APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **14**, 581–589 (2000)

Phenylacetylene carbonylation catalysed by Pd(II) and Rh(III) intercalated in zirconium phosphates[†]

Potenzo Giannoccaro,[1,2]* M. Aresta,[1,2] S. Doronzo[1] and Carla Ferragina[3]
[1]Dipartimento di Chimica, Università di Bari, Bari, Italy
[2]Centro CNR MISO, Università di Bari, Bari, Italy
[3]CNR-IMAI, Area della Ricerca di Roma, Monterotondo, Rome, Italy

Palladium(II) and rhodium(III) ions, or palladium(II) complexes (Pd-L) with bidentate *N*-donor ligands such as 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen), intercalated in the layers of zirconium hydrogen phosphate, in α or γ phases (α- or γ-ZrP), catalyze both single and double methoxo-carbonylation of phenylacetylene. The monocarbonylation products, $PhC(COOCH_3){=}CH_2$ (1) and its regio isomer $PhCH{=}CH(COOCH_3)$ (2) are obtained when phenylacetylene reacts, in methanol, under CO pressure (1–4 MPa), at temperatures of 80–130 °C. When the reaction is carried out under oxidative conditions using a CO/O_2 mixture, double-carbonylation products are obtained as well as monofunctionalized phenylacetylene. The double-carbonylation product $PhC(COOCH_3){=}CH(COOCH_3)$ (3) and the corresponding anhydride $PhCCO(\underbracket{O){=}CHCO}$ (4) are obtained when the process is carried out with a CO/O_2 mixture under pressure (2–4 MPa; pO_2 = 0.8 MPa) at 60–100 °C, using methanol or acetonitrile as solvent. When the reaction is carried out in the presence of tertiary amines such as NEt_3 or NPh_3, under mild pressure conditions (0.4–0.7 MPa) at 60–90 °C, the triple bond remains unchanged and the monocarboxylate $PhC{\equiv}CCOOCH_3$ (5) is isolated. Compound 5 is also prepared in a neutral medium when γ-Zr–Rh^{3+} is used as catalyst. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: phenylacetylene; metoxo-carbonylation; double-carbonylation; heterogeneous catalysis; reductive-carbonylation; oxidative-carbonylation

1 INTRODUCTION

The carbonylation of terminal and internal alkynes to afford mono- and di-carbonylation products has long been known.[1] Some palladium-based homogeneous systems have been described in recent years and mechanistic aspects have been elucidated.[2–6] Conversely, heterogeneous catalysts, which offer some advantages such as separation and recycling, have scarcely been studied.[7]

We have investigated zirconium and titanium phosphates, both α and γ- phases (α- or γ-ZrP; α- or γ-TiP), as a means for heterogenizing homogeneous catalysts by intercalation.[8–10]

Our studies have shown that not only does the insertion of transition-metal ions or complexes, usually employed in homogeneous catalysis, not alter their activity but in some cases even enhances it.[9] Thus the new heterogenized systems show at the same time all the advantages of both homogeneous and heterogeneous catalysts. In a way, they can be considered as models of heterogeneous catalysts working under homogeneous conditions. Eventual leaching of the metal ions from the matrix causes catalyst deactivation and may represent the main hindrance to their practical application. As an example, α-ZrP–Pd-L (L = bipy, phen) catalyzes the oxidative carbonylation of aniline, but, because of leaching, its activity decreases when it is recovered and re-used.[8] In contrast, rhodium(III)-based systems, such as α-and γ-ZrP–Rh(III) and γ-ZrP–Rh(III)-L (L = bipy; phen) under the same conditions, behave as stable catalysts.[9–10]

In this paper we describe the catalytic activity and the behaviour after recycling of α- and γ-ZrP–

---

* Correspondence to: Potenzo Giannoccaro, Dipartimento di Chimica, Università di Bari, Bari, Italy.

