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Preconversion Catalytic Deoxygenation of Phenolic Functional Groups

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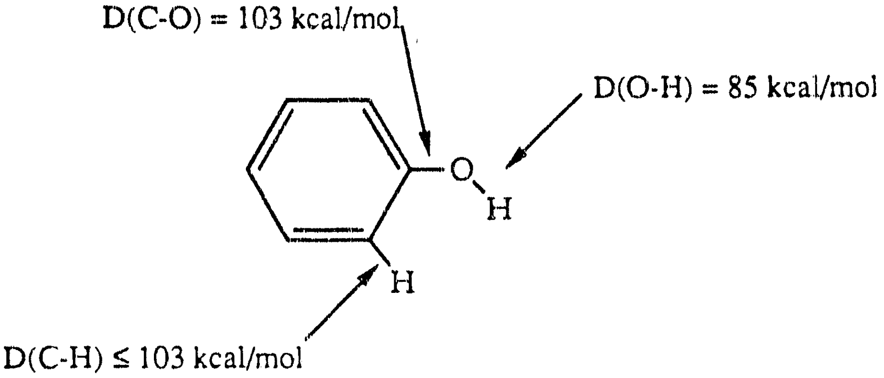
STATEMENT OF PROBLEM:

The deoxygenation of phenols is a conceptually simple, but unusually difficult chemical transformation to achieve. The phenolic C-O bond energy of 103 kcal/mol is as strong as a benzene C-H bond and over 10 kcal/mol stronger than the C-O bonds of methanol and ethanol.



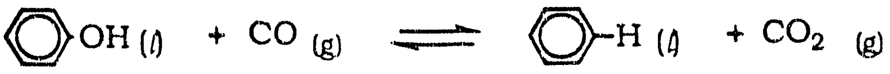
The consequence of this is that the hydrogenation/deoxygenation methods in current use require severe conditions and give low selectivities. The ongoing research described herein is based on the unprecedented, but thermodynamically promising, use of carbon monoxide as the oxygen atom acceptor for the catalytic deoxygenation of phenols.

SIGNIFICANCE OF PROBLEM:

Aryl carbon-oxygen bond cleavage is a chemical transformation of importance in coal liquefaction and the upgrading of coal liquids[1-9] as well as in the synthesis of natural products[10-17]. There have been numerous attempts to discover general methods for the cleavage of aryl carbon-oxygen bonds[13-15, 18-22]. All the stoichiometric organic methods for phenol deoxygenation have limited applications and involve expensive reagents. Catalytic methods for the hydrodeoxygenation (HDO) of phenols involve supported transition metal oxides, such as Mo/γ-Al$_2$O$_3$, Ni-Mo/γ-Al$_2$O$_3$, Co-Mo/γ-Al$_2$O$_3$, and Fe$_2$O$_3$/SiO$_2$. Typical phenol hydrodeoxygenation conditions involve hydrogen pressures in excess of 100 atm and temperatures in excess of 200°C. Under these conditions arene ring hydrogenation is generally found to compete with phenol deoxygenation; and the coproduct water is found to impair the activity of the catalysts.[1-5, 7, 8] This proposed research offers the possibility of effecting the selective catalytic deoxygenation of phenolic functional groups using CO.

RESEARCH BACKGROUND:

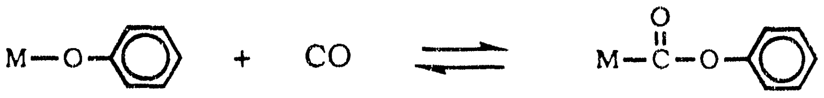
A program of research for the catalytic deoxygenation of phenols, via a low energy mechanistic pathway that is based on the use of the CO/CO_2 couple to remove phenolic oxygen atoms, is underway. The use of readily available CO as the repository for the phenolic oxygen atom provides both a highly thermodynamically favorable and a kinetically feasible pathway. The deoxygenation of phenols by CO, eq 1,



(1)

$$\Delta G_{298} = -20.7 \text{ kcal/mol}$$

is thermodynamically favorable by over 20 kcal/mol. However, prior to our studies[23], examples of oxygen atom transfers from phenols to CO did not exist. The key to our studies involves the exploitation of the insertion of CO into the M-O bonds of metal phenoxides, eq 2.



