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# Preconversion Catalytic Deoxygenation of Phenolic Functional Groups

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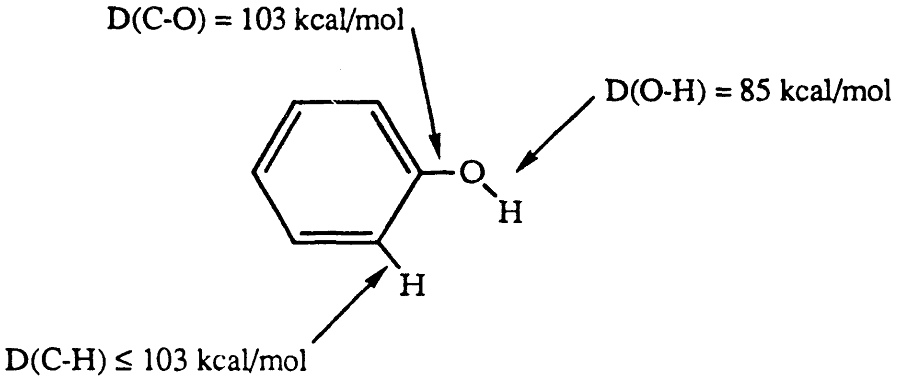
## STATEMENT OF PROBLEM:

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 $Mo/\gamma\text{-}Al_2O_3$, $Ni\text{-}Mo/\gamma\text{-}Al_2O_3$, $Co\text{-}Mo/\gamma\text{-}Al_2O_3$, and $Fe_2O_3/SiO_2$. 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.

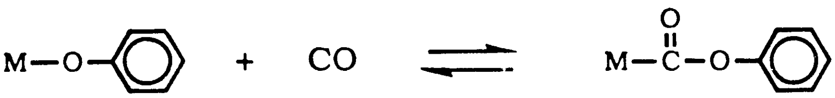
## RESEARCH BACKGROUND:

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,

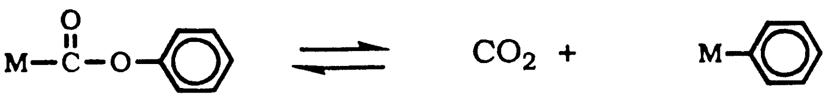

(1)

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

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.

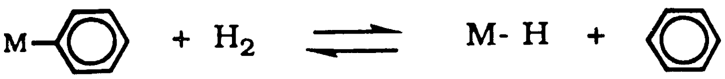

(2)

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

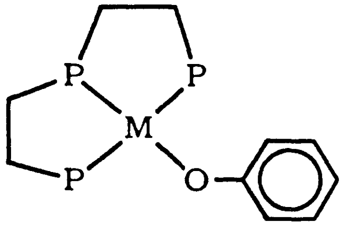

(3)

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 is useful for mechanistic studies because it provides the possibility to isolate the key intermediates, which are illusive in kinetically faster systems, like the Rh(triphos)OPh.

I. Preparation of Ir(triphos)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 four equivalents of triphenylphosphine and 1 atm of CO to synthesize *trans*-

$Ir(CO)(PPh_3)_2Cl$[25]. $^{31}P\{^1H\}$ NMR ($CDCl_3$) shows a singlet at 24.582 ppm. The CO stretch in the IR comes at 1955.2 $cm^{-1}$ in KBr as compared to the reported value of 1957 $cm^{-1}$ in $CHCl_3$[25].

$Ir(CO)(PPh_3)_2Cl$ was refluxed with triphos {bis(2-diphenylphosphinoethyl)phenylphosphine} in 50/50 mixture of $CH_2Cl_2$ and hexanes under a nitrogen atmosphere to yield a peach solid, $[Ir(triphos)PPh_3]Cl$. The $^{31}P\{^1H\}$ NMR ($CDCl_3$) is shown in figure 1.

