DOE/PC/93208--T7

Preconversion Catalytic Deoxygenation of Phenolic Functional Groups

DE-FG22-93PC93208

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Quarterly Technical Progress Report* for the period:

April 1, 1995 - June 30, 1995

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Abstract: The complex, [Rh(triphos)CO][PF_6] {triphos = bis(2-diphenylphosphinoethyl)phenyl phosphine}, **4**, has been reacted with a series of aryloxides, ROH {R = C_6H_5, C_6H_4-*p*-CH_3, C_6H_4-*p*-OCH_3}. The resulting aryloxycarbonyl complexes are observable by FTIR spectroscopy. These rhodium aryloxycarbonyl complexes decay to form Rh(triphos)OR, **1-3**, or [Rh(triphos)CO]PF_6, **4**, through the fac- and mer- isomers of Rh(triphos)(CO)OR. These reactions were followed by FT-IR, $^{31}P\{^1H\}$ VT-NMR, under reaction conditions where carbon monoxide both could and could not escape. The conditions under which the carbon monoxide could not escape enabled the observation of [Rh(triphos)$(CO)_2$]PF_6, **5**, by $^{31}P\{^1H\}$ NMR and FT-IR.

Introduction

Transition metal carbonyl complexes exhibit important reactivity central to organometallic chemistry. The activation of coordinated carbonyls to form acyls, hydroxycarbonyls, alkoxycarbonyls, formyls, and carbamoyls has been widely studied due to the importance of these nucleophilic adducts of coordinated carbonyls in catalytic processes, such WGS and hydroformylation.[1,2] The nucleophilic attack of phenoxides on coordinated carbonyls has been studied much less extensively. The phenoxycarbonyl is believed to be the important intermediate in the metal facilitated deoxygenation of phenols with carbon monoxide. Previously, phenoxycarbonyls were generated by reacting metal phenoxides with carbon monoxide.[3-8] Although Atwood and coworkers started with iridium phenoxide, they observed that carbon monoxide completely displaced the phenoxide to outer sphere before the phenoxycarbonyl was formed.[3-6] For this reason, carbonyl complexes and their reactivity with various aryloxides was explored.

Results and Discussion

The previously synthesized[9,10] complex, Rh(triphos)Cl, was used as the starting material for the synthesis of a series of rhodium triphos aryloxides, **1-3**, rhodium triphos carbonyl cation, **4**, and rhodium triphos bis(carbonyl) cation, **5**.

Rh(triphos)Cl, was reacted with excess NaOR {R = C_6H_5, C_6H_4-*p*-CH_3, C_6H_4-*p*-OCH_3} in acetone and stirred overnight. The solvent was removed and the solid was extracted into CH_2Cl_2 and precipitated with hexanes, to produce Rh(triphos)OR {**1**: R = C_6H_5, **2**: R = C_6H_5-*p*-CH_3, **3**: R = C_6H_5-*p*-OCH_3}. Other rhodium phenoxides have been synthesized, including $Rh(PPh_3)_3OPh$,[11] $Rh(PPh_3)_3OPh$-*p*-CH_3,[12] and *trans*-$Rh(PPh_3)_2(CO)OPh$.[13] The $^{31}P\{^1H\}$ NMR data of aryloxide complexes **1-3** are compared to each other and to the literature data of another rhodium trisphosphine phenoxide, Table 1. Notice that the $J(Rh\text{-}P_B)$ decreases from 164 Hz for the chloride complex to the 150 Hz range for the aryloxides, indicating that the Rh-OAr bond is stronger than the Rh-Cl bond. It is expected the the Rh-P_B coupling constant is most sensitive to the species located 180° away from it, since that is the ligand which shares the same orbitals with P_B. The relative trend of the strengths of the Rh-OAr bond should be indicated by Rh-P_B coupling constants, yet due to the closeness of these values in this series of phenoxides, no trend can be observed. The best nucleophile, *para*-methoxy-phenoxide, would be expected to have the strongest Rh-OAr bond, and the weakest Rh-P_B coupling.

Table 1. $^{31}P\{^1H\}$ NMR data of Rhodium Tris(phosphine) Aryloxides.

Compound	δP_A	δP_B	$J(Rh\text{-}P_A)$	$J(Rh\text{-}P_B)$	$J(P_A\text{-}P_B)$	Reference
16	39.2	110.4	153	149	33.1	
17	39.6	110.6	154	150	33.0	
18	39.5	110.4	153	148	32.0	
Rh(ttp)OPh *	3.31	18.04	137	147	54.0	14

* ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$

$[Rh(triphos)(CO)_2]^+$ is formed whenever a solution of Rh(triphos)Cl or Rh(triphos)OR {**1**: R = C_6H_5, **2**: R = C_6H_5-*p*-CH_3, **3** R = C_6H_5-*p*-OCH_3}, is placed under 1 atm of CO. The infrared spectra in THF shows two terminal carbonyl bands at 2050, 2008 cm^{-1} in THF. These infrared bands agree well with $[Rh(triphos)(CO)_2][PF_6]$, synthesized later, and with literature values of rhodium bis(carbonyl) complexes, Table 4. The $^{31}P\{^1H\}$ NMR spectra shows an A_2BX spin system ($\delta(P_A)$ = 64.4 ppm, $\delta(P_B)$ = 104.6 ppm) with $^2J(P_AP_B)$ = 22.8 Hz, $^1J(RhP_A)$ = 124 Hz, $^1J(RhP_B)$ = 90.1 Hz.

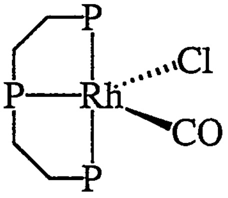
Rh(triphos)Cl was reacted with $AgPF_6$ in acetone to remove the chloride ligand, generating an acetone solvento complex. The flask was evacuated and then filled with carbon monoxide. The solution is stirred for one hour under CO, then precipitated with diethyl ether to yield [Rh(triphos)(CO)][PF_6], **4**. The ^1H NMR shows four multiplets for the triphos methylene protons at 2.23, 2.91, 3.15, 3.31 ppm and the phenyl protons in the 7.41 - 7.80 ppm region. The $^{31}P\{^1H\}$ NMR shows an A_2BX spin system ($\delta(P_A) = 55.6$ ppm, $\delta(P_B) = 104.7$ ppm) with $^2J(P_AP_B) = 28.2$ Hz, $^1J(RhP_A) = 128$ Hz, and $^1J(RhP_B) = 115$ Hz and $\delta(PF_6) = -144$ ppm. The related rhodium triphosphine carbonyl complex, [Rh{$PhP(CH_2CH_2CH_2PPh_2)_2$}(CO)][PF_6], was synthesized by Meek and coworkers.[15,16] The $^1J(RhP_B)$ value of 115.2 Hz for their complex agrees remarkably well with complex **4**. The infrared spectra shows one terminal carbonyl band at 2021 cm^{-1} in THF and 2026 cm^{-1} in KBr. PDMS shows a peak at *m/z* 637.3 corresponding to the loss of the carbonyl ligand in the gas phase. Other rhodium tris(phosphine) carbonyl complexes have been synthesized, see Table 2 for comparison of their IR data with **4**. Notice that the agreement of the $\upsilon(CO)$ bands is best for square planar cationic complexes with three phosphine ligands.

Table 2. IR Data of Rhodium Tris(phosphine) Mono(carbonyl) Complexes.