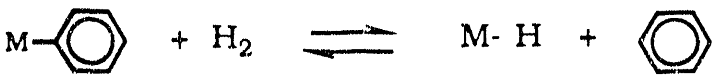
(2)

The subsequent decarboxylation, which affords CO_2 and a metal phenyl complex[23], has a high thermodynamic driving force, eq 3.

(3)

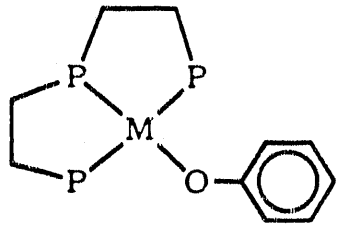
Benzene can be produced by protolysis or hydrogenation, eq 4-5.

(4)



(5)

Although our earlier work on the platinum complex, Pt(dppe)$(OPh)_2$, achieves the deoxygenation of phenols[23], this system fell short of our desired goals because the phenyl group produced from benzyne is eliminated along with an undeoxygenated aryloxycarbonyl group to yield the ester, phenylbenzoate. Moreover, the deoxygenation reaction is stoichiometric instead of catalytic. We are therefore focusing on systems which have significant promise as catalysts: Ir(triphos)OPh, [Pt(triphos)OPh]$^+$ and Rh(triphos)OPh. {triphos = bis(2-diphenylphosphinoethyl)phenylphosphine}.



M=Ir, Pt, and Rh

Our studies of phenol deoxygenation focus on monitoring the reactions for the elementary processes upon which catalytic activity will depend: CO insertion into M-OPh bonds, CO_2 elimination from aryloxy carbonyls {M-C(O)-O-Ph}, followed by formation of a coordinated benzyne intermediate.

RECENT EXPERIMENTAL RESULTS:

The Ir(triphos)OPh system has shown the ability to catalytically deoxygenate *p*-Cresol. This catalyst has been generated in the reaction mixture from the precursor, [Ir(triphos)η^4-cod]Cl. Many reactions have been prepared with varying amounts of Ir(triphos)η^4-cod]Cl, *p*-cresol, and NaOPh-*p*-Me. All reactions took place in a silicone oil bath at 55° so that *p*-cresol was the solvent. 1 atm of CO was introduced into each flask. Periodically, a gas-lock syringe was used to remove a sample of the headspace gas in order to monitor the disappearance of CO and the appearance of CO_2 by GC. After the amount of CO was diminished or completely depleted, the flasks were removed from the silicone oil bath and the organic products were distilled and analyzed by HPLC, to find amounts of toluene corresponding to the same order of magnitude as CO_2 evolved. The proposed mechanism follows as figure 1.

I. Preparation of Ir(triphos)(η^2-cod)Cl

[Ir(cod)Cl]$_2$, (cod = 1,5-Cyclooctadiene), was synthesized according to existing literature methods[24] and placed in a round bottom flask with two equivalents of triphos {bis(2-diphenylphosphinoethyl)phenylphosphine} in CH_2Cl_2. This forms [Ir(triphos)η^4-cod]Cl. $^{31}P\{^1H\}$ NMR ($CDCl_3$): doublet at 27 ppm, triplet at 65 ppm, ^2J=8 Hz. [Ir(triphos)η^4-cod]Cl, although not soluble in benzene, upon refluxing in benzene forms Ir(triphos)(η^2-cod)Cl, which is soluble in benzene. $^{31}P\{^1H\}$ NMR (C_6D_6): doublet at 39 ppm, triplet at 80 ppm, ^2J=10 Hz. See figure 2.

