

Iminophosphine-palladium(0) complexes as catalysts in the alkoxy-carbonylation of terminal alkynes

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Abstract

In the presence of methanesulfonic acid, the palladium(0)-olefin complexes: $[\text{Pd}(\eta^2\text{-ol})(\text{P-N})]$ [ol = dimethyl fumarate or fumaronitrile, P-N = 1-(Ph₂P)C₆H₄-2-CH=NR (R = CMe₃ or C₆H₄OMe-4)] catalyse the alkoxy-carbonylation of terminal alkynes. Moderately good rates are obtained when the catalysts are promoted with two equivalents of the free P-N ligand and a large excess of acid at 120°C. The catalytic data suggest that derivatives of the type $[\text{Pd}(\text{alkyne})(\text{P-N})_n]$ ($n = 2-3$) are the active catalytic species. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The carbonylation of 1-alkynes is a versatile reaction which allows to obtain in one step α,β -unsaturated carboxylic acids and their derivatives (Scheme 1) [1,2].

The successful application of this reaction requires the use of catalysts having high activity and selectivity. So far, the most efficient catalytic systems are those generated in situ by mixing together palladium acetate, a tertiary phosphine having a 2-pyridyl substituent (typically, 2-pyridyldiphenylphosphine), and a strong organic acid whose conjugate base is weakly coordinating (e.g. sulfonic acids) [3,4]. The high activity and selectivity of this system warrants its use not only in the commercial synthesis of important

large-scale chemical intermediates such as methacrylates [3,5] but also in the preparation of fine chemicals [6,7].

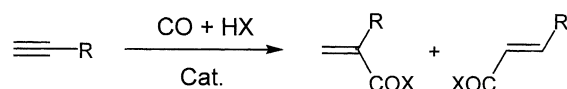
While studies on the mechanism of the reaction have shown that in the formation of the catalytic system palladium acetate can be replaced by other palladium compounds (for instance, $[\text{Pd}_2(\text{dba})_3]$ (dba = dibenzylideneacetone)) without loss in activity and selectivity [8], it appears that a unique role is played by the 2-pyridyl substituent present on the phosphorus ligand [3]. To explain the particular high activity obtained with such ligands it has been proposed that the nitrogen atom of the pyridyl moiety allows a fast transfer of protons to the substrate [4,8].

In this context, we have thought worthwhile to investigate the catalytic activity of palladium complexes with iminophosphine ligands. For this purpose, we deemed particularly well-suited as catalyst precursors iminophosphine-palladium(0)-olefin complexes having the structure depicted in Fig. 1 [9].

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X = OH, OR', NR'R'', etc.

Scheme 1.

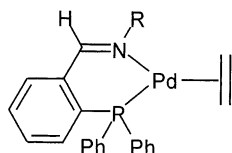


Fig. 1. Structure of imino-phosphine-Pd(0)-olefin complexes.

Indeed, we expect that the olefin would be easily replaced by the acetylenic substrate to produce a palladium(0) species involved in the catalytic cycle.

2. Results and discussion

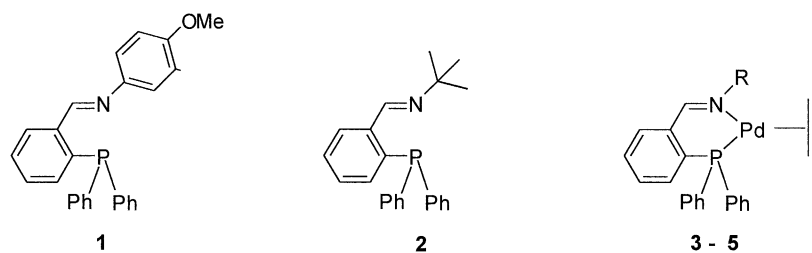
In our investigations we have chosen as model reaction the methoxycarbonylation of phenylacetylene.

The catalytic systems were prepared in situ by mixing together the appropriate palladium complex, variable amounts of the corresponding iminophosphine and $\text{CH}_3\text{SO}_3\text{H}$. The reaction studied and the catalysts used are reported in Scheme 2.

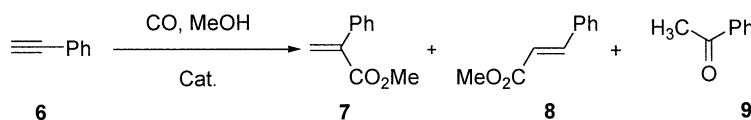
The reactions were carried out in a magnetically stirred stainless steel autoclave. Substrate conversion and product composition were determined by GLC using an internal standard. The experimental data obtained with complex **3** as catalyst precursor are reported in Table 1 together with the relevant reaction conditions.

