Mechanistic Studies of the Palladium-Catalyzed Reaction of Methanol with Bromobenzene and CO To Produce Methyl Benzoate. 1. Stoichiometric Study

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Abstract: The mechanism of the palladium-catalyzed carbomethoxylation of bromobenzene to methyl benzoate in the presence of methanol and triethylamine has been investigated with Cylindrical Internal Reflectance Fourier Transform Infrared Spectroscopy (CIR-FTIR). The synthesis of the proposed catalytic intermediate $Pd(Br)(C_6H_5)(P(C_6H_5)_3)_2$ (**1**) was carried out, and the reaction of this species with CO to form $Pd(Br)(COC_6H_5)(P(C_6H_5)_3)_2$ (**3**) was confirmed. Both complexes were characterized by IR and ^{31}P and ^1H NMR spectroscopy. The stability of **3** in the absence of CO suggests that the carbonylation of **1** is irreversible; its stability in the presence of triethylamine establishes that reductive elimination of benzoyl bromide is not facile. In the absence of CO, the conversion of **3** to methyl benzoate was found to be rapid when both methanol and triethylamine were present, but very slow in the presence of methanol alone. A series of experiments in which **3** was allowed to react with methanol and a variety of amines in the absence of CO demonstrated a direct relationship between the rate of reaction and the amine basicity. These observations point to a mechanism in which methanol is initially deprotonated by the amine, and the methoxide ion thus produced attacks the benzoyl complex directly yielding methyl benzoate. When reaction of the benzoyl complex with methanol and triethylamine was carried out with bromobenzene also present, regeneration of **1** was observed via CIR-FTIR and confirmed by IR and proton NMR spectroscopy. The carbomethoxy species, $Pd(Cl)(CO_2CH_3)(P(C_6H_5)_3)_2$, was shown to be stable in the presence of bromobenzene, triethylamine, and methanol at 90 °C, suggesting that this complex is not an active catalytic intermediate. These experiments substantiate the mechanism in Figure 8.

In the presence of phosphine modifiers, certain palladium complexes can function as homogeneous catalysts for the esterification of alcohols with various aryl, benzyl, or vinyl halides under moderate pressures of carbon monoxide.[1] A stoichiometric quantity of tertiary amine must be added to neutralize the HX produced. The production of methyl benzoate from bromobenzene and methanol (eq 1) is a representative example.

$$C_6H_5Br + CH_3OH + (C_2H_5)_3N + CO \xrightarrow[90\ °C,\ 40\ psi]{(C_6H_5)_3P,\ "Pd"} C_6H_5COOCH_3 + (C_2H_5)_3NH^+Br^- \quad (1)$$

Several mechanistic studies of such reactions have been carried out. Heck[1,2] has proposed that ester formation results from direct alcoholysis of a bromo(benzoyl)bis(phosphine)palladium complex **3**, producing bromohydridobis(phosphine)palladium (**5**). Reaction of this species with CO then eliminates HBr and forms a bis(phosphine)palladium carbonyl. Oxidative addition of bromobenzene and subsequent insertion of CO regenerates **3**.

Garrou and Heck[3] investigated the carbonylation of a variety of halobis(phosphine)organopalladium complexes. They found that after CO coordination occurs forming a halocarbonylbis(phosphine)organopalladium complex, migratory insertion of CO into the Pd-C bond takes place either with or without prior dissociation of a phosphine ligand. This raises the possibility that oxidative addition of bromobenzene could occur prior to CO coordination. They also found that with few exceptions, the final product was the benzoyl complex **3**, and in no case was reductive elimination of the acid halide observed. This evidence supports Heck's original hypothesis that the alcohol reacts directly with **3**, rather than with benzoyl bromide reductively eliminated from **3**.

Ozawa and co-workers[4] studied the related palladium-catalyzed double-carbonylation reaction in which an aryl halide reacts with a secondary amine and 2 mol of CO forming an α-keto amide. They noted that aryl iodides react faster than aryl bromides and that use of electron-withdrawing para substituents on the aryl bromides increases the reaction rate. Furthermore, the rate was zero order in iodobenzene, but first order when bromobenzene was used. On the basis of this and other data, Ozawa and co-workers concluded that oxidative addition of iodobenzene is relatively facile and that the subsequent CO coordination is the rate-limiting step. In the bromobenzene case, however, oxidative addition is slower and becomes rate-limiting. This work is consistent with a mechanism in which oxidative addition precedes CO coordination.