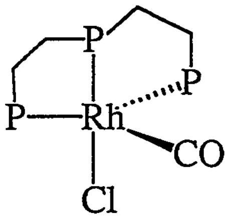
Compound	$\upsilon(CO)$, cm^{-1}	Solvent	Reference
4	2026	KBr	
Rh(ttp)(CO)Cl*	1956	Nujol	17
[Rh(ttp)(CO)][PF_6]*	2026	CH_2Cl_2	17
Rh(T)(CO)Cl†	1920	KBr	18
[Rh(PPh_3)$_3$(CO)][ClO_4]	2029	CH_2Cl_2	19
[Rh($PMePh_2$)$_3$(CO)][ClO_4]	2023	CH_2Cl_2	19

* ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$ † T = $CH_3C(CH_2PPh_2)_3$

Complex 4 was originally synthesized using NaPF$_6$ instead of AgPF$_6$. When silver was not used to efficiently remove the chloride, Rh(triphos)(CO)Cl was observed as an impurity in the [Rh(triphos)(CO)][PF$_6$], 4. Rh(triphos)(CO)Cl has two terminal carbonyl bands, υ(CO) = 2064, 1984 cm^{-1}, corresponding to the two possible isomers, facial and meridional, shown below.



mer



fac

The data in Table 2 show that the facial isomer of Rh(triphos)(CO)Cl has the lower energy terminal carbonyl band by comparison to the energy of the band of Rh(T)(CO)Cl {T = $CH_3C(CH_2PPh_2)_3$}, υ(CO) = 1920 cm^{-1}. Due to the steric constraints of the ligand T, the facial isomer is the only possible isomer of this complex. Rh(ttp)(CO)Cl is also in the facial arrangement as the chloride is located in the best sigma donating axial position. The three phosphines of ttp can be rearranged easily because of the three carbon spacer. The triphos ligand with the two carbon spacer does not exhibit the same ease of rearrangement. The meridional isomer of Rh(triphos)(CO)Cl would be expected to have a higher energy terminal carbonyl band, since the chloride is located in the equitorial position and it is not able to sigma donate as effectively. When the chloride doesn't sigma donate well, there is less electron density on the rhodium to backbond to the carbonyl, giving rise to the higher energy of the carbonyl band of *mer*-Rh(triphos)(CO)Cl. The *fac*- and *mer*-isomers of iridium triphos complexes have been previously observed.[20] PDMS of samples of 4 that contain Rh(triphos)(CO)Cl as an impurity show *m*/*z* 672.5, corresponding to Rh(triphos)Cl, as well as *m*/*z* 637.3, while pure samples of 4 show only the carbonyl loss peak at *m/z* 637.3. The appearance of the *m/z* of Rh(triphos)Cl indicates that there is chloride present, consistant with the inefficient removal of the chloride ligand using $NaPF_6$.

The ^{13}C-labeled version (**4***) of complex **4** was synthesized identically to **4**, only substituting the ^{13}C-labeled carbon monoxide. The $^{13}C\{^1H\}$ NMR spectra shows an AM_2BNX spin system ($\delta(C_AO) = 192.5$ ppm) with $^1J(RhC_A) = 83$ Hz, $^2J(C_AP_M) < 2$ Hz, $^2J(C_AP_N) = 87$ Hz. The $^{31}P\{^1H\}$ NMR spectra shows an A_2BMX spin system ($\delta(P_A) = 55.2$ ppm, $\delta(P_B) = 104.7$ ppm) with $^2J(P_AP_B) = 27.9$ Hz, $^2J(P_AC_M) < 2$ Hz, $^2J(P_BC_M) = 87$ Hz, $^1J(RhP_A) = 128$ Hz, and $^1J(RhP_B) = 114$ Hz. The large coupling constant between ^{13}CO (C_M) and P_B indicates a 180° arrangement of these ligands around the rhodium. The ^{13}CO to P_A coupling constant is very small indicating an approximate 90° arrangement. The infrared spectra shows the terminal carbonyl band at 1979 cm^{-1}. The Hook's Law prediction for this carbonyl band of **4***, considering $\upsilon(CO) = 2026$ cm^{-1} for **4**, is 1980 cm^{-1}.

$[Rh(triphos)(CO)][PF_6]$, **4**, was dissolved in THF and NaOPh was added as a solution in THF in 0.5 eq increments and monitored by infrared spectroscopy. Figure 1 shows a series of these IR spectra taken over time with increasing amounts of NaOPh. Notice that only moments after addition of NaOPh, the phenoxycarbonyl is observed at $\upsilon(CO) = 1709$ cm^{-1} (Figure 1 b), but after waiting 0.5 hr, this band has disappeared and the band for **4** at $\upsilon(CO) = 2021$ cm^{-1} has almost completely returned (Figure 1 c). The phenoxycarbonyl band reappears with additional NaOPh (Figure 1 d). The fact that the phenoxycarbonyl appears and then later disappears means that it is formed and decays by separate pathways. The proposed pathway for this reactivity is shown in Figure 4 and involves the initial formation of the phenoxycarbonyl, **A**, by direct nucleophilic attack of the phenoxide on the coordinated carbonyl. The decay can then occur because this square planar phenoxycarbonyl, **A**, can rearrange to a 5-coordinate phenoxide carbonyl complex, **B**. There are two isomers of **B**, because of the hindered movement of the connected phosphines. The *fac*-**B** is observed at 2005 cm^{-1} while *mer*-**B** is observed at 2058 cm^{-1}. These isomers are assigned with the same logic used to assign the isomers of the chloride version of this compound, discussed previously. Either isomer of **B** can lose a carbonyl ligand to form Rh(triphos)OPh, **1**, or revert to the starting material, **4**, by allowing the phenoxide to move to outer sphere. Attempts to isolate the phenoxycarbonyl, Rh(triphos)C(O)OPh, **A**, observed in the IR spectra at 1709 cm^{-1}, resulted only in [Rh(triphos)CO]PF_6, **4**, and Rh(triphos)OPh, **1**, by $^{31}P\{^1H\}$ NMR spectroscopy. These are the expected decay products from the 5-coordinate isomers of **B**. A similar reaction was repeated in an IR cell that is very gas-tight. The phenoxycarbonyl, **A**, was observed at 1702 cm^{-1} and the carbonyl phenoxycarbonyl complex, **C**, was observed at 1926, 1699 cm^{-1}. This formation of **C** is probably a result of the inability of carbon monoxide to escape from the cell after the 5-coordinate species, **B**, decays to Rh(triphos)OPh, **1**.

[Rh(triphos)(CO)][PF_6], **4**, was dissolved in THF and NaOPh-*p*-Me was added as a solution in THF in 0.5 eq increments and monitored by infrared spectroscopy. Figure 2 shows a series of these IR spectra taken over time with increasing amounts of NaOPh-*p*-Me. The carbonyl band at 1703 cm^{-1}, corresponding to the aryloxycarbonyl, Rh(triphos)C(O)OPh-*p*-Me, grows with addition of NaOPh-*p*-Me (Figure 2 b) and does not decay after waiting (Figure 2 c). This behavior differs from that of the phenyl version. It may be because the *para*-methyl group makes this aryloxide a stronger nucleophile. Despite the stronger nucleophilicity of the *para*-methyl phenoxide, the 5-coordinate carbonyl aryloxide complexes, ***fac*-B** and ***mer*-B**, are still observed at 2004 and 2057 cm^{-1}. Variable temperature $^{31}P\{^1H\}$ NMR spectroscopy was utilized to observe the reaction of **4** with NaOPh-*p*-Me at -80 °C. The species observed at -80 °C are small amounts of [Rh(triphos)$(CO)_2$]$^+$ and Rh(triphos)OPh-*p*-Me, **2**, and mostly [Rh(triphos)(CO)][PF_6], **4**. The only coalescence occurs between [Rh(triphos)$(CO)_2$]$^+$ and **4** at 0 °C. Complex **4** was the only species observed at 30 °C, although the remaining complex **2** may be buried in the noise. When a separate solution was prepared and heated to 50 °C, **2** and **4** were observed by $^{31}P\{^1H\}$ NMR spectroscopy. The 5-coordinate isomers of **B**, Figure 4, can be employed in the decay of the aryloxycarbonyl, once the solution is disturbed by isolation.

Although it was encouraging that a stronger nucleophile more persistantly formed the aryloxycarbonyl, its decay upon isolation caused us to strive for an even stronger nucleophile.

[Rh(triphos)(CO)][PF_6], **4**, was dissolved in THF and NaOPh-*p*-OMe was added as a solution in THF in 0.5 equivalent increments and monitored by infrared spectroscopy. Figure 3 shows a series of these IR spectra taken over time with increasing NaOPh-*p*-OMe. The aryloxycarbonyl, Rh(triphos)C(O)(OPh-*p*-OMe), **A**, was observed in the IR spectra at 1700 cm^{-1} (Figure 3 c). There was only one isomer of the 5-coordinate, ***fac*-B**, observed in the IR at 2002 cm^{-1}. The lack of observation of the meridional isomer of **B** is understandable as the para-methoxy group makes this aryloxide a good nucleophile and the most favorable position for sigma donation is in the axial position, as in ***fac*-B**, Figure 4.

