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Methylchloroformate synthesis *via* direct interaction of palladium di(methoxycarbonyl) complexes with $CuCl_2$: utilization in the synthesis of carbonates and carbamates

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Abstract

$ClCOOCH_3$ has been obtained in very good yield by reaction of $[PdL_2(COOCH_3)_2]$ [L_2 = 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen)] with $CuCl_2$. The *in situ* reaction of $ClCOOCH_3$ with alcohols or amines produces carbonates or carbamates.

1. Introduction

The cleavage of palladium–carbon bonds by copper(II) chloride leading to nucleophilic replacement of the organic group R by the chloride ion at palladium (reaction 1), is well documented [1,2].

$$[L_nPd^{II}\text{–}R] + 2CuCl_2 \longrightarrow [L_nPd^{II}\text{–}Cl] + RCl + 2CuCl \quad (1)$$

In contrast, the cleavage of the Pd–carbomethoxy bond (R=COOR') and the elimination of a chloro-compound (ClCOOR'), reaction (2), is quite unknown.

$$[L_nPd^{II}\text{–}COOR] + 2CuCl_2 \longrightarrow [L_nPd^{II}\text{–}Cl] + ClCOOR + 2CuCl \quad (2)$$

The carbomethoxy complexes of palladium are useful intermediates in many carboxylation processes as the –COOR can be transferred to a suitable substrate to afford, for example, carbonates, carbamates and oxalic acid esters [3].

We have prepared a new series of mono- and dimethoxycarbonyl complex of palladium(II) by reaction of $[PdL_2Cl_2]$ or $[PdL_2(OAc)_2]$ with CO and methanol and studied their reactivity towards copper chloride in order to ascertain the potential of the elimination of the carbomethoxy group as chloroformate for synthesis.

2. Results and discussion

New mono- and di-methoxycarbonyl complexes of palladium with N–N or P–N donor set ligands of formula $[PdL_2X_{2-n}(COOCH_3)_n]$ (n = 1, 2; X = Cl or OAc; L_2 = bipyridine (bipy), 1,10-phenanthroline (phen), *ortho*-(diphenylphosphino)dimethylaminobenzene (PN) or 2-(diphenylphosphinoethyl)pyridine (PNpy)] [4] have been prepared in good yields, following reaction (3).

$$[L_2PdX_2] + nCO + nCH_3OH \xrightarrow{B} [L_2PdX_{2-n}(COOCH_3)_n] + nHX \quad (3)$$

(n = 1 or 2; X = Cl or OAc)

The reactivity of some of these complexes towards copper compounds shows some very interesting features.

Di(methoxycarbonyl) complexes $[PdL_2(COOCH_3)_2]$ (**1**) (L_2 = bipy or phen) react at room temperature with $CuCl_2$ (**2**) to afford $ClCOOCH_3$ (**3**) in very good yield.

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* Dedicated to Professor G.P. Chiusoli on the occasion of his 70th birthday and in recognition of his important contributions to organometallic chemistry and its application to organic synthesis.

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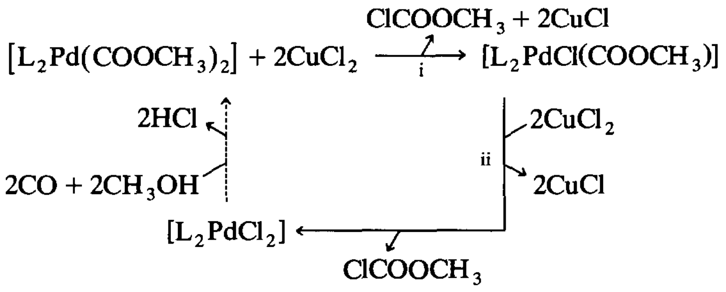


Scheme 1.

The overall stoichiometry requires 4 moles of copper per mole of palladium as indicated in eqn. (4).

$$\underset{(1)}{[L_2Pd(COOCH_3)_2]} + \underset{(2)}{4CuCl_2} \xrightarrow{THF} [PdL_2Cl_2] + 4CuCl + \underset{(3)}{2ClCOOCH_3} \quad (4)$$

The $ClCOOCH_3$ formation was demonstrated by GC analyses, and IR and mass spectra. The IR spectrum of the reaction solution shows a medium band at 1778 cm^{-1}, typical of $ClCOOCH_3$ [5]. The mass spectrum and GLC retention time were consistent with $ClCOOCH_3$, as indicated by comparison with a pure sample. The other reaction products were also isolated and characterized (see Experimental section).

