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REACTIONS OF PALLADIUM(II) COMPOUNDS WITH CARBON MONOXIDE IN ALCOHOL/AMINE SYSTEMS : A NEW ROUTE TO PALLADIUM(0) CARBONYL- AND CARBOALKOXY-PALLADIUM(II) COMPLEXES

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SUMMARY

Palladium(0) carbonyl complexes, $Pd(CO)(PPh_3)_3$, $Pd_3(CO)_3(PPh_3)_3$, and $Pd_3(CO)_3(PPh_3)_4$, can conveniently be prepared by the reaction of $(PPh_3)_2PdCl_2$ with carbon monoxide at room temperature in methanol/amine systems involving primary and secondary amines such as diethylamine and cyclohexylamine. These carbonyl complexes are interconvertible under suitable conditions. On the other hand, use of tertiary amines such as triethylamine and tri-n-butylamine in place of the above amines gives selectively a carbomethoxy complex $(PPh_3)_2PdCl(COOCH_3)$.

INTRODUCTION

In previous papers[1], we have reported that first examples of stable palladium(0) carbonyl complexes, $Pd(CO)(PPh_3)_3$ (I), $Pd_3(CO)_3(PPh_3)_3$ (II), and $Pd_3(CO)_3(PPh_3)_4$ (III), are prepared by the reduction of palladium(II) compounds with triethylaluminium or sodium borohydride in the presence of triphenylphosphine under carbon monoxide.

Recently, series of base/alcohol systems involving triethylamine and potassium hydroxide have been conveniently used as reducing agents. For example, tetrakis(triethyl phosphite)palladium(0) was prepared from potassium tetrachloropalladate(II) and triethyl phosphite by use of methanolic diethylamine[2].

We have now examined the reaction of $(PPh_3)_2PdCl_2$ with carbon monoxide in methanol/amine systems and found that the above palladium(0) carbonyl complexes are obtained by use of primary or secondary amines such as diethylamine and cyclohexylamine, while a carbomethoxy complex, $(PPh_3)_2PdCl(COOCH_3)$, is prepared by use of tertiary amines such as triethylamine and tri-n-butylamine.

RESULTS AND DISCUSSION

Preparation of palladium(0) carbonyl complexes by use of methanol/primary or secondary amine systems

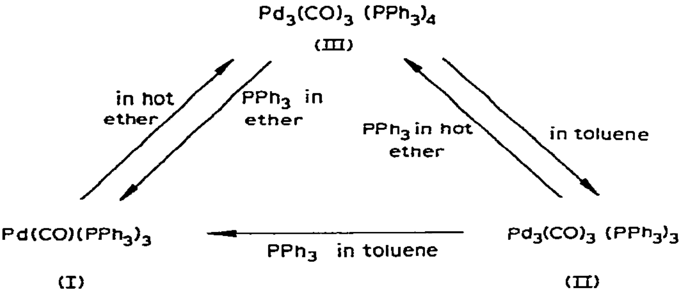
Palladium(0) carbonyl complexes can conveniently be prepared from $(PPh_3)_2PdCl_2$, carbon monoxide, methanol, and a primary or secondary amine at room temperature.

$$(PPh_3)_2PdCl_2+CO+CH_3OH+R_1R_2NH \rightarrow$$
$$\rightarrow \underset{(I)}{Pd(CO)(PPh_3)_3}+\underset{(III)}{Pd_3(CO)_3(PPh_3)_4}$$

$$R_1=C_2H_5, R_2=C_2H_5;\ R_1=\text{n-}C_4H_9, R_2=H;$$
$$R_1=C_6H_5, R_2=H;\quad R_1=C_6H_{11},\ R_2=H$$

When a suspension of $(PPh_3)_2PdCl_2$ in a methanol/primary or secondary amine (1/1) mixed solvent was stirred under carbon monoxide for several hours at room temperature, the original orange-yellow colour of the precipitate changed first to white and then rapidly to canary yellow. The infrared spectrum of the canary yellow precipitate showed strong absorption bands at 1955, 1845, and 1820 cm^{-1} assignable to $\nu(C{\equiv}O)$, indicating that it is a mixture of $Pd(CO)(PPh_3)_3$ (I) and $Pd_3(CO)_3(PPh_3)_4$ (III). However, $(PPh_3)_2PdCl_2$ dissolved completely in methanol/aniline system to give a reddish brown solution under carbon monoxide, from which the carbonyl complex (III) was gradually precipitated as yellow crystals. These carbonyl complexes were also obtained by using $(PPh_3)_2PdCl(NO_2)$ in place of $(PPh_3)_2PdCl_2$.