Finally, Stille and Wong[5] have suggested a markedly different route in which reaction of a dihalobis(phosphine)palladium species with methanol yields a halobis(phosphine)(carbomethoxy)palladium intermediate. The facility of this reaction and that of the subsequent reaction with methyl iodide or benzyl bromide yielding ester have been demonstrated.[6]

Despite these studies, the mechanism by which reaction 1 and related reactions occur is not well understood. It is unclear whether the active palladium complex reacts first with bromobenzene or methanol. If bromobenzene reaction occurs first, it would presumably be followed by CO insertion into the Pd-phenyl bond, but it is not known how the resulting benzoyl complex **3** reacts with methanol to produce ester. The mechanistic role of triethylamine is also not understood. One obstacle to mechanistic studies of this reaction is that most of the proposed intermediates have not been well-characterized. This is true in part because no thorough in-situ infrared studies of this system have been published.

Prior experimentation has shown that cylindrical internal reflectance coupled with Fourier transform infrared spectroscopy, CIR-FTIR, permits one to obtain high-quality in-situ infrared spectra.[7-13] Use of a well-stirred high-pressure autoclave with

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directly embedded CIR optics affords several experimental advantages in the study of solution reactions. Unlike other in-situ infrared techniques, the portion of the sample being analyzed is truly representative of the entire solution, since no unusual reactor geometry is required. Furthermore, the path length in a CIR–FTIR experiment is both considerably shorter and less sensitive to changes in temperture and pressure than in traditional infrared cells. These features reduce the likelihood of strong solvent bands obscuring portions of the spectrum and facilitate quantitative measurements. The in-situ nature of the technique allows one to continually monitor changes in concentrations of species in a solution without interrupting the experiment. A complete description of this technique and its applications was previously reported by Moser and co-workers.[7]

To clarify the mechanistic picture, we have used CIR–FTIR, together with standard spectroscopic methods, to study reaction 1. We have identified, isolated, and characterized a number of the proposed intermediates in the catalytic cycle. In addition, we have demonstrated the feasibility of several of the proposed mechanistic steps.

Experimental Section

Materials. Solvents (bromobenzene, triethylamine, 2,6-lutidine, *N,N*-dimethylpiperazine, *N*-methylmorpholine, *N*-methylpyrrolidine, *N*-methylpiperidine, methanol, benzene, chloroform-*d*, and diethyl ether) were purchased from Aldrich. Purification of bromobenzene, methanol, benzene, and triethylamine involved refluxing with an appropriate drying agent, distillation under nitrogen, and degassing by freeze–thaw under vacuum. The other amines were degassed by freeze–thaw and used without further purification. Chloroform-*d* was used as purchased. Anhydrous ether was degassed by bubbling nitrogen through 100 mL for 30 min. All solvents were stored and used in a nitrogen atmosphere. Tetrakis(triphenylphosphine)palladium was used as purchased from Strem.

Synthesis of $Pd(P(C_6H_5)_3)_2(C_6H_5)Br$. This synthesis was carried out by the general method reported by Fitton and Rick.[14] $Pd(P(C_6H_5)_3)_4$ (2.2 g) and bromobenzene (2 mL) were heated to reflux in benzene (10 mL) for 20 h to ensure complete conversion. The solvents were then removed in vacuo, and the light yellow solid was stirred vigorously with 40–50 mL of ether for 30 min. The solution was filtered, and the solid was placed in 40 mL of benzene and brought to the boiling point. The solution was then filtered hot, and the filtrate was cooled and all but 2 to 3 mL of the benzene was removed in vacuo. The resulting light yellow-cream solid was removed by filtration and dried. The average yield was 70%.

The product was characterized by elemental analysis, infrared spectroscopy, and NMR spectroscopy. Anal. (Galbraith Laboratories) ($PdBrP_2C_{42}H_{35}$) C, H, Br. Infrared spectrum (in chloroform-*d*): 3075, 3055 (s), 3005, 1562 (s), 1432 (s), 1057, 1025, 1015 cm^{-1}. ^1H NMR spectrum (in chloroform-*d*): two multiplets, 7.36, 7.33, 7.28, 7.23, 7.20, 7.15, 7.05 ppm and 6.46, 6.42, 6.36, 6.30, 6.13, 6.06, 5.95 ppm. ^{31}P NMR spectrum (in chloroform-*d*): 23.5 ppm (s).

