JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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A Heterogeneous Nickel Catalyst for the Hydrogenolysis of Aryl Ethers without Arene Hydrogenation

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Supporting Information

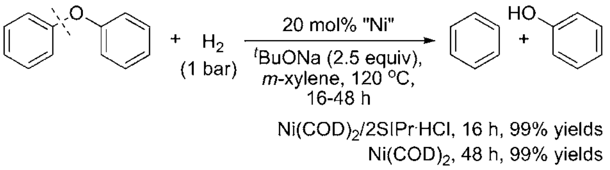
ABSTRACT: A heterogeneous nickel catalyst for the selective hydrogenolysis of aryl ethers to arenes and alcohols generated without an added dative ligand is described. The catalyst is formed *in situ* from the well-defined soluble nickel precursor $Ni(COD)_2$ or $Ni(CH_2TMS)_2(TMEDA)$ in the presence of a base additive, such as ^tBuONa. The catalyst selectively cleaves $C_{Ar}-O$ bonds in aryl ether models of lignin without hydrogenation of aromatic rings, and it operates at loadings down to 0.25 mol % at 1 bar of H_2 pressure. The selectivity of this catalyst for electronically varied aryl ethers differs from that of the homogeneous catalyst reported previously, implying that the two catalysts are distinct from each other.

Catalytic hydrogenolysis of the $C_{Ar}-O$ bond in aromatic ethers is a critical process for the conversion of the lignin component of plant biomass into aromatic hydrocarbons, feedstocks for the production of biofuels, and chemicals.[1−4] Typically, the hydrogenolysis of $C_{Ar}-O$ bonds is conducted over heterogeneous catalysts that require high temperatures (>250 °C) and pressures of hydrogen (>30 bar). These conditions lead to concomitant reduction of aromatic rings.[1,5−7] The poor chemoselectivity of heterogeneous catalysts for hydrogenolysis over hydrogenation wastes hydrogen and results in low yields of arene products. Therefore, the identification of catalysts that cleave $C_{Ar}-O$ bonds selectively would be a significant advance toward addressing the challenge of converting lignocellulose biomass into simple arenes.[3]

To address the problem of selective reduction of $C_{Ar}-O$ bonds in aryl ethers, several groups have developed catalytic systems that are based on soluble nickel complexes and hydride donors, such as silanes[8−10] and aluminohydrides.[10] Reactions with hydrogen would be more practical, and we recently reported a nickel-*N*-heterocyclic carbene catalyst for the selective reduction of the $C_{Ar}-O$ bond in aryl ethers with hydrogen at 1 bar of pressure.[10] The catalyst converted aryl ethers into arenes and alcohols in high yields without arene hydrogenation. Despite these advantages, the process required high catalyst loading (typically 20 mol % of Ni) and the SIPr carbene ligand.

Here we report a highly active heterogeneous and ligandless nickel catalyst[11] for the selective hydrogenolysis of diaryl, benzyl aryl, and benzyl alkyl ethers at much lower loadings (down to 0.25%) than the SIPr-Ni catalyst without carbenes or phosphines as auxiliary ligands. In contrast to most known heterogeneous systems, the catalyst operates at low hydrogen pressure (1 bar) and does not catalyze the hydrogenation of arenes. The regioselectivity of this system for cleavage of two different types of C−O bonds is orthogonal to that of the previously reported homogeneous nickel-carbene catalyst.[10]

The ligandless nickel catalyst reported here was discovered when studying the effects of ligands on the nickel-catalyzed hydrogenolysis of aryl ethers.[10] Initial studies showed that $Ni(COD)_2$ without added ligand was less reactive than the combination of $Ni(COD)_2$ and SIPr·HCl for the hydrogenolysis of diphenyl ether (eq 1).



(1)

However, we have now found that this ligandless system is more active than the SIPr-Ni catalyst for hydrogenolysis of the types of electron-rich diaryl ethers found in lignin.[1,12,13] Figure 1A provides data on the relative rates for reaction of electronically varied diaryl ethers in the presence of the two types of catalysts. Only 75% conversion of the di-*o*-anisyl ether to arene and aryl alcohol occurred in the presence of the Ni-SIPr system under the conditions that led to full conversion of the same ether in the presence of the ligandless system. In contrast, conditions that led to full conversion of the trifluoromethyl-substituted ether in the presence of the Ni-SIPr system occurred to only 41% conversion in the presence of the ligandless system and formed products from the reduction of both C−O and C−F bonds.

