# CHAPTER 3

## SELECTIVITY FOR HYDROGENOLYSIS VS. HYDROGENATION WITH RHODIUM AND IRIDIUM CATALYSTS IN THE CLEAVAGE OF ARYL ETHERS AS MODELS OF LIGNIN

## ABSTRACT

Hydrogenolysis and hydrogenation reactions of ethers and phenols relevant to the degradation of lignin were studied with a precatalyst consisting of biscycloocteneiridium(I)chloride in neat substrate at 180 °C. Rh/C was tested for comparison. With limiting $H_2$, arene-rich cleaved products were isolated. At higher $H_2$ pressure, hydrocarbon products were major. More hydrogenolysis was observed with Ir than with Rh. The relative rates of hydrogenolysis followed the trend: diaryl ether > phenol > aryl-alkyl ether ≈ alcohol ≈ dialkyl ether. Addition of mesoporous silica facilitated acid-catalyzed dehydration of alcohols and alkyl ethers, leading to exhaustive deoxygenation and hydrogenation when coupled with $H_2$/Ir catalysis.

## INTRODUCTION

Cleavage of the aryl C–O bond of aryl ethers represents a key transformation in the conversion of lignin to aromatic compounds useful as precursors in chemical synthesis or as fuel additives.[1] This transformation has been employed with homogeneous Ni catalysts for cross-coupling chemistry and for removal of oxygen-based directing groups with silanes.[2] Hydrogenolysis of aryl ethers was reported with Ni-N-heterocyclic carbene catalysts.[3] Mechanistic studies of intramolecular cleavage of aryl ether bonds has been studied with Rh(I)[4] and Ni(0).[4b,5] In the presence of micelles, hydrogenolysis/hydrogenation of aryl ethers was observed with Ni precursors.[6] A variety of heterogeneous catalysts have been investigated for the cleavage of aryl ethers. Systems based on Raney Ni,[7] Ni(cod)$_2$ (cod = 1,5-cyclooctadiene) and NaO$^t$Bu,[8] Rh/C in supercritical CO$_2$,[9] Ni/SiO$_2$[10] have been reported. Additionally, hydrodeoxygenation of phenols was reported with Pd/C/acid[11] and Ni/Nafion/SiO$_2$ catalysts.[10,12] Although recent experiments have focused on less stringent conditions, aryl C–O bond cleavage often requires high temperatures or pressures.[1c,7b,13] Hydrogenolysis effects deoxygenation without consumption of additional hydrogen for conversion of arenes to saturated hydrocarbons.[14] An important selectivity consideration is the extent of hydrogenolysis vs hydrodeoxygenation leading to products with different applications. Herein we report Ir catalysts for the cleavage of aryl ethers and comparative studies of hydrogenolysis vs. hydrodeoxygenation with Ir and Rh.

We have previously reported on the mechanism of intra- and intermolecular aryl C–O bond cleavage facilitated by Ni.[5] Phosphine ligands were screened with Rh and Ir precursors for potential intermolecular C–O bond cleavage reactivity in neat aryl ether substrate. $(Ir(COE)_2Cl)_2$ (coe = cyclooctene) was found to generate a catalyst that displays the desired reactivity in the presence of $H_2$ at 180 °C and in the absence of additional Lewis basic additives. Sulfided $Ir/Al_2O_3$ and $IrMo/Al_2O_3$ catalysts were reported to perform hydrogenolysis of diphenyl ether, albeit at much higher temperatures and pressures (350 °C, 137 atm $H_2$).[13b] Given the growing interest in the cleavage of aryl ethers relevant to biomass conversion, we investigated the behavior of the present Ir catalyst under a variety of conditions. For comparison, we also studied Rh/C, which has been studied previously. While in supercritical $CO_2$, C–O bond cleavage and hydrogenation of diphenyl ether to form cyclohexane and cyclohexanol has been observed,[9] with wood meal, in dioxane-water, phenolic products were obtained.[15] Since the products of cleavage of aryl ethers with Rh/C depend on reaction conditions and (or) nature of substrate, the Ir and Rh catalysts were studied under similar conditions.