[†] Presented at the XIIIth FECHEM Conference on Organometallic Chemistry, held 29 August–3 September 1999, Lisbon, Portugal.

Contract/grant sponsor: MURST; Contract/grant number: 9803026360.

Pd(II), α- and γ-ZrP–Pd(II)-L and γ-ZrP–Rh(III) towards the carbonylation of phenylacetylene. Preliminary results have been presented previously.[11]

2 EXPERIMENTAL

α- and γ-Pd(II)–zirconium phosphate (α- and γ-ZrP–Pd) and γ-Rh(III)–zirconium phosphate (γ-ZrP–Rh) were prepared by contacting the respective metastable ethanolic form of the exchanger α-$Zr(HPO_4)_2(EtOH)_2$ and γ-$Zr(PO_4)(H_2PO_4)(EtOH)_2$ with a Pd(II) or Rh(III) solution. α- and γ- [Pd(II)-ligands]–zirconium phosphate (α- and γ-ZrP–Pd-L) were prepared by contacting the α- and γ -ZrP-ligand intercalation compounds with palladium(II) Pd(II)] solution. Details of the preparation and characterization of compounds have been already reported.[10,12,13]

X-ray photoelectron spectra were taken with a Esca 3MK II spectrophotometer (Vacuum Generator Ltd) employing Al $K\alpha_{1,2}$ excitation (1486.6 eV) at a residual pressure of 10^{-9} Pa. The binding energy was calibrated by mecro of the $4f_{7/2}$ gold signal at 83.7 eV and sample charging was corrected by referencing to the C 1*s* line of contaminating carbon taken at 285.0 eV. The accuracy of the binding energies was estimated to ±0.1 eV. The spectra were usually recorded in the fixed analyser transmission (fat) mode at 20 eV.

Quantitative analyses of reaction products were carried out with a Varian GC 3300 using a VA-5ms, i.d. 0.53 mm, 15-m column. GC–MS analyses were performed using a Hewlett-Packard 5995 instrument. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer.

^{1}H-NMR spectra were recorded on a Varian XL 200 spectrometer and the chemical shifts are expressed in δ units with Me_4Si as internal standard.

All reactions were performed in a 55.6-ml stainless-steel autoclave. The catalyst, co-catalyst and reagents were introduced in a Pyrex test-tube placed inside the autoclave in order to prevent any contact with the metal. After reaction the autoclave was cooled, the reaction solution was analysed as described below and thereafter the solid catalyst was filtered off, washed with methanol or CH_3CN and re-used.

2.1 Phenylacetylene carbonylation

2.1.1 Reductive carbonylation

In a typical experiment the autoclave was charged with the catalyst (40 mg of α-$ZrH_{1.64}Pd_{0.18}(PO_4)_2{\cdot}2.5H_2O$; Pd, 5.52%), methanol (7 ml), phenylacetylene (0.5 ml, 4.54 mmol) and co-catalyst, if needed. The autoclave was sealed, the air was evacuated and CO was admitted up to 2–4 MPa. After reaction for 10 h at the temperature indicated in Table 2 (below), the autoclave was cooled and the contents were analysed (GLC, GC–MS, IR and NMR). The quantities of Phenylacetylene that had reacted and carbonylated products (**1** + **2**) that has formed were estimated by GLC, using toluene as an internal standard. The filtered reaction solutions, which display an IR band (s, br) centred at 1727 cm^{-1} [ν(CO)], were concentrated by evaporation, then water was added and the carbonylated products were extracted with ether. The ethereal layer was dried over $MgSO_4$,, then concentrated, and products **1** and **2** were separated by column chromatography (silica gel, 80 cm long, 2 cm i.d.) with a 1:4 CH_2Cl_2 hexane mixture. Compound **1** was eluted first. It was identified by comparison with an authentic Merck–Aldrich sample and by ^{1}H NMR, IR and mass spectra. The approximate molar ratio **1**/**2** was also determined by comparing the intensity of the ν(CO) bands of the separate compounds diluted with hexane to 10 ml.