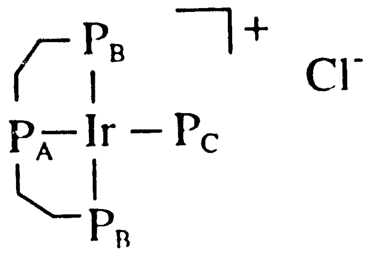
Ir(triphos)Cl was isolated by recrystallization of $[Ir(triphos)PPh_3]Cl$ in a LiCl saturated solution of THF with slow addition of diethyl ether. The pale yellow solid was collected in a filter frit and washed with diethyl ether to remove the triphenylphosphine and then washed with water to remove the excess LiCl. The $^{31}P\{^1H\}$ NMR ($CDCl_3$) is shown in figure 2.

Ir(triphos)Cl was also prepared by a second method. $[Ir(triphos)\eta^4$-cod]Cl was prepared by reacting $[Ir(cod)Cl]_2$, (cod = 1,5-Cyclooctadiene), with two equivalents of triphos in $CH_2Cl_2$. The x-ray crystal structure and $^{31}P\{^1H\}$ NMR ($CDCl_3$) spectra are shown in figure 3. Recrystallization of $[Ir(triphos)\eta^4$-cod]Cl in a LiCl saturated solution of THF with addition of hexanes yields a mixture of $[Ir(triphos)\eta^4$-cod]Cl and Ir(triphos)Cl, which can be seen in the $^{31}P\{^1H\}$ NMR ($CDCl_3$) in figure 4. The presence of both species lends credibility to the equilibrium first step of the proposed catalytic deoxygenation cycle shown in figure 5.

Ir(triphos)Cl is currently being reacted with NaOAr to form Ir(triphos)Ar.

## II. Catalytic deoxygenation of *p*-Cresol by $[Ir(triphos)\eta^4$-cod]Cl.

Several reactions were prepared with varying amounts of Ir(triphos)$\eta^4$-cod]Cl, *p*-cresol, and NaOPh-*p*-Me. The most efficient reactions to date occurred when five equivalents of NaOPh-*p*-Me were used. In some reactions, triethylamine was substituted for NaOPh-*p*-Me. Either base caused the reaction to proceed with approximately the same efficiency. All reactions took place in a silicon 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, the flasks were removed from the silicon 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 5.



