Interaction of $PdCl_2$-2-(β-diphenylphosphine)ethylpyridine Complex with Diols and CO: Synthesis of New Alkoxycarbonyl Complexes, Key Intermediates to Cyclic Carbonates

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$PdCl_2PN$ (PN = 2-(β-diphenylphosphine)ethylpyridine) was found to be effective in the promotion of the alkoxycarbonylation of diols [(1,2-hydroxyethane (HE); 1,2- and 1,3-hydroxypropane (1,2HP, 1,3HP), 1,2-, 1,3-, and 1,4-hydroxybutane (1,2HB, 1,3HB, 1,4HB)]. The relevant mono-alkoxycarbonyl complexes of the diols, of formula PdClPN(COO-R-OH), were isolated, characterized in solution, and studied for their reactivity. All complexes in the presence of different reagents release the alkoxycarbonyl group directly as cyclic carbonate or as chloroformate, which "in situ" converts into cyclic carbonate or other valuable carbonyl products. The structure of the complexes PdCl[(COO-CH_2-CH_2-CH_2(OH)](PN) (**4c**) and PdCl(COO-CH_2-CH(OH)-C_2H_5)(PN) (**4d**) was also derived by single-crystal X-ray diffraction.

1. Introduction

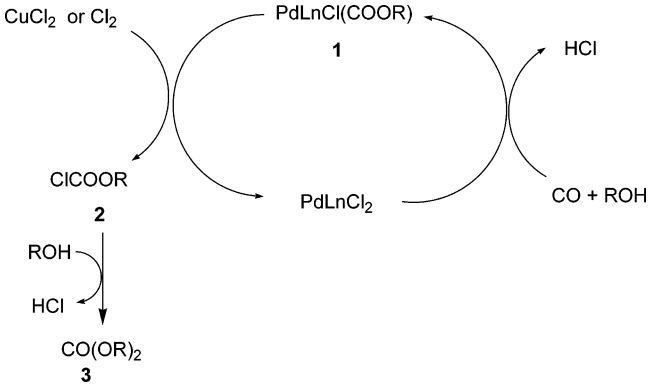
Transition and post-transition metal compounds have successfully been used as catalysts for the oxidative carbonylation of alcohols to give carbonates (reaction 1),[1] a process on stream for the synthesis of DMC.[2]

$$2\ ROH + CO + {}^1/_2\ O_2 \rightarrow CO(OR)_2 + H_2O \qquad (1)$$

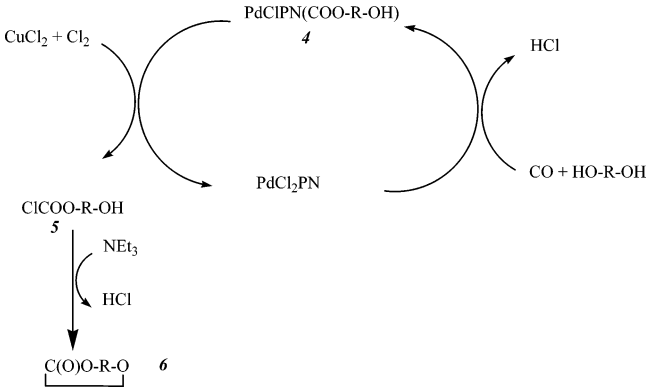
Alkoxycarbonyl complexes **1** are key intermediates that, by further reaction with alcohol, give carbonates. We have already shown that complexes **1** can be used for the synthesis of chloroformates **2**, and we have proposed a protocol for the conversion, through a double-step path, without the use of phosgene, of alcohols into either chloroformates or carbonates **3** (Scheme 1).[3]

Now we have found that this procedure can be applied to the alkoxy carbonylation of diols, which can be converted into the relevant chloroformates **5** or cyclic carbonates **6** (Scheme 2), which are precursors of polycarbonates.

Scheme 1. Double-Step Pathway for Converting Alcohols into Chloroformates or Carbonates



Scheme 2. Conversion of Diols into Chloroformates or Cyclic Carbonates



Cyclic carbonates are mostly prepared by transesterification of alkyl carbonates with diols in the presence of inorganic or organic catalysts.[4] Two five-membered cyclic carbonates have also been synthesized by direct carbonylation of ethylene glycol or 1-phenylethanediol,[5] but no attempt has been made so far

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Table 1. Some IR Spectroscopic Features of PdClPN(CO-OR-OH) Complexes

		IR (cm^{-1})		
HO-R-OH	complex **4**	OH	CO	C-O-C
1,2-HE	**a**	3415	1651	1085−1068
1,2-HP	**b**	3391	1659	1085−1055
1,3-HP	**c**	3430	1655	1070−1031
1,2-HB	**d**	3429	1661	1075−1028
1,3-HB	**e**	3439	1665	1068−1023
1,4-HB	**f**	3443	1634	1082−1053

for isolating or characterizing the relevant alkoxycarbonyl complexes **4**.

To the best of our knowledge, the only alkoxycarbonyl complex of a diol reported in the literature is the bipyridyl ruthenium complex, of formula $Ru(bipy)(CO)_2Cl(COOCH_2CH_2OH)$, isolated in the course of a study on a water gas shift process.[6]

We report here the first well-characterized examples of alkoxycarbonyl complexes of palladium, obtained by direct carbonylation of diols having from two to four carbon atoms and the procedure for converting the alkoxycarbonyl group into chloroformate or cyclic carbonate. The solid-state structure of complexes **4c** and **4d** was also derived by X-ray diffraction analysis.

2. Results and Discussion

2.1. Synthesis and Characterization of Complexes. By reacting $PdCl_2PN$ [(PN = 2-(*β*-diphenylphosphine)ethylpyridine)] with diols [(HO-R-OH) = 1,2-hydroxyethane (HE); 1,2- or 1,3-hydroxypropane (1,2HP; 1,3HP); 1,2-, 1,3-, or 1,4-hydroxybutane (1,2HB, 1,3HB, 1,4HB); diol/Pd = 4)], in CH_3CN, under carbon monoxide at atmospheric pressure and room temperature, in the presence of triethylamine as base, the alkoxycarbonyl complexes of formula PdClPN(COO-R-OH) (**4a**−**f**) were isolated in good yields (60−80%) as white-cream or yellow-cream microcrystalline products (reaction 2).

$$PdCl_2PN + CO + HO\text{-}R\text{-}OH \xrightarrow{NEt_3} \underset{\mathbf{4}}{PdClPN(COO\text{-}R\text{-}OH)} + NEt_3H^+Cl^- \quad (2)$$

All compounds are stable in the solid state and can be manipulated in the air for long periods without any appreciable modification. In solution, they are stable only at room temperature; upon heating ($T > 40$ °C) they decompose, with a reaction rate depending on the type of diol, giving metallic palladium and carbonate (see later).