It is worth noting that whereas the oxidative addition of **3** to a metal centre in a low oxidation state is a well known process and widely used as a general procedure for the preparation of methoxycarbonyl complexes [6] (reaction (5)), utilization of a methoxycarbonyl complex for the formation of chloroformate is unprecedented [7*].

$$[L_nPd^0 + ClCOOCH_3 \longrightarrow [L_nPdCl(COOCH_3)] \quad (5)$$

In order to gain an insight into the reaction mechanism, we have studied reaction (**4**) in detail and shown that it proceeds in two stages (Scheme 1).

Support for this reaction scheme comes from the following experimental observations.

The di(methoxycarbonyl) complex $[Pd(COOCH_3)_2(PPh_3)_2]$ and $CuCl_2$ react (molar ratio Cu/Pd = 2) to afford the stable, well known $[PdCl(COOCH_3)(PPh_3)_2]$ [6] (step i) that further reacts with $CuCl_2$ to afford $[PdCl_2(PPh_3)_2]$ (step ii).

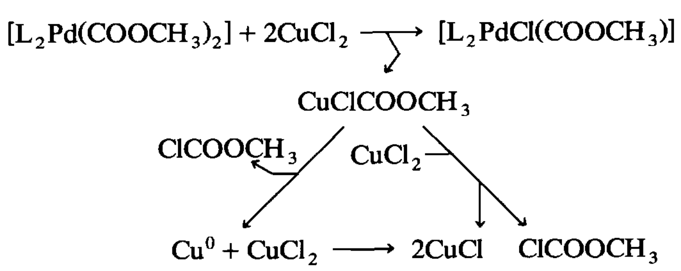
The di(methoxycarbonyl)complex $[Pd(COOCH_3)_2$ bipy] reacts with $CuCl_2$ (Cu/Pd = 4) to afford $[PdCl_2$bipy] and CuCl. This reaction also affords the mono(methoxycarbonyl) complex, which can be obtained in a pure form when PPh_3 and a Cu/Pd = 2, is used.

An authentic sample of mono(methoxycarbonyl) complex $[PdCl(COOCH_3)$bipy] reacts with $CuCl_2$ analogously (Cu/Pd = 2) to afford $[PdCl_2$bipy] and CuCl (step ii).

As far as the reaction mechanism is concerned, chloroformate formation may occur through one of the following pathways:

(a) a concerted attack by $CuCl_2$ on the Pd–$COOCH_3$ bond with formation of a Pd–Cl bond and $ClCOOCH_3$ (Fig. 1).

(b) Ligand substitution at Pd with formation of $CuCl(COOCH_3)$, that can either undergo a reductive elimination to afford Cu^0 which then reacts with Cu^{II} to give CuCl, or interacts with $CuCl_2$ to form the same products (Scheme 2).



Scheme 2.

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* Reference number with asterisk indicates a note in the list of references.

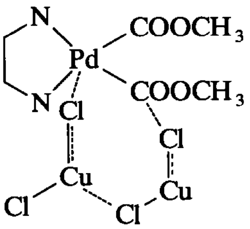

Fig. 1.

We favour route (b) as route (a) requires a three-centre reaction mechanism.

However, an alternative mechanism involving the formation of an unstable Pd^{III}- or Pd^{IV}-intermediate followed by a reductive elimination of chloroformate cannot be ruled out.

An example of the oxidative mechanism is the reaction of $[Pd(COOCH_3)_2bipy]$ with chlorine in THF. The intermediate Pd^{IV} complex can be detected but not isolated, as it gives readily $[PdCl_2bipy]$ and $ClCOOCH_3$ in quantitative yield (reaction (6)). It is known that palladium(IV) complexes stabilized by dinitrogen ligands easily undergo a reductive elimination [8].

$$\begin{aligned}&[Pd(COOCH_3)_2bipy] + 2Cl_2 \longrightarrow \\ &\qquad [PdCl_2(COOCH_3)_2dipy] \\ &\qquad\qquad \downarrow \qquad\qquad (6) \\ &\qquad [PdCl_2bipy] + 2ClCOOCH_3\end{aligned}$$

Reaction (4) requires perfectly dry solvents and reactants. If moisture is present, CO_2 is evolved and methanol is formed according to reaction (7). These are the main products also when $CuCl_2 \cdot 2H_2O$ reacts with **1** in anhydrous solvents.