The solution coming from reactions in acid medium was neutralized before extraction.

Compound **1**: ^{1}H NMR in $CDCl_3$ (δ): 7.31 (m, Ph), 5.97, 6.31 (d, each, $=CH_2$), 4.05 (s, CH_3). IR, ν(CO): 1728 cm^{-1} MS (*m/z*): 162 [M^+].

Compound **2**: ^{1}H NMR in $CDCl_3$ (δ): 7.51 (d, $=CH$), 7.31 (m, Ph), 6.05 (d, $=CH$), 4.05 (s, CH_3). IR, ν(CO): 1728 cm^{-1}. MS (*m/z*): 162 [M^+].

2.2 Oxidative carbonylation to afford double-carbonylation products

2.2.1 Reaction in methanol

The autoclave was charged as above, then filled with the CO/O_2 mixture at the total pressure indicated in Table 2 (below) and left to react under the conditions reported therein. After reaction, unreacted phenylacetylene and the products **3** and **4** were estimated by GLC. The IR spectra of the solution display bands at 1768 (w), 1730–1735 (s, br), 1635 (br, w) and 1588 cm^{-1} (w). Compounds **3** and **4** were separated by column cromatography using a CH_2Cl_2 hexane mixture. Compounds **4** was eluted first. No other carbonylated products were separated.

3: IR: 1730–1735 (s, br) and 1635 cm^{-1} (br, w). ^{1}H NMR in $CDCl_3$ δ: 7.4 (m, Ph), 6.2 (s, $=$CH), 4.31 (s, CH_3), 3.65 (s, CH_3). MS (*m/z*): 220 [M^+].

4: IR: 1768 and 1588 cm^{-1} (s). Addition of H_2SO_4 (1 ml, 5 M) followed by reflux in methanol for 0.5 h causes a decrease in the bands at 1768 and 1588 cm^{-1} (w), and the appearance of new bands at 1730–1735 and 1635 cm^{-1}, due to the conversion of **4** into **3**. MS (*m/z*) = 74 [M^+]

2.2.2 Reaction in CH_3CN

The autoclave was charged as described above using CH_3CN as solvent. GLC analyses and IR spectral provide evidence that the reaction mixture contains unreacted PhC$\equiv$CH, compound **4** and trace amounts of **3**.

2.3 Monocarbonylation without reducing the triple bond

2.3.1 Reaction with palladium catalyst

The autoclave was charged according to the above procedure. NEt_3 was added and a lower pressure of the CO/O_2 mixture was used (Table 3, below). GLC analyses and IR spectra of the reaction solution revealed the presence of unreacted PhC$\equiv$CH, and the single and double-carbonylation products **5** and **3**. Samples of pure **5** were prepared by methylation of PhC$\equiv$CCOOH purchased from Merck–Aldrich. Compounds **3** and **5** were separated by column chromatography.

5: IR: bands at 2231 cm^{-1} (vs), ascribed to ν(C$\equiv$C),[14] 1718 (vs), 1640 cm^{-1} (w), ascribed to ν(CO) MS (*m/z*): 160 [M^+].

2.3.2 Reactions with the rhodium catalyst

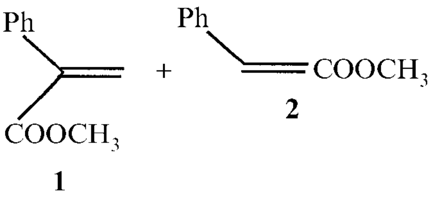
The autoclave was charged with γ-$ZrH_{0.86}Rh_{0.38}(PO_4)_2$ (40 mg), PhC$\equiv$CH (0.3 ml, 2.72 mmol) and methanol (7 ml). Then a CO/O_2 mixture was admitted to the desired pressure and the system was kept to react under the conditions given in Table 3 (below). The products were analysed as described above.