The inability to isolate the rhodium aryloxycarbonyl complexes can be explained in the scheme in Figure 4. Upon isolation, the aryloxycarbonyl complexes, **A**, can lose a carbonyl ligand through the *fac*- or *mer*- isomers of the 5-coordinate complex, Rh(triphos)(CO)OR, **B**, to form either Rh(triphos)OR or **4**. For a comparison of the IR data for the series of different aryl groups {R = C_6H_5, C_6H_4-*p*-CH_3, C_6H_4-*p*-OCH_3} and other complexes from literature, see Table 3. Cobalt, iridium, and platinum aryloxycarbonyls exhibit IR bands in the 1675 - 1715 cm^{-1} region.

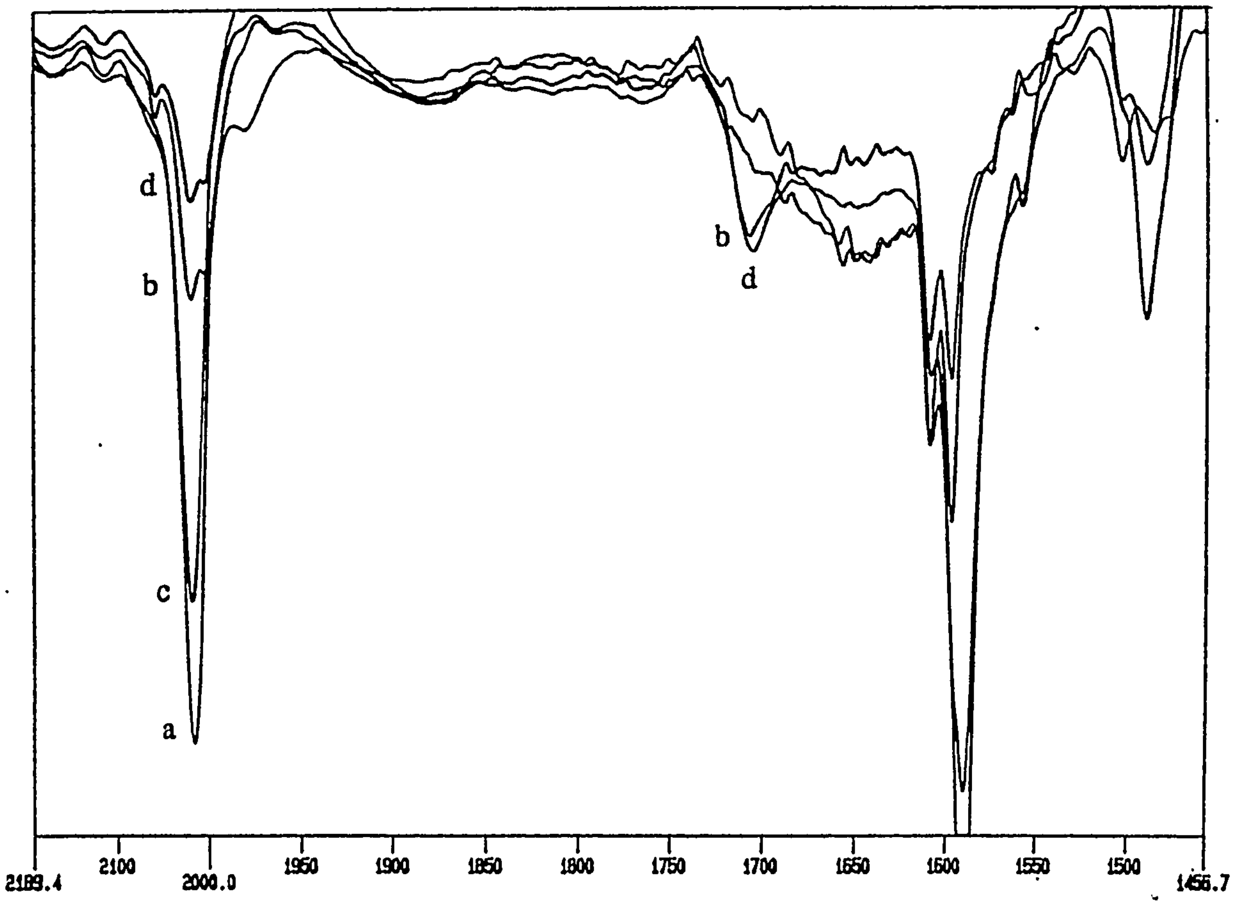


Figure 1. IR (THF) of the Reaction of 4 with NaOPh: a) 4 only, b) 0.5 eq of NaOPh, c) waited 0.5 hr, d) 1.0 eq of NaOPh.

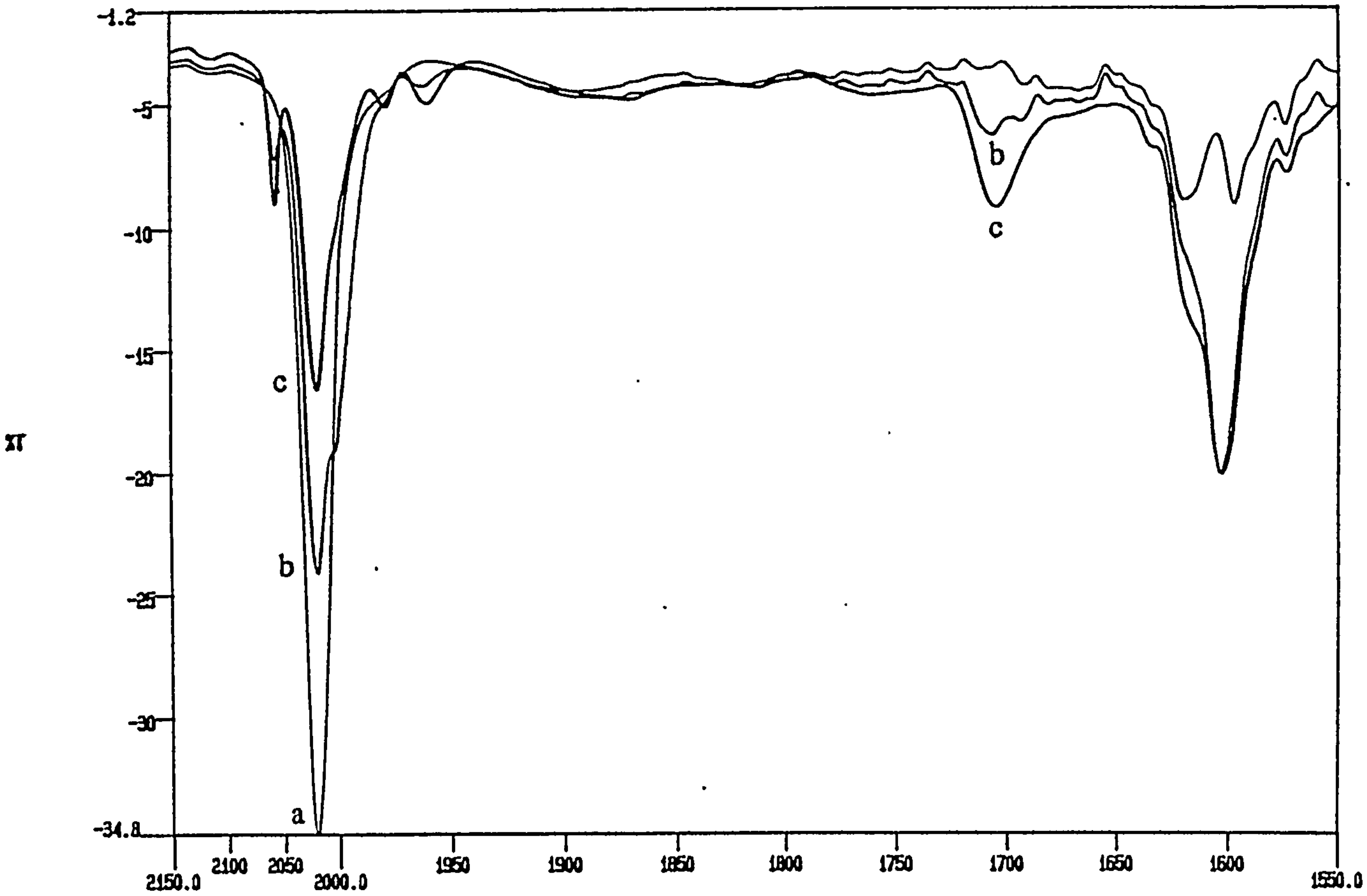


Figure 2. IR (THF) of the Reaction of 4 with NaOPh-*p*-Me: a) 4 only, b) 1.0 eq of NaOPh-*p*-Me, c) waited 0.5 hr.