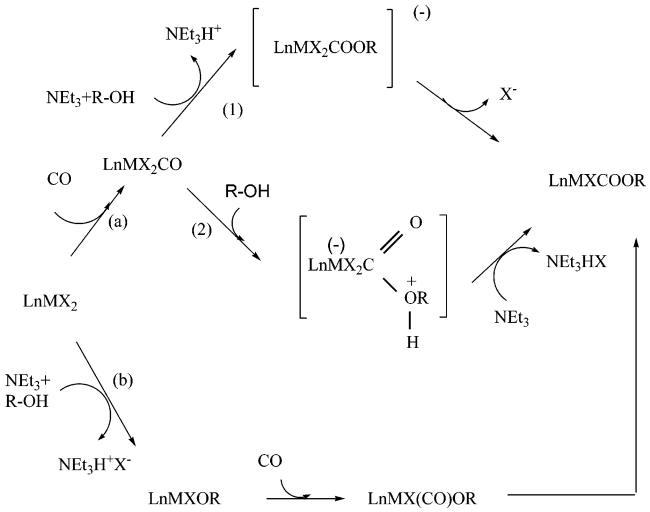
The complexes were characterized by analytical and spectroscopic data (IR, Table 1; NMR) and through the decomposition reactions with HCl. Molecular structures of **4c** and **4d** were derived by single-crystal X-ray diffraction.

Their IR spectra in Nujol show characteristic absorptions ascribable to the stretching of the free hydroxyl group of diol and to the ν(C═O) and ν(C−O−C) of the alkoxycarbonyl group (Table 1). The above values are consistent with the data found for other alkoxycarbonyl complexes of mono-alcohols.[4,7−9] All complexes react with HCl in methanol and develop, according to their formulation, one mole of CO per mole of complex (reaction 3 and Table 2). The gas evolved was measured using a gas buret and identified as CO by GC analysis.

Table 2. Decomposition of Complexes with HCl and CO Evolved

complex	mmol	*V* CO (mL)	CO (mmol)
4b	0.31	6.7	0.30
4a	0.24	5.0	0.22
4c	0.26	5.5	0.24
4d	0.24	5.1	0.23
4f	0.24	5.2	0.23

Scheme 3. Possible Routes for Alkoxycarbonylation of Mono-alcohols



$$PdClPNCO\text{-}OR\text{-}OH + HCl \rightarrow PdCl_2PN + CO + HO\text{-}R\text{-}OH \quad (3)$$

The decomposition of complexes under acid conditions suggests that the base NEt_3 plays a double role in the reaction. Its presence is needed for (i) shifting reaction 2 to the right by converting the strong acid HCl into the weak acid NEt_3HCl and (ii) promoting the deprotonation of diols during the formation of the alkoxy-carbonyl group (see Scheme 3).

Complexes **4a**−**f** have been fully characterized in solution by NMR (^1H, ^{13}C, ^{31}P) spectroscopy. In all the compounds, the P resonance of the PN ligand is within a narrow range, between 22 and 24 ppm. In the ^{13}C spectrum, the signal of the carboxyl carbon atom appears in the expected region (around 175 ppm) as a doublet because of coupling with the P atom of the chelating ligand. The $^2J_{C-Pd-P}$ coupling constants range between 14.2 and 15.3 Hz and are close to the value of 10−15 Hz found for *trans*-bis-phosphine-acyl and carbamoyl-Pd complexes.[10] The $^2J_{C-Pd-P}$ observed values suggest that complexes **4a**−**f** have a P−Pd−C(O)O *cis* arrangement. Such an arrangement has been documented for complexes **4c** and **4d** also in the solid state by X-ray diffraction analysis (see later). This result leads us to the conclusion that compounds **4c** and **4d** are configurationally stable complexes, which maintain their configuration also in solution.

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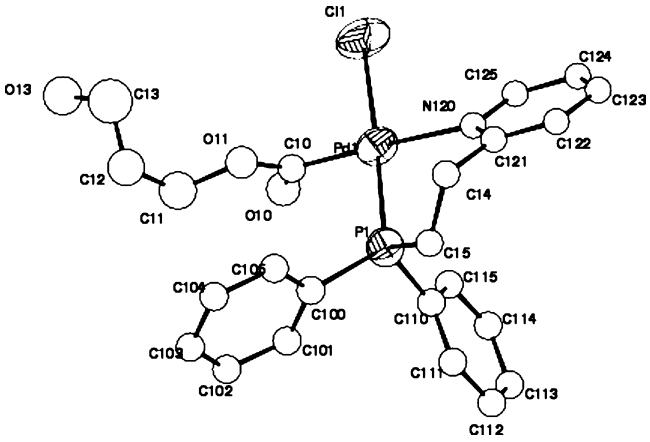

Figure 1. Perspective view of **4c**. Displacement ellipsoids are drawn at the 30% level of probability. Hydrogen atoms have been omitted for clarity.

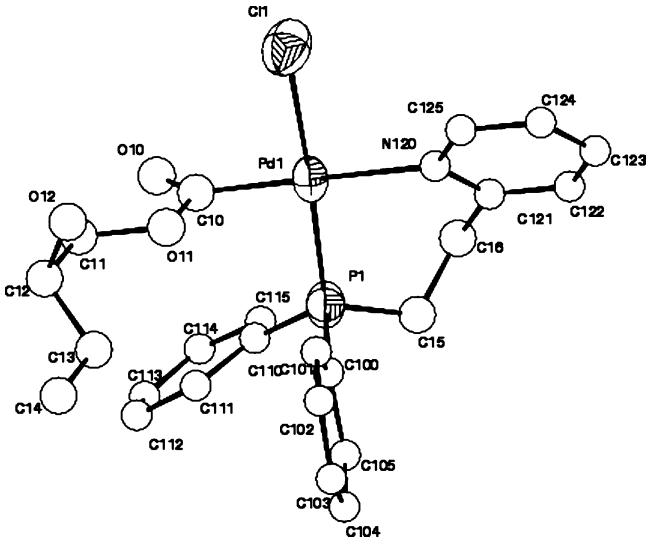

Figure 2. Perspective view of **4d**. Displacement ellipsoids are drawn at the 30% level of probability. Hydrogen atoms have been omitted for clarity.

The ^{13}C spectra of compounds **4a**, **4c**, and **4f** show a unique set of signals for both phenyl rings of the PN ligand. These signals are doublets because of coupling with the phosphorus atom of the ligand. However, in complexes **4b**, **4d**, and **4e** the presence of a chiral center in the diol chain makes the two phenyl rings diastereotopic and no longer equivalent. Also the CH_2P and CH_2Py protons of the PN ligand are, respectively, diastereotopic in complexes **4b**, **4d**, and **4e**. This may account for the different fine structure of the CH_2P and CH_2Py signals in **4b**, **4d**, and **4e** with respect to that exhibited by enantiotopic CH_2P and CH_2Py protons in complexes **4a**, **4c**, and **4f**.

In complex **4e** the resonance of the methyne proton has been unequivocally located by means of homonuclear decoupling experiments. The observed value at 3.63 ppm is too high field to support the formation of the regioisomer Cl(PN)Pd-C(O)-$OCH(CH_3)CH_2CH_2OH$[11] and is consistent with the reported formulation of **4e** as Cl(PN)Pd-C(O)$OCH_2CH_2CH(OH)CH_3$. Analogous considerations lead us to characterize the complex and **4b** and **4d** as 1-OH regioisomers. In the case of **4d**, this is also supported by X-ray analysis, which shows that the diol is bonded to the CO through the primary alcoholic group.

