystal X-ray diffraction (Figure 3). Intramolecular trapping of the arylnickel halide was crucial to the isolation of an NHCligated arylnickel phenoxide. The reaction of SIPr–Ni(η^{6} – C_6H_6) (14) with bromobenzene and NaOPh did not give products of this structural type (vide infra). Instead, biphenyl was observed by GC/MS and an unidentified Ni species was formed. In addition, no reaction of SIPr-Ni(η^6 -C₆H₆) (14) and dibenzofuran was observed below 80 °C. and decomposition was observed at 120 °C.

Scheme 7. Synthesis of Three-Coordinate Ni Metallacycle 18 Through Intramolecular Substitution



Metallacycle **18** was found to be thermally sensitive; heating a solution of metallacycle **18** in C_6D_6 at 120 °C for 1 hour provided a complex mixture of products with full conversion of metallacycle **18**. We did not observe dibenzofuran resulting from C–O bond-forming reductive elimination in significant quantities; this result is in agreement with Hillhouse's original findings that reductive elimination of C–O bonds from Ni^{II} alkoxide complexes occurs faster and in higher yield after oxidation of an alkyl or arylnickel alkoxide complex to a Ni^{III} species.⁴²⁻⁴⁴

The solid-state structure of **18** consists of a SIPr-ligated metallacycle in which the Ni^{II} atom adopts a distorted T-shaped geometry (C1–Ni1–O1 161.15(7)°, O1–Ni1–C28 97.91(6)°, C1–Ni1–C28 100.63(7)°).⁴⁵⁻⁴⁶ These bond angles are similar to those of the other three-coordinate Ni^{II} complexes.³⁰⁻³³ The C1–Ni1–O1 angle in metallacycle **18** is 12° smaller than the P–Pd–O angle of 173.1° in a T-shaped,

phosphine ligated arylpalladium phenoxide,⁴⁷ and this smaller angle leads to a geometry that is more distorted from a T-shape.

The NHC ligand in complex **18** is located trans to the phenoxide group. This configuration is consistent with a larger trans influence of a phenyl ligand than of a phenoxide ligand.⁴⁸ Consistent with this assertion are the relative trans influences shown by the lengths of the Ni–N bonds in TMEDA complex **16**. The Ni–N bond that is trans to the phenoxide ligand is 0.063(2) Å shorter than the Ni–N bond that is trans to the aryl ligand.



Figure 3. ORTEP diagram of metallacycle **18** (thermal ellipsoids at the 50% probability level). For clarity, one molecule in the asymmetric unit and all hydrogen atoms have been omitted. Values reported are averaged values of the 2 molecules in the asymmetric unit. Selected bond lengths (Å): Ni1–C1 = 1.859(2), Ni1–O1 = 1.793(1), and Ni1–C28 = 1.849(2). Selected bond angles (°): C1–Ni1–O1 = 162.33(7), O1–Ni1–C28 = 97.87(6), C1–Ni1–C28 = 99.55(7).

Reactivity of Metallacycle 18: To assess the relevance of metallacycle 18 to the catalytic hydrogenolysis, we conducted the reaction of dibenzofuran with H₂ catalyzed by the NHC-ligated η^6 -arene complex 14. The reaction of this diaryl ether catalyzed by complex 14 with added NaOt-Bu occurred at 140 °C to provide the corresponding phenol after acidic workup in 87% yield by GC analysis (see the Supporting Information for further experimental details). To assess initially whether the metallacycle 18 is competent to be an intermediate in this catalytic reaction, the hydrogenolysis of ether 8 catalyzed by 18 with excess NaOt-Bu was conducted. This reaction occurred to 94% conversion to form arene 10 in 63% yield (Table 2, Entry 7). The hydrogenolysis of dibenzofuran catalyzed by metallacycle 18 with added base gave 49% conversion with 49% yield of the corresponding phenol after acidic workup (see the Supporting Information for further experimental details).