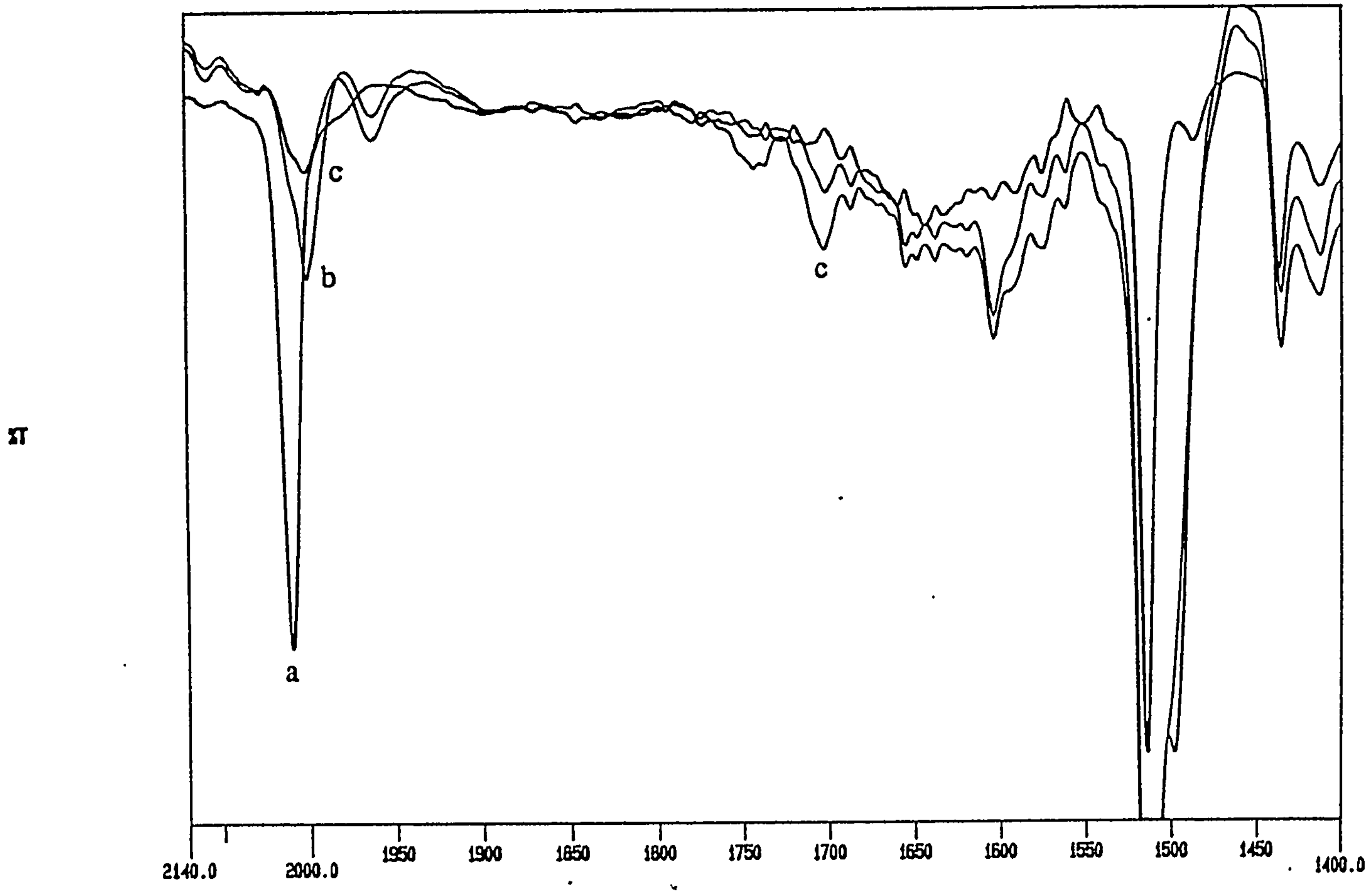


Figure 3. IR (THF) of the Reaction of 4 with NaOPh-*p*-OMe: a) 4 only, b) 3.0 eq of NaOPh-*p*-OMe, c) waited 0.5 hr.

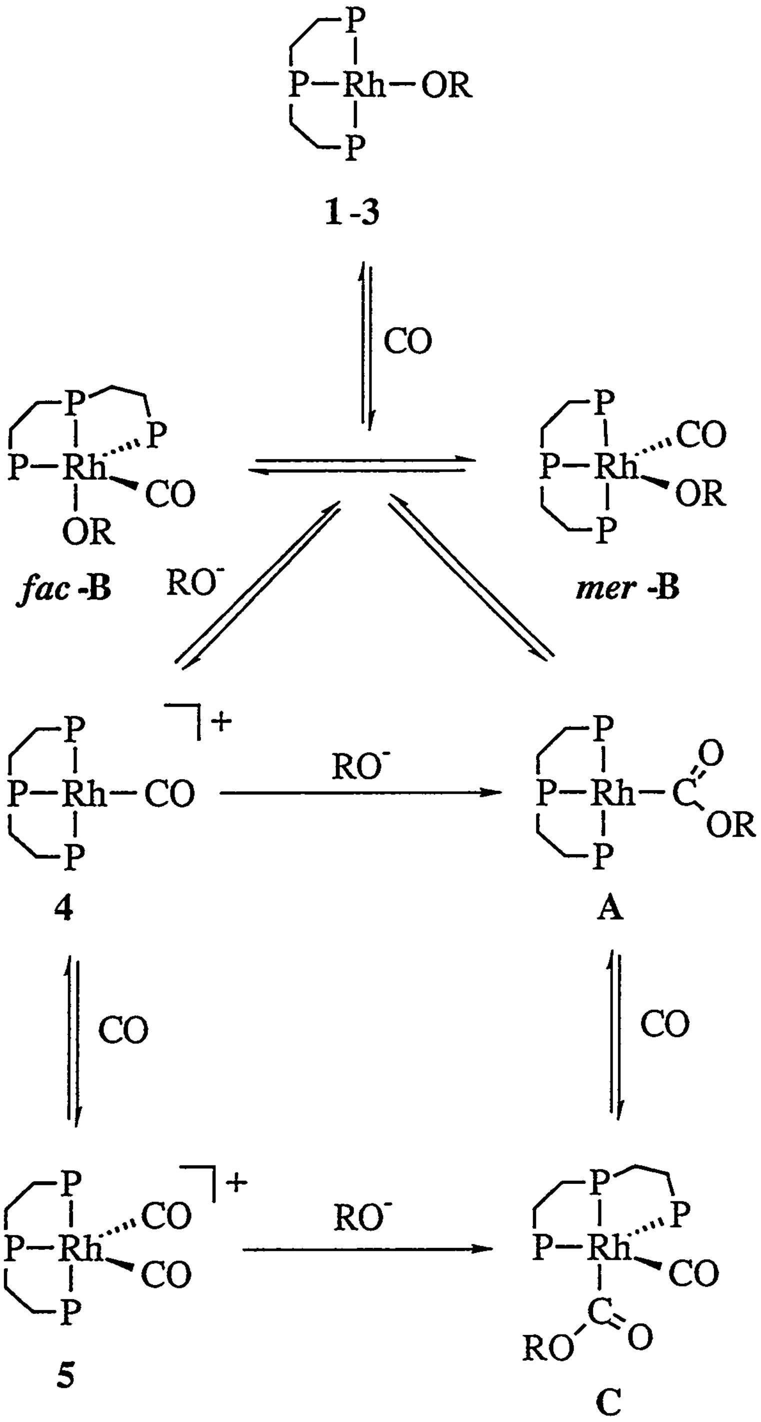


Figure 4. Proposed Scheme for the Reactivity of **4** with NaOR.

Table 3. IR Data from the Reactions of 4 with NaOR and Literature.