$$\begin{aligned}&[L_2Pd(COOCH_3)_2] + 4CuCl_2 \cdot 2H_2O \longrightarrow \\ &\qquad [PdL_2Cl_2] + 2CO_2 + 4CuCl \\ &\qquad + 2CH_3OH + 2HCl + 6H_2O \quad (7)\end{aligned}$$

2.1. *Synthesis of carbonates and carbamates*

If PhOH or CH_3OH are added under anhydrous conditions in the presence of NEt_3 to the mixture of **1** and **2** in THF, the corresponding carbonates, $PhOCOOCH_3$ and $CH_3OCOOCH_3$, are formed. The IR spectrum of the reaction mixture shows bands at 1759 and 1755 cm^{-1} for phenylmethylcarbonate and dimethylcarbonate, respectively.

When **1** reacts with copper(II) amine complexes $[(RNH_2)_2CuCl_2]$ ($R = Ph$ or ^nBu), carbamates are formed according to reaction (8). The stoichiometry has been proved by GLC determination of the organic products and isolation of the Pd^{II} and Cu^I compounds.

$$\begin{aligned}&[L_2Pd(COOCH_3)_2] + 4[CuCl_2(RNH_2)_2] \longrightarrow \\ &\qquad [L_2PdCl_2] + 4CuCl + 2RNHCOOCH_3 \\ &\qquad + 2RNH_2 \cdot HCl + 4RNH_2 \quad (8)\end{aligned}$$

Organic carbamates can also be obtained when reaction (4) is carried out in the presence of primary and secondary amines (Table 1).

TABLE 1. Carbamates synthesis *via* chloroformate

Amine	Carbamate	Yield [a]
$PhNH_2$	$PhNHCOOCH_3$	75
$n\text{-}BuNH_2$	$BuNHCOOCH_3$	79
$CyNH_2$	$CyNHCOOCH_3$	70
$PhNHCH_3$	$PhNCH_3COOCH_3$	72

[a] Yields determined by GLC and based on the initial palladium complex. In all experiments, 0.42 mmol of $[Pd(COOCH_3)_2bipy]$ were used.

3. Conclusions

The formation of chloroformate from a methoxycarbonyl ligand is unprecedented and deserves consideration for its synthetic applications, some of which are described in this paper. The overall process depicted in Scheme 1 may be of synthetic interest as $[PdL_2Cl_2]$ and CuCl, which are formed as well as chloroformate, can be transformed into $[PdL_2(COOCH_3)_2]$ and $CuCl_2$ by reaction with CO/CH_3OH and dioxygen, respectively. In this way a cycle with turnover number higher than 1 can be achieved. We are currently developing the synthetic aspect of the reaction (Scheme 1, dotted line).

4. Experimental details

All the solvents and reactants were reagent-grade quality dried, de-aerated and saturated with dinitrogen. THF was heated under reflux and distilled from sodium wire, and alcohols and amines were distilled from magnesium turnings and KOH pellets, respectively. $[Pd(COOCH_3)_2(PPh_3)_2]$ was prepared according to the literature method [3a]. $[Pd(OAc)_2L_2]$ complexes (L_2 = bipy or phen) were prepared in methanol by reaction of $Pd(OAc)_2$ with the appropriate ligand in a 1:1 ratio [9]. The Fluka Chemie commercial products $CuCl_2$ and $CuCl_2 \cdot 2H_2O$ were used as purchased. All reactions were carried out in dry dinitrogen by standard vacuum-line techniques.

IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer, GC-MS analyses were performed using a Hewlett Packard 5995 instrument. GC quantitative analyses for chloroformate, carbamates and carbonates were carried out with a Varian Vista 6000 gas chromatograph using a SP-2100/01% Carbowax column and toluene as internal standard.

4.1. General procedure for the preparation of palladium methoxycarbonyl complexes

4.1.1. Synthesis of 2,2'-bipyridine-[di(methoxycarbonyl)]palladium(II) [Pd(COOCH$_3$)$_2$bipy]

(a) Carbon monoxide was bubbled through a solution of [Pd(OAc)$_2$bipy] (0.850 g) in 20 ml of a freshly prepared methanol/NEt$_3$ (5 : 3) mixture, until the solution gradually turned pale green. The solution was cooled to 0°C and, upon stirring under CO for 2 h, gave a green microcrystalline product that was filtered, washed with cold methanol and dried *in vacuo* (0.552 g, yield 65%). Anal. Found C, 44.0; H, 3.5; N, 7.2. Pd, 27.7. $C_{14}H_{14}N_2O_4Pd$ calcd.: C, 44.17; H, 3.71; N, 7.35; Pd, 27.95%. IR: ν(C=O) 1634vs; ν(C–O–C) 1055vs, 1026s, 1016s cm^{-1}.