In previous papers[1], we have reported that an equilibrium exists between (I) and (III). It was now observed that all three palladium(0) carbonyl complexes, (I), (II), and (III), are interconvertible under suitable conditions. When the complex (III) dissolved in toluene, the colour of the solution turned to red. The addition of hexane to the solution gave the complex (II) as red crystals. By refluxing an ether suspension of the complex (II) in the presence of equimolar triphenylphosphine, complex (III) was obtained. On the other hand, recrystallization of the complex (II) from toluene/hexane in the presence of excess triphenylphosphine gave the complex (I).



Preparation of $(PPh_3)_2PdCl(COOCH_3)$ by use of methanol/tertiary amine systems

As described above, interaction of $(PPh_3)_2PdCl_2$ with carbon monoxide in methanol/primary or secondary amine systems produced palladium(0) carbonyl complexes in good yields. However, use of tertiary amines such as triethylamine, tri-n-butylamine, and tri-n-octylamine in place of the above amine afforded $(PPh_3)_2PdCl(COOCH_3)$ selectively, and palladium(0) carbonyl complexes were not obtained at room temperature.

$$(PPh_3)_2PdCl_2+CO+NR_3+CH_3OH \rightarrow$$
$$\rightarrow (PPh_3)_2PdCl(COOCH_3)+NR_3\cdot HCl$$
$$R=C_2H_5,\ \text{n-}C_4H_9,\ \text{and n-}C_8H_{17}$$

When a suspension of $(PPh_3)_2PdCl_2$ in a methanol/tertiary amine (1/1) mixed solvent was stirred under carbon monoxide for several hours at room temperature, the colour of the precipitate changed into white. The recrystallization of the precipitate from dimethylformamide/methanol gave white needles. The elemental analysis of the complex was in accord with the formula $(PPh_3)_2PdCl(COOCH_3)$. The reaction of the complex with methyl iodide and benzyl bromide at elevated temperature gave a quantitative amount of methyl acetate and methyl phenylacetate respectively. Treatment of the complex with hydrochloric acid in ether yielded methanol and $(PPh_3)_2PdCl_2$. Furthermore, the infrared spectrum showed two strong absorption bands at 1650 and 1065 cm^{-1} characteristic of the $-C(O)-O-C$ group and a band at 325 cm^{-1} assigned to $\nu(Pd-Cl)$. These results provide good evidence that the complex is $(PPh_3)_2PdCl(COOCH_3)$.

As described above, the colour of the suspension of $(PPh_3)_2PdCl_2$ in methanol/primary or secondary amine systems under carbon monoxide turned firstly to white and then rapidly to canary yellow at room temperature. However, the reaction at ca. $-70°$ afforded the white precipitate in a good yield. The infrared spectrum of the white precipitate showed that it was the carbomethoxy complex $(PPh_3)_2PdCl(COOCH_3)$. This indicates that the carbomethoxy complex is easily converted to palladium(0) carbonyl complexes under carbon monoxide in methanol/primary or secondary amine systems at room temperature, in contrast with its stability in methanol/tertiary amine systems.

When $(PPh_3)_2PdCl(NO_2)$ was used instead of $(PPh_3)_2PdCl_2$ in methanol/tertiary amine systems, palladium(0) carbonyl complexes were also formed as well as the carbomethoxy complex. Potassium hydroxide can also be used instead of amine to yield both complexes.