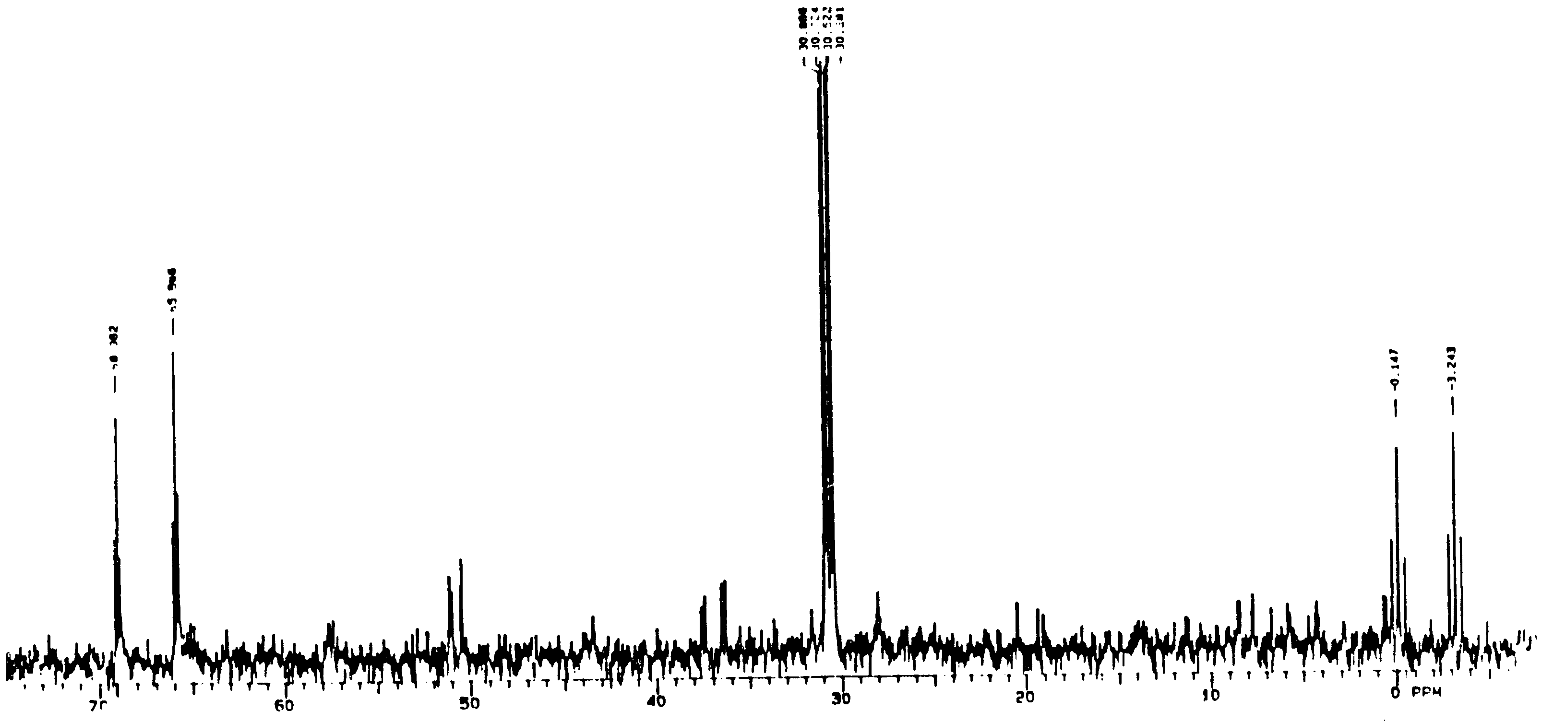
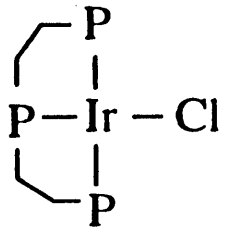


Figure 1.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$) of $[Ir(triphos)PPh_3]Cl$.

$J(P_A\text{-}P_B)$= 11.4 Hz; $J(P_B\text{-}P_C)$= 27.8 Hz; $J(P_A\text{-}P_C)$= 250.7Hz.