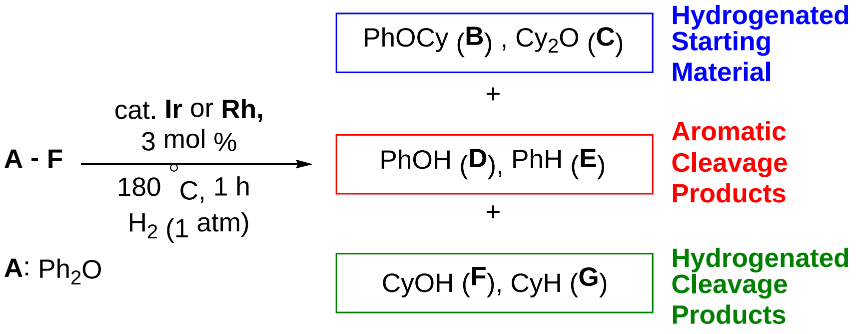
## RESULTS AND DISCUSSION

Reactions were performed in batch mode in Schlenk tubes with Teflon stoppers. The catalyst was generated *in situ* from $(Ir(COE)_2Cl)_2$ upon heating in neat substrate. Generally, increased temperature favored hydrogenolysis (arene) products vs. hydrogenation (alkane) products. At 180 °C, with 3 mol % catalyst loading and moderate $H_2$ pressure, substantial amounts of arenes were generated; therefore, these conditions were further investigated for various catalysts and substrates. Under the conditions studied, a limiting amount (3.3 equiv., 1 atm; 13.3 equiv., 4 atm) of $H_2$ was present.

Arenes were the major cleavage products (60%, 1:5 PhOH:PhH) using $(Ir(COE)_2Cl)_2$ as a precatalyst.[16] (Entry 1, Table 3.1) Rh/C afforded lower arene generation (40%) with benzene (36%) as major product overall and cyclohexanol (34%) major among the hydrogenated products (Entry 2). Increasing $H_2$ pressure to 4 atm resulted in full hydrogenation of the ether cleavage products with both Ir and Rh catalysts (Entries 5, 6). Only 16% $Cy_2O$ was observed with the Ir catalyst, whereas the yield of $Cy_2O$ was 46% using Rh/C.

Further studies were focused on limiting $H_2$ amounts, allowing for interrogation of the relative levels of hydro-genolysis and hydrogenation/deoxygenation. The products of the hydrogenolysis/hydrogenation of $Ph_2O$ were submitted to the same reaction conditions to better understand the observed selectivities (Table 3.1, Entries 9-23). For both the Rh- and Ir-catalyzed reactions, low conversions were observed with PhOCy and $Cy_2O$ (Entries 9, 10, 12, 13).

