



IR spectroscopic studies of the reversible equilibria between Rh(I)(triphos) aryloxides, aryloxycarbonyls, and carbonyls

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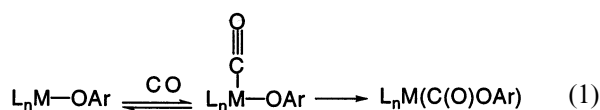
Abstract

The complex, $[\text{Rh}(\text{triphos})\text{CO}][\text{PF}_6]$ {triphos = bis(2-diphenylphosphinoethyl)phenyl phosphine}, **4**, reacts with aryloxides, ArO^- {Ar = C_6H_5 , C_6H_4 -*p*- CH_3 , C_6H_4 -*p*- OCH_3 }. The formation and subsequent chemistry of the resulting aryloxycarbonyl complexes were observed by FTIR spectroscopy. These aryloxycarbonyl complexes are formed and decay via different pathways involving the *fac*- and *mer*-isomers of $\text{Rh}(\text{triphos})(\text{CO})(\text{OAr})$. Decarbonylation of $\text{Rh}(\text{triphos})(\text{CO})(\text{OAr})$ forms $\text{Rh}(\text{triphos})\text{OAr}$, {Ar = C_6H_5 (**1**), C_6H_4 -*p*- CH_3 , (**2**) C_6H_4 -*p*- OCH_3 (**3**)}, while elimination of the aryloxide via a different pathway can also reform $[\text{Rh}(\text{triphos})\text{CO}][\text{PF}_6]$, **4**. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Reversible equilibria; Aryloxides; Aryloxycarbonyls; Carbonyls

1. Introduction

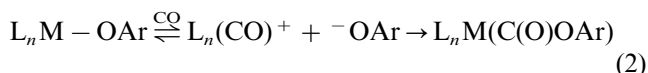
There are two principal mechanisms by which late transition metal aryloxy complexes can be carbonylated to their respective aryloxycarbonyls. The first is classical migratory insertion, where the aryloxy ligand migrates to a carbon monoxide *cis* to the aryloxy ligand, Eq. (1).



Bryndza concluded that this mechanism is important in the carbonylation of the platinum alkoxy complexes, $\text{Pt}(\text{dppe})(\text{OMe})(\text{R})$ (R = OMe, Me; dppe = 1,2 bis-(diphenylphosphino)ethane) [1] and we reported that

the carbonylation of $[\text{Pt}(\text{triphos})(\text{OAr})][\text{PF}_6]$ proceeds by a similar mechanism [2].

A second type of mechanism that must be considered in view of the lower M–OAr bond energies expected for late transition metal aryloxy complexes, is nucleophilic addition of the aryloxy to coordinated carbon monoxide. This involves substitution of a weakly bound aryloxy ligand by carbon monoxide, followed by nucleophilic addition of the displaced aryloxy to the carbonyl ligand Eq. (2).



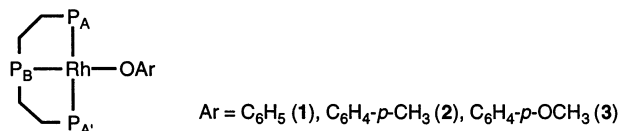
Atwood et al. found that nucleophilic addition of aryloxy to the coordinated carbon monoxide ligands of $[\text{Ir}(\text{CO})_2(\text{PPh}_3)_2]^+$ occurs during the reaction of $\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{OR})$ (R = Me, Ph) with carbon monoxide [3–6]. We describe reactions of a series of aryloxides { ArO^- ; Ar = C_6H_5 , C_6H_4 -*p*- CH_3 , C_6H_4 -*p*- OCH_3 } with $[\text{Rh}(\text{triphos})(\text{CO})]^+$ to afford aryloxycarbonyl complexes, $\text{Rh}(\text{triphos})(\text{C}(\text{O})\text{OAr})$. We also report FTIR spectroscopic studies of the reversible decarbonylation and aryloxy eliminations.

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2. Results and discussion

2.1. Preparation of aryloxide and carbonyl complexes

The previously reported complex, Rh(triphos)Cl [7,8] was used as the starting material for the synthesis of a series of rhodium aryloxide complexes, **1–3**. The complex Rh(triphos)Cl, was reacted with excess sodium aryloxide NaOAr {Ar = C₆H₅, C₆H₄-*p*-CH₃, C₆H₄-*p*-OCH₃} in acetone and stirred overnight. The solvent was removed and the solid was extracted into CH₂Cl₂ and precipitated with hexanes, to produce Rh(triphos)OAr {**1**: Ar = C₆H₅, **2**: Ar = C₆H₄-*p*-CH₃, **3**: Ar = C₆H₄-*p*-OCH₃}.



A few other rhodium aryloxides have been reported previously, including Rh(PPh₃)₃OC₆H₅ [9] Rh(PPh₃)₃OC₆H₄-*p*-CH₃ [10] and *trans*-Rh(PPh₃)₂(CO)OC₆H₅ [11]. In general, the Rh–P_B coupling constant is quite sensitive to the nature of the ligand *trans* to it. The magnitude of *J*(Rh–P_B) decreases from 164 Hz for Rh(triphos)Cl to ca. 150 Hz for the aryloxides, **1–3**, suggesting that chloride and aryloxides behave similarly as ligands to rhodium. The relative trend of the Rh–OAr bonding interactions also should be reflected in the Rh–P_B coupling constants, but due to the small difference in these values, no trend is evident. The magnitude of *J*(Rh–P_B) for **1–3** agrees well with the reported value of 147 Hz for *J*(Rh–P_B) of Rh(ttp)OC₆H₅ {ttp = Ph(PCH₂CH₂CH₂PPh₂)₂} [12].