Compound	υ(CO), cm^{-1}	Solvent	Reference
fac-Rh(triphos)(CO)OPh	2005	THF	
mer-Rh(triphos)(CO)OPh	2058	THF	
fac-Rh(triphos)(CO)OPh-*p*-Me	2004	THF	
mer-Rh(triphos)(CO)OPh-*p*-Me	2057	THF	
fac-Rh(triphos)(CO)OPh-*p*-OMe	2002	THF	
Rh(triphos)(C(O)OPh)	1709	THF	
Rh(triphos)(C(O)OPh-*p*-Me)	1703	THF	
Rh(triphos)(C(O)OPh-*p*-OMe)	1700	THF	
$Ir(PPh_3)_2(CO)_2(C(O)OPh)$	1985, 1938, 1675	KBr	4
$RhH(N(CH_2CH_2PPh_2)_3(C(O)OEt)$	1715	Nujol	21
[Pt(triphos)(C(O)OPh-*p*-Me)][PF_6]	1677	KBr	8
$Co(CO)_4(C(O)OPh)$	2121, 2060, 2047, 2034, 1693	n-heptane	22
$Co(CO)_4$(C(O)OPh-*p*-OMe)	2121, 2059, 2045, 2032, 1689	n-heptane	22
$Co(CO)_4$(C(O)OPh-*p*-^{t}Bu)	2117, 2054, 2042, 2028, 1703	n-heptane	22
$Co(CO)_3(PPh_3)(C(O)OPh)$	2064, 2080, 1987, 1684	n-heptane	22
$Co(CO)_3(PPh_3)$(C(O)OPh-*p*-OMe)	2063, 1997, 1985, 1688	n-heptane	22
$Co(CO)_3(PPh_3)$(C(O)OPh-*p*-^{t}Bu)	2063, 1997, 1986, 1684	n-heptane	22

[Rh(triphos)(^{13}CO)][PF$_6$], **4***, and NaOPh were dissolved in 1 mL CD$_2$Cl$_2$ and 0.2 mL THF. This experiment was undertaken in an effort to prove that the ^{31}P{^{1}H} NMR spectra of Rh(triphos)(C(O)OPh) was different from Rh(triphos)OPh, **1**. By ^{13}C-labeling the aryloxycarbonyl, there would be proof of which species was present by the observation or lack of observation of the P$_B$-^{13}C coupling constant. The reaction of **4*** with NaOPh was monitored by ^{31}P{^{1}H} NMR spectroscopy, showing the formation of Rh(triphos)OPh, **1**, as well as remaining **4***. The ^{31}P{^{1}H} NMR spectra shows complex **4*** in 75% as an A$_2$BMX spin system ($\delta(P_A) = 55.4$ ppm, $\delta(P_B) = 105.0$ ppm) with $^2J(P_AP_B) = 28.4$ Hz, $^2J(P_BC_M) = 84$ Hz, $^1J(RhP_A) = 128$ Hz, $^1J(RhP_B) = 118$ Hz and complex **1** in 25% as an A$_2$BX spin system ($\delta(P_A) = 39.3$ ppm, $\delta(P_B) = 110.5$ ppm) with $^2J(P_AP_B) = 33$ Hz, $^1J(RhP_A) = 153$ Hz, $^1J(RhP_B) = 149$ Hz. Notice that there was no ^{13}C coupling to the trans phosphine, P$_B$, as would be expected if Rh(triphos)(^{13}C(O)OPh) was the species observed instead of **1**. This sample was then isolated by precipitation with hexanes. The IR spectra in KBr shows υ(CO) = 1974, 1931 cm^{-1} and υ(C-C) = 1587, 1552 cm^{-1}. The band at 1974 cm^{-1} is **4***, while the bands at 1931, 1587, 1552 cm^{-1} may correspond to Rh(triphos)(^{13}CO)OPh.

Since the aryloxycarbonyl complexes, A in Figure 4, were decaying through the 5-coordinate isomers of **B**, starting from a 5-coordinate complex could avoid this decay pathway and enable the isolation of the aryloxycarbonyl complex. The most logical extra ligand to employ was another carbonyl. The addition of another carbonyl also served the purpose of increasing the electrophilicity of each carbonyl carbon, because the electron density back bonded into the carbonyls is decreased by being shared among two carbonyls.

[Rh(triphos)(CO)][PF$_6$], **4**, was dissolved in THF and carbon monoxide was bubbled through the solution, yielding [Rh(triphos)(CO)$_2$][PF$_6$], **5**. Attempts to isolate this bis(carbonyl) complex, **5**, result in the mono(carbonyl), **4**. The IR spectra in THF shows two terminal carbonyl bands, 2050, 2001 cm^{-1}. The ^{31}P{^{1}H} NMR spectra shows an A$_2$BX spin system ($\delta(P_A) = 64.0$ ppm, $\delta(P_B) = 104.9$ ppm) with $^1J(RhP_A) = 124$ Hz, $^1J(RhP_B) = 92$ Hz,

$^2J(P_AP_B) = 23$ Hz. There are other examples of rhodium tris(phosphine) bis(carbonyl) complexes. For comparison of their IR data with **5**, see Table 4.

Table 4. IR Data of Rhodium Tris(phosphine) Bis(carbonyl) Complexes.

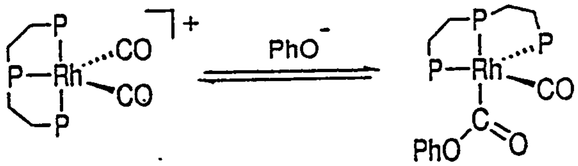
Compound	υ(CO), cm^{-1}	Solvent	Reference
5	2050, 2001	THF	
$[Rh(ttp)(CO)_2][PF_6]$*	2040, 1960	Nujol	17
$[Rh(T)(CO)_2][PF_6]$†	2060, 1980	KBr	18
$[Rh(PPh_3)_3(CO)_2][ClO_4]$	2048, 1987	CH_2Cl_2	19
$[Rh(PMePh_2)_3(CO)_2][ClO_4]$	2027, 1980	CH_2Cl_2	19

* ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$ † T = $CH_3C(CH_2PPh_2)_3$

$[Rh(triphos)(CO)][PF_6]$, **4**, was dissolved in THF and 1 atm of carbon monoxide was added to the solution to generate the bis(carbonyl), **5**. Next, a THF solution of NaOPh was added in increments of 0.5 equivalent at a time and monitored by infrared spectroscopy. The bis(carbonyl), **5**, bands at 2051, 2006 cm^{-1} disappear with addition of NaOPh, while new bands at 1926 and 1699 cm^{-1} grow in, shown in Figure 5. These new bands corresponding to the facial triphos isomer of Rh(triphos)(CO)(C(O)OPh), **C** in Figure 4. The meridional isomer of **C** is not observed, as the phenoxycarbonyl ligand is a much better nucleophile than any phenoxide and, therefore, must be in the axial positon, as it is in the facial isomer, **C**. Also notice that the phenoxycarbonyl is persistantly formed now that there two carbonyl ligands initially, consistant with the increased electrophilicity of the carbonyls. Attempts to isolate the aryloxycarbonyl were made, resulting only in $[Rh(triphos)CO]PF_6$, **4**, and Rh(triphos)OPh, **1**, from the loss of a carbonyl ligand and then decay through the 5-coordinate, **B**, shown in Figure 4.

$[Rh(triphos)(CO)][PF_6]$, **4**, was dissolved in THF and 1 eq of carbon monoxide was syringed into the solution to generate the bis(carbonyl), **5**, observable by IR, $\upsilon(CO) = 2051$, $2009\ cm^{-1}$. Next, a THF solution of NaOPh-*p*-OMe was added in increments of 0.5 equivalent at a time and the reaction was monitored by infrared spectroscopy with samples that were transferred via a syringe to a one piece infrared cell ($b = 8x10^{-3}$ mm), which was not gas-tight. After 1.5 eq NaOPh-*p*-OMe were added, the IR spectra shows $\upsilon(CO) = 2052, 2018, 1978, 1705\ cm^{-1}$ and $\upsilon(C\text{-}C) = 1600, 1513\ cm^{-1}$. The reaction appeared to have experienced a loss of carbonyl as some of the mono(carbonyl) species is observed at $2018\ cm^{-1}$ as well as the square planar aryloxycarbonyl complex at $1705\ cm^{-1}$.