To test whether this trend in reactivity also applies to the cleavage of two different $C_{Ar}-O$ bonds within the same ether, we conducted the hydrogenolysis of unsymmetrical diaryl ethers. As shown in Figure 1B, the ligandless nickel catalyst cleaved the $C_{Ar}-O$ bond adjacent to the most electron-rich arene ring of 4-hydroxy diphenyl ether to form 2 equiv of phenol as the sole product. In contrast, the SiPr-Ni catalyst preferentially cleaved the $C_{Ar}-O$ bond adjacent to the more electron-deficient ring to form predominantly hydroquinone (67%) and benzene (48%). These results on both the inter- and intramolecular competition experiments clearly indicate that

Received: August 30, 2012
Published: November 19, 2012

dx.doi.org/10.1021/ja3085912 | *J. Am. Chem. Soc.* 2012, 134, 20226−20229

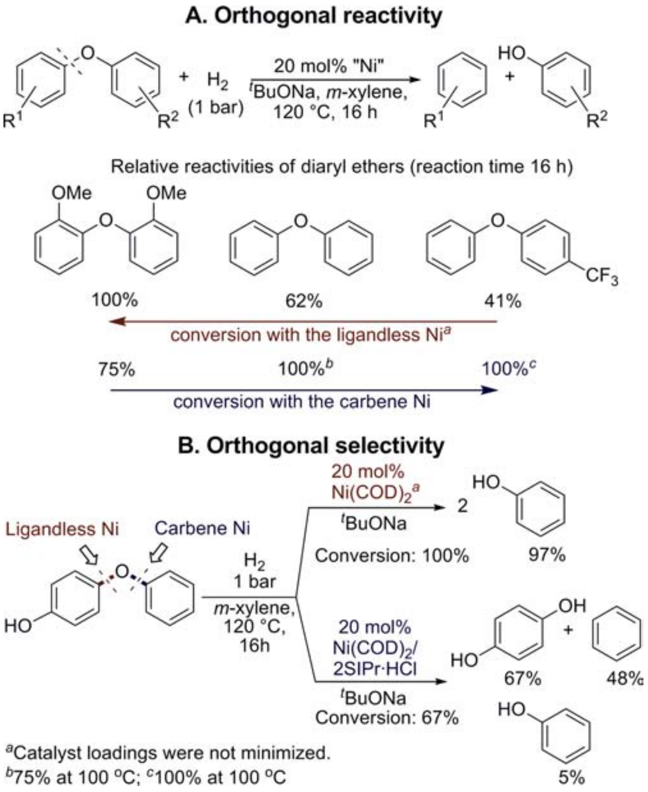


Figure 1. Differences in reactivity and selectivity between the ligandless and carbene-ligated nickel catalysts.

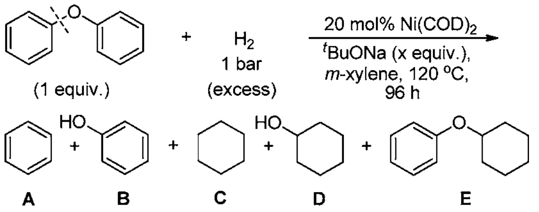
the catalytic species generated without added ligand is distinct from the species generated with added SIPr ligand.

The effect of the reaction components on the hydrogenolysis of diaryl ethers helped reveal the origin of the unusual regio- and chemoselectivity of the ligandless catalyst system. In particular, the ^{t}BuONa base had a dramatic influence on catalyst activity, stability, and chemoselectivity for hydrogenolysis of the C_{Ar}−O bond over hydrogenation of the aromatic ring (Table 1).

In the absence of ^{t}BuONa (Table 1, entry 1), the catalyst was not regioselective. Under these conditions, the products included benzene (58%), phenol (2%), cyclohexane (12%), cyclohexanol (53%), and phenyl cyclohexyl ether (6%) from competitive C_{Ar}−O bond hydrogenolysis and arene hydrogenation. In the presence of 0.2 equiv of ^{t}BuONa, with respect to diphenyl ether, the catalytic activity was low (Table 1, entry 2). However, the reaction conducted with 1 equiv of base occurred to a higher conversion (84%) and formed benzene (84%), phenol (77%), and only traces of cyclohexanol (Table 1, entry 3). The reaction with 2.5 equiv of base occurred to completion and formed benzene and phenol in nearly quantitative yields (Table 1, entry 4).[14]

The fate of the nickel in the absence of ^{t}BuONa was different from the fate in the presence of ^{t}BuONa. Under the reaction conditions in the absence of ^{t}BuONa, the nickel precursor rapidly formed a mirror on the walls of the vessel, leaving a colorless solution. In contrast, under the reaction conditions with 0.2 equiv of ^{t}BuONa, the nickel remained in solution. The solution was either black or dark brown, depending on the amount of base (see the Supporting Information for photographs).