The carbonyl complex [Rh(triphos)(CO)][PF₆] was prepared by treating Rh(triphos)Cl with AgPF₆ in acetone to remove chloride, generating an acetone solvento complex. The reaction flask was evacuated and then filled with carbon monoxide. The solution was stirred for 1 h under CO, then product was precipitated with diethyl ether to yield [Rh(triphos)(CO)][PF₆], **4**. The ¹H-NMR spectrum shows four multiplets for the triphos methylene protons at 2.23, 2.91, 3.15 and 3.31 ppm and the phenyl protons in the δ 7.41–7.80 ppm region. The ³¹P{¹H}-NMR spectrum is an A₂BX spin system (δ(P_A) = 55.6 ppm, δ(P_B) = 104.7 ppm) with ²*J*(P_AP_B) = 28.2 Hz, ¹*J*(RhP_A) = 128 Hz, and ¹*J*(RhP_B) = 115 Hz and δ(PF₆) = –144 ppm. The related rhodium triphosphine carbonyl complex, [Rh{PhP(CH₂CH₂CH₂PPh₂)₂}(CO)][PF₆], was reported by Meek and co-workers [13,14]. The ¹*J*(RhP_B) value of 115.2 Hz for their complex agrees well with that for complex **4**. The IR spectrum of **4** shows one terminal ν(CO) band at 2021 cm^{–1} in THF and at 2026 cm^{–1} in KBr. For comparison, other rhodium tris(phosphine)

carbonyl complexes have reported values of ν(CO) in the 2023–2029 cm^{–1} range [15,16].

2.2. Aryloxide additions to coordinated CO

The reactions of **4** with various aryloxides were monitored by IR spectroscopy. The complex [Rh(triphos)(CO)][PF₆], **4**, was dissolved in THF and NaOAr {Ar = C₆H₅, C₆H₄-*p*-CH₃, C₆H₄-*p*-OCH₃} was added as a solution in THF. Fig. 1 shows a series of IR spectra taken over time with increasing amounts of NaOC₆H₅. Immediately following addition of NaOC₆H₅, the phenoxycarbonyl product is observed at ν(CO) = 1709 cm^{–1} (Fig. 1b). Surprisingly, 30 min later, this band has disappeared and the original band for **4** at ν(CO) = 2021 cm^{–1} has almost completely been restored (Fig. 1c). The phenoxycarbonyl band reappears as additional NaOC₆H₅ is added (Fig. 1d). This ephemeral product formation followed by reversion to starting material cycle can be repeated several times by adding more NaOC₆H₅ and waiting. Significantly, two other carbonyl compounds, the *fac*- and *mer*-isomers of Rh(triphos)(CO)(OC₆H₅), also are observed in small quantities. The fact that both the *fac*- and *mer*-isomers of Rh(triphos)(CO)(OC₆H₅) are observed is consistent with the expectation that these isomers may have different stabilities but interconvert slowly because of the steric requirements of the triphos ligand. Similar behavior has been observed with *fac*- and *mer*-iridium triphos complexes [17]. The *fac*-Rh(triphos)(CO)(OC₆H₅) complex is characterized by ν(CO) = 2005 cm^{–1}, while *mer*-Rh(triphos)(CO)(OC₆H₅) is observed at ν(CO) = 2058 cm^{–1}. The assignments of these isomers are based on the energetic preference of the strongest σ and π-donor ligands in axial positions, as they would be in the *fac*-isomer. This σ/π donation results in increased backbonding to the equatorial carbonyl ligand and the lower energy ν(CO) band. It is important to note that the appearance of phenoxycarbonyl ν(CO) absorption and its subsequent disappearance (Fig. 1) implies that this species forms and decays by separate pathways. The observation of both the *fac*- and *mer*-isomers, the *fac*-isomer is considered more thermodynamically stable, implies that one of these is an intermediate in the formation of the phenoxycarbonyl complex, Rh(triphos)(C(O)OC₆H₅), while the other isomer is an intermediate in its decay.

The reaction of **4** with a more nucleophilic aryl oxide, NaOC₆H₄-*p*-CH₃, eliminates the reaction ‘rebound’ phenomenon observed with NaOC₆H₅. Fig. 2 shows a series of IR spectra taken over time with increasing amounts of NaOC₆H₄-*p*-CH₃. The ν(CO) band at 1703 cm^{–1}, corresponding to the aryloxycarbonyl, Rh(triphos)(C(O)OC₆H₄-*p*-CH₃), grows with addition of NaOC₆H₄-*p*-CH₃ (Fig. 2c) but does not decay