Heating both of these reactions to 85 °C caused the disappearance of the aryloxycarbonyl bands and the appearance of new bands in the 1992 - 1995 and 1933 - 1927 cm^{-1} regions. The structure of these species remains elusive, but may be the *fac*- and *mer*-isomers of Rh(triphos)(CO)R. In order to have a terminal carbonyl band as low in energy as $1930\ cm^{-1}$, the other ligand on the rhodium must be very nucleophilic. Hydride is a very nucleophilic ligand and the terminal carbonyl band of $Rh(PPh_3)_3(CO)H$ is reported at $1926\ cm^{-1}$, while the Rh-H stretch is reported at $2004\ cm^{-1}$.[23]



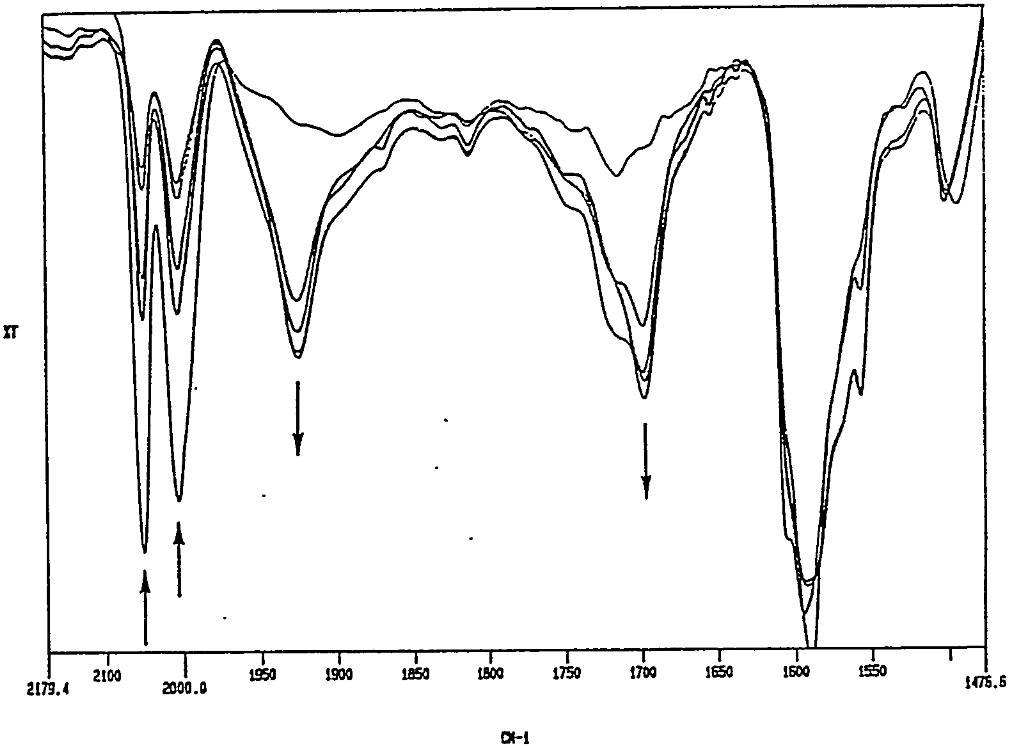


Figure 4. IR (THF) of the Reaction of **5** with NaOPh: a) **5** only, b) 1.0 eq of NaOPh, c) wait 0.5 hr, d) 1.0 eq of NaOPh more, e) wait 1.0 hr.

The rhodium complexes, Rh(triphos)Cl or **4**, were utilized to investigate phenol or alcohol catalytic deoxygenation under 1 atm of carbon monoxide. Numerous reactions were undertaken with alcohols (MeOH, EtOH) or phenols (PhOH, *p*-Me-PhOH, *p*-MeO-PhOH), bases (alkoxide, aryloxide, or Proton-Sponge), carbon monoxide and catalytic amounts of Rh(triphos)Cl or **4**. None of these reactions produced more than a fraction of an equivalent of CO_2. $[Rh(triphos)(CO)_2]^+$ was observed as the only species present by $^{31}P\{^1H\}$ NMR spectroscopy, during many of these reactions.

There are numerous reasons why complexes Rh(triphos)Cl and **4**. do not behave as catalysts for the deoxygenation of phenols and alcohols with carbon monoxide. This may be explained if the outer sphere nucleophilic attack on coordinated carbonyl is important. Most of these reactions didn't involve high enough concentrations of nucleophiles. Although when an extremely high concentration of nucleophile is used in a reaction of **4** with CO, NaOPh-*p*-OMe, and PhOH, the solubility becomes a problem as the rhodium complex precipitates out of solution. This product shows one terminal carbonyl band in the IR in KBr at 1939 cm^{-1} and an A_2BX spin system ($\delta(P_A) = 65.6$ ppm, $\delta(P_B) = 101.5$ ppm) with $^2J(P_AP_B) = 24.4$ Hz, $^1J(RhP_A) = 146$ Hz, $^1J(RhP_B) = 98$ Hz in the $^{31}P\{^1H\}$ NMR. This product is not $[Rh(triphos)(CO)_2]^+$ because the coupling constants are different, particularly $^1J(RhP_A)$ has increased from 124 to 146 Hz and $^1J(RhP_B)$ has increased from 90 to 98 Hz. The increase in the coupling constants indicates a neutral complex, while the low Rh-P_B coupling constant indicates that the complex is not square planar. This observed reactivity is the same as when reactions of **4** are monitored by IR to observe **5**, and the carbonyl aryloxycarbonyl complexes, **C**, Figure 4, are heated. This species formed is probably the facial isomer of Rh(triphos)(CO)R.

Complex **4**, $[Rh(triphos)CO][PF_6]$, can be nucleophilically attacked by aryloxides to form aryloxycarbonyl complexes. These aryloxycarbonyl complexes can not be isolated as they decay through a 5-coordinate carbonyl aryloxide species to form rhodium triphos aryloxide complexes and **4**. Starting with the 5-coordinate complex, **5**, the carbonyl aryloxycarbonyl complexes can be formed. The formation of the aryloxycarbonyl complexes results from the nucleophilic attack of the aryloxides on the coordinated carbonyl. .

Experimental Section

General Procedures: All reactions and manipulations were carried out under nitrogen using standard Schlenk and dry box techniques. Solvents were degassed and purified by distillation under nitrogen from the appropriate drying agents (sodium/benzophenone for THF, sodium for toluene, and CaH_2 for CH_2Cl_2 and hexanes). Triphos {bis(2-diphenylphosphinoethyl) phenylphosphine} was purchased from Aldrich Chemical Company and used as received. The complex Rh(triphos)Cl was synthesized according to the published literature procedure.[9,10,24] Carbon monoxide (99.5%) was purchased from Matheson Gas Company. NaOR {R = C_6H_5, C_6H_4-*p*-CH_3, C_6H_4-*p*-OCH_3} was prepared from ROH and NaH in THF and precipitated with hexanes. ^1H NMR spectra were recorded on Gemini 200, Varian XL-200, and QE-300 spectrometers with chemical shifts reported in ppm referenced to internal $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra were recorded on QE-300 and Varian XL-200 spectrometers at 121.4 MHz and 81.0 MHz, respectively, with chemical shifts reported in ppm referenced to external H_3PO_4. Headspace GC data were collected on a Carle Analytical Gas Chromatograph Series S with a Thermal Conductivity detector. Plasma desorption mass spectroscopy (PDMS) spectra were collected on an Applied Biosystems Bio-Ion 20R instrument. Fast atom bombardment (FAB) mass spectroscopy spectra were collected on Kratos MS25 or MS50 instruments. Infrared Spectra were recorded on Perkin Elmer 1710 and Mattson Galaxy Infrared Fourier Transform Spectrometers. Elemental analysis were performed by Dr. H.D. Lee of this department.

Preparation of Rh(triphos)OR, 1-3. Rh(triphos)Cl,[9,10] was reacted with excess NaOR {R = C_6H_5, C_6H_4-*p*-CH_3, C_6H_4-*p*-OCH_3} in acetone and stirred overnight. The solvent was removed and the solid was extracted into CH_2Cl_2 and precipitated with hexanes, to produce Rh(triphos)OR {**1**: R = C_6H_5, **2**: R = C_6H_5-*p*-CH_3, **3** R = C_6H_5-*p*-OCH_3}. Typical yields were near 70% with the major impurity being Rh(triphos)Cl. **1**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): A_2BX, $\delta(P_A) = 39.2$ ppm, $\delta(P_B) = 110.4$ ppm, $^2J(P_AP_B) = 33.1$ Hz, $^1J(RhP_A) = 153$ Hz, $^1J(RhP_B) = 149$ Hz. **2**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): A_2BX, $\delta(P_A) = 39.6$ ppm, $\delta(P_B) = 110.6$ ppm, $^2J(P_AP_B) = 33.0$ Hz, $^1J(RhP_A) = 154$ Hz, $^1J(RhP_B) = 150$ Hz. **3**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): A_2BX, $\delta(P_A) = 39.5$ ppm, $\delta(P_B) = 110.4$ ppm, $^2J(P_AP_B) = 32.0$ Hz, $^1J(RhP_A) = 153$ Hz, $^1J(RhP_B) = 148$ Hz.