Having established the catalytic competence of 18, we conducted reactions of 18 with hydrogen and base to de-

termine how the product of oxidative addition of the C–O bond of a diaryl ether would be converted to the free organic product and the starting Ni⁰ species. The reaction with all components in C₆D₆ proceeded with full conversion of **18** to give 96% yield of C₆D₆-ligated **12**, as determined by ¹H-NMR spectroscopy, and 83% yield of phenoxide **20**, as determined by GC analysis of the corresponding phenol after neutralization of the reaction (Scheme 8a).

Scheme 8. Stoichiometric Reactivity of Metallacycle 18 with a) NaOt-Bu and H_2 and b) with Et_3SiH and c) with H_2 .



This reaction of metallacycle **18** to form C_6D_6 -ligated **12** and phenoxide **20** could occur by several paths. To determine if the reaction requires only H₂ or both H₂ and NaO*t*-Bu, a series of reactions were conducted with the metallaycle and NaO*t*-Bu, H₂ surrogates, and H₂ itself. First, we treated metallacycle **18** with NaO*t*-Bu. Exposure of metallacycle **18** to 2.5 equivalents of NaO*t*-Bu at room temperature did not form any new species by ¹H-NMR spectroscopy; starting material **18** was recovered from this reaction in 87% isolated yield. Therefore, it seems likely that metallacycle **18** reacts with H₂ before it reacts with base.

Second, as a surrogate for H_2 , a solution of metallacycle **18** was allowed to react with excess Et_3SiH in the absence of NaOt-Bu (Scheme 8b). The reaction mixture immediately changed from the purple color indicative of metallacycle **18** to a light red color indicative of a SIPr–Ni⁰ complex; C₆D₆-ligated **12** and silyl ether **21** were formed in 93% and 96% yield, respectively. The identity of silyl ether **21** was confirmed by independent synthesis, as well as GC/MS analysis of the reaction mixture.

Third, the stoichiometric reaction of metallacycle **18** was performed with 1 atm of H₂ (Scheme 8c). This reaction was more complex than the reaction with silane. C₆D₆-complex **12** formed in 19% yield. In addition, the η^2 , κ^1 hydroxybiphenyl Ni⁰ complex **22** formed in 56% yield. The identity of complex **22** was confirmed by independent synthesis (see below), and the solid-state structure of complex **22** was determined by X-ray crystallography to be an adduct

of SIPr–Ni⁰ and phenol **23** (Figure 4). The phenolic hydroxyl group was found to coordinate to Ni in a bidentate fashion by a dative O–Ni interaction and an η^2 –arene interaction. Although the phenolic hydrogen was not located by X-ray diffraction, its presence was confirmed by a sharp stretch in the IR spectrum of **22** at 3572 cm⁻¹. In addition, the broad peak in the ¹H-NMR spectrum of **22** at 2.12 ppm that was assigned to the phenolic hydrogen was absent after addition of D₂O.

Complex 22 was prepared independently by the reaction of SIPr–Ni(η^6 –C₆H₆) (14) with 2-hydroxy-1,1-biphenyl (23). The reaction of SIPr–Ni(η^6 –C₆H₆) (14) with phenol 23 in pentane formed Ni complex 22 in 45% isolated yield. (Scheme 9). The formation of adduct 22 is specific to the reaction of metallacycle 18 to form hydroxybiphenyl 23 because this phenol can chelate Ni⁰ through the arene and hydroxyl groups.





This phenol fragment could form in the hydrogenolysis process by addition of H₂ across the Ni–O or Ni–C bond in metallacycle **18** to form an O–H or C–H bond. The resultant Ni–hydride could then form the O–H or C–H bond by reductive elimination to generate hydroxybiphenyl **23**, which would bind to Ni⁰ to produce complex **22**. We could not distinguish between these pathways experimentally, but it is clear that NaO*t*-Bu is not needed for the reaction of the arylnickel phenoxide with hydrogen.



Figure 4. ORTEP diagram of Ni complex **22** (thermal ellipsoids at the 50% probability level). For clarity, one molecule of phenol **23** in the asymmetric unit and all hydrogen atoms including the phenolic hydrogen have been omitted. Selected bond lengths (Å): Ni1–C1 = 1.932(4), Ni1–O1 = 2.002(2), Ni1–C28 = 2.282(4), and Ni1–C29 = 2.141(4).