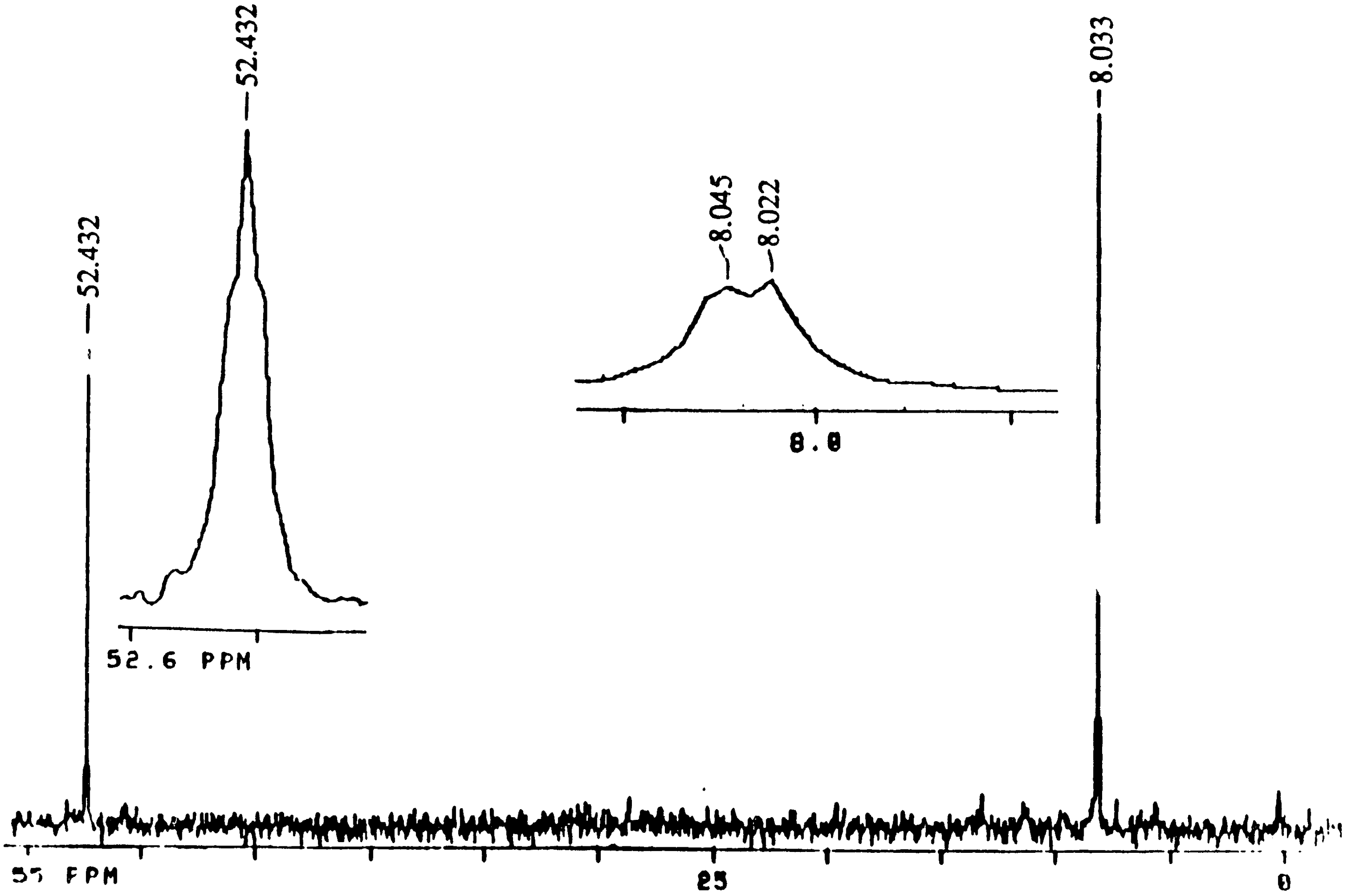


Figure 2.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$) of Ir(triphos)Cl. J(P-P)= 2 Hz.