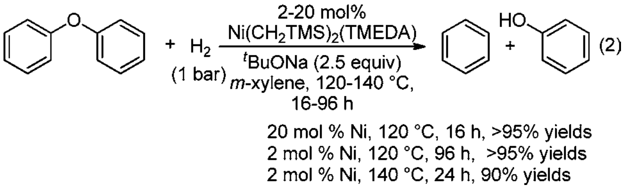
Table 1. Effect of Base and Nickel Precursor on Hydrogenolysis of Diphenyl Ether Catalyzed by the Ligandless Nickel[a]



			GC Yields				
entry	^{t}BuONa, equiv	conv., %	A, %	B, %	C, %	D, %	E, %
1	0	72[b]	58	2	12	53	6[c]
2	0.2	19[d]	18	8	0	8	0
3	1	84[d]	84	77	0	5	0
4	2.5	100	99	97	0	<5	0
5	5	100	99	96	0	<5	0

[a] Reaction conditions: diaryl ether (1 equiv), hydrogen (1 bar gauge pressure at rt), Ni(COD)$_2$ (0.2 equiv), ^{t}BuONa (0−5 equiv), m-xylene, 120 °C, 96 h. [b] Dimethylcyclohexanes were observed as products of m-xylene hydrogenation. [c] Uncorrected GC yield. [d] No further conversion was observed after 48 h.

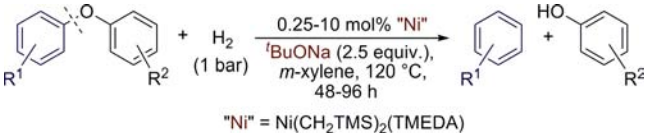
A change in the nickel precursor led to reactions that occur with lower loadings than those conducted with Ni(COD)$_2$. Reactions initiated by a series of well-defined nickel precursors for the model hydrogenolysis of diphenyl ether (Table S2) indicated that Ni(CH$_2$TMS)$_2$(TMEDA) generated a more active catalyst than Ni(COD)$_2$. Equation 2 summarizes the reactions of diphenyl ether initiated by Ni(CH$_2$TMS)$_2$(TMEDA). The reactions conducted with 20 mol % of Ni(CH$_2$TMS)$_2$(TMEDA) in place of Ni(COD)$_2$ formed benzene and phenol quantitatively in 16 h instead of 48 h. The same reaction with just 2 mol % of Ni(CH$_2$TMS)$_2$(TMEDA) occurred without any decrease in yield of the hydrogenolysis products after 96 h. The reaction at 140 °C led to 90% conversion to phenol and benzene after 24 h.



Tables 2 and 3 summarize the selective hydrogenolysis of various diaryl ethers with Ni(CH$_2$TMS)$_2$(TMEDA) as the precatalyst and ^{t}BuONa (2.5 equiv) as the base. These reactions occurred with just 1 bar of hydrogen pressure and ran to completion with 0.25−10 mol % Ni. No competing hydrogenation of arenes was observed.

Hydrogenolysis of the electron-neutral diphenyl, di-*m*-tolyl, and di-*p*-tolyl ethers formed arenes and phenols in excellent yields with 2−10 mol % of Ni (Table 2, entries 1−3). Ni(CH$_2$TMS)$_2$(TMEDA) also catalyzed the selective hydrogenolysis of di-*o*-anisyl ether, an electron-rich diaryl ether which is representative of the 4-O-5 structural motif in lignin. Di-*o*-anisyl ether formed anisole (99%) and guaiacol (99%) in excellent yields in the presence of only 0.25 mol % of the Ni catalyst (Table 2, entry 4). By contrast 10 mol % of the Ni catalyst was required for cleavage of the electron-deficient di-*m*-

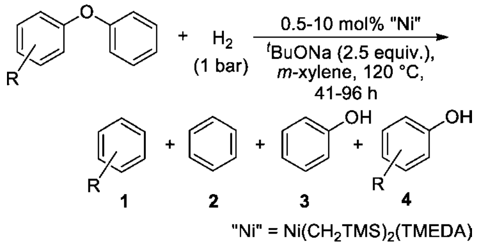
Table 2. Hydrogenolysis of Symmetrical Diaryl Ethers Catalyzed by the Ligandless Nickel Catalyst at Hydrogen Pressure of 1 bar[a]



entry	R	Ni, %	time, h	ArH, %	ArOH, %
1	H	2	96	99	99
2	*m*-Me	5	96	97	93
3	*p*-Me	10	96	94	91
4	*o*-OMe	0.25	48	99	99
5	*m*-OMe	10	48	68	70[b]

[a]Conditions: diaryl ether (1 equiv), hydrogen (1 bar gauge pressure at rt), $Ni(CH_2TMS)_2(TMEDA)$ (0.25–10 mol %), ${}^tBuONa$ (2.5 equiv), *m*-xylene, 120 °C. The yields of arenes and phenols were measured by GC after acidification and aqueous work up. [b]Total yield of 3-methoxyphenol (66%) and phenol (4%).