3 RESULTS AND DISCUSSION

α-ZrP–Pd(II), α- and γ-ZrP–Pd(II)-L [L = 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen)] catalyse the carbonylation of phenylacetylene, under both reductive and oxidative conditions, to afford mono- and di-carbonylation products.

The monocarbonylation product **1** and its regio isomer **2** are synthesized when phenylacetylene reacts with CO in methanol (Eqn [1]).

$$PhC\equiv CH + CO + CH_3OH \longrightarrow$$



[1]

The reaction requires a pressure of 2–4 MPa of CO and a temperature of 80–130 °C. The methyl ester of 2-phenylpropenoic acid **1**, which can be hydrogenated to α-arylpropionic acids that are used as non-steroidal anti-inflammatory drugs, is the main product. The conversion of the alkyne is in the range 70–90% and the selectivity of **1** with respect to the regio isomer **2** is about 80%. The compounds were isolated from the reaction mixture by standard column chromatography techniques and characterized by NMR, IR and GC–MS spectroscopy (for details see the Experimental section).

In Table 1 are summarized the most significant results showing how the reaction conditions influence the yield and selectivity. The catalytic activity, expressed by turnover frequency (tof) as moles of phenylacetylene reacted/g of metal per hour, increases with increasing temperature and CO pressure (Table 1, entries 1–6). The increase in temperature has no significant effect on the selectivity towards **1** or **2**, but causes a decrease in the conversion of phenylacetylene to the carbonylated products expressed as yield of $\mathbf{1}+\mathbf{2}$ (Table 1, entries 3–6). Evidence that dimer of phenylacetylene is the main by-product is given by GC–MS. Concerning the activity of the catalyst, the materials containing naked Pd(II) ions are more effective than the corresponding compounds containing Pd(II) complexes (entries 6–9). This behaviour can be explained tentatively on the basis of greater difficulty for phenylacetylene to reach the metal centre bonded to the intercalated bidentate ligand, due to steric hindrance.

Table 1 Reductive carbonylation of phenylacetylene[a]

Entry	Catalyst	T (°C)	p(CO) (MPa)	Phenylacetylene reacted (mmol)	Phenylacetylene reacted (%)	Yield of 1 + 2 (mmol)	Yield of 1 + 2 (%)	Yield of **1** (mmol)	Selectivity for **1** (%)	Turnover frequency, tof[b]
1	A	80	2	1.59	35	1.43	90	1.21	85	0.072
2	A	80	3	2.27	50	2.02	89	1.82	90	0.10
3	A	80	4	2.72	60	2.42	89	2.08	86	0.12
4	A	100	4	3.18	70	2.70	85	2.34	87	0.14
5	A	120	4	3.53	78	2.82	80	2.40	85	0.16
6	A	130	4	4.13	91	2.97	72	2.49	84	0.19
7	B	130	4	4.17	92	2.92	70	2.51	86	0.19
8	C	130	4	3.22	71	2.25	70	1.94	86	0.14
9	D	130	4	2.74	60	1.86	68	1.64	88	0.13
10	A + HCl(1:1)	120	4	4.09	90	3.23	79	2.91	90	0.18
11	A + HCl(1:2)	120	4	4.13	91	3.30	80	2.91	88	0.19
12	A + HBF(1:3)	120	4	4.08	90	3.26	80	2.94	90	0.18

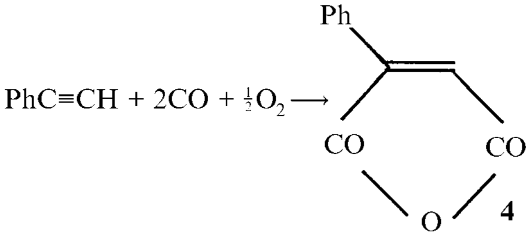
[a] In all the experiments, 7 ml of methanol and 0.5 ml (4.54 mmol) of phenylacetylene were used. Reaction time 10 h. Catalysts: A = α-$ZrH_{1.64}Pd_{0.18}(PO_4)_2{\cdot}2.5H_2O$, (5.52% Pd, 40 mg); B = γ-$ZrH_{1.62}Pd_{0.19}(PO_4)_2{\cdot}3.2H_2O$ (5.60% Pd, 40 mg); C = α-$ZrH_{1.60}Pd_{0.20}$(bi-py)$_{0.41}(PO_4)_2{\cdot}3.2H_2O$ (5.0% Pd, 50 mg); D = γ-$ZrH_{1.56}Pd_{0.22}$(phen)$_{0.44}(PO_4)_2{\cdot}3.5H_2O$ (5.22% Pd, 40 mg).