**Table 3.1. Hydrogenolysis/Hydrogenation of Diphenyl Ether (A) and Its Derivatives (B-F).**



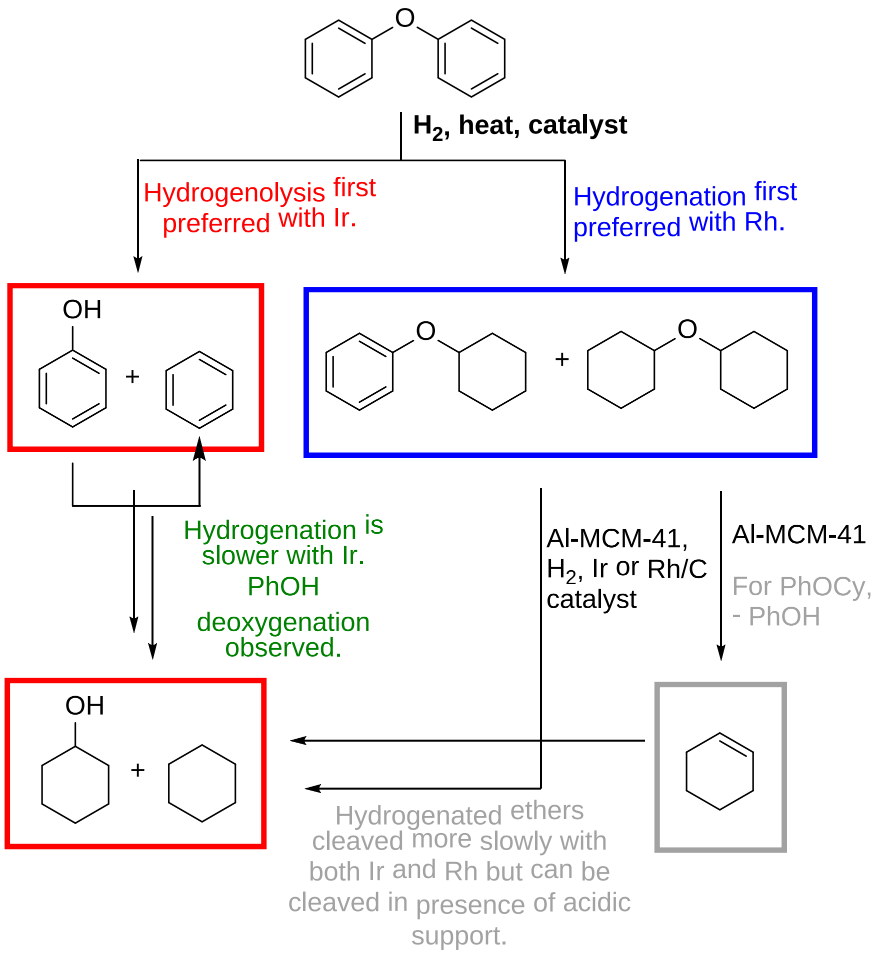
| Entry | Catalyst | Substrate | **B**, % | **C**, % | **D**, % | **E**, % | **F**, % | **G**, % |
|---|---|---|---|---|---|---|---|---|
| 1 | **Ir** | **A** | 2 | 3 | 9 | 50 | 16 | 12 |
| 2 | **Rh** | **A** | 17 | 6 | 4 | 36 | 34 | 5 |
| 3 | **Ir'** | **A** | 3 | 1 | 10 | 46 | 4 | 24 |
| 4 | **Ir*** | **A** | 0 | 2 | 10 | 40 | 0 | 27 |
| 5[a] | **Ir** | **A** | 0 | 16 | 0 | 0 | 23 | 59 |
| 6[a] | **Rh** | **A** | 0 | 46 | 0 | 0 | 26 | 25 |
| 7[a] | **Ir'** | **A** | 0 | 6 | 0 | 2 | 3 | 85 |
| 8[a] | **Ir*** | **A** | 0 | 0 | 0 | 0 | 0 | 102 |
| 9 | **Ir** | **B** | 92 | 2 | 0 | 3 | 0 | 1 |
| 10 | **Rh** | **B** | 65 | 15 | 0 | 3 | 11 | 1 |
| 11 | **Ir*** | **B** | 0 | 6 | 5 | 15 | 0 | 56 |
| 12 | **Ir** | **C** | 0 | 72 | 0 | 0 | 9 | 10 |
| 13 | **Rh** | **C** | 0 | 75 | 0 | 0 | 11 | 14 |
| 14 | **Ir*** | **C** | 0 | 0 | 0 | 0 | 0 | 99 |
| 15 | **Ir** | **D** | 0 | 1 | 4 | 44 | 24 | 20 |
| 16 | **Rh** | **D** | 0 | 17 | 0 | 2 | 70 | 15 |
| 17 | **Ir*** | **D** | 0 | 6 | 0 | 31 | 0 | 54 |
| 18 | **Ir** | **E** | 0 | 0 | 0 | 53 | 0 | 44 |
| 19 | **Rh** | **E** | 0 | 0 | 0 | 8 | 0 | 95 |
| 20 | **Ir*** | **E** | 0 | 0 | 0 | 20 | 0 | 84 |
| 21 | **Ir** | **F** | 0 | 26 | 0 | 0 | 70 | 4 |
| 22 | **Rh** | **F** | 0 | 16 | 0 | 0 | 38 | 37 |
| 23 | **Ir*** | **F** | 0 | 0 | 0 | 0 | 0 | 97 |

[a] 4 atm $H_2$ used. **Ir**: $(Ir(COE)_2Cl)_2$. **Rh**: Rh/C, 5 wt%. **Ir'**: $[(coe)_2IrCl]_2$ and MCM-41 (silica, mesostructured). **Ir***: $(Ir(COE)_2Cl)_2$ and Al-MCM-41 (aluminosilicate, mesostructured). Conversions: entry 1 – 95%; 3 – 94%, 4 – 92%, 2, 5-8 - 100%; for all other entries, recovered starting material shaded. Reactions neat in 1.000 mmol substrate. Quantification of yields by GC after extraction with 0.025 M solution of *n*-tridecane in $Et_2O$ using *n*-tridecane as an external standard. Reactions run in

duplicate; std. dev. < 5%. 1 atm $H_2$ = 3.3 equiv., 4 atm $H_2$ = 13.3 equiv. $H_2$ relative to substrate. See Experimental Section for further details.

A substantial portion of PhOH was converted to PhH (44%) with the Ir catalyst, while Rh/C led almost exclusively to hydrogenation (Entries 15, 16). High conversion of PhH to CyH (95%) was observed with Rh/C compared to moderate conversion using Ir (44%, Entries 18-19). Some etherification was observed from CyOH to afford $Cy_2O$ for both Ir and Rh/C (26% and 16%, respectively; Entries 21, 22).