Synthesis of $Pd(P(C_6H_5)_3)_2(COC_6H_5)Br$. CO was bubbled through 2 mL of a 0.1 M solution of **1** in chloroform for 30 min, during which time the color of the solution changed from very pale yellow to orange-yellow. The solution was capped and quickly placed into a nitrogen atmosphere. Methanol was added dropwise until precipitation of **3** was complete. This yellow-brown solid was washed with methanol and recrystallized from chloroform/methanol. Anal. ($BrC_{43}H_{35}OPdP_2$) C, H. Infrared spectrum (in chloroform-*d*): 3075, 3055, 3005, 1644 (s), 1445, 1432, 1302 cm^{-1}. ^1H NMR spectrum (in chloroform-*d*): two multiplets, 7.05, 7.17, 7.22, 7.29 ppm and 6.06, 6.31, 6.36 ppm. ^{31}P NMR spectrum: 18.8 ppm (s).

Physical Methods. Infrared spectra were recorded on a Nicolet 60SX FT-IR spectrometer equipped with an MCT (A or B) detector and integration and subtraction capabilities. Typically 300–1000 scans were taken per spectrum. Integrated peak intensities were used to calculate the product concentrations in the kinetic portions of the study. The CIR reactor was designed in this laboratory and manufactured for Barnes Analytical/Spectra Tech, Inc., Stamford, CT, by Parr Instrument Co.

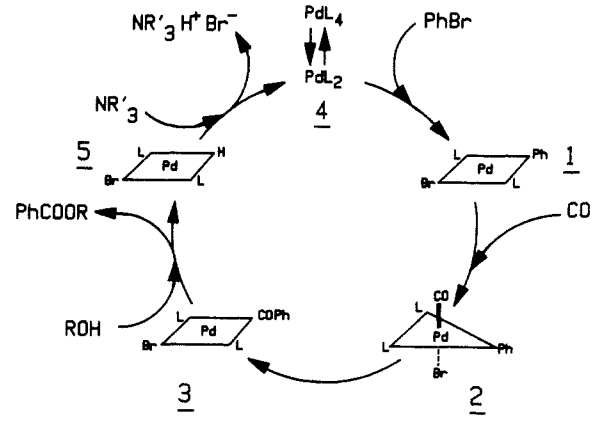

Figure 1. Modified Heck mechanism used as a basis in this study (L = triphenylphosphine, Ph = phenyl).

The silicon CIR crystals were also obtained from Barnes Spectra-Tech. Additional infrared spectra were acquired on a Perkin-Elmer 683 infrared spectrophotometer. A standard transmission cell with NaCl windows was used with the latter equipment.

^1H NMR spectra were measured on a Perkin-Elmer R24-B 60-MHz high-resolution NMR spectrometer. An external TMS standard was used. ^{31}P NMR spectra were measured on a Bruker WM250 at 101.27 MHz. An external H_3PO_4 standard was employed, and downfield shifts were assigned positive values. All NMR spectra were obtained from 0.1 M solutions in chloroform-*d*.

Gas chromatograms were obtained on a Perkin-Elmer Sigma 2000 gas chromatograph interfaced with a Perkin-Elmer 3600 data station. A 6-ft, $^1/_8$-in.-diameter column, Carbowax 20M on Chromosorb W, was used to effect the separation.

Results and Discussion

The starting point for this study was a modified Heck mechanism (Figure 1) involving oxidative addition of bromobenzene to a palladium(0) species (forming **1**), followed by CO coordination and insertion (producing **3**) and methanolysis yielding methyl benzoate and regenerating the palladium catalyst. This scheme was chosen on the strength of three observations. First, Fitton and Rick[14] have shown that oxidative addition of aryl halides to tetrakis(triphenylphosphine)palladium is facile. Second, the resulting haloorganobis(phosphine) complex readily coordinates CO and undergoes insertion, as reported by Garrou and Heck.[3] Third, in our preliminary CIR–FTIR studies of the active catalytic reaction in which methanol served as the solvent, we observed no evidence of carbonyl-containing intermediates at steady-state, suggesting that the dominant catalytic intermediate does not contain a carbonyl group. This observation is consistent with a rate-limiting step involving oxidative addition of bromobenzene to the bis(phosphine)palladium complex, as was suggested by Ozawa and co-workers.[4]

To examine the feasibility of this mechanism, we started with bromophenylbis(triphenylphosphine)palladium (**1**) and proceeded through the mechanism in discreet steps until we had returned to **1**. When possible, intermediates were isolated and characterized, and rates of individual steps were measured.