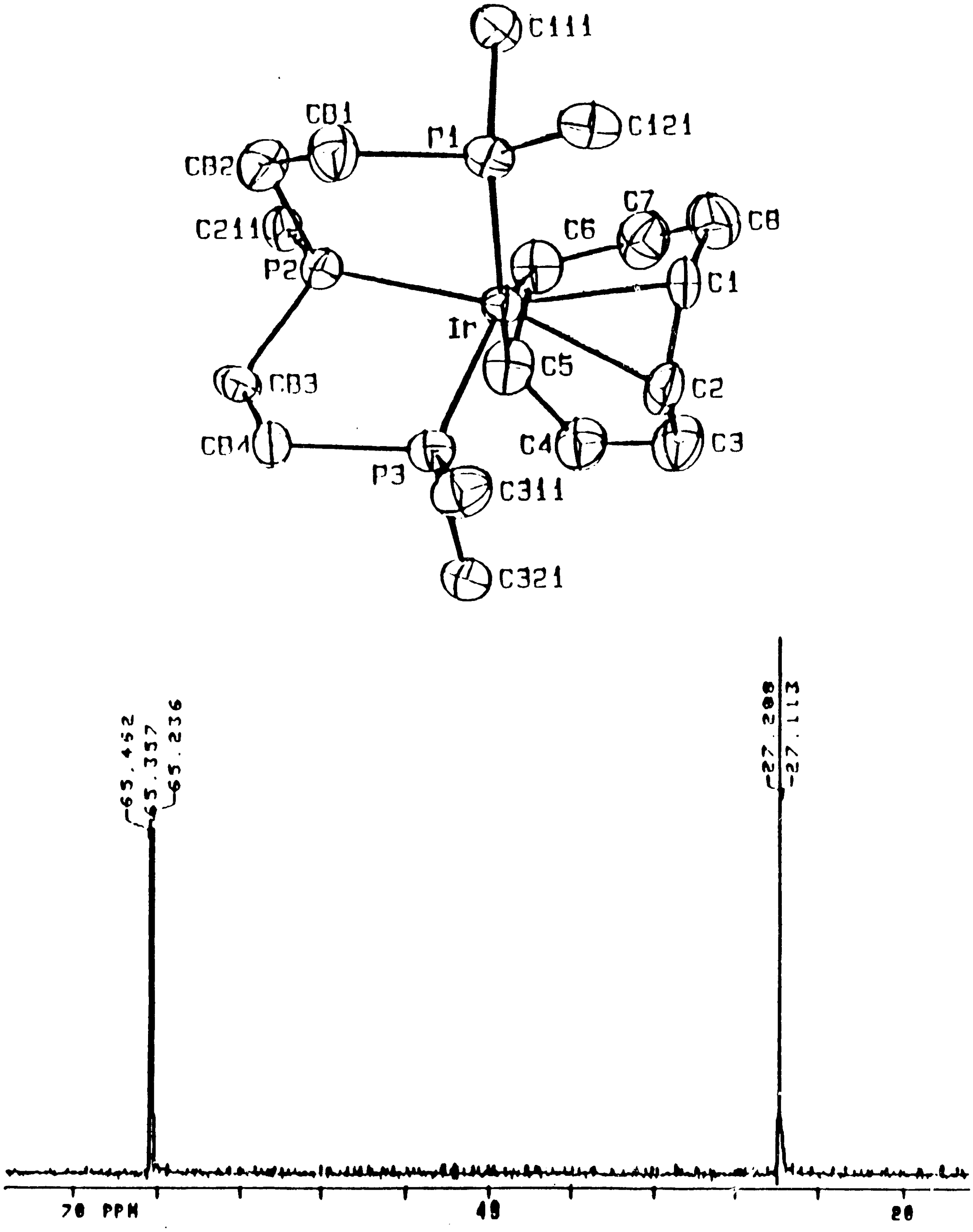


Figure 3.

Crystal structure and $^{31}P\{^1H\}$ NMR ($CDCl_3$) of [Ir(triphos)$\eta^4$-cod]Cl.

J(P-P)= 8 Hz.