**Figure 3.1. Proposed Mechanism for Hydrogenolysis/Hydrogenation Pathways for Ir and Rh Catalysts.**

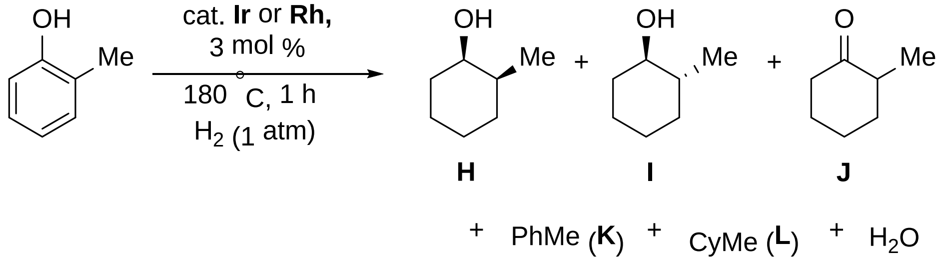


Trials with PhH as substrate indicate that Ir performs hydrogenation more slowly compared to Rh/C, allowing for longer residence times for benzene. With PhOH, Rh/C again performs primarily hydrogenation. Ir leads to cleavage of the aryl C–O bond of phenol to give benzene, a process that is competitive with hydrogenation. This phenol hydrogenolysis accounts for the higher yield of PhH relative to that of PhOH in reactions with $Ph_2O$ and represents a relatively mild method for total deoxygenation of aryl ethers with a preference for arene products. Hydrogenolysis of phenol has been previously reported for heterogenous Mo[17], Pd[11,18], and $Pt/H_2SO_4$[19] catalysts.

Given that alkyl ethers are cleaved slowly under these conditions, the mechanism of ether cleavage is proposed to first involve initial hydrogenolysis of the an aryl C–O bond as the major pathway. (Figure 3.1) If hydrogenation occurs first, the resulting alkyl ethers are significantly less reactive toward reductive cleavage. Since Rh is a better hydrogenation catalyst, the products funnel toward hydrogenated ether with lower yields of the cleaved products. The arenes formed upon aryl ether cleavage are further hydrogenated with Rh/C, while with Ir, hydrogenolysis of phenol to give benzene is a significant reaction pathway. Overall, the Ir catalyst leads to more cleavage as well as higher yields of arene products.

Mesoporous silica (MCM-41) and aluminosilicate (Al-MCM-41) were added to reaction mixtures to act as support for the *in situ* generated Ir catalyst. The CyOH:CyH ratio changed significantly: without additive, a 4:3 ratio was observed; with MCM-41, 1:6; with Al-MCM-41, only CyH was observed. These data suggest conversion of CyOH to CyH in the presence of mesoporous silica. In control experiments, both CyOH and $Cy_2O$ were converted to cyclohexene in the presence of Al-MCM-41 under $N_2$ at 180 °C in the absence of Ir. Under these conditions, 20% conversion of PhOCy to PhOH and cyclohexene was observed.

**Table 3.2. Hydrogenolysis/Hydrogenation of *o*-Methyl Phenol.**

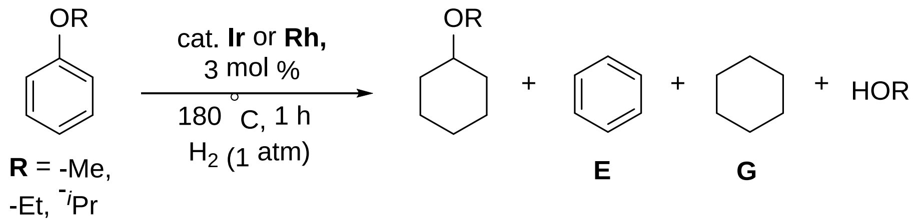


| Entry | Catalyst | Conversion, % | **H**, % | **I**, % | **J**, % | **K**, % | **L**, % |
|---|---|---|---|---|---|---|---|
| 1 | **Ir** | 85 | 4 | 4 | 9 | 40 | 9 |
| 2 | **Rh** | 100 | 14 | 23 | 42 | 1 | 14 |

**Ir**: $(Ir(COE)_2Cl)_2$. **Rh**: Rh/C, 5 wt%. Reactions neat in 1.0 mmol substrate. Quantification of yields by GC after extraction with 0.025 M solution of *n*-tridecane in $Et_2O$ using *n*-tridecane as an external standard. Reactions run in duplicate; std. dev. < 5%. 1 atm $H_2$ =3.3 equiv. See *SI* for further details.

Solid acids are known to mediate alkyl C–O bond cleavage of ethers and alcohols.[11b,20] In the presence of Ir/Al-MCM-41 and $H_2$, substrates CyOH or PhOH lead to CyH (Table 3.1; Entries 17 and 23); for PhOH, CyOH is not observed. These data indicate that subsequent to alkyl ether cleavage and alcohol dehydration facilitated by the acidic support, the resulted olefin is hydrogenated. Increasing $H_2$ pressure to 4 atm resulting in full conversion of $Ph_2O$ to CyH in the Ir/Al-MCM-41 system (Table 3.1, Entry 8). Consistent with our control reactions, good conversion of otherwise recalcitrant PhOCy and $Cy_2O$ to cleavage products was observed with Ir and Al-MCM-41 (Table 3.1, Entries 11 and 14). Thus, mesoporous silica complements hydrogenolysis by converting hydrogenated but not cleaved products that react slowly with Rh and Ir catalysts (alkyl ethers, alcohols) to alkenes and aromatics.