Synthesis of $Pd(P(C_6H_5)_3)_2(C_6H_5)Br$. To our knowledge, of the intermediates proposed in this mechanism, only **1** has been previously synthesized, isolated, and characterized. However, neither the complete infrared nor the NMR spectrum of **1** have been reported. We began our study by synthesizing and purifying **1** by the literature method. The synthesis and characterization are described in the Experimental Section. The infrared spectrum displays a characteristic palladium-bound phenyl C–C stretch at 1562 cm^{-1}. The ^1H NMR spectrum consists of two multiplets, centered at 7.05 and 6.25 ppm, which have relative intensities 6:1. The multiplet at 7.05 is therefore assigned to the phosphine phenyl protons, while the multiplet at 6.25 is assigned to the palladium-bound phenyl group. The latter multiplet occurs somewhat upfield due to shielding by electron density on the palladium. These assignments are consistent with those reported by Ozawa and co-workers for $Pd(Br)(C_6H_5)(P(CH_3)(C_6H_5)_2)_2$.[13] The ^{31}P NMR

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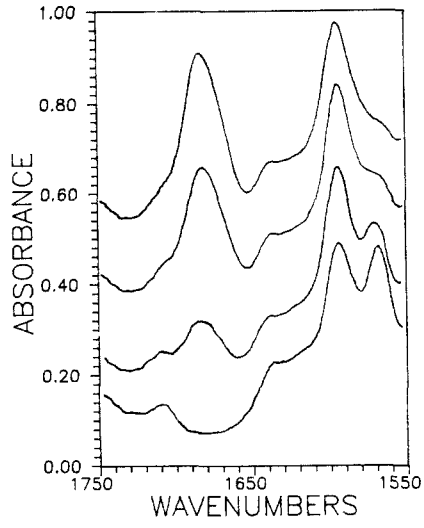

Figure 2. Reaction of 0.1 M $PdBr(C_6H_5)(P(C_6H_5)_3)_2$ with CO at 90 °C and 40 psi. The bottom spectrum was obtained just prior to CO pressurization. Successive spectra were obtained leading to the final (top) spectrum after 30 min of reaction.

spectrum consists of a singlet at 23.5 ppm, suggesting a trans configuration and consistent with literature data for analogous complexes.[15-18]

Carbonylation of $Pd(P(C_6H_5)_3)_2(C_6H_5)Br$. To reinforce the work of Garrou and Heck, we examined the reaction of **1** with carbon monoxide. CO was bubbled through a 0.1 M solution of **1** in $CDCl_3$ for 30 min at room temperature. An infrared spectrum of the resulting solution showed that the peak at 1562 cm^{-1}, due to the palladium-bound phenyl in **1**, was absent and that a new peak had appeared at 1648 cm^{-1}. Garrou and Heck reported that the C=O stretching frequency for **3** appears at 1650 cm^{-1}.[3] Furthermore, the ^1H NMR spectrum showed that the multiplet due to the phenyl previously bound to the metal had undergone a shift to lower field, consistent with the introduction of an electron-withdrawing functionality directly bound to it. The ^{31}P NMR spectrum consists of a singlet at 18.8 ppm, an upfield shift of 4.7 ppm from that of complex **1**. Ozawa and co-workers observed upfield shifts of 4–5 ppm for analogous carbonylated complexes.[15] On the basis of these observations, it is evident that **1** has been converted to the corresponding trans benzoyl complex **3**.

The carbonylation of **1** was also studied with the CIR–FTIR reactor. A 0.1 M solution of **1** in benzene was stirred at 90 °C under 40 psi of CO for 30 min. A series of spectra taken during the course of the reaction showed the disappearance of the peak at 1562 cm^{-1} and the simultaneous appearance of the benzoyl peak at 1648 cm^{-1} (see Figure 2). No evidence of the intermediate carbonyl complex **2** was observed. A pseudo-first-order plot of the conversion to **3** yielded a rate constant of 0.8 min^{-1}. Removal of the CO pressure and stirring under nitrogen for 2 h at 90 °C resulted in no loss of intensity of the benzoyl peak at 1648 cm^{-1}, implying that CO insertion is not reversible under these conditions.