The molecular structures, with the atom-labeling scheme adopted, are shown in Figures 1 and 2. As expected for tetracoordinated Pd(II) complexes, Pd[$PPh_2C_2H_4Py$]Cl[COO-CH_2-CH_2-CH_2-OH] (**4c**) and Pd[$PPh_2C_2H_4Py$]Cl[COO-CH_2-CH(OH)-C_2H_5] (**4d**) display a square planar coordination with Cl and P atoms in *trans* position to each other. The compounds exhibit a slight distortion from exact planarity at the metal center. The pyridine ligand shows an arrangement with an angle of 53.32° and 43.13° with respect to the coordination plane for the complexes **4c** and **4d**, respectively, while the O−C═O group is almost perpendicular with respect to coordination plane for both the molecules (dihedral angle between the Cl1P1N120C10 and O11C10O10 planes is 88.71° and 83.67° for **4c** and **4d**, respectively). The Pd−C(sp^2) bond distance values for both studied complexes indicate a back π-bonding character from the metal to the ligand for the Pd−C(O) bond in the complex, as the sum of covalent radii of Pd(II) and the sp^2 carbon is 2.05 Å.[3c,12] The Pd−Cl, Pd−P, and Pd−N bond distances are similar to that observed in the analogous PPh_3 complexes.[13] The Pd−N bond distances for **4d** are longer than that found in the $PdCl_2L_2$ (L_2 = *o*-diphenylphospino-*N*,*N*-dimethylbenzylamine) complex[14] and shorter than that observed in the same complex when a chlorine atom is substituted with a strong *trans* ligand.[15]

3. Reaction Mechanism and Reactivity of Complexes

It has already been ascertained by us and other authors that the alkoxy carbonylation of mono-alcohols can proceed through two mechanisms that differ in the sequence with which the CO and the alcohol interact with the metal center in the presence of a base (Scheme 3, routes a and b). According to route a in Scheme 3, the complex reacts first with the CO, giving a carbonyl intermediate, in which Pd is pentacoordinate, which undergoes nucleophilic attack by alcohol and evolves into the final product through pathway 1 or 2.[16] Through route b, the reaction starts with the formation, promoted by NEt_3, of an alkoxy complex, which by insertion of CO into the metal−alkoxy bond affords the alkoxy-carbonyl final species.[17] Route a appears to be the most probable in the case of diols. In fact, when the $PdCl_2$PN was allowed to interact with the diol and NEt_3 under a nitrogen atmosphere, the extraction of chloride ion with formation of NEt_3HCl was not observed. This seems to exclude route b.

Compounds **4a**−**f**, similarly to the alkoxy-carbonyl complexes having an alkoxy group coming from a mono-alcohol,[3] react, under nitrogen atmosphere, at room temperature with dry $CuCl_2$ or an halogen (Cl_2, I_2), to form the relevant chloroformate and regenerating the initial Pd complex, which can be recovered and reused (reactions 4 and 5 and Scheme 2).

(11) In 1,3-butandiol dimethylmethacrylate the methyne proton resonance was found at 5.11, while the OCH_2 signal was observed at 4.22 ppm.

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$$PdClPNCO\text{-}OR\text{-}OH + 2CuCl_2 \rightarrow PdCl_2PN + ClCO\text{-}OR\text{-}OH + 2\,CuCl \quad (4)$$

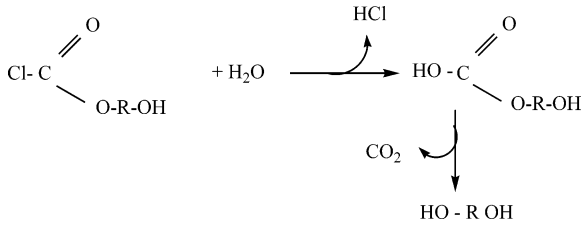
$$PdClPNCO\text{-}OR\text{-}OH + X_2 \rightarrow PdClXPN + XCO\text{-}OR\text{-}OH \quad (5)$$

$$(X_2 = Cl_2, I_2)$$

Reactions 4 and 5 were carried out by adding to the suspension of the complex in CH_3CN a CH_3CN solution containing dry $CuCl_2$ (Cu/Pd = 2) or the halogen (X_2/Pd = 1).

Chloroformates are formed in very high yields only if $CuCl_2$ and the reaction solvent are strictly anhydrous. Some amount of CO_2, which increases with increasing the water content, is also obtained. It is quite probable that CO_2 is formed by hydrolysis of the chloroformate, which evolves first to hydroxycarbonate and then decomposes to CO_2 and alcohol (Scheme 4).

Scheme 4. Hydrolysis of Chloroformate



It is possible to convert directly the alkoxycarbonyl group of complexes **4a**−**f** into cyclic carbonate, avoiding the chloroformate formation, by adding NEt_3 to the reaction mixture. Thus, the base is responsible for cyclization of chloroformate to cyclic carbonate **6**. It is very likely that the cyclization to carbonate occurs by intramolecular nucleophilic attack of the oxo group, coming from interaction between the base and the free OH of the alkoxycarbonyl ligand, on the carboxyl carbon. In this way, five- (**6a**, **6b**, **6d**), six- (**6c**, **6e**), and seven- (**6f**) membered cyclic carbonates (Figure 3) are synthesized by evolution of chloroformates coming respectively from the relevant complexes. The conversion of chloroformate to carbonates was monitored following the change of IR spectrum of the reaction solution. Solutions containing chloroformates display a medium-intensity band in the range 1778−1780 cm^{-1} due to the ν(C═O) of ClCO-O-R-OH. Addition of NEt_3 causes the shift of the CO stretching upon cyclic carbonate formation. The new absorptions are formed at 1807(s)−1776 (m), 1799(s), and 1800(s) cm^{-1}, respectively, for the five-membered cyclic carbonates (**6a**, **6b**, **6d**); at 1751 and 1748 cm^{-1} for the six-membered carbonates (**6c**, **6e**); and at 1757 cm^{-1} for the seven-membered carbonate **6f**. Carbonates were also identified by GC-MS. Molecular ions were observed for all compounds **6a**−**f** (see Experimental Section).

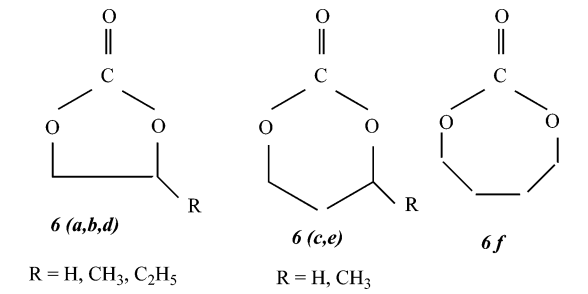
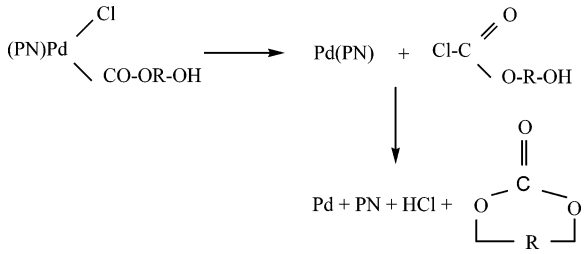


Figure 3. Five-, six-, and seven-membered carbonates.

Scheme 5. Decomposition of Pd Complexes upon Heating



Alkoxycarbonyl complexes are stable only in the solid state. In CH_3CN they decompose upon heating (T > 40 °C), giving metallic Pd and variable amounts of cyclic carbonate. Probably, upon heating, complexes undergo reductive elimination, giving chloroformate[1d] and the Pd(0) complex Pd(PN), which decompose respectively into carbonate and palladium black and free ligand (Scheme 5).