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Selected bond angles (°): C1–Ni1–O1 = 110.1(1), C1–Ni1– C28 = 152.4(1), C1–Ni1–C29 = 158.5(2).

Role of NaOt-Bu in the Ni-Catalyzed Hydrogenolysis of C-O Bonds: To regenerate the catalytic resting state, η^6 -arene complex 12 (if C₆D₆ is the reaction solvent), the bound arene must be replaced by C₆D₆. The reaction of 22 with excess NaOt-Bu in C₆D₆ occurred at room temperature to give a 1:3.75 mixture of starting 22 and η^6 -C₆D₆ 12 (Scheme 10). Deprotonation by NaOt-Bu to provide tbutanol and phenoxide 20 may provide a driving force for the generation of benzene-complex 12 from hydroxybiphenyl complex 22. The more electron rich phenoxide 20 should not bind to the electron-rich Ni⁰ as well as the neutral arene solvent or substrate. This assertion is supported by the reported high K_{eq} for replacement of toluene with 1,3,5-tris(trifluoromethyl)benzene in IPr-Ni(η^6 -C₇H₈). In contrast, the more electron rich 1,3,5-trimethoxybenzne does not give any product from displacement of toluene.²⁸

Scheme 10. Proposed Equilibrium of Phenol 22 and the Role of NaOt-Bu



To probe more generally how the phenol or phenoxide products could interact with the Ni⁰ product from reaction of H₂ with an arylnickel phenoxide complex, we conducted reactions of phenol and phenoxide with η^6 -arene Ni⁰ complex 14. No reaction was observed between Ni⁰ 14 and NaOPh. This result shows that binding of a neutral arene to the NHC-Ni⁰ fragment is favored over binding of an anion-ic phenoxide, as would be expected for this electron-rich Ni⁰ unit.

Scheme 11. Reaction of Ni⁰ with Phenol to generate Ni^I Dimer 24



In contrast, Ni⁰ **14** reacted with PhOH. This reaction did not produce a π -arene complex; rather it formed the new, orange, phenoxide bridged dimer **24** shown in Scheme 11. This complex was identified by single crystal X-ray diffraction (Figure 5) and was independently synthesized by the reaction of Sigman's Ni¹ dimer⁴⁹ [(SIPr)Ni(μ -Cl)]₂ with NaOPh (see the Supporting Information for further experimental details).

The ¹H-NMR spectrum of dimer **24** comprises 10 broad peaks at chemical shifts suggesting that the complex is paramagnetic. Indeed, the magnetic moment of dimer **24** is 2.89 μ B, indicating that complex **24** has 2 unpaired electrons and is most likely a Ni¹/Ni¹ dimer. We propose that dimer **24** forms by initial oxidative addition of Ni⁰ to the O–H bond in phenol to form SIPr–Ni(OPh)(H). Disproportionation of 2 molecules of SIPr–Ni(OPh)(H) would then provide SIPr–Ni(OPh)₂ and a Ni dihydride. Reductive elimination of H₂ from the latter complex would afford a Ni⁰ complex, which could react with SIPr–Ni(OPh)₂ to form **24**.



Figure 5. ORTEP diagram of dimer **24** (thermal ellipsoids at the 50% probability level). For clarity, all hydrogen atoms have been omitted. Selected bond lengths (Å): Ni1–Ni1' = 2.9710(7), Ni1–C1 = 1.880(2), Ni1–O1 = 2.020(1), Ni1–N1 = 1.354(2), and Ni1–N1 = 1.369(3). Selected bond angles (°): C1–Ni1–O1' = 156.12(8), C1–Ni1–O1 = 120.43(8), and O1–Ni1–O1' = 82.69(6).

