Preconversion Catalytic Deoxygenation of Phenolic Functional Groups

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Introduction to Catalytic Deoxygenation of Phenols by CO.

Recent research in our laboratories has established the viability of the catalytic deoxygenation of phenols by carbon monoxide. The deoxygenation of phenols is a problem of both fundamental and practical importance. The deoxygenation of phenols to arenes is a conceptually simple, yet a very 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 or ethanol.

\[
D(\text{C-O}) = 103 \text{ kcal/mol} \\
D(\text{O-H}) = 85 \text{ kcal/mol} \\
D(\text{C-H}) \leq 103 \text{ kcal/mol}
\]

Catalytic hydrodeoxygenation (HDO) of phenols over sulfided Mo/γ-Al₂O₃, Ni-Mo/γ-Al₂O₃, Co-Mo/γ-Al₂O₃ or other supported metal oxide catalysts can be achieved, at exceedingly high hydrogen pressures (> 100 atm) and temperatures (> 200 °C). Arene ring hydrogenation generally competes effectively with hydrodeoxygenation, and was found to occur an order of magnitude faster than HDO. As a consequence, most of the hydrogen is consumed in hydrogenation of the aromatic rings. HDO catalysts are easily poisoned. Moreover, the HDO side product, water, is found to dramatically impair HDO activity by occupying anion vacancies on the catalyst surfaces.

The inefficiency of catalysts for phenol deoxygenation in the presence of hydrogen can be attributed to the absence of a low energy mechanistic pathway for the hydrogenolysis of the strong phenol C-O bond. We are currently studying new transition metal catalysts for the efficient and selective deoxygenation of phenols using the CO/CO₂ couple to remove phenolic
oxygen atoms. The deoxygenation of phenols by CO, eq 1, is thermodynamically favored by over 20 kcal/mol; however, remarkably no commercial catalysts are yet available for this important reaction.

\[
\text{O}=\text{O} \quad (1) + \quad \text{CO} (g) \quad \xrightarrow{\Delta} \quad \text{H} \quad (l) + \quad \text{CO}_2 (g)
\]

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

The key to our studies involves the exploitation of the recently discovered insertion of CO into the M-O bonds of metal phenoxides, eq 2, and subsequent decarboxylation to afford CO\(_2\) and a metal phenyl complex,\(^1\) eq 3, which can produce benzene by protonation or hydrogenation, eq 4 and 5.

\[
\begin{align*}
\text{M} - \text{O} & \quad + \quad \text{CO} \quad \xrightarrow{\Delta} \quad \text{M} - \text{C} - \text{O} \quad (2) \\
\text{M} - \text{C} - \text{O} & \quad \xrightarrow{\Delta} \quad \text{M} - \text{C} - \text{H} \quad + \quad \text{CO}_2 \quad (3) \\
\text{M} - \text{C} - \text{H} & \quad + \quad \text{H}^+ \quad \xrightarrow{\Delta} \quad \text{M}^+ \quad + \quad \text{C} \quad (4) \\
\text{M} - \text{C} - \text{H} & \quad + \quad \text{H}_2 \quad \xrightarrow{\Delta} \quad \text{M} - \text{H} \quad + \quad \text{C} \quad (5)
\end{align*}
\]

In contrast to hydrodeoxygenation of phenols, for which no obvious low energy pathways exist for C-O bond rupture, the thermodynamic driving force for CO\(_2\) elimination, in eq 3, is high. Moreover, cooperative metal arene-\(\pi\) interactions or metal stabilized benzyne intermediates\(^1\) are likely to be important in facilitating the deoxygenation by CO\(_2\) loss.

Our initial phases of research focus on identifying catalyst requirements essential for low temperature deoxygenation of phenols. These studies make use of soluble transition metal catalysts and phenols. These well defined systems are chosen because they are amenable to facile characterization by routine spectroscopic methods (IR, NMR, UV-Vis) at modest
temperatures and pressures. The advantage of transition metal catalysts is that their study provides a richly detailed knowledge of fundamental chemical mechanisms for catalysis. Our ongoing studies focus on mono(aryloxide) potential catalysts of the class: Ir(triphos)(O-Ph), [Pt(triphos)(O-Ph)]⁺ and Rh(triphos)(O-Ph).