The carbonylation of the substrate proceeds only at temperatures higher than 100°C . Improved reaction rates are achieved adding to the catalyst some equivalents of free iminophosphine and an excess of methanesulfonic acid. The best results are obtained under the conditions of runs 2 and 3, i.e. using 1–2 mol of free ligand and 8 mol of acid per mole of catalyst.

The average turnover frequency number achieved under these conditions is ca. $50 \text{ (mol of substrate (mol of Pd)}^{-1} \text{ h}^{-1})$, which is much lower than that routinely obtained using 2-pyridyl containing arylphosphines, but higher than that obtained with PPh_3 [4]. Comparable reaction rates were



Cat.	P - N	Olefin
3	1	Dimethyl fumarate
4	1	Fumaronitrile
5	2	Dimethyl fumarate



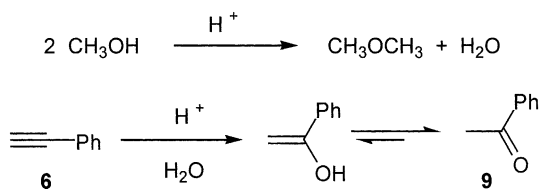
Scheme 2.

Table 1
Carbonylation of phenylacetylene in the presence of complex **3**^a

Run	1/3 (mol/mol)	H ⁺ /3 (mol/mol)	Conversion (%)	Product yield (%)			R (%) ^b
				7	8	9	
1	0	8.0	4	1	0	3	ca. 100
2	1.0	8.0	25	12	3	10	80
3	2.0	8.0	28	16	3	9	84
4	3.0	4.0	19	14	2	3	87
5	4.0	5.0	4	4	0	0	ca. 100

^a $T = 120^{\circ}\text{C}$; $t = 4\text{ h}$; $P(\text{CO}) = 28\text{ atm}$ at 25°C ; $\text{CH}_3\text{OH} = 20\text{ ml}$; phenylacetylene = 10 mmol; **3** = 0.0125 mmol; substrate/Pd = 800.

^b $R = [7/(7 + 8)]100$.



obtained previously under similar conditions employing tri(2-furyl)phosphine [10]. The regioselectivity towards the 2-substituted acrylate ester **7** is ca. 85%. Unfortunately, the chemo-selectivity is not complete because substantial amounts of acetophenone **9** are also formed. The formation of this side product can be accounted for by the sequence of reactions shown in Scheme 3.

These reactions are probably induced by the relatively high temperature and the high acid concentration required to improve the reaction rate.

As a matter of fact, looking at the data of Table 2 it is evident that the reaction rate increases

Table 2
Influence of the H⁺/3 ratio on the catalytic activity^a

Run	H ⁺ /3 (mol/mol)	Conversion (%)	Product yield (%)			R (%) ^b
			7	8	9	
1	2.0	8	7	1	3	88
2	4.0	16	10	2	4	83
3	8.0	25	12	3	10	80

^a $T = 120^{\circ}\text{C}$; $t = 4\text{ h}$; $P(\text{CO}) = 28\text{ atm}$ at 25°C ; $\text{CH}_3\text{OH} = 20\text{ ml}$; phenylacetylene = 10 mmol; **3** = 0.0125 mmol; **1/3** = 1; substrate/Pd = 800.

^b $R = [7/(7 + 8)]100$.

with increasing the H⁺/3 ratio, but at some expenses of the chemoselectivity since also the production of acetophenone grows. It is worth noting that also the regioselectivity decreases with increasing the H⁺/3 ratio.

From the data of the methoxycarbonylation of phenylacetylene carried out using the three different catalyst precursors (Table 3) it appears that the nature of both the imino substituent R and the olefin affects the reaction rate.

While the most important effect is brought about by the imino substituent R, the effect of the olefin is more intriguing. In fact, the catalytic activity decreases with increasing the π -accepting properties of the olefin. This finding suggests that the olefin initially present on the catalytic precursor is able to compete with the substrate in the coordination to the metal centre of the actual catalyst. Thus, the latter is likely to be a zero valent palladium species of the type $[\text{Pd}(\text{alkyne})(\text{P-N})_n]$ ($n = 2-3$) in equilibrium with the corresponding olefin complex $[\text{Pd}(\eta^2\text{-ol})(\text{P-N})_n]$ (fumaronitrile species of the type $[\text{Pd}(\eta^2\text{-ol})(\text{P-N})_2]$ has been isolated and characterised [9]) and ultimately with the catalyst precursors **3-5**. Accordingly, the difference in catalytic efficiency between **3** and **4** can be explained by taking into account that, owing to its higher π -electron accepting character, fumaronitrile is able to co-ordinate more firmly to the metal centre than dimethyl fumarate, thus, hindering the approach of the acetylenic substrate to the metal.