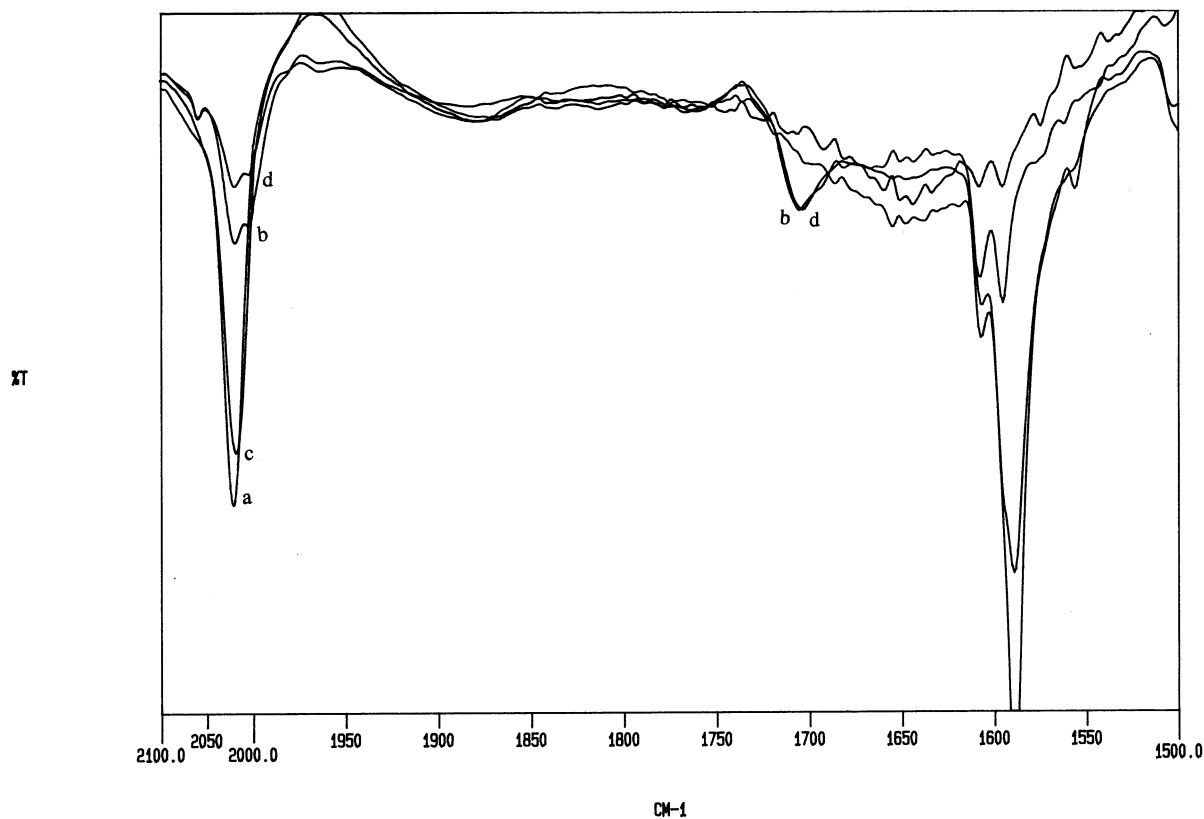


Fig. 1. IR (THF) of the reaction of **4** with NaOC_6H_5 : (a) **4** only (b) 0.5 equivalents of NaOC_6H_5 (c) 0.5 h after (b) (d) 0.25 additional equivalents of NaOC_6H_5 .

afterward (Fig. 2d). This behavior differs radically from that of the NaOC_6H_5 case. Again, both the *fac*- and *mer*-isomers of $\text{Rh}(\text{triphos})(\text{CO})(\text{OAr})$ are observed, but at $\nu(\text{CO})$ 2004 and 2057 cm^{-1} , respectively. The strongest nucleophile of the series, $\text{NaOC}_6\text{H}_4\text{-}p\text{-OCH}_3$, was also reacted with **4**. Fig. 3 shows the IR spectra taken over time after $\text{NaOC}_6\text{H}_4\text{-}p\text{-OCH}_3$ addition. The aryloxy carbonyl, $\text{Rh}(\text{triphos})(\text{C}(\text{O})\text{OC}_6\text{H}_4\text{-}p\text{-OCH}_3)$, was observed in the IR spectrum at 1700 cm^{-1} (Fig. 3c). Significantly, only the *fac*-isomer of $\text{Rh}(\text{triphos})(\text{CO})(\text{OC}_6\text{H}_4\text{-}p\text{-OCH}_3)$ is observed in the IR, $\nu(\text{CO}) = 2002 \text{ cm}^{-1}$. The fact that the *mer*-isomer is not observed is reasonable since the *para*-methoxy group makes this aryloxide a strong σ and π donor such that only the more stable *fac*-isomer is observed. The differences in persistence of formation of the aryloxy carbonyl complexes based on the nucleophilic strength of the aryloxide used indicates that the equilibrium conditions governing this set of reactions are highly reversible and nearly thermoneutral. A proposed reaction pathway, Fig. 4, involves the initial formation of one of the isomers of $\text{Rh}(\text{triphos})(\text{CO})(\text{OAr})$ by addition of the ArO^- to **4**, followed by the nucleophilic addition of the aryloxide to the coordinated carbonyl resulting in the square planar aryloxy carbonyl complex. We propose that the isomer formed initially is the

fac-isomer. One reason for this is the accumulation of the *fac*-isomer whenever the aryloxy carbonyl complex is observed (Fig. 1b, Fig. 2c, Fig. 3b). Another fact supporting this view is the more persistent formation of the aryloxy carbonyl species when the stronger nucleophiles, $\text{ArO}^- = \text{OC}_6\text{H}_4\text{-}p\text{-CH}_3$ and $\text{OC}_6\text{H}_4\text{-}p\text{-OCH}_3$, are used. These stronger nucleophiles favor the *fac*-isomer. A key point is that the decay pathway of the aryloxy carbonyl complex must differ from its formation pathway. The logic for this comes from the fact that the aryloxy carbonyl clearly can be formed but over time reverts to **4** plus aryloxide while a simple equilibrium between **4** plus aryloxide and the aryloxy carbonyl complex cannot be established. We suggest that decay of the aryloxy carbonyl complex occurs through the *mer*-isomer of $\text{Rh}(\text{triphos})(\text{CO})(\text{OAr})$, which is unstable with respect to **4** plus the aryloxide ligand. The *mer*-isomer becomes progressively less favored with the more nucleophilic aryloxides, and this explains the persistence of the aryloxy carbonyl complex when the more nucleophilic aryloxides are used.