The reaction of **14** with phenol to generate the Ni¹ dimer suggests an important effect of NaOt-Bu. Under base-free reaction conditions for C–O bond hydrogenolysis (such as Table 1, Entry 2), the phenol product generated would react with the Ni⁰ catalyst to produce dimeric Ni¹ phenoxides like 24. Despite the precedent for the intermediacy of NHC-Ni¹ dimers in cross-coupling and cycloaddition reactions,^{34, 50} our results on the hydrogenolysis of diaryl ether 8 in the absence of NaOt-Bu (Table 1, Entry 2) indicate that formation of dimer 24 leads to a loss of catalytic activity. The reaction of diaryl ether 8 with H₂ catalyzed by dimer 24 without added base proceeds to only 9% conversion, whereas the same reaction with added NaOt-Bu proceeds to full conversion of diaryl ether and formed arene 10 in 67% yield. Moreover, the hydrogenolysis of diaryl ether 8 with both H₂ and NaOt-Bu catalyzed by dimer 24 occurs at approximately the same initial rate as the hydrogenolysis catalyzed by Ni⁰ 14 (see the Supporting information for further experimental details). This result suggests that dimer 24 can re-enter the catalytic cycle when both H₂ and NaOt-

Scheme 12. Overall Proposed Mechanism for the Ni-Catalyzed Hydrogenolysis of Diaryl Ethers with NHC as Ligand



Bu are present. The same reaction in the absence of NaOt-Bu generates phenol, and the phenol reacts with Ni⁰ to produce the catalytically inactive dimer 24. The stoichiometric reaction of dimer 24 with H₂ and NaOt-Bu in C_6D_6 generated C_6D_6 -bound 12. We did not observe any intermediate species in this reaction providing insight into the mechanism for this transformation.

CONCLUSION

1. Mechanism of Ni-Catalyzed Hydrogenolysis of Diaryl Ethers: On the basis of the results described above, we conclude that the Ni catalyzed hydrogenolysis of diaryl ethers occurs by the mechanism shown in Scheme 12. Deprotonation of NHC salt 1, coordination to Ni⁰, hydrogenation of the cyclooctadiene ligand, and association of the aromatic reaction solvent proceeds under ambient conditions to provide η^6 -arene complex A. Complex A is the resting state of the catalytic reaction. The resting state A reacts reversibly with the diaryl ether substrate to form η^6 -diaryl ether complex B. The unsubstituted analog of B, η^6 -Ph-OPh complex 15, has been structurally characterized. Oxidative addition likely occurs from the η^2 -diaryl ether intermediate, rather than the η^6 isomer, as deduced by computation.²⁹

Kinetic studies show that reaction of the diaryl ether with SIPr–Ni⁰(η^6 –arene) to cleave the C–O bond is rate limiting. The direct oxidative addition of the C–O bond of the diaryl ether forms the three-coordinate complex **C**. The metallacyclic arylnickel phenoxide **18** has been prepared and represents the product of oxidative addition of dibenzofuran to Ni⁰ during catalytic hydrogenolysis of the diaryl ether C–O bond in this substrate. The reactivity of the three-coordinate complex **18** with hydrogen and

NaOt-Bu and the catalytic activity of 18 are consistent with the intermediacy of arylnickel phenoxides in the hydrogenolysis reactions. Complex C reacts with hydrogen to provide phenol D and arene-ligated E. This reaction presumably proceeds through a Ni-H intermediate. In the absence of NaOt-Bu, phenol **D** reacts with SIPr-Ni⁰ to generate Ni¹ dimers with bridging phenoxides. Dimer 24 has been prepared from the reaction of SIPr- $Ni(\eta^6-C_6H_6)$ (14) with phenol and structurally characterized. If NaOt-Bu is present, phenol **D** reacts with the base to form phenoxide **G**, which does not react with the Ni^{0} species. Replacement of the arene product with solvent would then regenerate resting state A and close the catalytic cycle. Replacement of the arene product with substrate can also occur, but the arene solvent is present in higher concentrations and binds more strongly to Ni⁰ than the aryl ether substrate.

2. Comparison of Experimental and Computational Mechanisms for the Ni-Catalyzed Cleavage of C–O Bonds: The main steps of the mechanism of the catalytic hydrogenolysis in Scheme 12 most closely resemble the steps computed by Surawantanawong.²⁹ Surawantanawong calculated the barrier for oxidative addition of the C–O bond in diaryl ether 8 to SIPr-Ni⁰ to be 26.2 kcal/mol from Ni(COD)₂. This value is consistent with our kinetic data showing that this step is rate limiting. Our kinetic data show that the overall catalytic hydrogenolysis occurs with a ΔG^{\ddagger} of 26.0 kcal/mol when SIPr–Ni(η^6 –C₆H₆) (14) was the catalyst.