**Table 3.3. Hydrogenolysis/Hydrogenation of Anisole, Ethoxybenzene, and Isopropoxybenzene.**



| Entry | Ru | Catalyst | Conversion (%) | E, % | Gm % |
|---|---|---|---|---|---|
| 1 | -Me | **Ir** | 31 | 14 | 5 |
| 2 | -Me | **Rh** | 26 | 3 | 0 |
| 3 | -Et | **Ir** | 59 | 27 | 9 |
| 4 | -Et | **Rh** | 88 | 9 | 14 |
| 5 | -$^i$Pr | **Ir** | 65 | 21 | 23 |
| 6 | -$^i$Pr | **Rh** | 92 | 5 | 17 |

**Ir**: $(Ir(COE)_2Cl)_2$. **Rh**: Rh/C, 5 wt%. Reactions neat in 1.0 mmol substrate. Quantification of yields by GC after extraction with 0.025 M solution of *n*-tridecane in $Et_2O$ using *n*-tridecane as an external standard. Reactions run in duplicate; std. dev. < 5%. 1 atm $H_2$ = 3.3 equiv. See **Experimental Details** for further details.

Reactions with *o*-methyl phenol and phenyl alkyl ethers (Tables 3.2 and 3.3) were pursued to determine the effect of increasing steric bulk on the product distribution. Products corresponding to C–O bond cleavage were major with the Ir catalyst (40% PhMe, 9% CyMe). Conversion to deoxygenation products was low in the case of Rh (15% for PhMe and CyMe combined). Phenyl alkyl ethers with larger alkyl groups showed increased conversion for both Ir and Rh catalysts. This could be a consequence of the increased boiling points of the substrates within the series, with the lighter substrates being heated to above their boiling temperature and likely partitioning substantially in the gas phase. For each substrate, the Ir catalyst shows more conversion to the deoxygenated arene product (PhH) than the Rh catalyst (19 vs.

3% for methyl, 36 vs. 23% for ethyl, and 44 vs. 22% *i*-propyl substituents, respectively). These data further highlight the difference in selectivity between the two systems, with preference for hydrogenolysis vs. hydrogenation for Ir compared to the Rh catalyst. A labeling study to determine if aryl-alkyl ether cleavage proceeded by a mechanism of oxidative addition, β-hydride abstraction, and reductive elimination as previously reported by our group[5] was complicated by deuterium scrambling. (see *Experimental Details*, "Additional Experiments")

## CONCLUSIONS

In summary, catalytic hydrogenolysis and hydrogenation of aryl-aryl ethers and aryl-alkyl ethers were studied using commercially available precursors. Rh- and Ir-catalyzed systems were both shown to hydrogenolyze aryl-aryl ethers. Investigations into the mechanism of these reactions show that alcohols, aryl alkyl ethers, and dialkyl ethers are more difficult to cleave than their diaryl ether counterparts. Thus, an effective catalyst for aryl ether cleavage carries out hydrogenolysis more rapidly than hydrogenation. Moderate amounts of arene products were observed in the case of limiting $H_2$ pressure and could be isolated prior to hydrogenation; hydrocarbon products could be obtained using higher $H_2$ pressures (4 atm). Cleavage of the aryl C–O bond of phenol by iridium was observed, demonstrating full deoxygenation of aryl ethers. In the presence of mesoporous silica, acid-catalyzed cleavage of alkyl-ethers occurred complementing the reactivity of the Ir-only catalyst and leading to exhaustive deoxygenation and hydrogenation of diaryl ethers.