Attempts to isolate any of the aryloxy carbonyl complexes, $\text{Rh}(\text{triphos})(\text{C}(\text{O})\text{OAr})$ $\{\text{Ar} = \text{C}_6\text{H}_5, \text{C}_6\text{H}_4\text{-}p\text{-CH}_3, \text{C}_6\text{H}_4\text{-}p\text{-OCH}_3\}$ netted only $[\text{Rh}(\text{triphos})\text{CO}]\text{PF}_6$, **4**, and the corresponding aryloxide, $\text{Rh}(\text{triphos})\text{OAr}$, **1–3**, as observed by $^{31}\text{P}\{^1\text{H}\}$ -NMR. The equilibrium

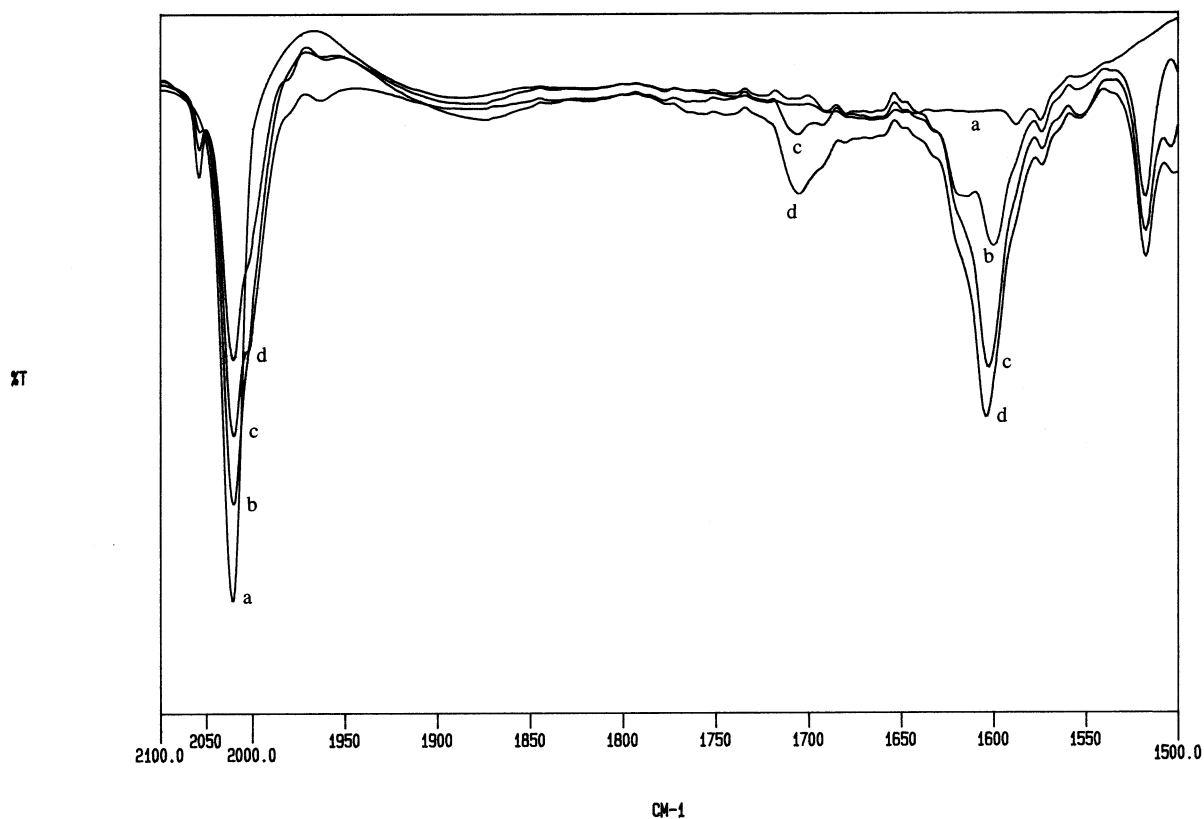


Fig. 2. IR (THF) of the reaction of **4** with $\text{NaOC}_6\text{H}_4\text{-}p\text{-CH}_3$: (a) **4** alone (b) after addition of 1.0 equivalents of $\text{NaOC}_6\text{H}_4\text{-}p\text{-CH}_3$ (c) after addition of another 0.5 equivalents of $\text{NaOC}_6\text{H}_4\text{-}p\text{-CH}_3$ (d) 0.5 h after (c).