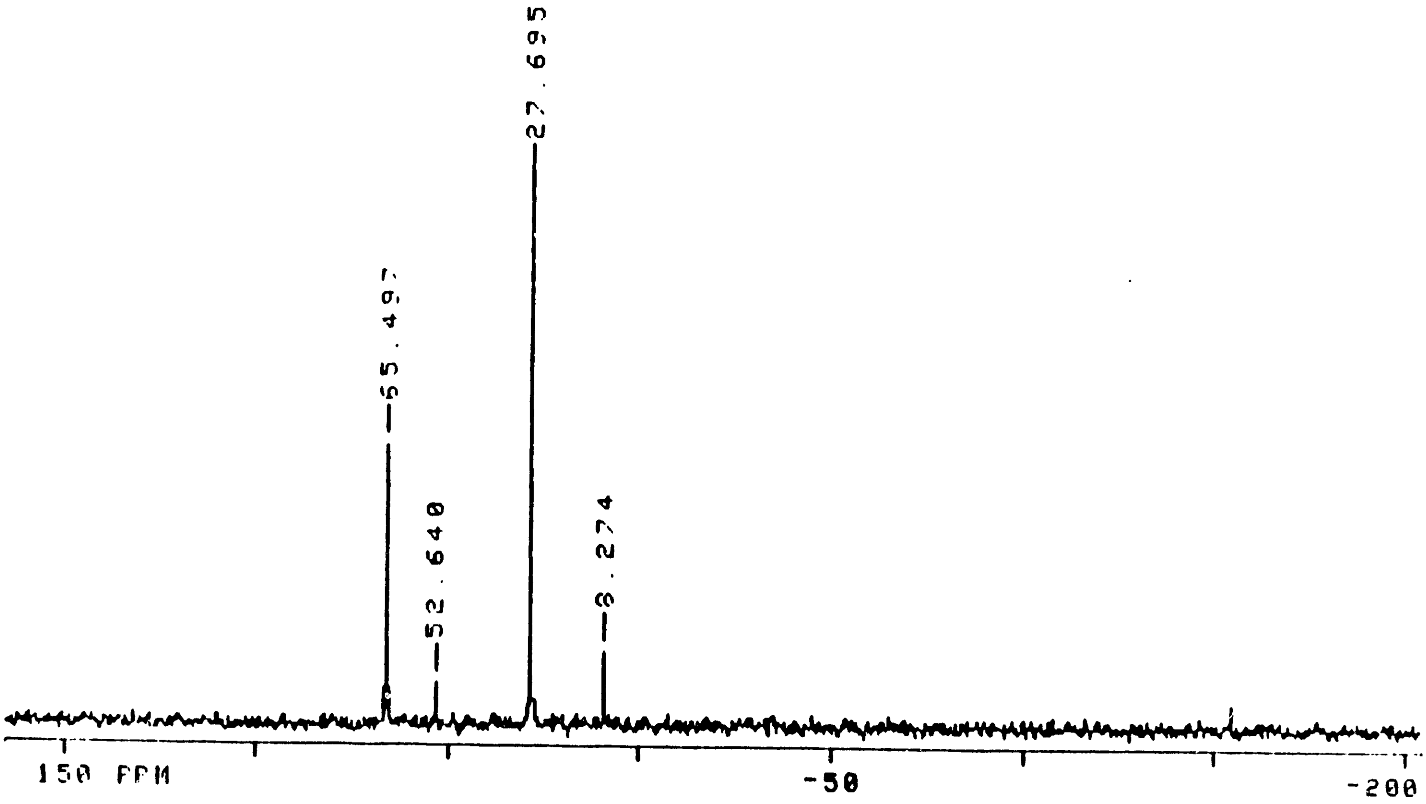


Figure 4.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$) of Ir(triphos)Cl and [Ir(triphos)$\eta^4$-cod]Cl