Reductive Elimination of Benzoyl Bromide from 3. Although Garrou and Heck had not observed reductive elimination of the acid halide from the benzoyl complex, the possibility remained that an unfavorable equilibrium involving the acid halide could be the primary route to ester, since it is known that the benzoylammonium salt produced by reaction of the acid halide with amine reacts rapidly with methanol to form the methyl ester.[19] To examine this possibility, we studied the reaction of the benzoyl complex **3** with triethylamine in the absence of CO. The addition of a tenfold excess of triethylamine to the 0.1 M solution of **3** resulted in no loss of intensity of the benzoyl peak after 20 min at 90 °C. This stability of **3** in the presence of amine implies that formation of benzoyl bromide from **3** does not occur at a significant rate, since benzoyl bromide would immediately react with the amine to form the benzoylammonium salt.[19]

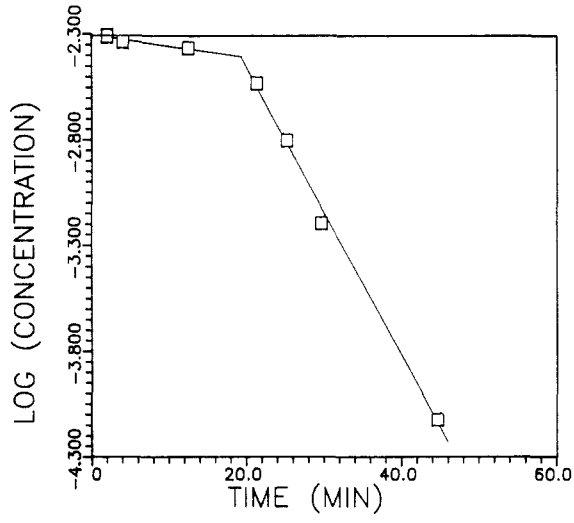

Figure 3. First-order plot (based on *3*) of the disappearance of **3** in the presence of approximately 1 M methanol (first 20 min) and 1 M methanol and 1 M triethylamine (after the first 20 min).

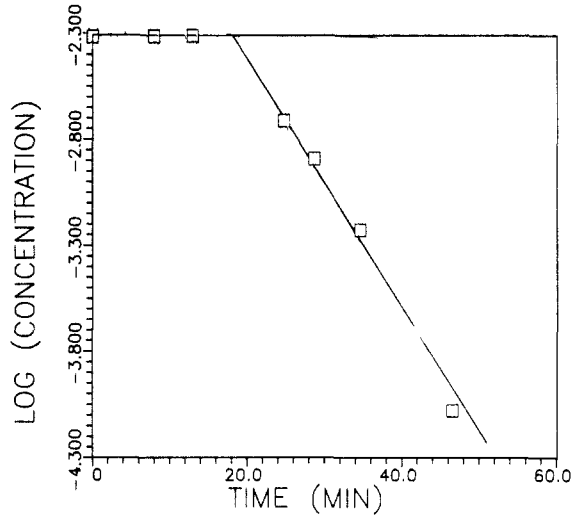

Figure 4. First-order plot (based on **3**) of the disappearance of **3** in the presence of approximately 1 M triethylamine (first 20 min) and 1 M triethylamine and 1 M methanol (after the first 20 min).

Reaction of 3 with Methanol and Triethylamine in the Absence of CO. The reactivity of **3** with methanol was then studied in both the presence and absence of triethylamine. When a 0.1 M solution of **3** was allowed to react at 90 °C under a nitrogen atmosphere with a tenfold excess of methanol in the CIR reactor, a very slow rate of methyl benzoate formation was observed. However, when a tenfold excess of triethylamine was added as well, rapid formation of methyl benzoate was observed (Figure 3). Similarly, addition of only 0.4 mL of methanol to 9.6 mL of the previously unreactive solution of **3** with triethylamine led to rapid production of ester (Figure 4). It is evident that both alcohol and amine are necessary for facile conversion of **3** to ester. It is possible that the amine could be activating the methanol by deprotonating it. The methoxide thus produced would be a far more effective nucleophile and could react with **3** to produce ester directly. These data do not enable one to discern whether this nucleophilic attack occurs directly on the carbonyl group or on the palladium center. In this latter case, the subsequent ester-forming step via reductive