Table 3. Hydrogenolysis of Unsymmetrical Diaryl Ethers Catalyzed by the Ligandless Nickel Catalyst at Hydrogen Pressure of 1 bar[a]



entry	R	Ni, %	time, h	ArH, %		ArOH, %	
				1	2	3	4
1	*o*-Me	10	96	22	60	17	63
2	*m*-Me	5	48	18	82	17	75
3	*p*-Me	5	48	13	85	11	81
4	*p*-^{t}Bu	5	48	3	90	3	90
5	*o*-OMe	0.5	48	45	54	44	53
6	*m*-OMe	10	48	21	46	22	45
7	*p*-OMe	10	48	15	8	18	2
8	*o*-OH	5	48	80	9	80	–
9	*m*-OH	10	48	75	8	75	–
10	*p*-OH	0.5	41	97	–	97	–

[a]See Table 2 for details of the experimental setup.

anisyl ether to form anisole (68%) and *m*-methoxyphenol (66%) (Table 2, entry 5).

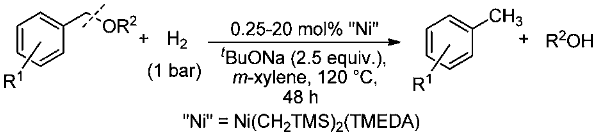
The hydrogenolysis of unsymmetrical diaryl ethers (Table 3) provided further insight into the electronic effects on the reaction. Alkyl-substituted diaryl ethers (Table 3, entries 1–4) were cleaved in good yields (80–99%) to the corresponding arenes and phenols with 5–10 mol % Ni. The regioselectivity of these reactions favored arene and phenol products from cleavage of the C_{Ar}–O bond adjacent to the unsubstituted ring. However, the hydrogenolysis of substrates bearing oxygenated substituents favored arene and phenol products from the cleavage of the C_{Ar}–O bond adjacent to the more electron-rich arene ring (Table 3, entries 5–10).

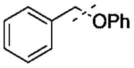
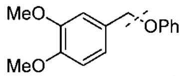
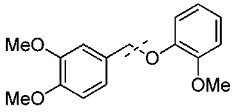
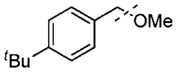
The unsymmetrical 4-O-5 lignin structural model *o*-anisyl phenyl ether was cleaved to arenes (99%) and phenols (98%) in excellent yields (Table 3, entry 5) in the presence of 0.5 mol % of the nickel catalyst. Recall that di-*o*-anisyl ether (Table 2, entry 4) reacted quantitatively in the presence of 0.25 mol % of the Ni catalyst. The loadings of the ligandless catalyst required for full cleavage of the 4-O-5 lignin model substrates were 40 and 80 times lower than that required by the Ni carbene catalyst,[10] reflecting a directing effect of *o*-methoxy substituents. The *m*- and *p*-constitutional isomers (Table 3, entries 6 and 7) of *o*-anisyl phenyl ether were less reactive under the hydrogenolysis reaction conditions.

Diaryl ethers that contain a free phenolic group also underwent hydrogenolysis with high selectivity. From the cleavage of *o*-, *m*-, and *p*-hydroxy diphenyl ethers (Table 3, entries 8–10) with 0.5–10 mol % Ni, 2 equiv of phenol were obtained in good to high yields (75–97%).

The ligandless nickel system also catalyzes the hydrogenolysis of benzyl aryl and benzyl methyl ether, which are two additional types of linkages in lignin (Table 4). Benzyl aryl ethers were converted to methyl-substituted arenes and phenols in excellent yields in the presence of 0.25–2 mol % of the nickel catalyst (Table 4, entries 1–3). Benzyl methyl ether was unreactive under standard reaction conditions, but full conversion could be achieved in the presence of 1 equiv of $AlMe_3$ (Table 4, entry 4).