There are recent reports that styrene can be dicarboxylated with alcohol and carbon monoxide in the presence of triethylamine and palladium chloride[3], and that diesters can conveniently be prepared from a variety of olefins and acetylenes with carbon monoxide at low pressure, an alcohol, and palladium chloride, with or without mercuric chloride as a cocatalyst[4]. In these reactions, "carboalkoxypalladium chloride" has been suggested as an intermediate, but no evidence for its existence was obtained. We have now succeeded in the isolation of a carboalkoxypalladium complex $(PPh_3)_2PdCl(COOCH_3)$ directly from $(PPh_3)_2PdCl_2$, carbon monoxide, tertiary amine, and methanol, although a similar complex $(PPh_3)_2PdCl(COOC_2H_5)$ has been prepared by the oxidative addition of ethyl chlorocarbonate to tetrakis(triphenylphosphine)palladium(0)[5].

EXPERIMENTAL

All preparations and recrystallizations were carried out in an atmosphere of carbon monoxide or nitrogen. Solvents were purified by the usual methods and used after distillation under nitrogen. Amines were obtained commercially and used without further purification. The dichlorobis(triphenylphosphine)palladium(II), $(PPh_3)_2PdCl_2$, was prepared by the published method[6]. The chloronitrobis(triphenylphosphine)palladium(II), $(PPh_3)_2PdCl(NO_2)$, was prepared by boiling a mixture of $(PPh_3)_2PdCl_2$ and $NaNO_2$ in ethanol/water under reflux for 5 h. (Found: C, 60.93; H, 4.46; N, 2.50; Cl, 5.1. $C_{36}H_{30}Cl_2P_2Pd$ calcd.: C, 60.68; H, 4.24; N, 1.97; Cl, 4.98 %.)

All reactions of $(PPh_3)_2PdCl_2$ and $(PPh_3)_2PdCl(NO_2)$ with carbon monoxide in methanol/amine systems are very similar, so several typical examples are described below.

Reaction of $(PPh_3)_2PdCl_2$ with carbon monoxide in methanol/diethylamine system

A suspension of $(PPh_3)_2PdCl_2$ (0.270 g, 0.386 mmole) in methanol (5 ml) and diethylamine (5 ml) was stirred under carbon monoxide for 3 h at room temperature. The original orange-yellow colour of the precipitate changed first to white and then rapidly to canary yellow. The precipitate was washed with methanol several times and dried *in vacuo*. The infrared spectrum showed that it was a mixture of $Pd(CO)(PPh_3)_3$ (I) and $Pd_3(CO)_3(PPh_3)_4$ (III). It dissolved in toluene (10 ml) to give a red solution. The addition of hexane (20 ml) to this solution at −20° afforded $Pd_3(CO)_3(PPh_3)_3$ (II) as red crystals (0.112 g, 61.5%). (Found: C, 57.70; H, 4.15. $C_{57}H_{45}O_3P_3Pd_3$ calcd.: C, 57.53; H, 3.82%.)

Reaction of $(PPh_3)_2PdCl_2$ with carbon monoxide in methanol/aniline system

A suspension of $(PPh_3)_2PdCl_2$ (0.270 g, 0.386 mmole) in methanol (5 ml) and aniline (5 ml) was stirred under carbon monoxide for 3 h at room temperature. The originally orange-yellow precipitate dissolved completely within half an hour to give a reddish brown solution and then orange-yellow crystals of $Pd_3(CO)_3(PPh_3)_4$ (III) were gradually precipitated within 3 h; these were washed with methanol, ether, and hexane several times and dried *in vacuo* (0.150 g, 81.8%). (Found: C, 61.63; H, 4.12. $C_{75}H_{60}O_3P_4Pd_3$ calcd.: C, 62.00; H, 4.17%.)

Reaction of $(PPh_3)_2PdCl(NO_2)$ with carbon monoxide in methanol/cyclohexylamine system

The reaction was carried out as above, except that $(PPh_3)_2PdCl(NO_2)$ (0.207 g, 0.296 mmole) was used instead of $(PPh_3)_2PdCl_2$. $Pd_3(CO)_3(PPh_3)_3$ (II) was obtained as red crystals (0.108 g, 94.1%).