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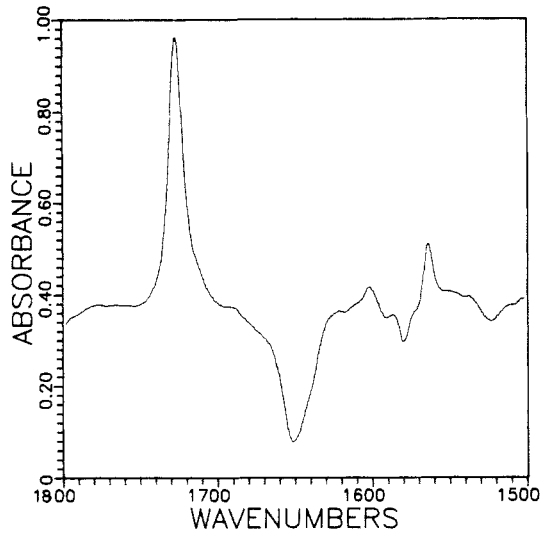

Figure 5. CIR–FTIR spectrum of the changes during reaction of **3** with methanol, triethylamine, and bromobenzene at 90 °C under nitrogen. The final spectrum (after 60 min) was ratioed to the initial spectrum; thus changes in concentrations appear as positive and negative peaks, depending on whether the species was produced or consumed, respectively.

elimination of the methoxyl and benzoyl groups would have to be very rapid.

The reaction of 0.1 M **3** with 1 M methanol, 1 M triethylamine, and 1 M bromobenzene at 90 °C under nitrogen resulted in the rapid formation of methyl benzoate and disappearance of **3** as observed in the CIR–FTIR. A difference spectrum of this reaction (Figure 5) displayed positive bands at 1727 and 1600 cm^{-1}, indicative of the formation of methyl benzoate, and a negative peak at 1648 cm^{-1}, indicative of the depletion of **3**. The simultaneous appearance of the peak at 1562 cm^{-1} indicated that the bromophenylbis (phosphine)palladium (**1**) was being regenerated. The palladium catalyst was recovered from the solution and isolated by recrystallization from benzene. The NMR spectrum of this complex confirmed that it was **1**. The identity of the ester was verified by gas chromatography. Thus the catalytic loop had been completed.

When the preceding experiment was repeated without the bromobenzene, formation of palladium–carbonyl clusters was observed, along with methyl benzoate production (see Figure 6). Hidai[6] has attributed the peak at 1855 cm^{-1} to $Pd_3(P(C_6H_5)_3)_4(CO)_3$. The broad band around 1910 cm^{-1} is likely due to a Pd–CO homopolymer of the type described by Goggin and Mink.[20] A possible explanation is that in the absence of bromobenzene, the bis(phosphine) complex formed after the methyl benzoate producing step scavenges dissolved CO and forms clusters. A number of studies have shown that palladium–carbonyl–phosphine systems readily form clusters and that these clusters are quite stable.[21-27]

If **4** is produced as an intermediate, it should react rapidly with triphenylphosphine to form tetrakis(triphenylphosphine)palladium, in the absence of the competing oxidative addition of bromobenzene. When the experiment above was repeated, again without bromobenzene, but with two added moles of triphenylphosphine per mole of palladium, cluster formation was substantially suppressed. In addition, the intensity of the free phosphine peak at 1583 cm^{-1} weakened as the reaction progressed, indicating that triphenylphosphine was being taken up by the palladium catalyst. A difficulty in the identification of these species arises because the tetrakis(triphenylphosphine)palladium also has a peak at 1583 cm^{-1}, although it has a weaker absorbance. Presumably, some of the **4** being formed reacted with the free triphenylphosphine to form tetrakis(triphenylphosphine)palladium, rather than being converted to clusters. This is consistent with the observation that when the reaction is carried out in a catalytic fashion, the use of excess phosphine is necessary to prevent catalyst decomposition via cluster formation.