Reactions with CO. $[Rh(triphos)(CO)_2]^+$ is formed whenever a solution of Rh(triphos)Cl or Rh(triphos)OR {**1**: R = C_6H_5, **2**: R = C_6H_5-*p*-CH_3, **3** R = C_6H_5-*p*-OCH_3} is placed under 1 atm of CO. Yield (by NMR) = 100%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): A_2BX, $\delta(P_A) = 64.4$ ppm, $\delta(P_B) = 104.6$ ppm, $^2J(P_AP_B) = 22.8$ Hz, $^1J(RhP_A) = 124$ Hz, $^1J(RhP_B) = 90.1$ Hz. IR (THF): $\upsilon(CO) = 2050, 2008$ cm^{-1}.

Preparation of [Rh(triphos)(CO)][PF$_6$], 4. Rh(triphos)Cl (0.156 g, 0.23 mmol) was reacted with $AgPF_6$ (0.058 g, 0.23 mmol) in 15 mL acetone. The AgCl was filtered off, leaving a solution of the acetone solvento complex. The flask was evacuated, then filled 1 atm carbon monoxide and the solution was stirred for 1 hour. Diethyl ether (10 mL) was used to precipitate 0.16 g of [Rh(triphos)(CO)][PF$_6$], **4**. Yield = 86%. ^1H NMR (CD_2Cl_2): $\delta(CH_2) = 2.23$ ppm (m, 2H), $\delta(CH_2) = 2.91$ ppm (m, 2H), $\delta(CH_2) = 3.15$ ppm (m, 2H), $\delta(CH_2) = 3.31$ ppm (m, 2H), $\delta(Ph) = 7.41 - 7.80$ ppm (m, 25H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): A_2BX, $\delta(P_A) = 55.6$ ppm, $\delta(P_B) = 104.7$ ppm, $\delta(PF_6) = -144$ ppm, $^2J(P_AP_B) = 28.2$ Hz, $^1J(RhP_A) = 128$ Hz, $^1J(RhP_B) = 115$ Hz. IR (KBr): $\upsilon(CO) = 2026$ cm^{-1}. IR (THF): $\upsilon(CO) = 2021$ cm^{-1}. PDMS: *m/z* 637.3 (loss of CO). Anal Calcd for $C_{35}H_{33}F_6RhOP_4$: C, 51.85; H, 4.11. Found: C, 51.54; H, 4.06.

Preparation of [Rh(triphos)(^{13}CO)][PF$_6$], 4*. Rh(triphos)Cl (0.23 g, 0.34 mmol) was reacted with $AgPF_6$ (0.089 g, 0.32 mmol) in 20 mL acetone to remove the chloride ligand as AgCl, generating an acetone solvento complex. The flask was evacuated, then filled 1 atm ^{13}C-labeled carbon monoxide and the solution was stirred for 1 hour. Diethyl ether (15 mL) was used to precipitate 0.24 g of [Rh(triphos)(^{13}CO)][PF$_6$], 4*. Yield = 87%. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): AM$_2$NX, δ(C$_A$≡O) = 192.5 ppm, ^1J(RhC$_A$) = 83 Hz, ^2J(C$_A$P$_N$) = 87 Hz, ^2J(C$_A$P$_M$) > 2 Hz. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): A$_2$BMX, δ(P$_A$) = 55.2 ppm, δ(P$_B$) = 104.7 ppm, ^2J(P$_A$P$_B$) = 27.9 Hz, ^2J(P$_A$C$_M$) < 2 Hz, ^2J(P$_B$C$_M$) = 87 Hz, ^1J(RhP$_A$) = 128 Hz, ^1J(RhP$_B$) = 114 Hz. IR (KBr): υ(CO) = 1979 cm^{-1}.

Reactions of 4 with NaOR {R = C_6H_5, C_6H_5-*p*-CH_3, C_6H_5-*p*-OCH_3}.

[Rh(triphos)(CO)][PF$_6$], 4, (0.047 g, 0.058 mmol) was dissolved in 2.5 mL THF and NaOPh was added in 0.5 eq increments in THF to a 5 mL reaction flask with a septa. After each addition of NaOPh, a sample was transferred via a syringe to an infrared cell (b = 8x10^{-3} mm), which is not gas-tight. IR (THF): After 0.5 eq NaOPh was added, υ(CO) = 2058, 2020, 2005, 1709 cm^{-1} and υ(C-C) = 1589, 1497 cm^{-1}; After 0.5 eq of waiting, υ(CO) = 2020 cm^{-1}; After 0.5 eq more NaOPh was added, υ(CO) = 2058, 2020, 2005, 1710 cm^{-1} and υ(C-C) = 1590, 1500 cm^{-1}; After 0.5 hr of waiting, υ(CO) = 2020 cm^{-1}; This oscillation can be repeated several times until the υ(C-C) bands grow large enough to make the υ(CO) bands difficult to see in the noise. ^{31}P{^{1}H} NMR (THF/CD$_2$Cl$_2$): (4) 60% A$_2$BX, δ(P$_A$) = 55.4 ppm, δ(P$_B$) = 105.3 ppm, ^2J(P$_A$P$_B$) = 27.8 Hz, ^1J(RhP$_A$) = 128 Hz, ^1J(RhP$_B$) = 112 Hz; (1) 40% A$_2$BX, δ(P$_A$) = 39.4 ppm, δ(P$_B$) = 110.5 ppm, ^2J(P$_A$P$_B$) = 30.5 Hz, ^1J(RhP$_A$) = 152 Hz, ^1J(RhP$_B$) = 150 Hz.

[Rh(triphos)(CO)][PF$_6$], 4, (0.080 g, 0.099 mmol) was dissolved in THF (4 mL). A sample (0.10 mL) of this solution was placed in a gas-tight solution infrared cell (b = 0.019 cm) with septas over the ports. Periodically, NaOPh in THF was injected into the cell. IR (THF): After 1.2 eq of NaOPh was added, υ(CO) = 2047, 2020, 1926, 1702, 1699 cm^{-1} and υ(C-C) = 1588, 1556, 1487, 1437 cm^{-1}; Waiting does not cause the disappearance of these bands; More NaOPh causes the growth of υ(CO) = 1926, 1699 cm^{-1}.

[Rh(triphos)(CO)][PF$_6$], 4, (0.106 g, 0.13 mmol) was dissolved in 6 mL THF and NaOPh-*p*-Me was added in 0.5 eq increments in THF. After each addition of NaOPh-*p*-Me, a sample was transferred via a syringe to an infrared cell (b = 8x10^{-3} mm), which was not gas-tight. IR (THF): After 1.0 eq NaOPh-*p*-Me was added, υ(CO) = 2057, 2021, 2004, 1703 cm^{-1} and υ(C-C) = 1600, 1516 cm^{-1}; After 0.5 hr of waiting, υ(CO) = 2058, 2022, 2004, 1703 cm^{-1} and υ(C-C) = 1602, 1517 cm^{-1}; The band at 1703 cm^{-1} grows with addition of NaOPh-*p*-Me.

[Rh(triphos)(CO)][PF$_6$], **4**, (0.039 g, 0.048 mmol) was dissolved in CD$_2$Cl$_2$ (1 mL) and frozen to 77 K. NaOPh-*p*-Me (0.015 g, 0.12 mmol) was dissolved in 0.1 mL of THF and added to the solution of **4** at 77 K. The sample was allowed to warm to dry ice/diethyl ether temperature (-100 °C) and placed in the Varian XL200 NMR spectrometer at -80 °C and spectra were taken as the sample was warmed to 25 °C. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$/THF) at -80°C: (**4**) 90% A$_2$BX, δ(P$_A$) = 54.7 ppm, δ(P$_B$) = 105.2 ppm, ^2J(P$_A$P$_B$) = 28.4 Hz, ^1J(RhP$_A$) = 127 Hz, ^1J(RhP$_B$) = 114 Hz; (**2**) 5% A$_2$BX, δ(P$_A$) = 38.5 ppm, δ(P$_B$) = 110.2 ppm, ^2J(P$_A$P$_B$) = 32.9 Hz, ^1J(RhP$_A$) = 153 Hz, ^1J(RhP$_B$) = 148 Hz; (**5**) 5% A$_2$BX, δ(P$_A$) = 64.5 ppm, δ(P$_B$) = 105.0 ppm, ^2J(P$_A$P$_B$) = 22.9 Hz, ^1J(RhP$_A$) = 124 Hz, ^1J(RhP$_B$) = 84 Hz. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$/THF) at 30°C: (**4**) A$_2$BX, δ(P$_A$) = 55.6 ppm, δ(P$_B$) = 104.9 ppm, ^2J(P$_A$P$_B$) = 28 Hz, ^1J(RhP$_A$) = 128 Hz, ^1J(RhP$_B$) = 115 Hz.