This provides a series of compounds which are expected to have the following order of reactivity toward CO insertion: Rh(triphos)(O-Ph) > Ir(triphos)(O-Ph) > [Pt(triphos)(O-Ph)]⁺.

**Recent Results on the Mechanism of CO Insertion into Metal-Oxygen Bonds of Phenoxides.** The term "insertion" is used in organometallic chemistry to describe a wide variety of reactions where an incoming group ends up between a metal and a previously bonded ligand. For carbonyl insertions into metal-alkyl bonds a large body of kinetic and mechanistic work is available, and is the subject of several reviews.¹⁻⁵ For all the transition metals an example of carbon monoxide reacting with a metal alkyl (M-R) to produce a metal acyl (M-C(=O)-R) is known. A variety of detailed mechanistic pathways are available for these reactions.⁶

The first carbonyl insertion reaction to be studied in detail was the carbonylation of CH₂Mn(CO)₅. Infrared spectroscopy was used by Calderazzo to study this system.⁷,⁸ Flood later re-examined this reaction using ¹³C NMR and confirmed the stereochemistry at the manganese.³,⁹ Specifically in Flood's work, treatment of CH₃Mn(CO)₅ with ¹³CO yields only (CH₃C(O))Mn(CO)₄(¹³CO), where the labeled carbon monoxide is situatedcis to the acyl group, eq. 1.
In addition, the product distribution after insertion was studied with cis CH₃Mn(CO)₄₁³CO). The migration of carbon monoxide into the Mn-Me bond of cis CH₃Mn(CO)₄₁³CO) would give a distribution of products where only the cis terminal manganese carbonyls would contain the ¹³C label, eq. 2. In the reverse case, methyl migration, the ratio of cis/trans ¹³C labeled terminal manganese carbonyls would be 2:1, eq. 3. A ratio of 2:1 was reported on the basis of IR ¹³C stretching frequencies,¹⁰ and ¹³C NMR integration⁹, confirming the methyl migration pathway.

For carbon monoxide insertion into platinum group alkyls one could be tempted by the available coordination site to propose a similar migratory insertion mechanism with a five coordinate intermediate.¹¹,¹² While this simple insertion mechanism is known for some square planar platinum alkyls, a second mechanism is more prevalent.¹³ The second mechanism involves dissociation of phosphine and formation of a cis four coordinate alkyl carbonyl derivative, M XR(CO)L. Insertion then proceeds through a T-shaped 14-electron intermediate followed by phosphine filling the vacant site.¹³,¹⁴ These reactions are faster for palladium than for platinum, and are faster for triarylphosphine complexes; both observations are consistent with a mechanism involving displacement of phosphine. The necessity for ligand dissociation is underlined by the inability of organoplatinum complexes containing chelating phosphine ligands
to undergo carbonyl insertion reactions. This mechanism is the one most commonly seen for carbonylation of platinum alkyls. Formation of a five coordinate intermediate dominates the process in a few cases, but only after isomerization of the alkyl group to the apex of a square pyramidal configuration.

For the late transition metal alkoxides several examples of carbonyl insertion into the metal alkoxide bond are known. However, little solid kinetic or mechanistic information has been reported. The best defined examples are those of Atwood for Ir(CO)(OPh)(PPh$_3$)$_2$,\textsuperscript{15-18} Bryndza for Pt(dppe)(OMe)$_2$,\textsuperscript{19,20} and [Pt(triphos)(O-Ph)]$^+$ described here.

There are two principal mechanisms by which late transition metal aryloxy complexes can be carbonylated to their respective aryloxycarbonyls. The first is classical migratory insertion,\textsuperscript{1-3,8} where the aryloxy ligand migrates to a carbon monoxide cis to the aryloxy ligand, eq. 4.

\[
\text{L}_n\text{M}-\text{OAr} \xrightleftharpoons{\text{CO}} \text{L}_n\text{M} \rightarrow \text{L}_n\text{M} (\text{CO}) \text{OAr}
\]  

(4)