Support for this reaction course is derived from the observation that it is possible to convert quantitatively the alkoxycarbonyl group into cyclic carbonate by heating a CH_3CN solution of the alkoxycarbonyl complex in the presence of PPh_3 and NEt_3 (reaction 5). The presence of triphenylphosphine stabilizes the Pd^0 complex as $Pd(PN)(PPh_3)_2$ or as $Pd(PPh_3)_4$, in the presence of a large excess of PPh_3.

$$PdClPNCOO\text{-}R\text{-}OH + 4\,PPh_3 + NEt_3 \rightarrow Pd(PPh_3)_4 + \mathbf{6a}-\mathbf{f} + NEt_3{\cdot}HCl + PN \quad (5)$$

4. Conclusion

We have demonstrated for the first time that the carbonylation of diols to cyclic carbonates, under palladium catalysis, proceeds through the formation of alkoxycarbonyl intermediates, and mono-alcohol carbonylation to linear carbonates proceeds similarly. The first series of alkoxycarbonyl complexes of diols, PdClPN(COO-R-OH), with the free OH group of the diols bonded to either terminal or internal carbon, have been synthesized and fully characterized. All complexes in the presence of proper promoters release the alkoxycarbonyl group as chloroformate, which may evolve to cyclic carbonate most likely by intramolecular nucleophilic attack of the free OH on the carboxyl carbon. Unlike alkoxycarbonyl of mono-alcohols, which require an oxidant ($CuCl_2$, Cl_2, I_2, Br_2) as promoter for converting the alkoxycarbonyl group into the carbonate, complexes with diols are able to give cyclic carbonates also by simple heating of their solution in the presence of a coordinating ligand (PPh_3). Under these conditions, however, the process cannot be carried out catalytically, as the palladium is released as Pd(0) (Scheme 5), which is not able to form alkoxycarbonylate diols. In contrast, the use of $CuCl_2$ or of a halogen, which reacts with the alkoxycarbonyl complex and releases palladium as Pd(II), re-forms the initial complex, $PdCl_2PN$ (Scheme 2), producing a catalytic carbonylation of diols.

5. Experimental Section

All preparations, reactions, and manipulations were carried out under the proper gas (dinitrogen or carbon monoxide) using standard vacuum-line techniques. Solvents and reactants (diols, NEt_3, $CuCl_2$, I_2) were Aldrich products and were used without further purification. The PN ligand and the relevant Pd complex, $PdCl_2(PN)$, were synthesized according to the literature.[18] IR spectra were recorded on a Shimadzu IR-Prestige-21 spectrophotometer. GC separations and analyses of samples, both in solution and in gas phase, were

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Table 3. Experimental Data for the X-ray Diffraction Studies

	4c	4d
formula	$C_{23}H_{25}O_3PdPClN$	$C_{24}H_{27}O_3PdPClN$
dimension mm	0.200 ×.0140 × 0.025	0.280 × 0.200 × 0.020
shape, color	plate, light yellow	plate, light yellow
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
cell params at 295 K		
a, Å	8.9999 (3)	11.0551 (14)
b, Å	19.5797 (8)	12.4848 (17)
c, Å	13.1775 (4)	19.6466 (24)
α, deg	90	103.269 (8)
β, deg	93.117 (2)	97.059 (8)
γ, deg	90	89.976 (9)
V, Å^3	2321.1 (6)	2918.4 (4)
cell params from	2363 reflns	4362 reflns
Z	4	4
D_{calcl}, g cm^{-3}	1.533	1.396
radiation	Mo Kα	Mo Kα
F(000)	1088	1120.0
mol wt	536.284	550.331
scan type	*φ*, *ω*	*φ*, *ω*
scan speed, deg/min	≤0.167	≤0.167
2*θ* range, deg	2−25	2−21
index ranges	$-10 \le h \le 10$	$-10 \le h \le 11$
	$-23 \le k \le 23$	$-12 \le k \le 12$
	$-15 \le l \le 15$	$-19 \le l \le 19$
no. of reflns measd	42 456	63 390
no. of unique data	3965	7040
no. of params	130	143
R1	0.039[a]	0.059[a]
wR2	0.043[b]	0.064[c]
no. of obsd reflns	904	1162
criterion for observations[d]	$F_o > 3\sigma(F_o)$	$F_o > 5\sigma(F_o)$
goodness of fit on F^2	0.961	1.085
peak, hole in final diff Fourier map	0.275, −0.415	0.702, −0.665

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$ with $w = 1/\sigma(F_o)^2$. [c] $w'^{1/2} = [w' \times (1 - ((F_o - F_c)/6(F - F_c)_{estimated})^2)^2]^{1/2}$, where $w'^{1/2} = [1.0/[A[0] \times t[0]'(x) + A[1] \times t[1]'(X) + ... + A[NP - 1] \times t[NP - 1]'(x)]]^{1/2}$. *A*[*i*] are the coefficients of a Chebyshev series in *t*[*i*]′(*x*), with $x = F_c/F_c(max)$.[25] [d] Goodness-of-fit $= [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* the number of parameters.

performed using a Varian Chromopack CP3800 GC connected to a Varian Star chromatographic workstation. A CP Sil 8 CB 30 m, 0.53 i.d. capillary column, connected to a FID detector, was used for solution analysis, whereas a 2 m, i.d. 2.0 mm, Restek's Shincarbon ST packed column connected to a TCD detector was used for separating gaseous samples (CO, CO_2). MS spectra were recorded on a Shimadzu GC/MS QP5050A using an HP-5 MS 30 m column.

NMR spectra were run on a Bruker AM 500 instrument. ^{1}H and ^{13}C chemical shifts are in ppm versus TMS and were referenced to the solvent peak. ^{31}P resonances are reported in ppm and were calibrated with respect to 85% H_3PO_4.

Single crystals, suitable for X-ray analysis, of complexes **4c** and **4d** were mounted on a glass rods without protection from air. Collection of X-ray diffraction data was performed by a Bruker AXS X8APEX system equipped with a four-circle Kappa goniometer and a 4K CCD detector. Relevant crystal data and experimental parameters for the studied complex are summarized in Table 3, while selected bond and angles are reported in Tables 4 and 5. All data were collected at ambient temperature using a combination of $\phi-\omega$ scans and Mo Kα radiation ($\lambda = 0.71073$ Å). Cell refinement and data reduction were performed with the SAINT[19] and SADABS programs.[20] The structures were resolved by direct methods and successive difference Fourier synthesis using the SIR2002 program.[21] Structure refinements were carried out in space group $P2_1/n$ and in $P\bar{1}$, respectively, for **4c** and **4d**, with the CRYSTAL program.[22] All non-H atoms in the crystal structure were refined anisotropically, while H atoms were added at calculated positions (aromatic H, C−H = 0.93 Å, $U_{iso} = 1.2U_{iso}$ of the parent carbon; CH_2 hydrogens, C−H = 0.97 Å, $U_{iso} = 1.2U_{iso}$ of the parent carbon; O−H hydrogens, C−H = 0.82 Å, $U_{iso} = 1.5U_{iso}$ of the parent oxygen) and were refined isotropically.