(b) The yellow suspension of [PdCl$_2$dipy] (0.400 g) in 30 ml of a freshly prepared methanol/NEt$_3$ (5 : 3) mixture was allowed to react for 48 h with stirring with carbon monoxide at room temperature. The suspension turned greenish-yellow. The collected product was suspended in 20 ml of methanol/NEt$_3$ (5 : 3) mixture and allowed to react with CO for a further 12 h. The green product was filtered, washed with methanol and dried *in vacuo* (0.342 g, yield 75%). Anal. Found: C, 44.0; H, 3.6; N, 7.1. Pd, 27.7%.

4.1.2. 2,2'-Bipyridinechloro(methoxycarbonyl)palladium(II) [PdCl(COOCH$_3$)bipy]

(a) To a stirred green suspension of [Pd(COOCH$_3$)$_2$bipy] (0.450 g, 1.18 mmol) in 15 ml of benzene, 3 ml of a methanol solution of HCl (0.4 N) were added dropwise at room temperature. There was rapid evolution of CO (26.1 ml) and the suspension gradually turned greenish-yellow. The collected product was washed with methanol and dried *in vacuo* (0.358 g, yield 85%). IR: ν(C=O) 1634vs; ν(C–O–C) 1055vs, 1026s, 1016s cm^{-1}. Anal. Found, C, 39.8; H, 2.99; Cl, 9.9; N, 7.7; Pd, 29.9. $C_{12}H_{11}ClN_2O_2Pd$ calcd.: C, 40.36; H, 3.10; Cl, 9.93; N, 7.84; Pd, 29.80%.

(b) The yellow suspension of [PdCl$_2$bipy] (0.400 g) in 20 ml of a freshly prepared methanol/NEt$_3$ (5 : 3) mixture, was stirred overnight in a carbon monoxide atmosphere at room temperature. The suspension turned greenish-yellow and the product was filtered, washed with methanol and dried *in vacuo* (0.342 g, yield 80%). Anal. Found: C, 39.9; H, 2.8; Cl, 9.5; N, 7.7; Pd, 29.7%. (Samples prepared according to this procedure can be slightly impure of PdCl$_2$bipy or of Pd(COOCH$_3$)$_2$bipy.)

4.2. Chloroformate synthesis and stoichiometry of the reaction

A suspension of [Pd(COOCH$_3$)$_2$bipy] (0.160 g, 0.42 mmol) in 3 ml of THF and CuCl$_2$ (0.226 g, 1.68 mmol) in 4 ml of THF were separately charged into the branches of an inverted Y-shaped glass reactor. The reactor was closed and the contents mixed. After 1 h of stirring, the liquid phase of the reaction mixture was analyzed. The IR spectrum showed a band at 1778 cm^{-1} due to chloroformate, confirmed by the GC-MS spectrum and GLC analysis. Mass spectrum: m/z, 94 (M$^+$, 2% relative intensity), 65 (11%), 63 (33%), 59 (100%), 44 (7%). The GC quantitative analysis gave 0.062 g of $ClCOOCH_3$ (yield = 80% based on the initial palladium complex).

The solid reaction residue was filtered off and the components ([PdCl$_2$dipy] and CuCl) were separated by adding a methanol solution (10 ml) containing bipy (1.7 mmol). The pale-yellow residue was filtered off and identified as [PdCl$_2$(dipy)] by elemental analyses and the IR spectrum. Anal. Found: C, 35.8; H, 2.2; Cl, 21.2; N, 8.3; Pd, 31.7. $C_{10}H_8Cl_2N_2Pd$ calcd.: C, 35.99; H, 2.42; Cl, 21.26; N, 8.40; Pd, 31.91%.

The red-brown solution collected after the removal of methanol *in vacuo*, gave a brown solid whose elemental analyses indicated CuCl(bipy). Anal. Found: C, 46.8; H, 3.0; Cl, 14.1; Cu, 24.8; N, 10.7. $C_{10}H_8ClCuN_2$ calcd.: C, 47.07; H, 3.16; Cl, 13.89; Cu, 24.90; N, 10.97%.