A second plausible mechanism is nucleophilic addition of a displaced aryloxide to coordinated carbon monoxide. This mechanism must be considered in view of the dissociative mechanisms observed for platinum alkyl carbonylation\textsuperscript{13,14} and the lower M-OAr bond energies expected for late transition metal aryloxy complexes.\textsuperscript{21} This mechanism would proceed by substitution of a weakly bound aryloxide ligand with carbon monoxide, followed by nucleophilic addition of the displaced aryloxide to the carbonyl ligand, eq. 5.

\[
\text{L}_n\text{M}-\text{OAr} \xrightleftharpoons{\text{CO}} \text{L}_n\text{M} (\text{CO})^+ + \text{OAr} \rightarrow \text{L}_n\text{M} (\text{CO}) \text{OAr}
\]  

(5)

It was concluded by Bryndza that migratory insertion, eq. 4, is involved in the carbonylation of the platinum alkoxy complexes, Pt(dppe)(O-Me)(R) (R = OMe, Me), eq. 6.\textsuperscript{20}
This conclusion was based on low temperature (-80°C) $^{13}$C NMR studies, whereby a five coordinate carbon monoxide platinum adduct was observed, with a chemical shift of 184.9 ppm ($^1 J(C-Pt) = 1753$ Hz) with no coupling to phosphorus observed. In the $^1$H NMR spectrum, the methoxy protons in Pt(dppe)(O-Me)$_2$ are equivalent, indicating a square pyramidal structure for this intermediate. Warming the solution to -20°C results in coalescence of the platinum adduct resonance with that of free carbon monoxide. These observations suggest that the first step of the carbonylation of Pt(dppe)(O-Me)(R) (R = OMe, Me) is a pre-equilibrium coordination of carbon monoxide to form a square pyramidal intermediate. The prospect of methoxide dissociation was ruled out by examining CD$_2$OD exchange with the complex. Under these conditions, methoxide/methanol exchange occurs more than three orders of magnitude slower than carbonylation. Furthermore, in the presence of carbon monoxide, the deuterium incorporation into the final methoxycarbonyl is less than 5%, the detection limit of proton integration.

Atwood et al. determined that nucleophilic attack on coordinated carbon monoxide was the mechanism for carbon monoxide insertion into the Ir-O bond of Ir(CO)(O-Ph)(PPh$_3$)$_2$.$^{17}$ During the reaction of Ir(CO)(O-Ph)(PPh$_3$)$_2$ with carbon monoxide, the formation of an Ir(CO)$_3$(PPh$_3$)$_2^+$ intermediate is observed spectroscopically. Infrared spectra taken during the course of the carbonylation reaction show the growth and then the loss of IR signals assigned to [Ir(CO)$_3$(PPh$_3$)$_2^+$]. The amount of this intermediate is dependent on phenoxide nucleophilicity, with the intermediate being undetectable in the presence of more nucleophilic alkoxides.

\[
\begin{align*}
\text{OC} & \text{Ir} \text{-PPh}_3 \quad 2 \text{CO} \quad \text{OC} \text{-PPh}_3 \\
R = \text{Me, Ph}
\end{align*}
\]

Trogler found that the increased tendency toward heterolytic dissociation complicated the reaction of carbon monoxide with trans-PtH(O-Ph)(PEt$_3$)$_2$. Reaction with carbon monoxide yields trans-Pt(CO)$_2$(PEt$_3$)$_2$ as the major product, indicating reductive elimination as the
dominant reaction pathway. However, some PtH(PEt₃)₃⁺ is produced as a result of the increased tendency of late transition metal alkoxides toward heterolytic dissociation.

Experimental Section

General Experimental Descriptions

Carbon monoxide (research grade) was purchased from Matheson and used without further purification. Acetonitrile, methylene chloride, and THF were freshly distilled from CaH₂ under a nitrogen atmosphere. THF was freshly distilled from sodium benzophenone ketal. Deuterated acetonitrile (99.9%) was purchased from Cambridge Isotope Labs, stored under nitrogen, and used as received. All reactions and manipulations were carried out under a nitrogen atmosphere using a nitrogen filled glovebox (Vacuum Atmospheres).

³¹P NMR spectra were recorded on a Varian XL-200 spectrometer. ³¹P NMR spectra were referenced to external 85% H₃PO₄ and were all proton decoupled.