X-ray data collection of **4d** evidences the presence of some peak broadening. In addition residuals (about 1 e/Å^3) in Fourier difference maps in the structure refinement are found, suggesting the presence of disordered solvent (ethyl ether) in the unit cell. This consideration is supported by the occurrence of large voids ($V = 272$ Å^3) in the crystal lattice. To take care of the contribution of disordered solvent, the data reflections were processed by means of the SQUEEZE program.[23]

Table 4. Selected Geometrical Parameters (Å, deg) of Complex 4c

Pd1−C10	1.964 (19)	C10−O11	1.31(2)
Pd1−N120	2.134(7)	C10−O10	1.21(2)
Pd1−P1	2.237(4)	P1−C15	1.840(15)
Pd1−Cl1	2.364(4)	P1−C110	1.806(9)
P1−C100	1.809(9)		
Cl1−Pd1−P1	176.79(19)	Cl1−Pd1−N120	92.32(33)
N120−Pd1−P1	89.29(31)	Cl1−Pd1−C10	88.32(53)
N120−Pd1−C10	175.30(80)		

Table 5. Selected Geometrical Parameters (Å, deg) of Complex 4d

Pd1−C10	1.910(29)	C10−O11	1.401(19)
Pd1−N120	2.172(9)	C10−O10	1.202(20)
Pd1−P1	2.268(8)	P1−C15	1.850(29)
Pd1−Cl1	2.353(10)	P1−C110	1.794(11)
P1−C100	1.783(13)		
Cl1−Pd1−P1	176.8(4)	Cl1−Pd1−N120	92.62(39)
N120−Pd1−P1	90.32(29)	Cl1−Pd1−C10	88.83(33)
N120−Pd1−C10	178.20(40)		

5.1. Synthesis of Complexes. Synthesis of PdCl(PN) (COO-CH_2-CH_2-OH) (4a). To a suspension of $PdCl_2$(PN) (0.400 g, 0.85 mmol) in CH_3CN (10 mL) were added, under nitrogen atmosphere, 1,2-hydroxyethane (190 μL, 3.41 mmol; HE/Pd = 4) and NEt_3 (1 mL). Nitrogen was pumped off and carbon monoxide was admitted (0.1 Mpa). The mixture was allowed to react under stirring at room temperature for ca. 4 h. Upon reaction, the yellow initial $PdCl_2$(PN) complex dissolves, giving an orange solution, from which a yellow-cream product begins to precipitate. The CO uptake at this time (8−10 mL, 0.36−0.44 mmol) indicates that the reaction progress is only about 50%. The mixture was concentrated to one-half its volume, diethyl ether (5 mL) was added, and the mixture was allowed to react with CO for a further 12 h at room temperature. After this period the color of the solution turned to pale yellow and the suspension product increased. The product was filtered, washed twice with a cold mixture of Et_2O-CH_3CN (4:1; 6 mL), to dissolve impurities of triethylammonium chloride, and dried in vacuo (0.310 g, yield 69%). The mother liquor was kept overnight at −10 °C to afford a second fraction of product, with NEt_3·HCl as an impurity. The salt impurities were dissolved as above, and further pure product was obtained (0.050 g, total yield 80%).

(19) *Siemens SMART, SAINT* (version 4.0); Siemens Analytical X-ray Instrument Inc.: Madison, WI, 1996.

(20) Sheldrik, G. M. *SADABS*; University of Göttingen: Germany, 1996.

(21) Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *Sir2002: a new Direct Methods program for automatic solution and refinement of crystal structures*. *J. Appl. Crystallogr.* **2003**, *36*, 1103.

(22) Watkin, D. J. *CRYSTALS, a programmable program*. In *Crystallographic Computing 6−A Window on Modern Crystallography* (H. D. Flack, L. Parkanyl, and K. Simon, Eds.); Oxford Science Publications: Oxford, UK, 1992.

(23) v. d. Sluis, P.; Speck, A. L. *Acta Crystallogr.* **1990**, *A46*, 194−201.

Anal. Calcd for $C_{22}H_{23}ClNO_3PPd$: Pd, 20.34; Cl, 6.78; P, 5.92. Found: Pd, 20.25; Cl, 6.71; P, 5.88. ^{1}H NMR (CD_2Cl_2, 500 MHz, 293 K): δ 2.43 (m, 2H, $CH_{2(PN)}$), 2.61 (br unresolved tr, 1H, OH), 3.37 (dm, 2H, $CH_{2(PN)}$, J = 28.3 Hz), 3.44 (br unresolved m, 2H, CH_2OH), 3.81 (pseudo-tr, 2H, OCH_2, J = 4.7 Hz), 7.24−7.33 (m, 2H, H_β,Py atoms), 7.42−7.54 (m, 6H, H_{Ph}), 7.70−7.80 (m, 5H, H_γ,Py and H_{Ph}), 9.26 (partially resolved dd, 1H, H_α',Py, J = 5.4 and 1.2 Hz). ^{13}C NMR (CD_2Cl_2, 125 MHz, 293 K): δ 61.40 (CH_2-OH), 67.46 (OCH_2), 176.69 (d, C(O)O, J_{CP} = 15.3 Hz); 25.23 (d, CH_2P, J_{CP} = 30.5 Hz), 35.06 (d, CH_2Py, J_{CP} = 4.8 Hz), 123.46 and 125.06 (C β,Py atoms), 139.56 (C_γ,Py), 153.02 (C_α',Py) and 159.64 (d, C_α,Py, J_{CP} = 2.9 Hz); 129.11 (d, $C_{meta,Ph}$, J_{CP} = 10.5 Hz), 131.54 (d, $C_{ipso,Ph}$, J_{CP} = 51.5 Hz), 131.57 (d, $C_{para,Ph}$, J_{CP} = 1.9 Hz), 133.34 (d, $C_{ortho,Ph}$, J_{CP} = 12.4 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202 MHz, 293 K): δ 24.47.

Synthesis of PdCl(PN)(COO-CH$_2$-CH(OH)-CH$_3$) (4b). $PdCl_2$(PN) (0.300 g, 0.64 mmol), CH_3CN (8 mL), 1,2-hydroxypropane (190 μL, 2.59 mmol; HP/Pd = 4), and NEt_3 (1 mL) were charged in a glass reactor and allowed to react under stirring with carbon monoxide at atmospheric pressure and room temperature until the initial yellow Pd complex dissolved. The resulting orange solution was concentrated to one-half its volume, and after the addition of diethyl ether (8 mL) it was kept under stirring to react with CO for a further 24 h in order to drive the reaction to completion. The reactor was cooled at −10 °C for 12 h, and the precipitated yellow-cream alkoxy-carbonyl complex was filtered off, washed with a cold mixture of Et_2O-CH_3CN (4:1), and dried (0.260 g, yield 60%). More product was isolated by concentration and cooling of the mother liquor.