loss of carbon monoxide, Fig. 4, allows for the formation of $\text{Rh}(\text{triphos})\text{OAr}$, **1–3**. One way to block the pathway by which the aryloxy carbonyl decays is to occupy an additional vacant site on rhodium. This was attempted with an additional carbonyl ligand. The presence of a second carbonyl also serves the purpose of increasing the electrophilicity at the carbonyl carbon atoms. The complex $[\text{Rh}(\text{triphos})(\text{CO})][\text{PF}_6]$, **4**, was dissolved in THF and carbon monoxide was bubbled through the solution, yielding $[\text{Rh}(\text{triphos})(\text{CO})_2][\text{PF}_6]$, **5**. Attempts to isolate the bis(carbonyl) complex, **5**, led only to recovery of **4**. However, the IR spectrum of **5** in THF clearly shows two terminal $\nu(\text{CO})$ bands at 2051 and 2006 cm^{-1} . The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum is an A_2BX spin system ($\delta(\text{P}_\text{A}) = 64.0$ ppm, $\delta(\text{P}_\text{B}) = 104.9$ ppm) with $^1J(\text{RhP}_\text{A}) = 124$ Hz, $^1J(\text{RhP}_\text{B}) = 92$ Hz and $^2J(\text{P}_\text{A}\text{P}_\text{B}) = 23$ Hz. Related examples of rhodium tris(phosphine) bis(carbonyl) complexes show similar spectroscopic data [15,16]. The dicarbonyl complex, $[\text{Rh}(\text{triphos})(\text{CO})_2][\text{PF}_6]$, **5**, was generated in situ by the introduction of 1 atm carbon monoxide over a THF solution of $[\text{Rh}(\text{triphos})(\text{CO})][\text{PF}_6]$, **4**. Next, a THF solution of NaOC_6H_5 was added in increments of 0.5 equivalents and the reactions were monitored by IR spectroscopy. The bis(carbonyl), **5**, bands at 2051 and 2006 cm^{-1} are replaced during the addition of NaOC_6H_5 by new bands at 1926 and 1699 cm^{-1} , Fig.

5. These new bands correspond to *fac*- $\text{Rh}(\text{triphos})(\text{CO})(\text{C}(\text{O})\text{OC}_6\text{H}_5)$. The *mer*-isomer is not observed as there is a strong preference for the phenoxycarbonyl ligand to occupy an axial position, as it does in the *facial*-isomer. The phenoxycarbonyl is formed and persists now that there are two carbonyl ligands. The fact that the *mer*-isomer is not observed in this experiment further supports our view that aryloxy carbonyl deinsertion occurs through the *mer*-isomer. Attempts to isolate the phenoxycarbonyl, $\text{Rh}(\text{triphos})(\text{CO})(\text{C}(\text{O})\text{OC}_6\text{H}_5)$, were made, resulting only in $[\text{Rh}(\text{triphos})\text{CO}]\text{PF}_6$, **4**, and $\text{Rh}(\text{triphos})\text{OC}_6\text{H}_5$, **1**. Again, the inevitable loss of a carbonyl ligand allows for the usual pathway to phenoxycarbonyl ligand collapse to carbon monoxide and phenoxide, shown in Fig. 4.

3. Conclusion

Complex **4**, $[\text{Rh}(\text{triphos})\text{CO}][\text{PF}_6]$, is attacked at CO by aryloxide nucleophiles to form aryloxy carbonyl complexes. These aryloxy carbonyl complexes cannot be isolated as they decay through a five-coordinate aryloxy carbonyl species to form rhodium triphos aryloxide complexes, **1–3**, and **4**. By starting with the five-coordinate bis(carbonyl) complex, **5**, the carbonyl aryloxy car-

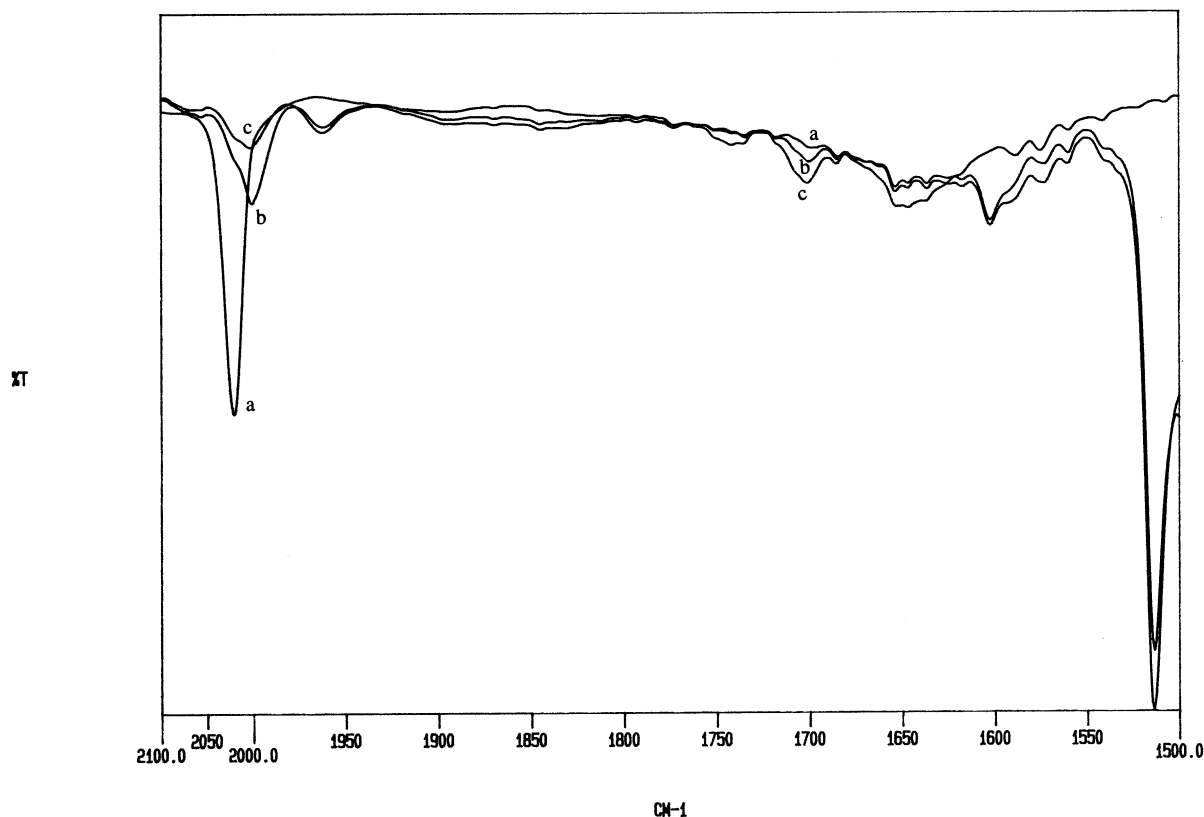


Fig. 3. IR (THF) of the reaction of **4** with NaOC₆H₄-*p*-OCH₃: (a) **4** alone (b) after addition of 3.0 equivalents of NaOC₆H₄-*p*-OCH₃ (c) 0.5 h after (b).