Kinetic Experiments

Rates of carbonylation of 2a-c were followed by ³¹P{¹H} NMR at ambient temperatures under carbon monoxide pressure. In a typical experiment, a pressure NMR tube (Wilmad) was charged in an inert atmosphere box with a d³-acetonitrile solution of one of the platinum aryloxy complexes, 2a-c. Experiments with excess aryloxide ligand required a 1:1 d³-acetonitrile : THF solvent mixture. An initial ³¹P{¹H} NMR spectrum was taken before the tube was pressurized (10 - 134 psi gauge) with carbon monoxide according to the procedure in chapter 3. Thereafter, ³¹P{¹H} NMR spectra were taken at regular intervals, Figure 1. These intervals were controlled by arraying the PAD parameter in the Varian XL software package. A typical array in seconds is PAD(1) = 5, 5, 60, 60, 60, 600, 600, 600, 600, 600, 6000, 6000, 6000, 6000, 6000. Increasing the PAD delay during the experiment in this manner utilizes the software constrained
18 data points more effectively and provides a good balance between obtaining at least 4 half lives of data and accurately collecting data during the early part of the experiment.
Figure 1. Overlaid $^{31}\text{P}^{1\text{H}}$ spectra showing the disappearance of resonances corresponding to the aryloxide, 2b, and the appearance of the aryloxy carbonyl, 3b.
Figure 2. $^{31}\text{P}(^1\text{H})$ spectra showing the disappearance of *trans* phosphine associated with phenoxide and the appearance of the *trans* phosphine of the aryloxy carbonyl.
Figure 3. Reaction profile of the carbon monoxide insertion reaction.

Figure 4. Plot of $-\ln[\text{Pt-Phenoxide}]$ vs. time for the disappearance of 2b.
Figure 1-2 shows a series of plots of the peak intensities for the starting aryloxide at 74.7 ppm and product aryloxycarbonyl at 91.1 ppm. Signals corresponding to the starting aryloxy complexes 2a-c and the carbonylated aryloxycarbonyl products, 3a-c, were integrated and these integrations were used in the kinetic data analysis. In the resulting reaction profile, Figure 3, it can be seen that the products are quantitatively produced from the reactants. Because this reaction is under pseudo first order conditions, plotting -ln[Pt-Phenoxide] vs. time gives a slope equal to the observed rate constant, $k_{obs}$, Figure 4.

Spin lattice relaxation times ($T_1$) for 2a were determined by inversion recovery for $P_A$ (4.8 s) and $P_B$ (3.4 s). To obtain accurate integrations a 6 second recycle rate was used with a 2 second acquisition time and minimized spectral width. It should be noted that care must be taken in obtaining these integrations; baseline correction must be turned off and each full spectrum must be individually phased.

The concentration of carbon monoxide in acetonitrile was determined by Henry’s Law. These calculations were based on the calibrated total volume of the tube and mole fraction solubility of carbon monoxide in propionitrile ($\chi = 6.30\times10^{-4}$). Under these conditions the carbon monoxide concentration in solution is greater than the Pt complex, ~80 mM vs ~20 mM, and pseudo first order conditions exist. While these concentration differentials do not meet the strictest definitions of pseudo first order conditions, commonly a 10-100 fold excess of reagent, the reader is reminded of the low solubility of carbon monoxide in these solvents. This poor solubility requires high pressures to achieve the reported concentrations, and results in the presence of a large excess of carbon monoxide being present in the head space. The head space then acts as a reservoir to keep the carbon monoxide concentration constant, the important requirement of pseudo first order kinetics. Furthermore, given that the rates being studied are quite slow, there should not be interference from the $\text{CO}_{sol}/\text{CO}_{gas}$ equilibrium.

Results and Discussion
The kinetics of carbonylation are first order in [2a-c] to better than four half-lives, Figure 3, Table 1. Varying the carbon monoxide pressures from 50 to 134 psi also indicated that the observed rates were first order in [CO], Figures 5, Table 2. The reaction shows no observable dependence on the presence of excess aryloxide in solution. The addition of up to 37 equivalents of aryloxide to the solution does not affect the rate, Table 2. These observations are consistent with associative kinetics and suggest quite clearly that the carbonylations of 2a-c do not proceed by initial dissociation of the aryloxide ligand.