Anal. Calcd for $C_{23}H_{25}ClNO_3PPd$: Pd, 19.81; Cl, 6.60; P, 5.77. Found: Pd, 19.79; Cl, 6.55; P, 5.73. ^{1}H NMR ($CDCl_3$, 500 MHz, 293 K): δ 0.93 (d, 3H, CH_3, J = 6.5 Hz), 2.38 (m, 2H $CH_{2(PN)}$), 2.60 (br, OH), 3.33 (dm, 2H, $CH_{2(PN)}$, J = 28.1 Hz), 3.47 and 3.74−3.81 (two multiplets, 1H and 2H, respectively, diastereotopic OCH_2 and CH), 7.18−7.28 (m, H_β,Py and H_β',Py), 7.36−7.50 (m, H_{Ph}), 7.68−7.76 (m, H_γ,Py and H_{Ph}), 9.30 (br dd, H_α',Py, $J \approx$ 5 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz, 293 K): δ 18.07 (CH_3), 65.61 and 71.35 (OCH_2 and CH), 176.12 (d, C(O)O, J_{CP} = 15.3 Hz); 24.94 (d, CH_2P, J_{CP} = 29.6 Hz), 34.62 (d, CH_2Py, J_{CP} = 4.8 Hz), 123.23 and 124.56 (C_β,Py atoms), 139.08 (C_γ,Py), 153.06 (C α',Py) and 159.00 (d, C_α,Py, J_{CP} = 2.9 Hz); 128.82 (d, $C_{meta,Ph}$, J_{CP} = 10.5 Hz) and 128.84 (d, $C_{meta,Ph}$, J_{CP} = 10.5 Hz), 130.91 (d, $C_{ipso,Ph}$, J_{CP} = 52.4 Hz) and 131.04 (d, $C_{ipso,Ph}$, J_{CP} = 51.5 Hz), 131.27 (d, br, $C_{para,Ph}$, J_{CP} = 2.9 Hz) and 131.30 (d, partially overlapped, $C_{para,Ph}$), 132.94 (d, $C_{ortho,Ph}$, J_{CP} = 12.4 Hz) and 132.96 (d, $C_{ortho,Ph}$, J_{CP} = 11.4 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, 293 K): δ 22.34.

Synthesis of PdCl(PN)(COO-CH$_2$-CH$_2$-CH$_2$(OH) (4c). $PdCl_2$(PN) (0.600 g, 1.28 mmol), CH_3CN (12 mL), 1,3-hydroxypropane (372 μL, 5.13 mmol; HP/Pd = 4), and NEt_3 (1.5 mL) were reacted with CO for 4 h, as described above. The volume of the resulting orange solution was reduced by concentration to about 5 mL and after addition of diethyl ether (10 mL) was allowed to react with CO for a further 12 h. Successive cooling of the reaction mixture to −10 °C gave compound **4c** as white-cream crystals, which were filtered off, washed with Et_2O-CH_3CN (4:1), and dried (0.547 g, yield 79%).

Anal. Calcd for $C_{23}H_{25}ClNO_3PPd$: Pd, 19.81; Cl, 6.60; P, 5.77; C, 51.51; N, 2.61; H, 4.60. Found: Pd, 19.82; Cl, 6.63; P, 5.74; C, 51.27; N, 2.79; H, 4.59. ^{1}H NMR (CD_2Cl_2, 500 MHz, 293 K): δ 1.48 (quint, CH_2, 2H, J = 5.9 Hz), 2.29 (br, 1H, OH), 2.44 (m, 2H, $CH_{2(PN)}$), 3.39 (dm, $CH_{2(PN)}$, 2H, J = 28.1 Hz), 3.44 (br tr, 2H, J = 5.7 Hz, CH_2OH), 3.76 (tr, 2H, OCH_2, J = 5.9 Hz), 7.24−7.32 (m, 2H, H_β,Py and H_β',Py), 7.42−7.52 (m, 6H, H_{Ph}), 7.70−7.77 (m, 5H, H_γ,Py and H_{Ph}), 9.25 (br d, 1H, H_α',Py, J = 5.5 Hz). ^{13}C NMR (CD_2Cl_2, 125 MHz, 293 K): δ 32.37 (CH_2), 59.52 (CH_2-OH), 63.35 (OCH_2), 177.21 (d, C(O)O, J_{CP} = 14.2 Hz); 25.43 (d, CH_2P, J_{CP} = 30.5 Hz), 35.30 (d, CH_2Py, J_{CP} = 4.8 Hz), 123.40 and 124.95 (C β,Py atoms), 139.46 (C_γ,Py), 153.03 (C α',Py) and 159.54 (d, C_α,Py, J_{CP} = 2.9 Hz); 129.06 (d, $C_{meta,Ph}$, J_{CP} = 11.9 Hz), 131.46 (d, $C_{para,Ph}$, J_{CP} = 2.3 Hz), 131.71 (d, $C_{ipso,Ph}$, J_{CP} = 51.5 Hz), 133.30 (d, $C_{ortho,Ph}$, J_{CP} = 11.1 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202 MHz, 293 K): δ 24.38.

Synthesis of PdCl(COO-CH$_2$-CH(OH)-CH$_2$-CH$_3$)(PN) (4d). $PdCl_2$(PN) (0.500 g, 1.07 mmol), CH_3CN (12 mL), 1,2-hydroxybutane (382 μL, 4.26 mmol; 1,2HB/Pd = 4), and NEt_3 (1.25 mL) were allowed to react with CO under the conditions described above, until the initial Pd complex dissolved (about 2 h). The resulting orange solution was concentrated to ca. 5 mL and after addition of Et_2O (10 mL) was allowed to react with CO for a further 36 h. Then the mixture was cooled at −10 °C for 5 days to give compound **4d** as white crystals with NEt_3·HCl as an impurity. The complex was purified by washing with a mixture of Et_2O-CH_3CN (4:1) and dried (0.330 g, yield 56%). More product was isolated by concentration and cooling of the mother liquor.

Anal. Calcd for $C_{24}H_{27}ClNO_3PPd$: Pd, 19.31; Cl, 6.43; P, 5.61. Found: Pd, 19.27; Cl, 6.47; P, 5.58. ^{1}H NMR ($CDCl_3$, 500 MHz, 293 K): δ 0.80 (t, 3H, CH_3, J = 7.5 Hz) 1.20−1.34 (m, 2H CH_2), 2.37 (m, 2H, $CH_{2(PN)}$), 2.70 (br, 1H, OH), 3.31 (dm, 2H, $CH_{2(PN)}$, J = 28.1 Hz), 3.46−3.56 and 3.86 (two multiplets, 2H and 1H respectively, diastereotopic OCH_2 and CH), 7.18−7.28 (m, 2H, H_β,-Py and H_β',Py), 7.37−7.48 (m, 6H, H_{Ph}), 7.67−7.76 (m, 5H, H_γ,-Py and H_{Ph}), 9.32 (br dd, 1H, H_α',Py, $J \approx$ 5.5 and 1.5 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz, 293 K): δ 9.80 (CH_3), 25.62 (CH_2), 70.79 and 70.10 (OCH_2 and CH), 175.96 (d, C(O)O, J_{CP} = 15.3 Hz); 24.93 (d, CH_2P, J_{CP} = 29.6 Hz), 34.55 (d, CH_2Py, J_{CP} = 4.8 Hz), 123.22 and 124.52 (C_β,Py atoms), 139.04 (C_γ,Py), 153.11 (C_α',Py) and 158.99 (d, C_α,Py, J_{CP} = 2.9 Hz); 128.82 (d, $C_{meta,Ph}$, J_{CP} = 11.4 Hz), 130.87 (d, $C_{ipso,Ph}$, J_{CP} = 51.5 Hz) and 131.11 (d, $C_{ipso,Ph}$, J_{CP} = 51.5 Hz), 131.27 (d, br, $C_{para,Ph}$), 132.96 (t, $C_{ortho,Ph}$, J_{CP} = 12.4 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, 293 K): δ 22.19.