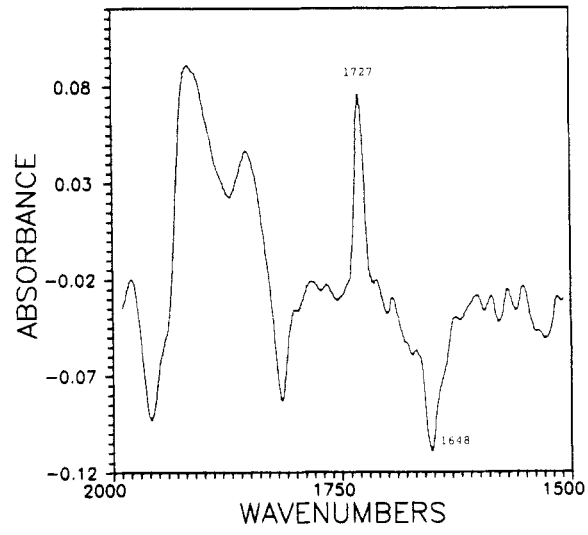

Figure 6. CIR–FTIR spectrum of the changes during reaction of **3** with methanol and triethylamine under nitrogen and in the absence of bromobenzene. The final spectrum was ratioed to the initial spectrum; thus changes during this period appear as positive or negative peaks, depending on whether the species was produced or consumed, respectively.

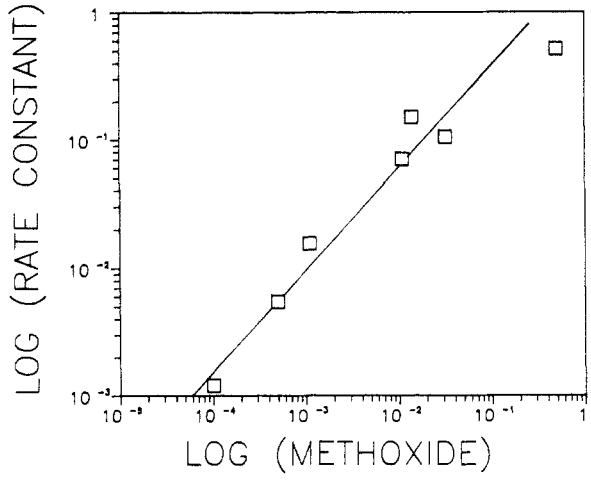

Figure 7. First-order rate constants for the reaction of $PdBr(COC_6H_5)(P(C_6H_5)_3)_2$ at 90 °C with 1 M methanol and a variety of 1 M amines as a function of the resulting estimated methoxide ion concentration (calculated on the basis of amine pK_a values in water).

Reaction of 3 with Methanol in the Presence of a Variety of Amines in the Absence of CO. The hypothesis that the amine plays a role in activating the methanol by deprotonating it was examined by measuring the rates of reaction of the benzoyl complex **3** with methanol in the presence of a variety of amines of differing basicity. The amines used were 2,6-lutidine (pK_a = 6.5), *N*-methylmorpholine (pK_a = 7.40), *N*,*N*-dimethylpiperazine (pK_a = 8.1), *N*-methylpiperidine (pK_a = 10.08), *N*-methylpyrrolidine (pK_a = 10.32), and triethylamine (pK_a = 11.01). The pseudo-first-order rate constant for the disappearance of **3** is plotted as a function of the estimated concentration of methoxide ion

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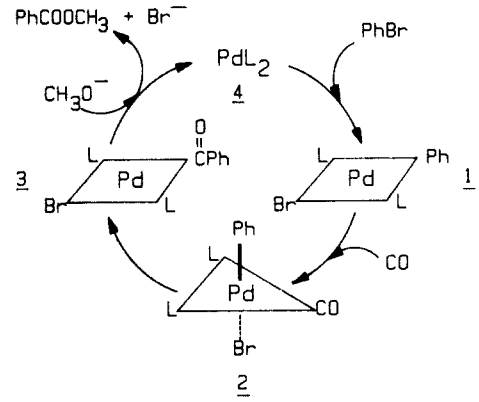

Figure 8. Proposed reaction mechanism in which methoxide ion (produced by deprotonation of methanol by amine) directly attacks the benzoyl complex **3**, resulting in the production of methyl benzoate and regeneration of the catalytic intermediate PdL_2 (L = triphenylphosphine, Ph = phenyl).

(calculated based on the pK_b of the amine in water) in Figure 7. An additional data point arises from an experiment in which methoxide ion (prepared from sodium metal and methanol) was injected directly into the reactor to a concentration of 0.5 M. Figure 7 demonstrates a clear relationship between the ability of the amine to deprotonate the methanol and the resulting rate of reaction of **3**. This provides additional evidence that the amine serves to convert the methanol to methoxide ion, which is sufficiently nucleophilic to attack the benzoyl complex **3** (Figure 8).