bonyl complex, Rh(triphos)(CO)(C(O)OAr), can be formed persistently. This set of reactions comprises a highly reversible equilibrium, which can be perturbed by a change in nucleophilic strength of the aryloxides, or by the presence of carbon monoxide. A surprising

mechanistic detail is that addition of weaker nucleophile aryloxides such as phenoxide to **4** leads to the prompt formation of a phenoxycarbonyl species, but as equilibrium is re-established the phenoxycarbonyl species ultimately reverts to [Rh(triphos)CO]PF₆, **4**, and Rh(triphos)OC₆H₅, **1**.

4. Experimental section

4.1. 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, CaH₂ for CH₂Cl₂ and hexanes, 4A Linde molecular sieves for acetone). 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 [7,8]. Carbon monoxide (99.5%) was purchased from Matheson Gas Company. The compound NaOAr {Ar = C₆H₅, C₆H₄-*p*-CH₃, C₆H₄-*p*-OCH₃} was pre-

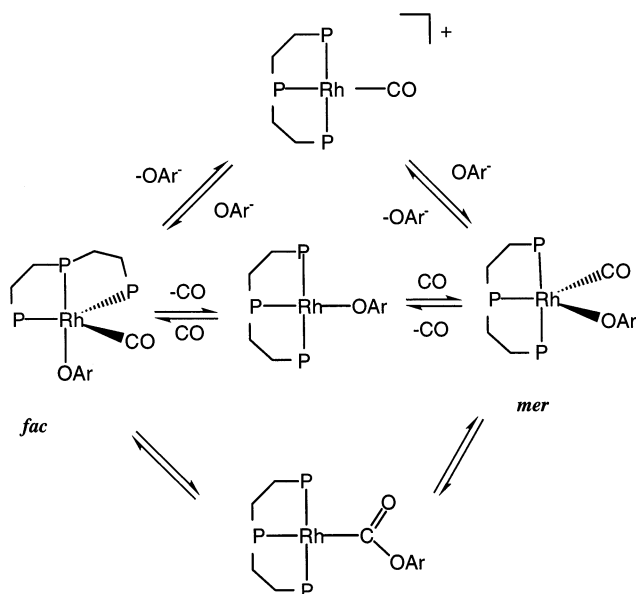


Fig. 4. Proposed scheme for the reactivity of **4** with aryl oxides.