## EXPERIMENTAL SECTION

### General considerations

Substrates diphenyl ether, phenyl cyclohexyl ether, phenol, benzene, cyclohexanol, *o*-cresol, anisole, and *tert*-butylbenzene were purchased commercially. Dicyclohexyl ether[21] was synthesized according to literature. Alkyl-aryl ethers ethoxybenzene and isopropoxybenzene were synthesized from phenol through substitution with alkyl iodides (ethyl iodide and isopropyl iodide) following an adapted literature procedure[22] and matched previously reported spectra (PhOEt,[23] PhO$^i$Pr[24]). *tert*-butylbenzene-$d_1$ was prepared from 1-bromo-4-(*tert*-butyl)benzene from treatment with *n*-BuLi followed by quenching with excess $D_2O$ and matched previously reported spectra.[25] Commercially available cyclohexane, *cis*-2-methylcyclohexanol, *trans*-2-methylcyclohexanol, 2-methylcyclohexanone, toluene, methylcyclohexane were used as received as standards for GC calibration. Manipulations were conducted in a $N_2$-filled glovebox or using standard Schlenk technique under $N_2$ unless otherwise specified. Alumina and 3 Å molecular sieves were activated by heating under vacuum at 200 °C for at least 12 h prior to use. Silica, mesostructured, MCM-41 type (hexagonal) was purchased from Sigma-Aldrich: unit cell size = 4.5 - 4.8 nm; pore size = 0.98 $cm^3/g$ pore volume, 2.1 – 2.7 nm pore size; spec. surface area ca. 1000 $m^2/g$. Aluminosilicate, mesostructured, MCM-41 (hexagonal): aluminum, ca. 3%; unit cell size = 4.6 – 4.8 nm; pore size = 1.0 $cm^3/g$ pore volume, 2.5 – 3 nm pore size; spec. surface area ca. 940 – 1000 $m^2/g$. Mesostructured silica (“MCM-41”) and mesostructured aluminosilica (“Al-MCM-41”) were heated in an oil bath under vacuum. This oil bath was and held at 150 °C for 16 h before use. Celite® was purchased commercially and used as received. $Et_2O$ used in catalyst loading and benzene used as substrate were dried by Grubbs' method[26] and placed over 3 Å molecular sieves prior to use. Diphenyl ether, phenyl cyclohexyl ether, anisole, dicyclohexyl ether, ethoxybenzene, and isopropoxybenzene were stirred over $CaH_2$ overnight, filtered through alumina, and stored over 3 Å molecular sieves in a nitrogen-filled glovebox prior to use.

Analysis of reactions with substrates *tert*-butylbenzene and *o*-cresol by gas chromatograph was performed on an Agilent 6850 FID gas chromatograph equipped with a flame ionization detector and DB-Wax polyethylene glycol capillary column. Runs were performed using the following program: hold at 40 °C for 4 minutes, ramp temperature at 50 °C min $^{-1}$ to 90 °C, hold at 90 °C for 4 minutes, ramp temperature at 75 °C min$^{-1}$ to 300 °C, hold at 300 °C for 4 minutes.

Analysis of reactions with all other substrates by gas chromatography was performed on an Agilent 6890N instrument using a flame ionization detector and DB-1 capillary column (10 m length, 0.10 mm diameter, 0.40 μm). Runs used the following program: hold at 40 °C for 3 minutes, ramp temperature at 50 °C min$^{-1}$ to 290 °C, hold at 290 °C for 5 minutes.

Analysis of reactions with all substrates by gas chromatograph mass spectrometry (GC-MS) was performed on an Agilent 6890 instrument equipped with an HP-5MS 30 m x 0.25 mm x 0.50 μm capillary column (Agilent). The GC was interfaced to an Agilent 5973N mass selective detector.

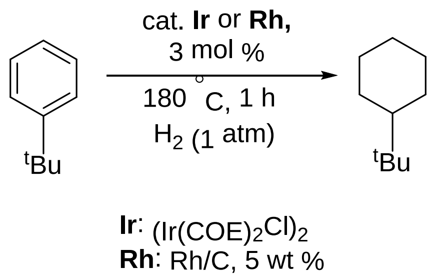
**Procedures for Hydrogenolysis/Hydrogenation Studies.** Procedure B was used for protic substrates phenol, cyclohexanol, and *o*-cresol; Procedure A was used for all other substrates.