The reaction stoichiometry (Cu/Pd = 4) was deduced by carrying out the reaction with an excess of Cu^{II} and titrating the Cu^{II} residue by iodometry according to the following procedure: [Pd(COOCH$_3$)$_2$bipy] (0.160 g, 0.42 mmol) and an excess CuCl$_2$ (0.282 g, 2.10 mmol; Cu/Pd = 5) were allowed to react as described above. Acetic acid and potassium iodide were added to a de-aerated aqueous suspension of the solid residue of the reaction and the liberated iodine was titrated with a standard 0.1 N $Na_2S_2O_3$ solution. To reach the starch end point, 4.5 ml of solution, corresponding to 0.45 mmol of unreacted Cu^{II}, were needed.

4.3. Reaction of [Pd(COOCH$_3$)$_2$(PPh$_3$)$_2$] with CuCl$_2$ (1 : 2 molar ratio)

[Pd(COOCH$_3$)$_2$(PPh$_3$)$_2$] (0.350 g, 0.47 mmol) in THF (4 ml) and CuCl$_2$ (0.126 g, 0.93 mmol), were allowed to react as described above. The IR spectrum of reaction solution showed a band at 1778 cm^{-1}. The solid residue of the reaction was filtered off and its components ([PdCl(COOCH$_3$)(PPh$_3$)$_2$] and CuCl) were separated by adding a methanol solution containing bipy (0.90 mmol) as described above. The flesh-coloured residue was filtered off and identified as [PdCl(COOCH$_3$)(PPh$_3$)$_2$]. IR: ν(C=O) 1672s, 1656m; ν(C–O–C) 1068vs cm^{-1}. Anal. Found: Cl, 4.8; P, 8.4; Pd, 14.4. $C_{38}H_{33}ClO_2P_2Pd$ calcd.: Cl, 4.89; P, 8.55; Pd, 14.67%.

4.4. Reaction of [PdCl(COOCH$_3$)bipy] with CuCl$_2$ (1:2 molar ratio)

[PdCl(COOCH$_3$)bipy] (0.150 g, 0.42 mmol) and CuCl$_2$ (0.113 g, 0.84 mmol) were allowed to react as reported above. After reaction, the IR spectrum of the solution showed a weak band at 1778 cm^{-1}. CuCl was separated from the solid mixture as CuCl(bipy) and the residue was characterized as [PdCl$_2$bipy] by IR and elemental analyses. The IR spectrum was identical with authentic material prepared from PdCl$_2$ and bipyridine in CH$_3$CN. Anal. Found: C, 35.9; H, 2.3; Cl, 21.1; N, 8.2; Pd, 31.7. $C_{10}H_8Cl_2N_2Pd$ calcd.: C, 35.99; H, 2.42; Cl, 21.26; N, 8.40; Pd, 31.91%.

4.5. Carbonate synthesis via the in situ reaction of chloroformate with alcohols

Methylphenyl carbonate

[Pd(COOCH$_3$)$_2$bipy] (0.114 g, 0.30 mmol) and CuCl$_2$ (0.161 g, 1.2 mmol) were allowed to react as reported above. NEt$_3$ (0.5 ml) and an excess of PhOH (0.200 g) were added to the reaction mixture. After stirring (1 h), GLC quantitative analysis suggested 0.071 g of methylphenyl carbonate (78% yield). IR: (ν CO) 1759 cm^{-1}. Mass spectrum: m/z (relative intensity) 152 (M$^+$, 60%), 108 (40%), 94 (30%), 93 (24%), 78 (84%), 77 (40%), 65 (100%), 59 (21%), 39 (62%).

Dimethyl carbonate

The reaction was carried out in the same way in the presence of CH$_3$OH (1 ml). GLC quantitative analysis suggested 0.041 g of carbonate (76% yield). IR: ν(CO) 1755 cm^{-1}. MS: 90 (M$^+$, 3%), 59 (40%), 45 (100%), 44 (9%).

4.6. Carbamates synthesis

4.6.1. Via chloroformate intermediate

(a) PhNHCOOCH$_3$: PhNH$_2$ (0.5 ml) was added to the chloroformate obtained by treating [Pd(COOCH$_3$)$_2$bipy] (0.160 g, 0.42 mmol) and CuCl$_2$ (0.226 g, 1.68 mmol). The IR spectrum of the resulting solution shows a band at 1737 cm^{-1} due to PhNHCOOCH$_3$ (0.101 g, yield 80%). MS: 151 (M$^+$, 68%), 120 (13%), 119 (65%), 106 (100%), 92 (46%), 77 (39%), 65 (89%), 59 (37%), 39 (74%).