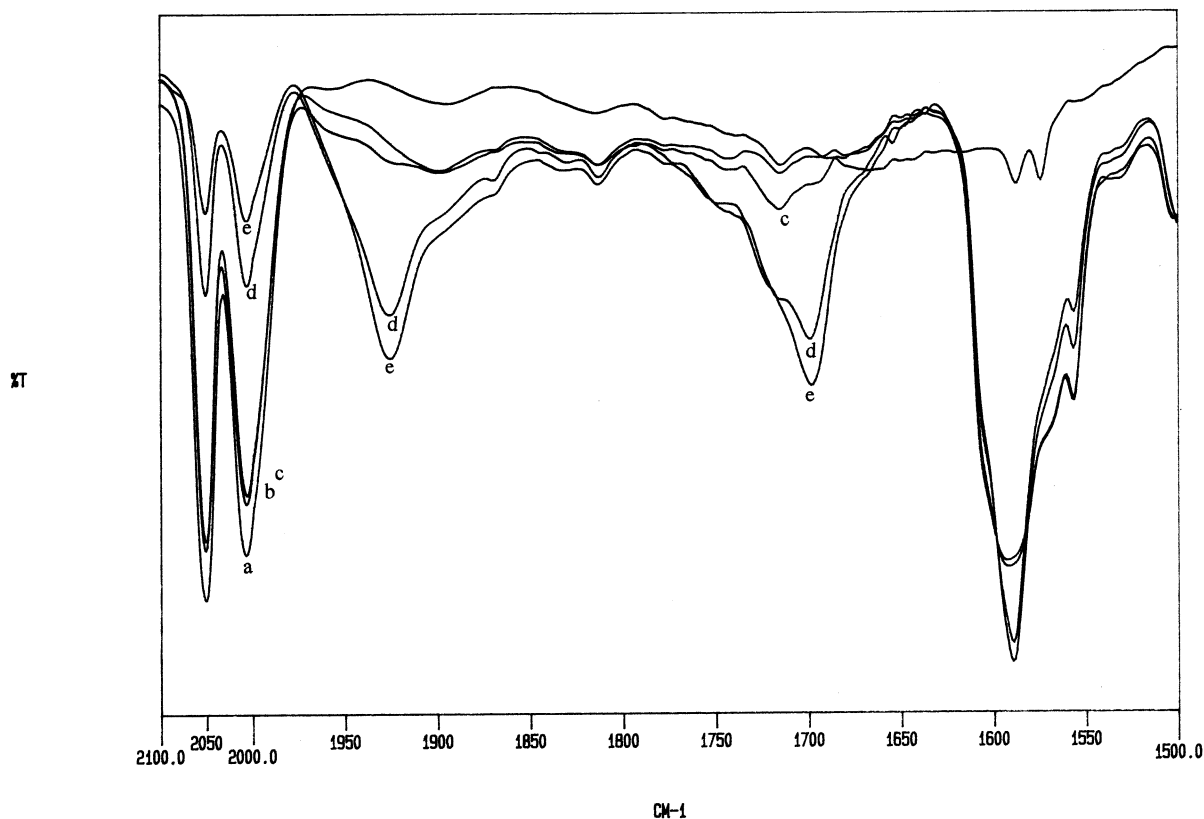


Fig. 5. IR (THF) of the reaction of **5** with NaOC_6H_5 : (a) **5** alone (b) after addition of 2.0 equivalents of NaOC_6H_5 (c) 0.5 h after (b) (d) after addition of another 1.0 equivalents of NaOC_6H_5 (e) 0.5 h after (d).

pared from ArOH 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 . $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were recorded on QE-300 and Varian XL-200 spectrometers at 121.4 and 81.0 MHz, respectively, with chemical shifts reported in ppm referenced to external 85% H_3PO_4 . Plasma desorption mass spectroscopy (PD MS) spectra were collected on an Applied Biosystems Bio-Ion 20R instrument. IR Spectra were recorded on Perkin Elmer 1710 and Mattson Galaxy Infrared Fourier Transform Spectrometers. Elemental analysis were performed by H.D. Lee of this department.

4.2. Preparation of $\text{Rh}(\text{triphos})\text{OAr}$, **1–3**

$\text{Rh}(\text{triphos})\text{Cl}$ [7,8] was allowed to react with excess NaOAr ($\text{Ar} = \text{C}_6\text{H}_5$, $\text{C}_6\text{H}_4\text{-}p\text{-CH}_3$, $\text{C}_6\text{H}_4\text{-}p\text{-OCH}_3$) in acetone and stirred overnight. The solvent was removed and the solid was extracted into CH_2Cl_2 and precipitated with hexanes, to produce $\text{Rh}(\text{triphos})\text{OAr}$ (**1**: $\text{Ar} = \text{C}_6\text{H}_5$, **2**: $\text{R} = \text{C}_6\text{H}_4\text{-}p\text{-CH}_3$, **3**: $\text{R} = \text{C}_6\text{H}_4\text{-}p\text{-OCH}_3$). Typical yields were near 70% with the major impurity being $\text{Rh}(\text{triphos})\text{Cl}$. **1**: $^{31}\text{P}\{^1\text{H}\}$ -NMR (CD_2Cl_2): A_2BX , $\delta(\text{P}_\text{A}) = 39.2$ ppm, $\delta(\text{P}_\text{B}) = 110.4$

ppm, $^2J(\text{P}_\text{A}\text{P}_\text{B}) = 33.1$ Hz, $^1J(\text{RhP}_\text{A}) = 153$ Hz, $^1J(\text{RhP}_\text{B}) = 149$ Hz. **2**: $^{31}\text{P}\{^1\text{H}\}$ -NMR (CD_2Cl_2): A_2BX , $\delta(\text{P}_\text{A}) = 39.6$ ppm, $\delta(\text{P}_\text{B}) = 110.6$ ppm, $^2J(\text{P}_\text{A}\text{P}_\text{B}) = 33.0$ Hz, $^1J(\text{RhP}_\text{A}) = 154$ Hz, $^1J(\text{RhP}_\text{B}) = 150$ Hz. **3**: $^{31}\text{P}\{^1\text{H}\}$ -NMR (CD_2Cl_2): A_2BX , $\delta(\text{P}_\text{A}) = 39.5$ ppm, $\delta(\text{P}_\text{B}) = 110.4$ ppm, $^2J(\text{P}_\text{A}\text{P}_\text{B}) = 32.0$ Hz, $^1J(\text{RhP}_\text{A}) = 153$ Hz, $^1J(\text{RhP}_\text{B}) = 148$ Hz.

4.3. Preparation of $[\text{Rh}(\text{triphos})(\text{CO})][\text{PF}_6]$, **4**

The compound $\text{Rh}(\text{triphos})\text{Cl}$ (0.156 g, 0.23 mmol) was allowed to react 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 h. Diethyl ether (10 ml) was used to precipitate 0.16 g of $[\text{Rh}(\text{triphos})(\text{CO})][\text{PF}_6]$, **4**. The yield was 86%. ^1H -NMR (CD_2Cl_2): $\delta(\text{CH}_2) = 2.23$ ppm (m, 2H), $\delta(\text{CH}_2) = 2.91$ ppm (m, 2H), $\delta(\text{CH}_2) = 3.15$ ppm (m, 2H), $\delta(\text{CH}_2) = 3.31$ ppm (m, 2H), $\delta(\text{Ph}) = 7.41\text{--}7.80$ ppm (m, 25H). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CD_2Cl_2): A_2BX , $\delta(\text{P}_\text{A}) = 55.6$ ppm, $\delta(\text{P}_\text{B}) = 104.7$ ppm, $\delta(\text{PF}_6) = -144$ ppm, $^2J(\text{P}_\text{A}\text{P}_\text{B}) = 28.2$ Hz, $^1J(\text{RhP}_\text{A}) = 128$ Hz, $^1J(\text{RhP}_\text{B}) = 115$ Hz. IR (KBr): $\nu(\text{CO}) = 2026$ cm^{-1} . IR (THF): $\nu(\text{CO}) = 2021$ cm^{-1} . PDMS: m/z 637.3 (loss of CO). Anal. Calc. for

$C_{35}H_{33}F_6RhOP_4$: C, 51.85; H, 4.11. Found: C, 51.54; H, 4.06.