**Hydrogenolysis/Hydrogenation Procedure A.** In a $N_2$-filled glovebox, an 80 mL Schlenk tube (ca. 5 mm x 16 mm) fitted with a Teflon screw cap was charged with a stir bar (3 x 12.7 mm). 5 wt % Rh/C (61.7 mg, 0.030 mmol, 0.03 equiv.) or $((coe)_2IrCl)_2$ (13.4 mg, 0.015 mmol, 0.015 equiv.) was transferred to the reaction vessel as a suspension in a minimum of $Et_2O$. Addition of a minimum of $Et_2O$ and transfer of the resulting suspension was completed once more to ensure near-quantitative transfer of catalyst. For reactions with MCM-41 or Al-MCM-41, a 20 mL scintillation vial was charged with a stir bar, mesoporous silica (100 mg), $(Ir(COE)_2Cl)_2$ (13.4 mg, 0.015 mmol, 0.015 equiv.), and 5 mL $Et_2O$ to afford an orange solution with white precipitate. This solution was stirred for a minimum of 3 h. The suspension and stir bar were transferred to the reaction vessel. Addition of a minimum of $Et_2O$ to the scintillation vial and transfer of the resulting suspension was completed to ensure near-quantitative transfer of catalyst. Solvent was removed from the reaction vessel under reduced pressure. For reactions with $(Ir(COE)_2Cl)_2$, an orange powder was observed. For reactions with $(Ir(COE)_2Cl)_2$ and mesoporous silica, a light orange powder was observed. For reactions with Rh/C, a black powder was observed. Substrate (1.00 mmol) was then added using a 250 μL syringe. The reaction vessel was sealed and removed from the glovebox. On a Schlenk line, the reaction vessel was cooled to 77 K with liquid nitrogen and the headspace was evacuated. For the addition of *ca.* 4 atm $H_2$, *ca.* 3.3 equiv., the evacuated reaction vessel was pressurized at 77 K, then sealed and warmed to room temperature. For the addition of *ca.* 1 atm $H_2$, *ca.* 13.3 equiv., the reaction vessel was sealed, allowed to warm to room temperature, then pressurized with *ca.* 1 atm $H_2$ and sealed again. The reaction vessel was subsequently placed in a silicone oil bath pre-heated to 180 ºC such that only a small amount of the Schlenk tube below the level of the Teflon screw cap was not submerged in oil. The reaction was left stirring vigorously in the oil bath for 1 h. After 1 h, the vessel was removed from the oil bath and allowed to cool for 10 min. A suspension of black precipitate in a colorless solution was observed. The reaction vessel was then chilled for 15 min. by submerging in an ice water bath such that only a small amount of the Schlenk tube below the level of the Teflon screw cap was not submerged in ice water. The reaction vessel was then opened and 9 mL of a 0.025 M solution of *n*-tridecane in $Et_2O$ was added. The reaction vessel was resealed, shaken vigorously for 15 s, then the reaction mixture was pushed through a plug of Celite. 0.4 mL of this solution was further diluted with 0.8 mL of a 0.025 M solution of *n*-tridecane in $Et_2O$. Yields were then determined by GC. Reported yields are the average of duplicate runs. On average, standard deviations between runs were below 5%.

**Hydrogenolysis/Hydrogenation Procedure B.** Procedure B is similar to Procedure A, but the addition of substrate differs. For Procedure B, substrates were added to the reaction vessel charged with rhodium or iridium catalyst on a Schlenk line under a counter flow of $N_2$ at room temperature. The rest of Procedure A was then followed as described above.

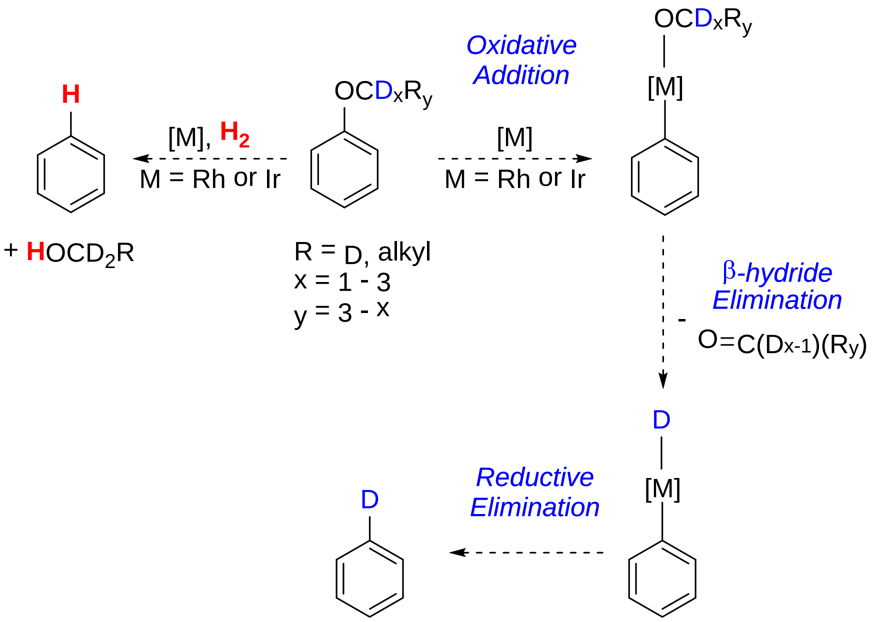
## Additional Experiments: Hydrogenolysis/Hydrogenation of *tert*-Butylbenzene-d$_1$