Synthesis of PdCl(PN)(COO-CH$_2$-CH$_2$-CH(OH)-CH$_3$ (4e). $PdCl_2$(PN) (0.600 g, 1.28 mmol), CH_3CN (15 mL), 1,3 hydroxybutane (460 μL, 5.13 mmol; 1,3-HB/Pd = 4), and NEt_3 (1.5 mL) were allowed to react with CO under the conditions described above, until the initial Pd complex dissolved (about 3 h). The resulting orange solution was concentrated to one-half of its volume. The suspension was separated by filtration and purified by washing as described above, whereas the filtered solution, after addition of Et_2O (5 mL), was left at −10 °C for 5 days. White crystals of **4e**, with a slight impurity of ammonium salt, were obtained, which were purified by washing with a cold mixture of Et_2O-CH_3CN (5:1) and dried (0.371 g total, yield 53%). More product was obtained as described above.

Anal. Calcd for $C_{24}H_{27}ClNO_3PPd$: Pd, 19.31; Cl, 6.43; P, 5.61; C, 52.38; N, 2.55; H, 4.95. Found: Pd, 19.28; Cl, 6.45; P 5.56; C, 52.15; N, 2.93; H, 5.08. ^{1}H NMR (CD_2Cl_2, 500 MHz, 293 K): δ 1.01 (d, 3H, CH_3, J = 6.1 Hz), 1.24−1.43 (m, 2H, diastereotopic CH_2), 2.43 (m, 3H, OH and $CH_{2(PN)}$), 3.38 (dm, $CH_{2(PN)}$, J = 28.0 Hz), 3.60 (dt, 1H, diastereotopic OCH_2, J = 11.1 and 5.7 Hz), 3.63 (m, 1H, CHOH, J = 3.5 and 8.9 Hz), 3.93 (m, 1H, diasterotopic OCH_2, J = 4.9, 8.1, and 10.8 Hz), 7.24−7.31 (m, 2H, H_β,Py and H_β',Py), 7.42−7.52 (m, 6H, H_{Ph}), 7.68−7.77 (m, 5H, H_γ,Py and H_{Ph}), 9.23 (br dd, 1H, H_α',Py, J = 5.7 and 1.5 Hz). The resonance of the methyne proton has been unequivocally located by means of homonuclear decoupling experiments. ^{13}C NMR (CD_2Cl_2, 125 MHz, 293 K): δ 23.36 (CH_3), 38.64 (CH_2), 63.59 (OCH_2), 64.94 (CHOH), 177.08 (d, C(O)O, J_{CP} = 15.0 Hz); 25.45 (d, CH_2P, J_{CP} = 30.5 Hz), 35.25 (d, CH_2Py, J_{CP} = 5.7 Hz), 123.41 and 124.97 (C_β,Py atoms), 139.48 (C_γ,Py), 153.10 (C_α',Py) and 159.60 (d, C_α,-Py, J_{CP} = 2.9 Hz); 129.08 (d, $C_{meta,Ph}$, J_{CP} = 11.7 Hz) and 129.10 (d, partially masked, $C_{meta,Ph}$, $J_{CP} \approx$ 11 Hz), 131.44 (d, $C_{para,Ph}$, J_{CP} = 2.9 Hz) and 131.52 (d, $C_{para,Ph}$, J_{CP} = 2.9 Hz), 131.67 (d, $C_{ipso,Ph}$, J_{CP} = 51.5 Hz) and 131.80 (d, $C_{ipso,Ph}$, J_{CP} = 51.5 Hz), 133.26 (d,

$C_{ortho,Ph}$, J_{CP} = 11.8 Hz) and 133.44 (d, $C_{orthp,Ph}$, J_{CP} = 12.1 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 293 K): δ 24.31.

Synthesis of PdCl(PN)(COO-CH_2-CH_2-CH_2-CH_2(OH) (4f). $PdCl_2$(PN) (0.600 g, 1.28 mmol), CH_3CN (15 mL), 1,4-hydroxybutane (454 μL, 5.12 mmol; 1,4-HB/Pd = 4), and NEt_3 (1,5 mL) were allowed to react with CO under the conditions described above for about 3 h. The resulting solution, after concentration to ca. 5 mL, addition of Et_2O (5 mL), and further 48 h reaction with CO, was left overnight at −10 °C to afford white **4f** contaminated with NEt_3·HCl. The mixture was separated by filtration and purified by washing. The filtered solution, after addition of Et_2O (5 mL) and cooling at −10 °C for 5 days, produced white crystals of **4f**, slightly contaminated with ammonium salt, which was purified by washing with Et_2O−CH_3CN (4:1) and dried (0.380 g total, yield 54%). More product could be obtained as described above.

Anal. Calcd for $C_{24}H_{27}ClNO_3PPd$: Pd, 19.31; Cl, 6.43; P, 5.61. Found: Pd, 19.26; Cl, 6.41; P 5.57. ^1H NMR (CD_2Cl_2, 500 MHz, 293 K): δ 1.24−1.40 (m, 4H, CH_2CH_2), 2.18 (br, OH), 2.44 (m, 2H, $CH_{2(PN)}$), 3.39 (dm, 2H, $CH_{2(PN)}$, J = 28.1 Hz), 3.45 (tr, 2H, CH_2OH, J = 6.2 Hz,), 3.64 (tr, 2H, OCH_2, J = 6.4 Hz), 7.24−7.31 (m, 2H, H_β,Py and $H_{\beta'}$,Py), 7.40−7.51 (m, 6H, H_{Ph}), 7.66−7.76 (m, 5H, H_γ,Py and H_{Ph}), 9.23 (br d, 1H, $H_{\alpha'}$,Py, J = 5.4 Hz). ^{13}C NMR (CD_2Cl_2, 125 MHz, 293 K): δ 25.60 (CH_2), 29.53 (CH_2), 62.21 (CH_2OH), 66.13 (OCH_2), 176.35 (d, C(O)O, J_{CP} = 14.6 Hz); 25.51 (d, CH_2P, J_{CP} = 29.6 Hz), 35.31 (d, CH_2Py, J_{CP} = 4.6 Hz), 123.33 and 124.94 (C_β,Py atoms), 139.43 (C_γ,Py), 152.93 ($C_{\alpha'}$,Py) and 159.58 (d, C_α,Py, J_{CP} = 2.8 Hz); 129.00 (d, $C_{meta,Ph}$, J_{CP} = 11.7 Hz), 131.38 (d, $C_{para,Ph}$, J_{CP} = 2.9 Hz), 131.81 (d, $C_{ipso,Ph}$, J_{CP} = 51.5 Hz), 133.29 (d, $C_{ortho,Ph}$, J_{CP} = 11.8 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 293 K): δ 24.53.

5.2. Reaction of the Complexes 4a−f with HCl. In a typical reaction the alkoxycarbonyl complex **4b** (0.168 g, 0.31 mmol), in CH_3CN (3 mL), and a methanol solution of 3 M HCl (2 mL) were separately charged into the two branches of an inverted Y-shaped glass reactor. The reactor was connected to a gas buret, the contents were mixed, and the CO evolved was measured at ambient temperature and pressure (6.7 mL at 21 °C, 0.1 MPa) and analyzed by GC. Trace amounts of CO_2 were found.

The decomposition of the other complexes was performed in the same way. The weighed amounts of complexes and volume of CO evolved are reported in Table 2.

5.3. Reaction of Alkoxycarbonyl Complexes 4a−f with $CuCl_2$: Synthesis of Cyclic Carbonates via Chloroformate. All the reactions were performed in the above-described inverted Y-shaped glass reactor.