Table 4. Hydrogenolysis of Benzyl Ethers Catalyzed by the Ligandless Nickel Catalyst at Hydrogen Pressure of 1 bar[a]

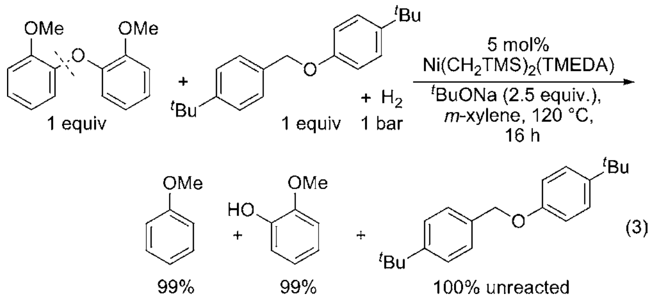


Entry	Benzyl ether	Ni, %	$ArCH_3$, %	R^2OH, %
1[b]		2	98	95
2		2	81	87
3		0.25	93	98
4		20	99[c]	Nd

[a]See Table 2 for details of the experimental setup. [b]96 h. [c]In the presence of $AlMe_3$ (1 equiv).

Having observed the cleavage of the C–O bonds in various ethers, we evaluated the relative reactivity of these ethers toward the ligandless system (for the full primary data, see Figures S1–S5). We observed that diaryl ethers and benzyl aryl ethers reacted at comparable rates, and both underwent hydrogenolysis faster than did benzyl alkyl ethers. Even though unactivated diaryl and benzyl aryl ethers reacted at comparable rates (Figure S2), the electron-rich di-*o*-anisyl ether was selectively reduced in the presence of the electron-neutral *p*-*tert*-butylbenzyl *p*-*tert*-butylphenyl ether (eq 3). This reduction of an unactivated diaryl ether in the presence of a benzyl aryl ether is unusual.

To gain preliminary insight into the phase and structure of the ligandless catalyst, we conducted hydrogenolysis reactions catalyzed by $Ni(COD)_2$ and $Ni(CH_2TMS)_2(TMEDA)$ with



(3)

added mercury. Although there are exceptions, mercury is a poison for heterogeneous catalysts and typically has little effect on the activity of homogeneous catalysts.[15,16] The activity of the ligandless nickel catalyst for the hydrogenolysis of diphenyl ether was completely suppressed by an excess of added mercury (Table S4). This result contrasts the lack of an effect of mercury on the hydrogenolysis of aryl ethers catalyzed by the SIPr-Ni system.[10] These data suggest that heterogeneous nickel clusters or particles catalyze the hydrogenolysis reactions conducted without an added dative ligand. Indeed, TEM analysis (Figures S6−S10) of an aliquot of a reaction mixture revealed the presence of 2.5 ± 0.4 nm nickel particles. X-ray EDS analysis of these nanoparticles indicated that they contain both nickel and sodium. Caubère and Fort[17−19] have shown that ^{t}BuONa can stabilize nickel nanoparticles, and we propose that the ^{t}BuONa stabilizes the "ligandless" system of our studies.

In conclusion, we have developed a highly active heterogeneous nickel catalyst for selective hydrogenolysis of diaryl, benzyl aryl, and benzyl alkyl ethers to form arenes and alcohols as the exclusive products. The activity and selectivity of this catalyst for hydrogenolysis of the C—O bonds of aryl ethers results from having generated the catalyst in the presence of ^{t}BuONa. The catalyst generated in the absence of ^{t}BuONa displays low reactivity at low pressures of hydrogen and low selectivity for hydrogenolysis over hydrogenation. In contrast, the catalyst generated from the well-defined soluble nickel precursor Ni(CH$_2$TMS)$_2$(TMEDA) with ^{t}BuONa base operates at hydrogen pressure as low as 1 bar and loadings as low as 0.25 mol %. Future work will be aimed at the characterization of this catalyst and the development of supported catalytic systems that display the same selectivity for hydrogenolysis over hydrogenation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, Tables S1−S4, Figures S1−S10, photographs of reaction mixtures, reaction progress graphs. 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.

■ ACKNOWLEDGMENTS

We thank Energy and Biosciences Institute for support of this work as well as the Molecular Foundry and Virginia Altoe for TEM analysis. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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(14) The identity of the base also affected the catalytic activity. Reactions conducted with various bases (2.5 equiv) in the model hydrogenolysis of diphenyl ether (Table S1) for 16 h showed that the highest conversions were obtained in the presence of ^{t}BuONa (62%) and ^{t}PentONa (70%). The reactions conducted in the presence of ^{t}BuOK or ^{t}BuOLi and reactions conducted with less bulky alkoxide bases containing hydrogens α to oxygen, such as OMe and O^{i}Pr, led to low conversions (<15%). No hydrogenolysis occurred from reactions with weaker bases. Given the similar efficiency of ^{t}BuONa and ^{t}PentONa, we chose to conduct further studies with ^{t}BuONa (2.5 equiv) as the base.
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