[Rh(triphos)(CO)][PF$_6$], **4**, (0.068 g, 0.083 mmol) and NaOPh-*p*-Me (0.019 g, 0.14 mmol) were dissolved in 1 mL THF-d$_8$. The sample was heated overnight at 50 °C. ^{31}P{^{1}H} NMR (THF-d$_8$): (**2**) 70% A$_2$BX, δ(P$_A$) = 40.7 ppm, δ(P$_B$) = 110.8 ppm, ^2J(P$_A$P$_B$) = 33.5 Hz, ^1J(RhP$_A$) = 145 Hz, ^1J(RhP$_B$) = 159 Hz; (**4**) 30% A$_2$BX, δ(P$_A$) = 56.1 ppm, δ(P$_B$) = 106.8 ppm, ^2J(P$_A$P$_B$) = 28.0 Hz, ^1J(RhP$_A$) = 128 Hz, ^1J(RhP$_B$) = 114 Hz. A small amount of CO$_2$, corresponding to 8x10^{-7} moles in the entire sample was observed by headspace GC.

[Rh(triphos)(CO)][PF$_6$], **4**, (0.011 g, 0.014 mmol) was dissolved in 4 mL THF and NaOPh-*p*-OMe was added in 0.5 eq increments in THF. After each addition of NaOPh-*p*-OMe, a sample was transferred via a syringe to an infrared cell (b = 8x10^{-3} mm), which was not gas-tight. IR (THF): After 3.0 eq NaOPh-*p*-OMe was added, υ(CO) = 2019, 2002, 1700 cm^{-1} and υ(C-C) = 1602, 1513 cm^{-1}.

Reactions of 4* with NaOPh. [Rh(triphos)(^{13}CO)][PF$_6$], **4***, (0.050 g, 0.061 mmol) and NaOPh (0.014 g, 0.12 mmol) were dissolved in 1 mL CD$_2$Cl$_2$ and 0.2 mL THF. The reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy. ^{31}P{^{1}H} NMR (THF/CD$_2$Cl$_2$): (**4***) 75% A$_2$BMX, δ(P$_A$) = 55.4 ppm, δ(P$_B$) = 105.0 ppm, ^2J(P$_A$P$_B$) = 28.4 Hz, ^2J(P$_B$C$_M$) = 84 Hz, ^1J(RhP$_A$) = 128 Hz, ^1J(RhP$_B$) = 118 Hz; (**1**) 25% A$_2$BX, δ(P$_A$) = 39.3 ppm, δ(P$_B$) = 110.5 ppm, ^2J(P$_A$P$_B$) = 33 Hz, ^1J(RhP$_A$) = 153 Hz, ^1J(RhP$_B$) = 149 Hz. The sample was isolated by precipitation with hexanes (1 mL). IR (KBr) = υ(CO) = 1974, 1931 cm^{-1}, υ(C-C) = 1587, 1552 cm^{-1}.

Preparation of [Rh(triphos)(CO)$_2$][PF$_6$], 5. [Rh(triphos)(CO)][PF$_6$], **4**, was dissolved in THF and carbon monoxide was bubbled through the solution, yielding [Rh(triphos)((CO)$_2$][PF$_6$], **5**. Attempts to isolate this bis(carbonyl) complex, **5**, resulted in the mono(carbonyl), **4**. Yield (by NMR) = 100%. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): A$_2$BX, δ(P$_A$) = 64.0 ppm, δ(P$_B$) = 104.9 ppm, ^2J(P$_A$P$_B$) = 23 Hz, ^1J(RhP$_A$) = 124 Hz, ^1J(RhP$_B$) = 92 Hz. IR (THF): υ(CO) = 2050, 2001 cm^{-1}.

Reactions of 5 with NaOR {R = C$_6$H$_5$, C$_6$H$_5$-*p*-CH$_3$, C$_6$H$_5$-*p*-OCH$_3$}.

[Rh(triphos)(CO)][PF$_6$], **4**, (0.32 g, 0.39 mmol) was dissolved in THF (16 mL) and 1 atm of carbon monoxide is added to the solution to generate the bis(carbonyl), **5**. Next, a THF solution of NaOPh was added in increments of 0.5 equivalent at a time. This reaction was monitored by infrared spectroscopy with samples that were transferred via a syringe to an infrared cell (b = 8x10^{-3} mm), which was not gas-tight. IR (THF): After 2.0 eq NaOPh was added, υ(CO) = 2051, 2006, 1926, 1698 cm^{-1} and υ(C-C) = 1589, 1489 cm^{-1}. This sample was heated at 85 °C in a sealed tube for 2.5 hours. IR (THF): υ(CO) = 2005, 1931 cm^{-1} and υ(C-C) = 1606, 1591, 1490 cm^{-1}. This sample was then heated at 85 °C in a sealed tube for 15 days. IR (THF): υ(CO) = 1992, 1933 cm^{-1} and υ(C-C) = 1606, 1594 cm^{-1}. No CO$_2$ was observed by headspace GC. The product was then isolated by precipitation with hexanes. IR

(KBr): υ(CO) = 1988 cm^{-1}, υ(C-C) = 1589, 1481, 1435 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): A_2BX, δ(P_A) = 61.4 ppm, δ(P_B) = 151.3 ppm, $^2J(P_AP_B)$ = 24 Hz, $^1J(RhP_A)$ = 133 Hz, $^1J(RhP_B)$ = 74 Hz.

[Rh(triphos)(CO)][PF_6], **4**, (0.22 g, 0.27 mmol) was dissolved in THF (4 mL) and 1 eq of carbon monoxide was syringed into the solution to generate the bis(carbonyl), **5**, observable by IR, υ(CO) = 2051, 2009 cm^{-1}. Next, a THF solution of NaOPh-*p*-OMe was added in increments of 0.5 equivalent at a time. This reaction was monitored by infrared spectroscopy with samples that were transferred via a syringe to an infrared cell (b = 8x10^{-3} mm), which was not gas-tight. IR (THF): After 1.5 eq NaOPh-*p*-OMe was added, υ(CO) = 2052, 2018, 1978, 1705 cm^{-1} and υ(C-C) = 1600, 1513 cm^{-1}. This sample was then heated at 86 °C in a sealed tube for 3 days. IR (THF): υ(CO) = 1995, 1937, 1742 cm^{-1}, υ(C-C) = 1601, 1513 cm^{-1}. A small amount of CO_2 was observed by headspace GC.

Reactions of Rh(triphos)Cl or 4 with CO, NaOR, and ROH. The rhodium complexes, Rh(triphos)Cl or **4**, were ultilized to investigate their ability to deoxygenate phenols or alcohols under 1 atm of carbon monoxide. Numerous reactions were undertaken with alcohols (MeOH, EtOH) and phenols (PhOH, *p*-Me-PhOH, *p*-OMe-PhOH), bases (alkoxide, aryloxide, or Proton-Sponge), carbon monoxide and catalytic amounts of Rh(triphos)Cl or **4**. None of these reactions produced more than a fraction of an equivalent of CO_2. $[Rh(triphos)(CO)_2]^+$ was observed as the only species present, by $^{31}P\{^1H\}$ NMR spectroscopy, during many of these reactions.

The most interesting result from a reaction of this type occured when the concentration of aryloxide was extremely high. Heating complex **4** (0.050 g, 0.062 mmol) with NaOPh-*p*-OMe (1.35 g, 9.3 mmol), PhOH (0.15 g, 1.6 mmol), and 1 atm of carbon monoxide in 2 mL THF in a sealed Schlenk tube at 50 °C for 24 hours resulted in the formation of 0.05 g of yellow solid. IR (KBr): υ(CO) = 1939 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): A_2BX, δ(P_A) = 65.6

ppm, $\delta(P_B) = 101.5$ ppm, ${}^2J(P_AP_B) = 24.4$ Hz, ${}^1J(RhP_A) = 146$ Hz, ${}^1J(RhP_B) = 98$ Hz. There was no CO_2 detected from the headspace of this reaction by GC.

Acknowledgement. We thank the Department of Energy and the American Chemical Society Petroleum Research Fund. A.M.G. thanks Amoco Chemical and the Department of Education for a National Needs Fellowship.

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