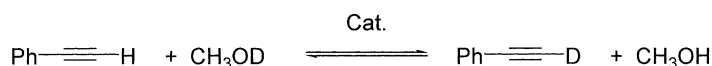
As far as the reaction mechanism is concerned, we assume that the same sequence of reactions involved in the case of Drent's system is at work here [8]. This assumption is justified not only by the similarity of the two systems, but also by the observation that

Table 3
Carbonylation of phenylacetylene in the presence of complex **3–5**^a

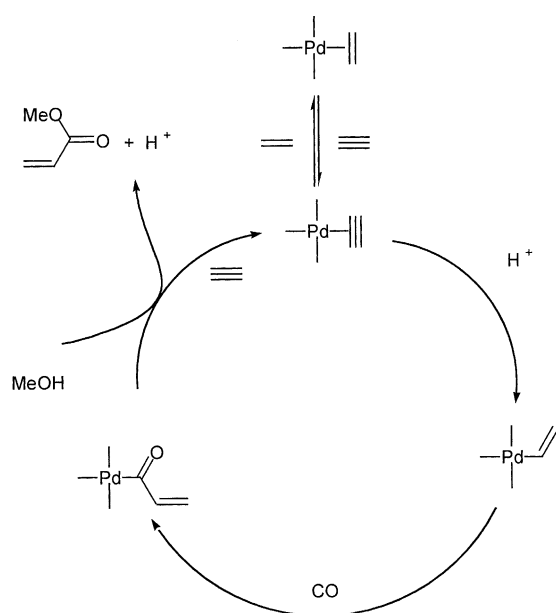
Run	Catalyst	P–N/catalyst (mol/mol)	H ⁺ /Pd (mol/mol)	Conversion (%)	Product yield (%)			R (%) ^b
					7	8	9	
1	3	2.0	8.0	35	21	5	9	81
2	4	1.0	8.0	26	10	2	14	83
3	4	2.0	8.0	23	9	2	12	82
4	5	2.0	8.0	11	4	1	6	80

^a $T = 120^{\circ}\text{C}$; $t = 4\text{ h}$; $P(\text{CO}) = 15\text{ atm}$ at 25°C ; $\text{CH}_3\text{OH} = 20\text{ ml}$; phenylacetylene = 10 mmol; catalyst = 0.0125 mmol; $\text{CH}_3\text{SO}_3\text{H} = 0.1\text{ mmol}$; substrate/Pd = 800.

^b $R = [7/(7 + 8)]100$.



Scheme 4.



Scheme 5.

both catalysts are able to promote the unusual H/D exchange depicted in Scheme 4 [8].¹

Starting from a $[\text{Pd}(\text{alkyne})(\text{P}-\text{N})_n]$ species, the catalytic cycle (Scheme 5) would imply: (i) a

¹ GC–MS analyses show that the residual phenylacetylene recovered after carbonylation experiments carried out with CH_3OD is partially deuterated.

metal-assisted protonation of the alkyne to give a palladium(II)-vinyl intermediate; (ii) CO insertion into the metal–carbon bond to afford a palladium-acyl intermediate and (iii) methanolysis of this latter derivative which leads to the desired ester [8,10]. In the sequence of reactions of Scheme 5, the key step is the formation of the σ -vinyl complex. Evidences supporting the formation of such type of intermediate by reaction of palladium(0) species with alkynes and acids have been reported by us [8] and others [11–14].

As far as the effect of the imino substituent R is concerned, it should be noted that in the complexes $[\text{Pd}(\eta^2\text{-ol})(\text{P}-\text{N})_2]$ ($\text{P}-\text{N} = \mathbf{1}$ or $\mathbf{2}$, ol = fumaronitrile) the iminophosphines act as P-monodentate ligands [9]. Therefore, we expect that such a ligating mode would be further stabilised by almost complete protonation of the free imino function in the presence of an excess of methanesulfonic acid (palladium complexes with protonated imino ligands are well-documented [15]). If the iminophosphines act as P-monodentate ligands, the lower activity displayed by complex **5** (as compared to complex **3**) may be rationalised on the basis of the higher steric hindrance of the *t*-butyl groups.

With the aim to improve the catalytic efficiency we have studied the influence of the carbon monoxide pressure and of the solvent. The relevant data are listed in Tables 4 and 5.