(b) ^{n}BuNHCOOCH$_3$: the compound (79% yield) was prepared as reported above using ^{n}BuNH$_2$. IR: (ν CO) 1726 cm^{-1}. MS: 131 (M$^+$, 9%), 88 (100%), 59 (17%), 57 (12%), 44 (52%).

4.6.2. Via copper amine complexes

(a) ^{n}BuNHCOOCH$_3$: [Pd(COOCH$_3$)$_2$bipy] (0.160 g, 0.42 mmol) was treated under dinitrogen with [CuCl$_2$(^{n}BuNH$_2$)$_2$] (0.471 g, 1.68 mmol) suspended in THF (8 ml). The carbamate was obtained in 80% yield.

(b) PhNHCOOCH$_3$: the compound was obtained (yield 80%), according to the above procedure, by reaction of [Pd(COOCH$_3$)$_2$bipy] (0.160 g, 0.42 mmol) with [CuCl$_2$(PhNH$_2$)$_2$] (0.538 g, 1.68 mmol).

4.7. Reaction of di(methoxycarbonyl) complexes

4.7.1. With chlorine

Chlorine was bubbled through a green suspension of [Pd(COOCH$_3$)$_2$bipy] (0.350 g) in THF (15 ml) at room temperature. The suspension rapidly turned yellow and the formation of ClCOOCH$_3$ was shown by IR spectroscopy band at 1778 cm^{-1}, and GC techniques. The solid reaction product was filtered, washed with methanol and dried *in vacuo* (0.290 g, yield 95%). The compound was identified as PdCl$_2$bipy by IR spectrum and analyses. Found: C, 35.9; H, 2.3; N, 8.2; Pd, 31.7; Cl, 21.1%.

4.7.2. With CuCl$_2$ · 2H$_2$O: CO$_2$ determination

A suspension of [Pd(COOCH$_3$)$_2$bipy] (0.160 g, 0.42 mmol) in 2 ml of THF and CuCl$_2$ · 2H$_2$O (0.286 g, 1.68 mmol) in 4 ml of THF were charged separately in the two branches of an inverted Y-shaped glass reactor that was connected to a gas burette. The reactants were mixed and the gas evolved (16.5 ml) was identified as CO$_2$ by IR spectroscopy (band in solution at 2336 cm^{-1}) and gas chromatography.

References and notes

1 R. A. Sheldon and J. K. Kochi, in: *Metal-Catalyzed Oxidation of Organic Compounds*, Academic Press, 1981, and refs. therein.

2 H. Stangl and R. Jira, *Tetrahedron Lett., 41* (1970) 3589; J.-E. Bäckvall, *Tetrahedron Lett., 5* (1977) 467 and refs. therein; J.-E. Bäckvall and R. E. Nordberg, *J. Am. Chem. Soc., 102* (1980) 393; P. M. Henry, *J. Org. Chem., 39* (1974) 3871; P. M. Henry, *J. Am. Chem. Soc., 94* (1972) 7305.

3 (a) F. Rivetti and U. Romano, *Chim. Ind., 62* (1980) 7 and refs. therein; (b) F. Rivetti and U. Romano, *J. Organomet. Chem., 174* (1979) 221; D. Fenton and P. J. Steinwand, *J. Org. Chem., 5* (1974) 701; Ph. Bréchot, Y. Chauvin, D. Commereuc and L. Saussine, *Organometallics, 9* (1990) 26; P. Giannoccaro, C. F. Nobile and M. Latronico, *Inorg. Chim. Acta, 175* (1990) 133 and refs. therein.

4 P. Giannoccaro, unpublished; some details have been presented at the VII-I.S.H.C. Lyon France, *P120* (1990) 377.

5 C. J. Pouchert, *The Aldrich Library of Infrared Spectra*, Aldrich Chemical Company, 1970.

6 S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto and K. Ataka, *J. Am. Chem. Soc.*, *95* (1973) 3180.

7 Ethyl chloroformate from decomposition of a supposed ethoxycarbonyl complex, ethyl acetate, Pd^0 and other products were observed in the stoichiometric carbonylation of ethanol promoted by $PdCl_2$. M. Graziani, P. Uguagliati and G. Carturan, *J. Organomet. Chem.*, *27* (1971) 275.

8 P. K. Beyrs, A. J. Canty, P. R. Traill and A. A. Watson, *J. Organomet. Chem.*, *390* (1990) 399.

9 C. D'Agostino, *Thesis*, University of Bari, Bari, Italy.