The conversion of $Pd_3(CO)_3(PPh_3)_4$ (III) to $Pd_3(CO)_3(PPh_3)_3$ (II)

$Pd_3(CO)_3(PPh_3)_4$ (III) (0.203 g, 0.142 mmole) dissolved in toluene (10 ml) to give a red solution. After addition of hexane (20 ml) to the solution, $Pd_3(CO)_3(PPh_3)_3$ (II) was obtained as red crystals (0.121 g, 72.1%).

The conversion of $Pd_3(CO)_3(PPh_3)_3$ (II) to $Pd_3(CO)_3(PPh_3)_4$ (III)

When an ether suspension of $Pd_3(CO)_3(PPh_3)_3$ (II) (0.294 g, 0.247 mmole) was refluxed in the presence of triphenylphosphine (0.070 g, 0.267 mmole) under carbon monoxide, the original red colour of the precipitate turned to orange-yellow. The precipitate was separated by filtration, washed with ether, and dried to give $Pd_3(CO)_3(PPh_3)_4$ (III) (0.305 g, 86.2%).

The conversion of $Pd_3(CO)_3(PPh_3)_3$ (II) to $Pd(CO)(PPh_3)_2$ (I)

Triphenylphosphine (0.475 g, 1.83 mmole) was added to a red solution of $Pd_3(CO)_3(PPh_3)_3$ (II) (0.183 g, 0.154 mmole) in toluene (10 ml) and the colour of the solution turned to yellow. After addition of hexane (20 ml) to the solution at 0°, $Pd(CO)(PPh_3)_3$ was obtained as cream-yellow crystals (0.316 g, 74.8%).

Reaction of $(PPh_3)_2PdCl_2$ with carbon monoxide in methanol/tri-n-octylamine system

A suspension of $(PPh_3)_2PdCl_2$ (0.283 g, 0.405 mmole) in methanol (5 ml) and tri-n-octylamine (5 ml) was stirred for 3 h at room temperature under carbon monoxide and the originally orange-yellow colour of the precipitate changed to white. After washing with methanol and toluene, the precipitate was recrystallized from dimethylformamide/methanol to give $(PPh_3)_2PdCl(COOCH_3)$ as white needles (0.278 g, 74.9%: decompn. 175–185°). (Found: C, 62.42; H, 4.76; Cl, 4.60. $C_{38}H_{33}O_2ClP_2Pd$ calcd.: C, 62.98; H, 4.58; Cl, 4.88%.)

Reaction of $(PPh_3)_2PdCl(NO_2)$ with carbon monoxide in methanol/triethylamine system

A suspension of $(PPh_3)_2PdCl(NO_2)$ (0.153 g, 0.215 mmole) in methanol (5 ml) and triethylamine (5 ml) was stirred under carbon monoxide for 3 h at room temperature and the original orange-yellow colour of the precipitate turned to pale yellow. After washing with methanol, the precipitate was dissolved in toluene (10 ml) and the solution filtered. The addition of hexane (20 ml) to the red filtrate at −20° afforded $Pd_3(CO)_3(PPh_3)_3$ (II) as red crystals (0.100 g, 53.5%). On the other hand, the white residue was recrystallized from dimethylformamide/methanol, giving $(PPh_3)_2PdCl(COOCH_3)$ as white needles (0.260 g, 37.5%).

Reaction of $(PPh_3)_2PdCl(COOCH_3)$ with methyl iodide or benzyl bromide

The reaction of $(PPh_3)_2PdCl(COOCH_3)$ (0.312 g, 0.431 mmole) with methyl iodide (2 ml) or benzyl bromide (2 ml) was carried out in a glass tube for 2 h at 90° or 140° respectively. Methyl acetate or methyl phenylacetate, in quantitative amount, was detected, respectively, in the reaction mixture by gas chromatography.

Reaction of $(PPh_3)_2PdCl(COOCH_3)$ with hydrochloric acid

When concentrated hydrochloric acid (0.05 ml) was added to an ether suspension of $(PPh_3)_2PdCl(COOCH_3)$ (0.262 g, 0.362 mmole) at room temperature, the original white precipitate turned orange-yellow. After separating the precipitate by filtration, it was recrystallized from dimethylformamide. $(PPh_3)_2PdCl_2$ was obtained as orange-yellow crystals. Methanol was detected in the filtrate by gas chromatography.

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