Table 1  Pseudo first order rate constants for the carbonylation of the aryloxy complexes (2a-d).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_{obs} \times 10^{-4}$</th>
<th>Hammett $\sigma^{25}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pt(triphos)(O-C$_6$H$_4$-F)][PF$_6$] (2d)</td>
<td>1.703</td>
<td>0.06</td>
</tr>
<tr>
<td>[Pt(triphos)(O-C$_6$H$_4$-H)][PF$_6$] (2c)</td>
<td>2.308</td>
<td>0.00</td>
</tr>
<tr>
<td>[Pt(triphos)(O-C$_6$H$_4$-Me)][PF$_6$] (2b)</td>
<td>1.252</td>
<td>-0.17</td>
</tr>
<tr>
<td>[Pt(triphos)(O-C$_6$H$_4$-O-Me)][PF$_6$] (2a)</td>
<td>1.031</td>
<td>-0.27</td>
</tr>
</tbody>
</table>
Figure 5. Dependence of the observed rate of para methyl-phenoxide disappearance on carbon monoxide pressure for \([\text{Pt(triphos})(\text{C(O)O-C}_6\text{H}_4-p\text{-Me})][\text{PF}_6]\) (2b).

Table 2. Dependence of the observed rate of carbon monoxide insertion into \([\text{Pt(triphos)}(\text{O-C}_6\text{H}_4-p\text{-Me})][\text{PF}_6]\) on carbon monoxide pressure.

<table>
<thead>
<tr>
<th>PSI</th>
<th><a href="mM">Pt</a></th>
<th><a href="mM">CO</a></th>
<th>(k_{\text{obs}}) (10^{-4})</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>16.4</td>
<td>41</td>
<td>0.67</td>
<td>0.994</td>
</tr>
<tr>
<td>74</td>
<td>12.6</td>
<td>61</td>
<td>0.98</td>
<td>0.993</td>
</tr>
<tr>
<td>100</td>
<td>13.6</td>
<td>82</td>
<td>1.25</td>
<td>0.984</td>
</tr>
<tr>
<td>134</td>
<td>17.3</td>
<td>110</td>
<td>1.91</td>
<td>0.980</td>
</tr>
</tbody>
</table>
Figure 6. Plot of the change in the observed rate of para methyl-phenoxide disappearance vs. carbon monoxide concentration for [Pt(triphos)(C(O)O-C₆H₄-p-Me)][PF₆] (2b).

Table 3. Pseudo first order rate constants for the carbonylation of [Pt(triphos)(O-C₆H₄-Me)][PF₆] (2b) in the presence of excess phenoxide. Pressure is 100 psi, [CO] = 82 mM.

<table>
<thead>
<tr>
<th>eq. of excess phenoxide</th>
<th>kobs (E⁻⁴)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>1.16</td>
<td>.974</td>
</tr>
<tr>
<td>19</td>
<td>1.16</td>
<td>.993</td>
</tr>
<tr>
<td>37</td>
<td>1.49</td>
<td>.982</td>
</tr>
<tr>
<td>none</td>
<td>1.36</td>
<td>.962</td>
</tr>
</tbody>
</table>
While these observations rule out a dissociative pathway, two associative pathways can still be considered. The first pathway involves classical migratory insertion: axial association of carbon monoxide with the square planar complex followed by insertion into the Pt-aryloxide bond, eq. 8.