[b] In mol phenylacetylene reacted (g Pd)$^{-1}$ h^{-1}.

The influence on the reaction rate of some Brönsted acids has also been tested and will be discussed later.

When the carbonylation of phenylacetylene is carried out at 60–100 °C under oxidative conditions, using a mixture of CO/O_2 at a total pressure of 1–4 MPa ($p(O_2) = 0.2$–0.8 MPa), the double carbonylation is accomplished. $PhC(COOCH_3){=}CH(COOCH_3)$ (**3**) and the corresponding anhydride $PhCCO(\underbrace{O){=}CHC}O$ (**4**) are obtained, depending on whether the reaction solvent is methanol or acetonitrile, respectively (Eqns [2], [3]). The yield of the reaction in methanol is in the range 70–85% (Table 2), whereas in CH_3CN, compound **4** is synthesized in 75–80% yield. Small amounts of **4** (5–6%) were also obtained in methanol. In both cases the main by-product is the phenylacetylene dimer. As, in principle, $PhC(COOCH_3){=}CH(COOCH_3)$ can be in *cis* and *trans* forms, attempts at their separation by column chromatography were made. We found that the prevalent structure is *Z*, according with the well-known *cis* character of CO insertion reaction.[15] The trend of the tof values shows that the activity increases with increasing temperature (Table 2, entries 1–5) and the pressure of the CO/O_2 mixture (entries 5–8). The materials that intercalate the complexes are less effective than those containing Pd(II) alone (entries 5 and 9–11). The effect of some additives, such as $NEt_3CH_3{}^+I^-$ HCl and HI, as promoters is also shown. Whereas $NEt_3CH_3{}^+I^-$ does not show any promoting effect (Table 2, entry 14), HCl and HI improve the activity. The best results are obtained with a molar ratio HX/Pd of 2:1 (Table 2, entries 15, 16). A higher ratio does not improve the activity but causes a lowering of the catalyst stability (see below).

$$\begin{gathered} PhC \equiv CH + 2CO + 2CHOH + \tfrac{1}{2}O_2 \longrightarrow \\ \underset{\mathbf{3}}{PhC(COOCH_3) = CH(COOCH_3)} \end{gathered} \qquad [2]$$



4

[3]

When the oxidative carbonylation of phenylacetylene is carried out in the presence of an organic base such as NEt_3 or NPh_3, the monocarboxylate species, $PhC{\equiv}CCOOCH_3$, (**5**), leaving the triple bond unchanged, is obtained (Eqn [4]). The higher conversion yield (55–70%) is obtained between 60–90 °C under mild pressures of a CO/O_2 mixture (0.4–0.7 MPa; $p(O_2) = 0.2$ MPa) (Table

Table 2 Oxidative carbonylation of phenylacetylene[a]