II. Preparation of Ir(triphos)(η^2-coe)Cl

[Ir(coe)$_2$Cl]$_2$, (coe = Cyclooctene), was synthesized according to existing literature methods[25] and placed in a round bottom flask with two equivalents of triphos {bis(2-diphenylphosphinoethyl)phenylphosphine} in benzene. Two products are formed from this reaction. The one that remains soluble in benzene is Ir(triphos)(η^2-coe)Cl. $^{31}P\{^1H\}$ NMR (C_6D_6): doublet at 39 ppm, triplet at 80 ppm, ^2J=10 Hz. See figure 3.

III. Work in progress

The isolation of the η^2-cod species is one step closer to the isolation of Ir(triphos)Cl, which will be reacted with NaOPh to synthesize Ir(triphos)OPh. Mechanistic studies of this catalytic cycle will be continued.

CONCLUSION:

For the first time, the deoxygenation of a phenol by CO to afford a hydrocarbon product and CO_2 has been demonstrated. Catalytic activities observed previously with Ir(triphos)OAr are not high because of the equilibrium existing with the coordinated cod ligand. The isolation of the η^2-cod species lends credibility to this equilibrium loss of the cod ligand in the proposed mechanism. When Ir(triphos)Cl can be prepared without the cod ligand, catalytic efficiencies are expected to improve significantly. We will then begin to assess catalytic activity for deoxygenation of a wide variety of differently substituted phenols and ultimately coal liquids.

Proposed Catalytic Cycle

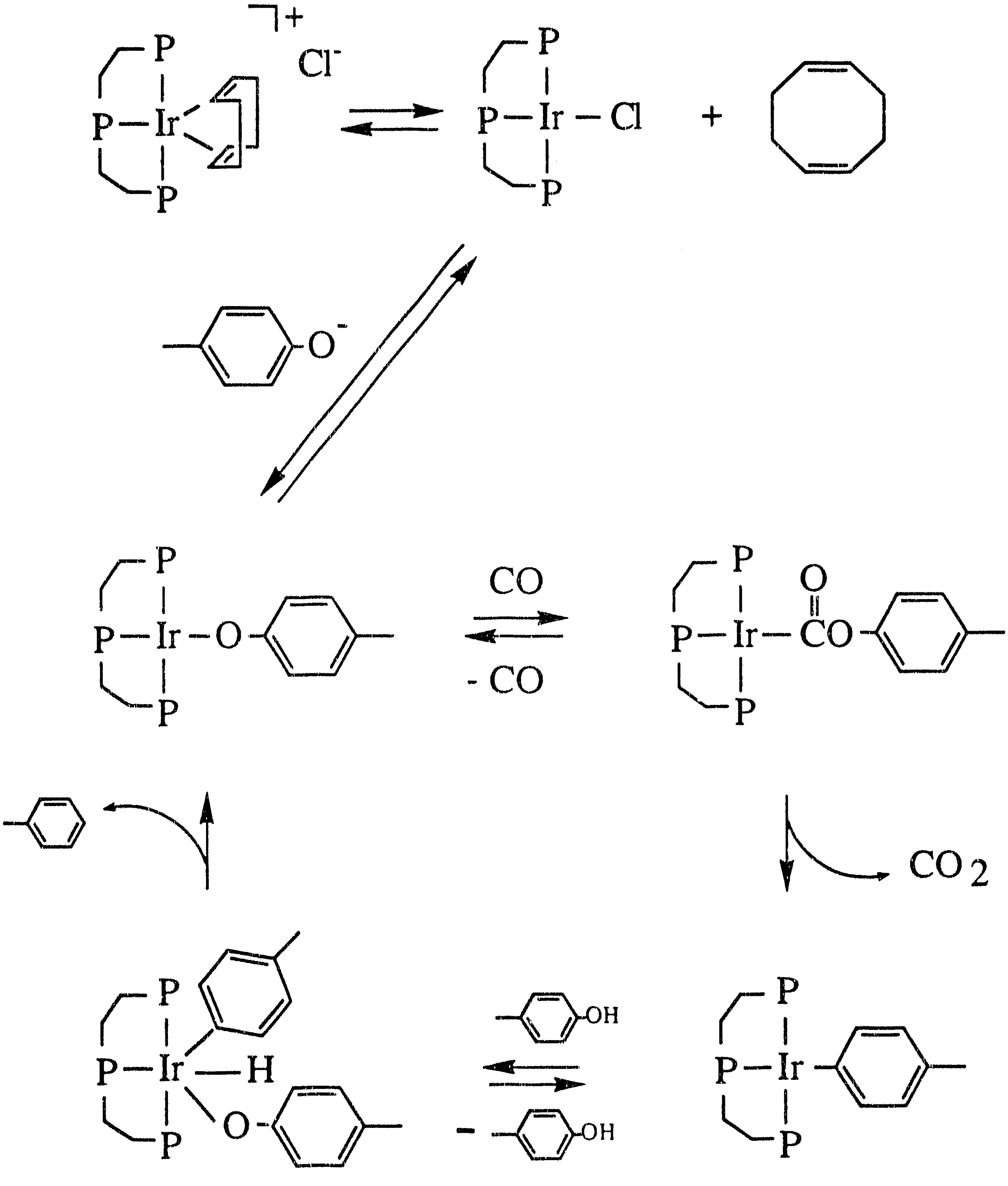
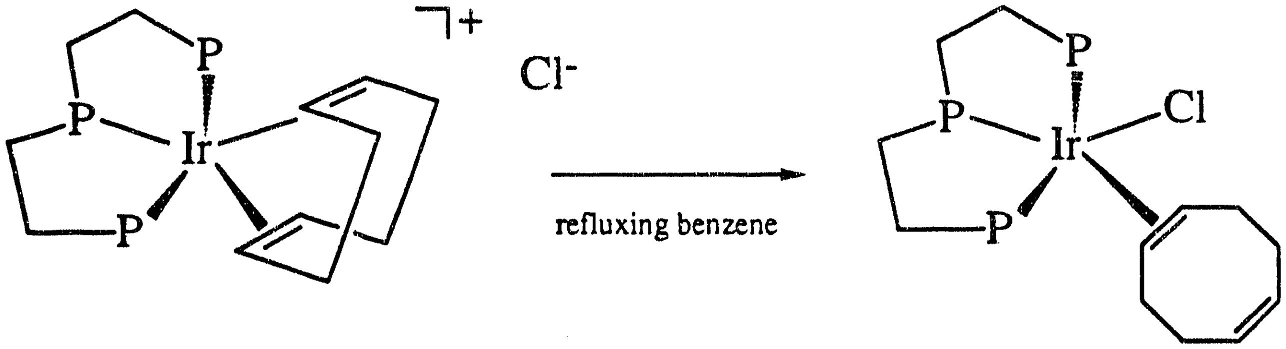