Computations reported by Chung and coworkers suggested that the oxidative addition of the C–O bond to anionic Ni-alkoxide **5** proceeded with a lower barrier than the oxidative addition of the C–O bond to a neutral spe-

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cies. We have not been able to isolate or observe anionic Ni complexes with compositions like that of **5**. In addition, our kinetic experiments show that the initial rate of the reaction is zero-order in NaOt-Bu and first order in diaryl ether. These data, coupled with the observed resting state, show clearly that reaction of the diaryl ether does not occur to an anionic species formed by the combination of the neutral resting state and NaOt-Bu.

At this time, we cannot explain why our experimental results do not match with Chung's computations of a lower-energy pathway through anionic Ni⁰ complexes. The catalytic cycle computed by Chung starts from Ni(SIPr)₂ (11) and did not include the formation of SIPr-Ni(η^6 -arene). Our experimental data indicates that the catalytic resting is SIPr-Ni(η^6 -arene) and not Ni(SIPr)₂ (11) at elevated temperatures in aromatic solvents.

Surawantanawong and coworkers proposed two energetically feasible pathways for the reaction of threecoordinate C with H_2 .²⁹ A Ni dihydride species was not located computationally. Instead, complex C could bind H₂ and react directly through sigma-complex assisted metathesis²⁹ to produce phenol **D** and a Ni–hydride. Reductive elimination of the hydride would then provide the arene product. Alternatively, three-coordinate C could isomerize to a Ni complex with the aryl ligand trans to the NHC. This species would then undergo sigma-complex assisted metathesis to form the C-H bond and reductive elimination would form the O-H bond. In both cases, O-H bond formation has the higher barrier of approximately 19 kcal/mol. We have not experimentally observed any intermediate Ni species in the reaction of metallacycle 18 with H₂ to distinguish between these two mechanistic possibilities.

The mechanism for the hydrogenolysis of aryl ethers by a Ni catalyst varies substantially with ligand, reductant, and substrate. Martin carefully examined the mechanism of the silanolysis of C–O bonds in aryl methyl ethers catalyzed by a phosphine-ligated Ni complex and concluded that the catalytic pathway involves Ni¹ intermediates.²¹ In this case, the barrier to direct oxidative addition of the C– O bond to a Ni⁰ complex to form a Ni^{II} complex was calculated to be 40.4 kcal/mol from Ni(COD)₂ and free phosphine. The authors concluded that the largest energetic barrier in a catalytic cycle involving phosphineligated Ni^I species would be only 31.6 kcal/mol. A catalytic cycle involving Ni^I species was also consistent with their observed kinetic and EPR spectroscopic data.

In contrast to Martin's system for C–O bond cleavage, our system has SIPr as a ligand, H_2 as a reductant, and diaryl ethers as substrate. The direct oxidative addition of the diaryl ether to Ni⁰ without involvement of hydrogen or base in this system is supported by our kinetic data.

In general, this work on NHC-ligated nickel complexes that cleave the C–O bonds in diaryl ethers complements Martin's detailed analysis of the mechanism for silanolysis of C–O bonds catalyzed by phosphine-bound Ni¹ complexes.²³ These two studies illustrate the large changes in mechanism that can be caused by small modifications in a catalytic system and reagent. Although computational proposals suggested anionic Ni⁰ intermediates,²⁵ and experimental studies in similar systems suggested Ni¹ intermediates,²¹ our data indicate that oxidative addition of aryl ethers occurs to a neutral Ni⁰ species in the catalyst system we investigated containing a hindered NHC ligand. Overall, we hope that exploration of mechanisms for Ni-catalyzed reactions will lead to new catalyst design for the cleavage of strong C–O bonds.

ASSOCIATED CONTENT

Additional experimental details and procedures and spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests

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