**Table 3.4. Hydrogenolysis/Hydrogenation of *tert*-Butylbenzene.**



| | | GC Yields | | |
|---|---|---|---|---|
| Entry | Catalyst | Conversion, % | Hydrogenated Product | Mass Balance |
| 1 | **Ir** | 73 | 67 | 94 |
| 2 | **Rh** | 96 | 96 | 100 |

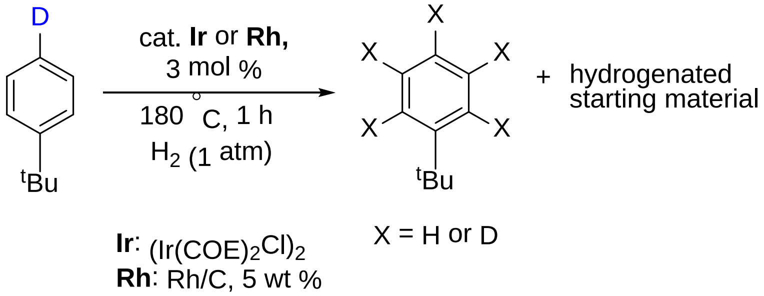
**Figure 3.2. Proposed Mechanisms for Hydrogenolysis of Aryl-Alkyl Ethers with and without H$_2$.**



A deuterium labeling study was designed to determine if hydrogenolysis of aryl-alkyl ethers proceeds through addition of H$_2$ across the aryl C-O bond or through oxidative addition, β-hydride elimination, and reductive elimination (without $H_2$) as previously reported by our group for nickel species.[5]

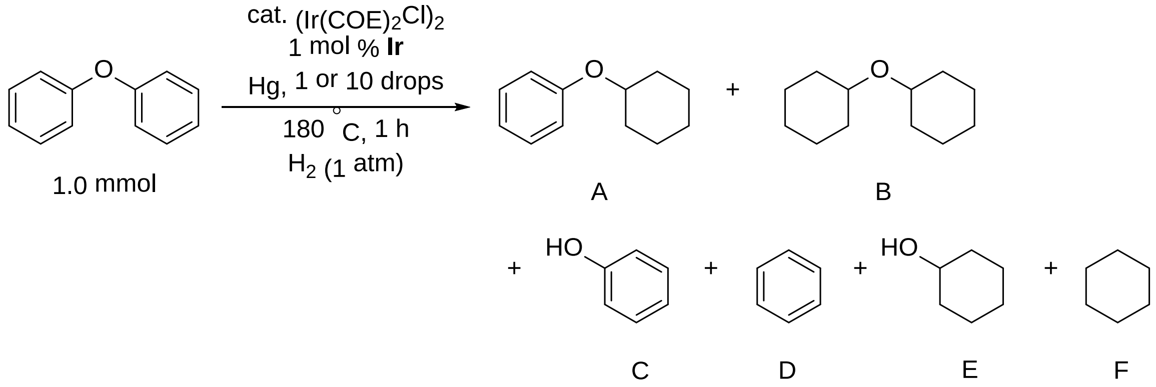
As a control, a $d_1$-labeled aromatic (*tert*-butylbenzene-$d_1$) was subjected to standard reaction conditions (180 °C, 1 atm $H_2$) for 30 min. to determine if scrambling would preclude identification of $d_1$-labeled aromatic products of hydrogenolysis/hydrogenation of labeled aryl-alkyl ethers. This reaction was performed according to *Hydrogenolysis/Hydrogenation Procedure B*. The product extracted in $Et_2O$/*n*-tridecane was diluted to a concentration of *ca.* 3 μmol and analyzed by GC-MS. Under hydrogenolysis/hydrogenation reaction conditions for 30 min., *tert*-butylbenzene-$d_1$ (m/z = 135) incorporates H atoms to afford *tert*-butylbenzene-$d_0$ (m/z = 134) and incorporates D atoms (up to m/z = 138). Scrambling of the deuterium labels thus prevented exclusion of a mechanistic pathway through labeling of aryl-alkyl ethers.

**Figure 3.3. Hydrogenation of *tert*-Butylbenzene-$d_1$.**



## Additional Experiments: Hydrogenolysis/Hydrogenation of Diphenyl Ether: Mercury Drop Test

### Table 3.5. Hydrogenolysis/Hydrogenation of Diphenyl Ether: Hg$^0$ Drop Test.[16b]



| | | | GC Yields (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Hydrogenated Ether | | Arene Cleavage Products | | Hydrogenated Cleavage Products | | Mass Balance |
| Entry | Hg | Conversion | A | B | C | D | E | F | |
| 1 | 1 drop | 21 | 2 | 0 | 0 | 1 | 0 | 2 | 85 |
| 2 | 10 drops | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 90 |

Hg added on Schlenk line using a glass pipet under counterflow of $N_2$ before pressurizing with $H_2$.

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