Possible Involvement of a Carbomethoxy Intermediate. In a separate series of experiments, the reactivity of the carbomethoxy complex, $Pd(P(C_6H_5)_3)_2(CO_2CH_3)Cl$, was examined to investigate the alternate mechanism suggested by the work of Stille and Wong.[5] This complex was synthesized according to the method published by Hidai[6] and confirmed by the infrared spectrum as reported by Hidai and the ^1H NMR spectrum as reported by Stille and Wong. In four separate experiments, solutions of the carbomethoxy complex were brought to 90 °C in the presence of bromobenzene and triethylamine. In the first experiment, the solution contained 1 M triethylamine in benzene under a pressure of 50 psi of CO. The solution was rapidly heated to 90 °C, and bromobenzene was injected. The solution was stirred at 90 °C for 4 hours. In the second experiment, the procedure of the first experiment was repeated, but the CO was omitted and methanol was used as the solvent. In the third experiment, a solution of the carbomethoxy complex in 1 M triethylamine, 1 M bromobenzene, and benzene under 50 psi of CO was heated to 90 °C and stirred overnight. In the fourth experiment a chloroform solution of the carbomethoxy complex was injected directly into a 90 °C benzene solution which was 1 M in both triethylamine and bromobenzene. In all four experiments, GC and CIR/FTIR analyses of the final solution revealed only minute traces of methyl benzoate (less than 2% yield based on the moles of chloro(carbomethoxy)bis(triphenylphosphine)palladium(II) charged to the reactor). In experiments 2-4 the carbomethoxy complex was observed via CIR/FTIR to be relatively stable at 90 °C in the presence of triethylamine and bromobenzene. This indicates that formation of a carbomethoxy intermediate which subsequently reacts with bromobenzene and/or triethylamine is not a facile route to ester formation and this system. The possibility remains that in systems containing more reactive organic halides, such as methyl iodide, this mechanism may become important, as has been proposed by Stille and Wong.[5]

Conclusions

The study of the individual steps in the palladium-catalyzed carbomethoxylation of bromobenzene with use of a CIR–FTIR reactor yielded the following conclusions. (1) The general mechanism shown in Figure 8 has been demonstrated on a stoichiometric basis. The conversion of **1** to the corresponding benzoyl complex **3** is quite rapid and appears to be irreversible. The intermediacy of the carbonyl complex **2**, although not observed, is implied by the work of Garrou and Heck.[3] Both methanol and triethylamine are required for facile reaction of $Pd(P(C_6H_5)_3)_2(C_6H_5CO)(Br)$ to form methyl benzoate. Furthermore, the rate of this reaction increases with the basicity of the amine. This suggests that the amine facilitates the reaction of methanol with **3** by converting methanol to methoxide ion. Direct reaction of methoxide ion, rather than methanol, with **3** is the principal mechanism of methyl benzoate production. The other product is probably bis(triphenylphosphine)palladium, as is implied by its reactions with carbon monoxide to form clusters, with free triphenylphosphine to form tetrakis(triphenylphosphine)palladium, and with bromobenzene to regenerate **1**. (2) Two key intermediates, $Pd(P(C_6H_5)_3)_2(C_6H_5)(Br)$ and $Pd(P(C_6H_5)_3)_2(C_6H_5CO)(Br)$, have been characterized by infrared and NMR spectroscopy. (3) Reductive elimination of benzoyl bromide from $Pd(P(C_6H_5)_3)_2(C_6H_5CO)(Br)$ is inoperative as a route to methyl benzoate formation. (4) Reaction of bromobenzene with a palladium–carbomethoxy intermediate is not a significant mechanism for methyl benzoate production.

Acknowledgment. The authors are grateful to the Dow Chemical Company for providing the funding for this project and in particular Dr. Philip Garrou, who provided numerous technical suggestions. We are indebted to Barnes Spectra-Tech who provided much of the CIR hardware for this study, and to the National Science Foundation (CPE-82 18110) for an FTIR equipment grant and a research grant (CPE-82 03278) supporting the development of CIR–FTIR reactors. We also acknowledge Dr. Paul Inglefield of the Worcester Consortium NMR Facility (supported by NSF Grant CHE77-09059), who ran the ^{31}P NMR spectra.