# Proposed Catalytic Cycle

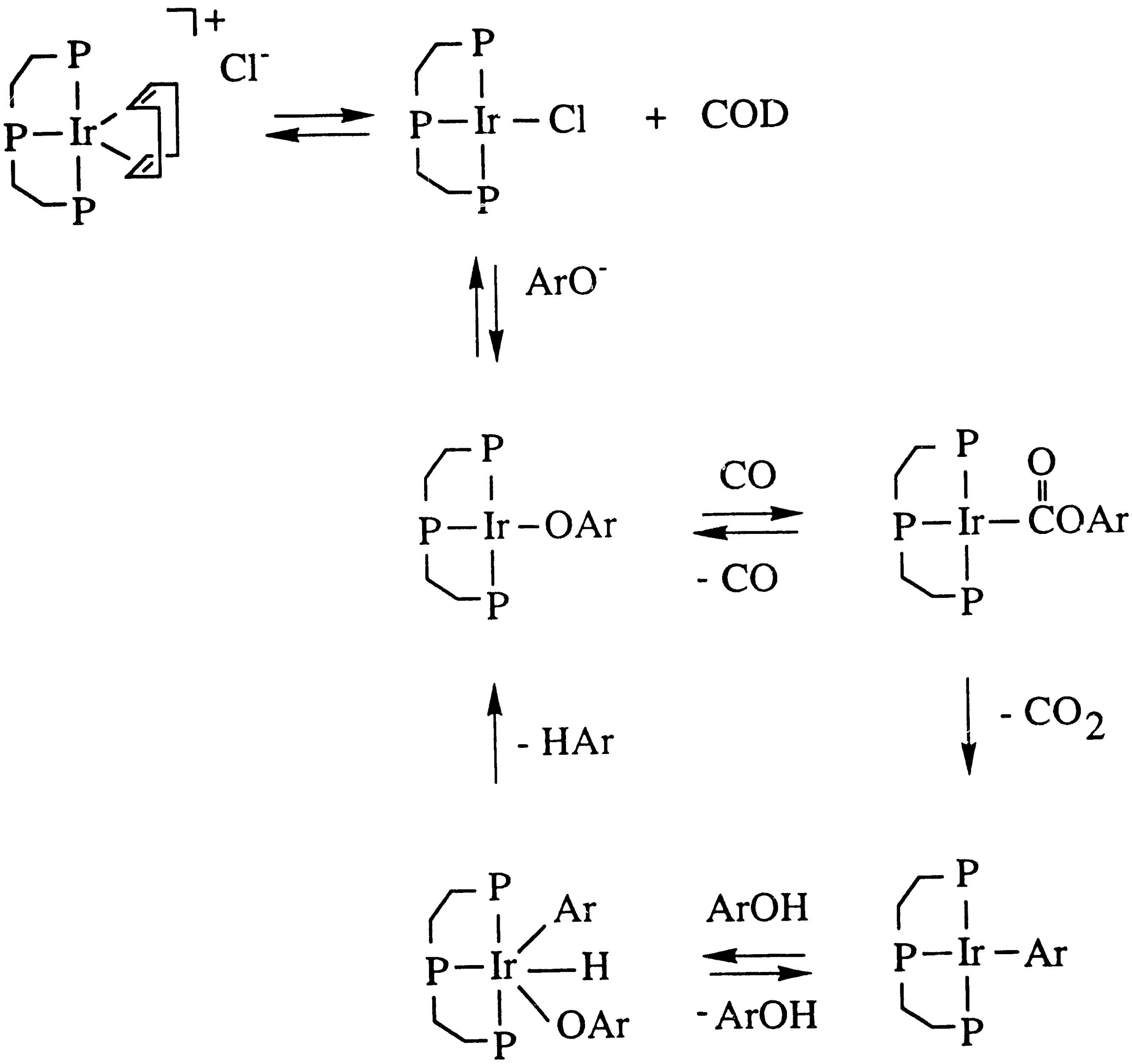


Figure 5.

### III. Attempted preparation of Rh(triphos)Cl

$Rh(PPh_3)_3Cl$ was purchased from Aldrich and reacted with triphos according to literature methods[25]. The $^{31}P\{^1H\}$ NMR showed a mixture of products. We are currently investigating the possibility of the formation of $[Rh(triphos)PPh_3]Cl$. When synthesized, Rh(triphos)Cl will be reacted with NaOAr to form Rh(triphos)OAr.

### IV. Work in progress

Reactions are being setup to see if Ir(triphos)Cl exhibits increased catalytic activity over $[Ir(triphos)\eta^4\text{-cod}]Cl$. The $CO_2$ elimination step has evidence of a benzyne intermediate in the $Pt(dppe)(OPh)_2$ system. Trapping experiments using furan are underway to see if the benzyne intermediate also exists in the Ir(triphos)OPh system.

## CONCLUSION:

For the first time, the deoxygenation of a phenol by C≡O to afford a hydrocarbon product and $CO_2$ has been demonstrated. Catalytic activities observed to date with Ir(triphos)OAr are not high because of the equilibrium existing with the coordinated cod ligand. Now that Ir(triphos)Cl can be prepared without the cod ligand, catalytic effiencies should improve.

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