Synthesis of 1,3-Dioxan-2-one (6c). Complex **4c** (0.096 g, 0.18 mmol), in CH_3CN (1.5 mL), and 0.050 g (0.37 mmol) of dry $CuCl_2$, in CH_3CN (3 mL), were separately charged into the two branches of the glass reactor. The copper solution was added to the suspension of the complex, which caused its solubilization and subsequently the precipitation of a yellow product. The IR spectrum of the reaction solution displays a strong band at 1778 cm^{-1} and a weak band at 1751 cm^{-1}, due respectively to chloroformate Cl-$COO(CH_2)_3$-OH and to small amounts of cyclic carbonate **6c**. NEt_3 (3 mL), added to the reaction mixture, caused an immediate conversion of the chloroformate into carbonate, as evidenced by the IR spectrum, which showed the extinction of the band at 1778 cm^{-1} and the reinforcement of the one at 1751 cm^{-1}. The carbonate was characterized by GC-MS and quantitatively analyzed by GC (found 0.15 mmol, 83%). MS (*m*/*z*) (relative intensity %): 102 (M^+, 13), 58 (25), 57 (47), 43 (15), 29 (100%).

Synthesis of 1,3-Dioxolan-2-one (6a). Complex **4a** (0.101 g, 0.19 mmol), in CH_3CN (1.5 mL), and $CuCl_2$ (0.057 g, 0.42 mmol) were reacted as described above, and the IR spectrum of the reaction solution displayed a strong band at 1778 cm^{-1} due to the chloroformate Cl-$COO(CH_2)_2$-(OH) (**5a**) and two weak intensity bands at 1807 and 1774 cm^{-1} ascribed to the cyclic carbonate **6a**. Addition of NEt_3 caused the complete conversion of **5a** to the relevant cyclic carbonate **6a**. MS (*m*/*z*): 88 (M^+, 52), 58 (9), 43 (65), 29 (100).

Synthesis of 4-Methyl-1,3-dioxolan-2-one (6b). Complex **4b** (0.088 g, 0.16 mmol), in CH_3CN (1.5 mL), and $CuCl_2$ (0.048 g, 0.35 mmol) were reacted, and the IR spectrum of the reaction solution displayed a strong band at 1779 cm^{-1} due to the chloroformate Cl-$COO(CH_2)CH$-$(OH)CH_3$ (**5b**). Addition of NEt_3 caused the complete conversion of **5b** into the relevant cyclic carbonate **6b**, as evidenced by the IR spectrum, which showed a new band at 1751 cm^{-1}. MS (*m*/*z*): 102 (M^+, 2), 87 (10), 57 (64), 43 (73), 29 (100).

Synthesis of 4-Ethyl-1,3-dioxolan-2-one (6d). Complex **4d**, (0.106 g, 0.19 mmol), in CH_3CN (1.5 mL), and $CuCl_2$ (0.056 g, 0.41 mmol) were reacted, and the IR spectrum of the reaction solution displayed a strong band at 1779 cm^{-1} due to the chloroformate Cl-$COOCH_2CH(OH)CH_2CH_3$ (**5d**). Addition of NEt_3 caused the complete conversion of **5d** into the relevant cyclic carbonate **6d**, as evidenced by the IR spectrum, which showed a new band at 1801 cm^{-1}. MS (*m*/*z*): 116 (M^+, 1), 87 (25), 71 (2), 44 (16), 43 (100), 42 (56), 29 (30).

Synthesis of 4-Methyl-1,3-dioxan-2-one (6e). Complex **4e** (0.99 g, 0.18 mmol), in CH_3CN (1.5 mL), and $CuCl_2$ (0.057 g, 0.42 mmol) were reacted, and the IR spectrum of the reaction solution displayed a strong band at 1778 cm^{-1} due to the chloroformate Cl-$COO(CH_2)_2$-$CH(OH)CH_3$ (**5e**) and a weak intensity band at 1749 cm^{-1} ascribed to the cyclic carbonate 4-methyl-1,3-dioxan-2-one (**6e**). Addition of NEt_3 (0.3 mL) caused the complete conversion of **5e** to the relevant cyclic carbonate **6e**. MS (*m*/*z*): 116 (M^+, 2,5), 101 (19), 86 (100), 71 (4), 58 (40), 44 (24), 43(45), 42 (50), 29 (43).

Synthesis of 1,3-Dioxacycloheptan-2-one (6f). Complex **4f** (0.150 g, 0.27 mmol), in CH_3CN (1.5 mL), and $CuCl_2$ (0.080 g, 0.59 mmol) were reacted, and the IR spectrum of the reaction solution displayed only one band in the carbonyl range at 1778 cm^{-1} due to the chloroformate Cl-$COO(CH_2)_4$-OH (**5f**). Addition of NEt_3 caused the complete conversion of **5f** into the relevant cyclic carbonate **6f**, evidenced by the IR spectrum, which displayed a band at 1757 cm^{-1}. MS (*m*/*z*): 116 (M^+, 4), 71 (6), 57 (5), 44 (22), 43 (29), 42 (100), 41 (50), 29 (23).

5.4. Reaction of Alkoxycarbonyl Complexes 4a−f with I_2: Synthesis of Chloroformate. Complex **4c** (0.091 g, 0.17 mmol), in CH_3CN (2 mL), and I_2 (0.044 g, 0.17 mmol), in CH_3CN (2,5 mL), were separately charged into the two branches of the glass reactor. The iodine solution was added to the suspension of the complex, which caused its solubilization and subsequently the precipitation of a brown product. The IR spectrum of the reaction solution displays a strong band at 1778 cm^{-1}, due to the chloroformate Cl-$COO(CH_2)_3$-OH (**5c**), which was identified indirectly both by the relevant cyclic carbonate **6c** and by the reaction product with aniline. Addition of aniline to a solution of **5c** gave the expected derivative carbamate $PhNHCOO(CH_2)_3OH$, which was recognized by MS [(*m*/*z*, M^+ 194, 119, 116, 115, 93(100%), 91, 65, 47)]. The mass spectrum of the reaction solution exhibits two further signals attributable respectively to phenyl isocyanate and 1,3-hydroxypropane, deriving from thermal decomposition of $PhNHCOO(CH_2)_3OH$.[24]

The reaction with other complexes was carried out in the same manner. The relevant chloroformates were characterized as cyclic carbonates and carbamate derivatives.

(24) Rivetti, F.; Romano, U.; Sassanelli, M. U.S. Patent FCS 4514339, 1985.

(25) Carruthers, B. J.; Watkin, D. J. *Acta Crystallogr*. **1979**, *A35*, 698.

5.5. Reaction of Alkoxycarbonyl Complexes with PPh_3 and NEt_3. Typical reaction: to a suspension of complex **4b** (0.102 g, 0.19 mmol) in CH_3CN (4 mL) were added, under nitrogen, PPh_3 (0.95 mmol; PPh_3/Pd = 5) and NEt_3 (0.4 mL). The mixture was heated at 60 °C for 3 h. During this period the initial white-cream complex dissolved, giving a yellow solution from which $Pd(PPh_3)_4$ precipitated. The IR spectrum of the reaction solution displayed a band at 1751 cm^{-1}, ascribed to cyclic carbonate **6b**, whose formulation was confirmed by a mass spectrum.

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Supporting Information Available: X-ray crystallographic data in CIF format for complexes **4c** and **4d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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