4.4. Reaction of **4** with $NaOC_6H_5$

The compound $[Rh(\text{triphos})(CO)][PF_6]$, **4**, (0.047 g, 0.058 mmol) was dissolved in 2.5 ml THF and $NaOC_6H_5$ was added in 0.5 equivalent increments in THF to a 5 ml reaction flask with a septum. After each addition of $NaOC_6H_5$, a sample was transferred via a syringe to an IR cell ($b = 8 \times 10^{-3}$ mm). IR (THF): After 0.5 equivalents $NaOC_6H_5$ was added, $\nu(CO) = 2058, 2020, 2005, 1709\text{ cm}^{-1}$ and $\nu(C-C) = 1589, 1497\text{ cm}^{-1}$; After 0.5 h, $\nu(CO) = 2020\text{ cm}^{-1}$; After a further 0.5 equivalents $NaOC_6H_5$ was added, $\nu(CO) = 2058, 2020, 2005, 1710\text{ cm}^{-1}$ and $\nu(C-C) = 1590, 1500\text{ cm}^{-1}$; After an additional 0.5 h, $\nu(CO) = 2020\text{ cm}^{-1}$. This oscillation can be repeated several times until the $\nu(C-C)$ bands grow large enough to make the $\nu(CO)$ bands difficult to see in the noise. $^3P\{^1H\}$ -NMR (THF/ CD_2Cl_2): (**4**) 60% A_2BX , $\delta(P_A) = 55.4$ ppm, $\delta(P_B) = 105.3$ ppm, $^2J(P_AP_B) = 27.8$ Hz, $^1J(RhP_A) = 128$ Hz, $^1J(RhP_B) = 112$ Hz; (**1**) 40% A_2BX , $\delta(P_A) = 39.4$ ppm, $\delta(P_B) = 110.5$ ppm, $^2J(P_AP_B) = 30.5$ Hz, $^1J(RhP_A) = 152$ Hz, $^1J(RhP_B) = 150$ Hz.

4.5. Reaction of **4** with $NaOC_6H_5$ - p - CH_3

The compound $[Rh(\text{triphos})(CO)][PF_6]$, **4**, (0.106 g, 0.13 mmol) was dissolved in 6 ml THF and $NaOC_6H_5$ - p - CH_3 was added in 0.5 equivalent increments in THF. After each addition of $NaOC_6H_5$ - p - CH_3 , a sample was transferred via a syringe to an IR cell ($b = 8 \times 10^{-3}$ mm). IR (THF): After 1.0 equivalents $NaOC_6H_5$ - p - CH_3 was added, $\nu(CO) = 2057, 2021, 2004, 1703\text{ cm}^{-1}$ and $\nu(C-C) = 1600, 1516\text{ cm}^{-1}$; After 0.5 h, $\nu(CO) = 2058, 2022, 2004, 1703\text{ cm}^{-1}$ and $\nu(C-C) = 1602, 1517\text{ cm}^{-1}$; The $\nu(CO)$ band at 1703 cm^{-1} grows with the addition of $NaOC_6H_5$ - p - CH_3 .

4.6. Reactions of **4** with $NaOC_6H_5$ - p - OCH_3

The compound $[Rh(\text{triphos})(CO)][PF_6]$, **4**, (0.011 g, 0.014 mmol) was dissolved in 4 ml THF and $NaOC_6H_5$ - p - OCH_3 was added in 0.5 equivalent increments in THF. After each addition of $NaOC_6H_5$ - p - OCH_3 , a sample was transferred via a syringe to an IR cell ($b = 8 \times 10^{-3}$ mm). IR (THF): $\nu(CO) = 2019, 2002, 1700\text{ cm}^{-1}$; $\nu(C-C) = 1602, 1513\text{ cm}^{-1}$.

4.7. Preparation of $[Rh(\text{triphos})(CO)_2][PF_6]$, **5**

The compound $[Rh(\text{triphos})(CO)][PF_6]$, **4**, was dissolved in THF and carbon monoxide was bubbled through the solution, yielding $[Rh(\text{triphos})(CO)_2][PF_6]$, **5**. Attempts to isolate this bis(carbonyl) complex, **5**,

resulted in the mono(carbonyl), **4**. Yield (by NMR) was 100%. $^3P\{^1H\}$ -NMR (CD_2Cl_2): A_2BX , $\delta(P_A) = 64.0$ ppm, $\delta(P_B) = 104.9$ ppm, $^2J(P_AP_B) = 23$ Hz, $^1J(RhP_A) = 124$ Hz, $^1J(RhP_B) = 92$ Hz. IR (THF): $\nu(CO) = 2051, 2006\text{ cm}^{-1}$.

4.8. Reactions of **5** with $NaOC_6H_5$

The compound $[Rh(\text{triphos})(CO)][PF_6]$, **4**, (0.32 g, 0.39 mmol) was dissolved in THF (16 ml) and 1 atm of carbon monoxide was added to the solution to generate the bis(carbonyl), **5**. Next, a THF solution of $NaOC_6H_5$ was added in increments of 0.5 equivalents at a time. This reaction was monitored by IR spectroscopy with samples that were transferred via a syringe to an IR cell ($b = 8 \times 10^{-3}$ mm). IR (THF): $\nu(CO) = 2051, 2006, 1926, 1698\text{ cm}^{-1}$ and $\nu(C-C) = 1589, 1489\text{ cm}^{-1}$.

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