The carbonylation rate increases with increasing the $P(\text{CO})$ until a maximum is reached at ca.15 atm, whereas at higher pressures the catalytic activity

Table 4
Influence of $P(\text{CO})$ on the catalytic activity^a

Run	$P(\text{CO})$ (atm)	Conver- sion (%)	Product yield (%)			R (%) ^b
			7	8	9	
1	4	23	10	2	11	83
2	10	23	11	2	10	85
3	15	35	21	5	9	81
4	20	31	18	3	10	86
5	28	28	16	3	9	84

^a $T = 120^\circ\text{C}$; $t = 4$ h; $\text{CH}_3\text{OH} = 20$ ml; phenylacetylene = 10 mmol; **3** = 0.0125 mmol; **1/3** = 2; $\text{CH}_3\text{SO}_3\text{H} = 0.1$ mmol; substrate/Pd = 800.

^b $R = [7/(7 + 8)]100$.

decreases. Such behaviour is rather usual in carbonylation reactions and can be accounted for by admitting that at higher pressure carbon monoxide is able to compete with some reactant for the coordination to the metal centre [8,10], whereas at low pressure the rate determining step is the CO insertion.

As far as the solvent influence is concerned, the best reaction rates are observed in methanol which probably takes advantage of the fact that it also participates to the reaction [3]. The catalytic efficiency is much lower in dichloromethane and almost disappears in other solvents such as toluene or tetrahydrofuran.

Finally, it is to remark that the catalytic activity of these systems is not restricted to aryl-substituted terminal alkynes. Aliphatic terminal alkynes such as 1-heptyne or disubstituted alkynes, such as diphenylacetylene or 2-butyne, are also carbonylated, albeit at a reduced rate.

Table 5
Influence of the solvent on the catalytic activity^a

Run	Solvent	Conver- sion (%)	Product yield (%)			R (%) ^b
			7	8	9	
1	CH_3OH^c	35	21	5	9	81
2	CH_2Cl_2^d	16	11	3	2	78

^a $T = 120^\circ\text{C}$; $t = 4$ h; $P(\text{CO}) = 15$ atm at 25°C ; phenylacetylene = 10 mmol; **3** = 0.0125 mmol; **1/3** = 2; $\text{CH}_3\text{SO}_3\text{H} = 0.1$ mmol; substrate/catalyst = 800.

^b $R = [7/(7 + 8)]100$.

^c $\text{CH}_3\text{OH} = 20$ ml.

^d An amount of 18 ml of CH_2Cl_2 and 50 mmol of CH_3OH .

3. Conclusions

This work shows that palladium(0) complexes containing iminophosphine ligands are able to catalyse the alkoxy-carbonylation of alkynes. Unfortunately, the efficiency of this system is not very high since the maximum observed rate is of ca. 50 catalytic cycles h^{-1} . Moreover, neither the chemoselectivity nor the regioselectivity of the reaction are complete.

It appears that the reaction proceeds with a mechanism similar to that reported for the system $\text{Pd}(\text{OAc})_2/\text{CH}_3\text{SO}_3\text{H}/2$ -pyridyldiphenylphosphine. Therefore, it is rather difficult to explain the large (ca. three order of magnitude) difference in catalytic activity displayed by the two systems. Electronic and steric factors can be invoked: indeed, Drent has already shown that subtle modifications of the ligand structure can lead to huge effects on the reaction rate [3,4].

4. Experimental

4.1. Materials and instruments

All the operations were carried out under argon in Schlenk-type glassware. Commercial solvents (C. Erba) were purified following methods described in [16]. The ligands **1–2** and the complexes **3–5** were prepared as described in [9]. Phenylacetylene (Aldrich) and 1-heptyne (Aldrich) were distilled prior to use; CH_3OD (Aldrich), 2-butyne (Aldrich) and methanesulfonic acid (Aldrich) were used as received. High purity CO was obtained by SIAD. The carbonylation experiments were carried out in a magnetically stirred stainless steel autoclave (total volume ca. 150 ml). Conversion and yield of the reactions were determined by GLC on a Hewlett–Packard 5830 II series gaschromatograph, using mesitylene as internal standard. GLC–MS analyses were carried out on a HP 5830 II series gaschromatograph interfaced to a Hewlett–Packard 5971 mass detector.

4.2. Carbonylation experiments

To illustrate the carbonylation procedure the experimental details for run 3 of Table 1 are reported. Under inert atmosphere, a Schlenk flask containing a small magnetic bar is charged with 20 ml of CH_3OH , 8.0 mg

(0.0125 mmol) of complex **3**, 9.9 mg (0.025 mmol) of iminophosphine **1**, 1.02 g (10.0 mmol) of phenylacetylene, 9.6 mg (0.1 mmol) of $\text{CH}_3\text{SO}_3\text{H}$ and 83 mg (0.7 mmol) of mesitylene. The resulting solution is transferred via cannula into the autoclave, which is then pressurised with CO. The reactor is maintained at the desired temperature ($\pm 1^\circ\text{C}$) by circulating a thermostatic fluid. At the end of the reaction the residual gas is vented off and the composition of the raw reaction mixture determined by GLC.

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