The second pathway involves an associative substitution of aryloxide for carbon monoxide, eq. 9-10, followed by nucleophilic addition of the displaced aryloxide to the coordinated carbon monoxide, eq. 11.
In order to distinguish between the two mechanisms that describe associative kinetics with carbon monoxide, aryloxide ligand exchange and crossover were examined. When one equivalent of NaOC\textsubscript{6}H\textsubscript{4}-p-R' (R' = OMe, H) is added to a solution of [Pt(triphos)(OC\textsubscript{6}H\textsubscript{4}-p-Me)][PF\textsubscript{6}] (2b) the \textsuperscript{31}P{\textsuperscript{1}H} NMR shows two products at equilibrium in solution, Figure 7, eq. 12. These two products can be identified as [Pt(triphos)(OC\textsubscript{6}H\textsubscript{4}-p-Me)][PF\textsubscript{6}] (2b) and [Pt(triphos)(OC\textsubscript{6}H\textsubscript{4}-p-R')][PF\textsubscript{6}] (2a or 2c). The reaction is slow enough to enable the observation of two distinct species on the NMR time scale, and the reaction is complete within 20 min. This brackets the rate constant for exchange between 10\textsuperscript{2} s\textsuperscript{-1} to 10\textsuperscript{-1} s\textsuperscript{-1}. These NMR studies also facilitate the measurement of relative stability constants for the different platinum aryloxy complexes, 2a-e. Equilibrium constants of 0.75 ± 0.2 for the [Pt(triphos)(OC\textsubscript{6}H\textsubscript{4}-p-OMe)]\textsuperscript{+} (2a) / [Pt(triphos)(OC\textsubscript{6}H\textsubscript{4}-p-Me)]\textsuperscript{+} (2b) system, 0.31 ± 0.2 for the [Pt(triphos)(OPh)]\textsuperscript{+} (2c) / [Pt(triphos)(OC\textsubscript{6}H\textsubscript{4}-p-Me)]\textsuperscript{+} (2b) system, and 0.23 ± 0.2 for the [Pt(triphos)(OPh)]\textsuperscript{+} (2c) / [Pt(triphos)(OC\textsubscript{6}H\textsubscript{4}-p-OMe)]\textsuperscript{+} (2a) system were obtained. These equilibrium constants should be considered within the context of the essentially thermoneutral behavior reported earlier for the exchange of platinum methoxides with methanol.\textsuperscript{26} When the equilibrated mixtures of platinum aryloxide complexes are reacted with carbon monoxide at 100 psi, both insertion products appear together at rates comparable to those seen for the same aryloxide complexes alone, Table 3.
Pt-OPh-Me (2b) + Na-OPh-OMe
Mixing time = 16 min

Pt-OPh-Me (2b) + Na-OPh-OMe
Mixing time = 16 min

Figure 7. Phenoxide self exchange, upper spectrum shows products at equilibrium after 16 minutes.
Aryloxide exchange is at least a factor of 1,000 times faster than carbon monoxide insertion. Since aryloxide ligand exchange in these systems is so facile, aryloxide displacement by carbon monoxide is also expected to be rapid, eq. 10. Thus, unless carbon monoxide coordination profoundly affects the rate of aryloxide dissociation, it is difficult to seriously consider aryloxide dissociation as the rate determining step in the carbonylation of 2a-e.

The rate of carbon monoxide insertion is also related to the electronic effects introduced by the *para* substituents of the aryloxides, Table 1. The rate of carbonylation for the more nucleophilic aryloxides is slower than the less nucleophilic aryloxides, Figure 8. These rates also correlate well with Hammett $\sigma$ values, Figure 9.\textsuperscript{27} Clearly, the opposite trend would be observed if nucleophilic addition of the displaced aryloxide, eq. 11, was the rate determining step. The presence of excess aryloxide would also affect the rate if nucleophilic addition to coordinated carbon monoxide were rate determining. This was not observed. These results remove nucleophilic addition of displaced aryloxide to coordinated carbon monoxide, eq. 11, as a reasonable rate determining step. Overall, the facility of aryloxide exchange together with the decreased rates of carbonylation for platinum complexes of more nucleophilic aryloxide ligands

### Table 4. Insertion rates for complexes 2 (a-c), at 100 psi as pure compounds and as exchanging mixtures.

<table>
<thead>
<tr>
<th></th>
<th>$k_{obs} \times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pure Compounds</strong></td>
<td></td>
</tr>
<tr>
<td>[Pt(triphos)(O-C\textsubscript{6}H\textsubscript{4}-Me)][PF\textsubscript{6}] (2b)</td>
<td>1.252</td>
</tr>
<tr>
<td>[Pt(triphos)(O-C\textsubscript{6}H\textsubscript{4}-O-Me)][PF\textsubscript{6}] (2a)</td>
<td>1.031</td>
</tr>
<tr>
<td><strong>Equilibrated mixture</strong></td>
<td></td>
</tr>
<tr>
<td>[Pt(triphos)(O-C\textsubscript{6}H\textsubscript{4}-Me)][PF\textsubscript{6}] (2b)</td>
<td>0.781</td>
</tr>
<tr>
<td>And [Pt(triphos)(O-C\textsubscript{6}H\textsubscript{4}-O-Me)][PF\textsubscript{6}] (2a)</td>
<td>0.840</td>
</tr>
</tbody>
</table>
cannot be reconciled with the carbon monoxide induced aryloxide dissociation mechanism summarized in eq. 9-11.