Figure 1.



^{31}P{^{1}H} NMR
doublet at 27.2 ppm
triplet at 65.4 ppm
^{2}J = 9.1 Hz

^{31}P{^{1}H} NMR
doublet at 39.6 ppm
triplet at 80.0 ppm
^{2}J = 10.3 Hz

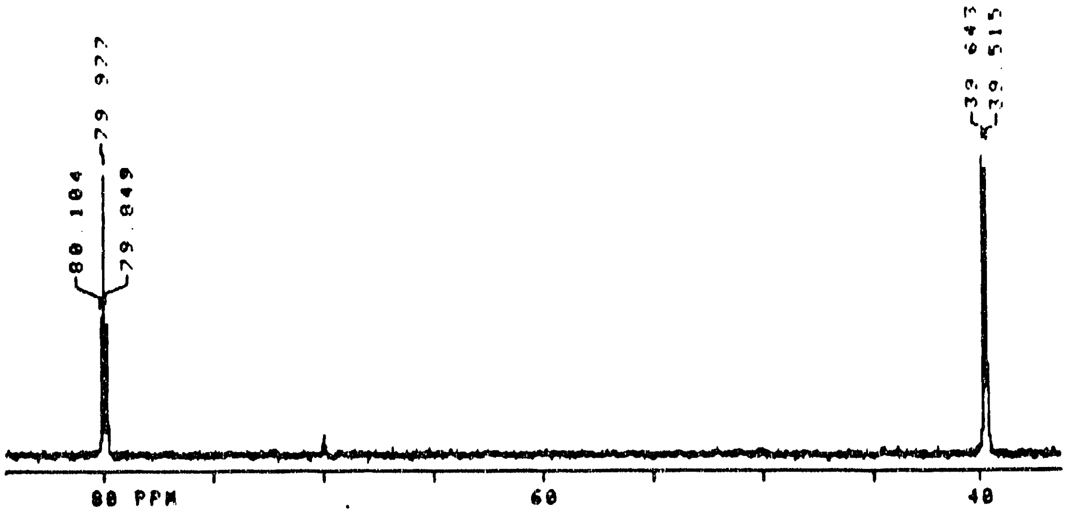
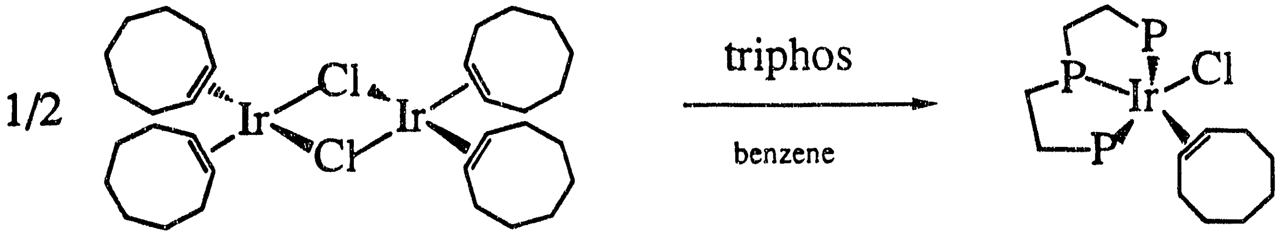


Figure 2.



$^{31}P\{^1H\}$ NMR
doublet at 39.6 ppm
triplet at 80.0 ppm
^2J = 10.3 Hz

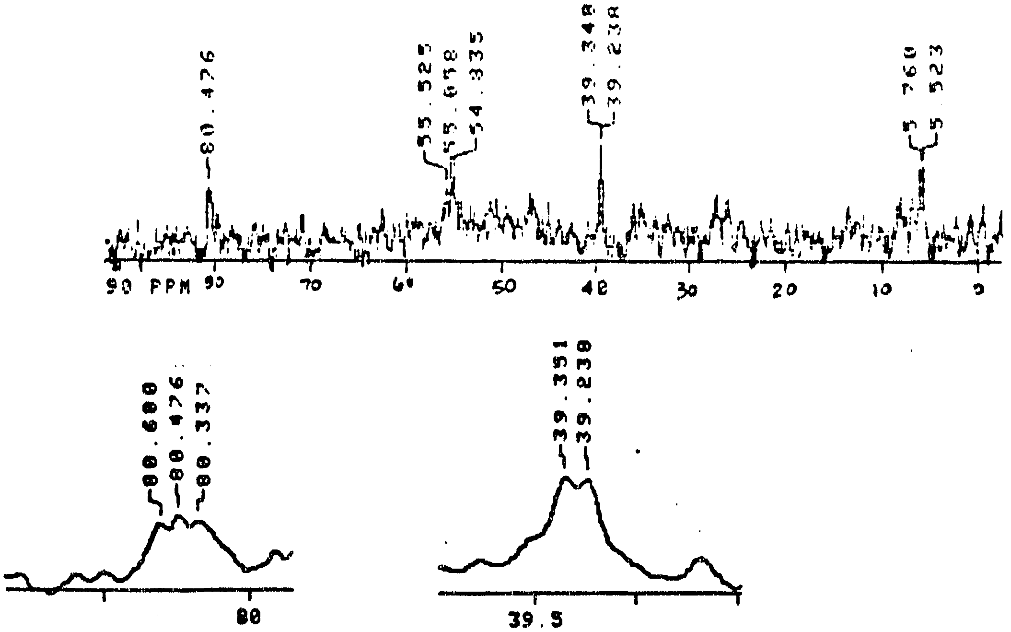


Figure 3.

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