Figure 8. Dependence of the observed rate aryloxycarbonyl formation on the aryloxide substituent.
The relative stability constants of the aryloxide complexes 2a-c and the electronic influence of p-substituents on the aryloxide ligands both indicate the importance of Pt - O bond breaking in the carbonylation mechanism. When ΔG, calculated from the relative stability constants, is compared to ΔE_a, calculated from relative rates for carbonylation, a linear relationship is found, Figure 10. For example, the ΔG for the [Pt(triphos)(O-Ph-Me)]^+ (2b) / [Pt(triphos)(O-Ph-OMe)]^+ (2a) equilibrium is calculated to be 0.71 kJ/mol and ΔE_a is 0.48 kJ/mol. In the [Pt(triphos)(O-Ph-Me)]^+ (2b) / [Pt(triphos)(O-Ph)]^+ (2c) equilibrium, ΔG is 2.87 kJ/mol and ΔE_a is 1.52 kJ/mol. Finally for the [Pt(triphos)(OPh)]^+ (2c) / [Pt(triphos)(OC_6H_4p-OMe)]^+ (2a) equilibrium ΔG is 3.59 kJ/mol and ΔE_a is 1.99 kJ/mol.

Figure 9. Correlation of the observed rate to Hammett Sigma of the phenoxide substituents.
From this linear free energy relationship it can be seen that differences in Pt - O bond energy, determined from the relative stability constants, contribute to the activation energy for carbonylation. This supports the notion that Pt - O bond breaking is important in the formation of the transition state. This is further supported by the dependence of the observed rates of carbon monoxide insertion on aryloxyde ligand p-substitution. More nucleophilic aryloxyde ligands are slower to carbonylate since a stronger Pt - O bond must be broken. Together these data support our assertion of a classical migratory insertion pathway, eq. 4, for the carbonylation of 2a-e. While little is known of the structure of the transition state involved, we find that approximately half of the difference in Pt - O ground state bond energies is
contributed to the activation energy for carbonylation. We also note that migratory insertion of carbon monoxide only occurs into the Pt - O bond of Pt(dppe)(Me)(OMe), and not the available Pt - C bond.\textsuperscript{20} This preference was attributed to the interaction of the oxygen lone pairs with the carbonyl $\pi^*$ orbital, Figure 11.

![Figure 11. Interaction of the carbonyl $\pi^*$ orbital with the aryloxide oxygen lone pair.](image)

Thus, part of the C - O bond is formed prior to complete Pt - O bond cleavage.\textsuperscript{29} This effect would stabilize the transition state and accelerate the rates for the more nucleophilic aryloxides, a trend opposite to that observed experimentally. In the [Pt(triphos)(O-Ph)]$^+$ system we believe that a transition state model like that shown in Figure 11 is plausible for the carbonylation of aryloxides, but in our system the influence of Pt - O bond breaking relative to C - O bond making dominates.

It is interesting to note that while we arrive at the same mechanistic conclusion as Bryndza, regarding the carbonylation of platinum aryloxide complexes, the two systems have differing exchange conditions. In the Pt(dppe)(OMe)$_2$ system, methoxide exchange is found to be slow with respect to insertion.\textsuperscript{20} In the aryloxide systems, 2a-e, aryloxide exchange is faster than insertion. Yet, in both systems, the mechanism of carbonylation is a classical migratory insertion of the alkyl or aryloxide ligand to coordinated carbon monoxide.
List of References


(24) At the time of writing no accurate solubility data for carbon monoxide in acetonitrile exists in the literature.


(27) A plot of the rate of carbon monoxide insertion versus Hammet Sigma gives a best fit line of $k_{\text{obs}} = 5.16 \text{ s} + 2.20$.