Entry	Catalyst	T (°C)	$p(CO + O_2)$ (MPa)	Phenylacetylene reacted		Yield of **3** (mmol)	Selectivity for **3**	Yield of **4**	Selectivity for **4**	Turnover frequency, tof
				(mmol)	(%)					
1	A	60	4	2.04	45	1.59	78	0.14	7	0.23
2	A	70	4	2.95	65	2.30	78	0.15	5	0.33
3	A	80	4	3.18	70	2.42	76	0.16	5	0.36
4	A	90	4	3.86	85	2.97	77	0.23	6	0.44
5	A	100	4	4.31	95	3.27	76	0.17	4	0.49
6[b]	A	110	4	4.22	93	2.74	65	0.16	5	0.64
7	A	100	3	3.86	85	2.89	75	0.19	5	0.44
8	A	100	2[c]	3.41	75	2.66	78	0.13	4	0.38
9	B	100	4	4.32	95	3.41	79	0.13	3	0.48
10	C	100	4	3.04	67	2.34	77	0.15	5	0.38
11	D	100	4	2.99	66	2.21	74	0.12	4	0.36
12[d]	A	100	4	3.72	82	—	—	2.86	77	0.42
13[d]	C	100	4	2.54	56	—	—	2.03	80	0.32
14[b]	A + $NEt_3CH_3^+I^-$	100	4	3.18	70	2.42	76	0.13	4	0.48
15[b]	A + HCl(1:2)	100	4	3.36	74	2.58	77	0.16	5	0.51
16[b]	A + HI(1:2)	100	4	3.38	74	2.64	78	0.14	4	0.51
17[b]	A + HI(1:4)	100	4	3.37	74	2.63	78	0.13	4	0.51

[a] In all the experiments the catalysts A–D were as described in the footnote to Table 1; 40 mg of catalyst and 0.5 ml (4.54 mmol) phenylacetylene were used with 7 ml methanol as solvent, unless stated therefore. Reaction time was 4 h, except where indicated.
[b] Reaction time 3 h.
[c] $pO_2 = 0.2$ MPa.
[d] In CH_3CN.

3). At higher pressures, a decrease in the selectivity towards **5** and an increase in double-carbonylation products are obtained (Table 3, entries 1, 5,6). Interestingly, the use of γ-ZrP–Rh(III) does not require any base for the synthesis of **5**.

$$\mathrm{PhC \equiv CH + CH_3OH + CO + \tfrac{1}{2}O_2 \longrightarrow PhC \equiv CCOOCH_3 + H_2O} \qquad [4]$$

The literature data show that monocarboxylate products of alkynes have also been prepared under mild condition of temperature and pressure with multicomponent catalytic systems such as Pd(II)–Cu(II), Pd(II)–Cu(I)–O_2 or Pd(II)–KI–I_2, working mainly under homogeneous conditions and in the presence of a base.[16]

3.1 Stability of catalysts and reaction mechanism

The practical application of a catalyst requires that its activity be maintained over time and after recycling. To check the stability of catalysts, they were left to react under the conditions indicated in Tables 4 and 5; thereafter they were recovered by filtration in air and re-used. This procedure was repeated several times. In each reaction the products were analysed and the tof calculated. The trend in the tof values versus cycles is reported in Tables 4 and 5 for reductive and oxidative processes respectively. The results show that the catalysts working under reductive condition slowly lose their activity. The tof values decrease by 15–20% after each cycle (Table 4, entries 1–5). The deactivation is reached after 9–10 cycles for the catalysts containing naked palladium ions. Catalysts formed by intercalated metal complexes are more stable and lose their activity more slowly (Table 4, entries 6–8).

X-ray photoelectron spectra of materials before they are to be used in catalysis show a signal at 338.5 eV for α-ZrP–Pd(II) and at 338.6 eV for α-ZrP–Pd(bipy), attributed to the binding energy of $3d_{5/2}$ levels of the Pd(II). Materials recovered after the first cycle show a strong signal at 335.4 eV, assigned to the binding energy of Pd(0), and a weaker signal at 338.5 eV characteristic of Pd(II).[17] Whilst the intensity of the latter decreases quickly

Table 3 Carbonylation of phenylacetylene without reducing the triple bond[a]

Entry	Catalyst	T (°C)	$p(CO + O_2)$ MPa	$PhC{\equiv}CH$ reacted (mmol)	(%)	Yield of $PhC{\equiv}CCOOCH_3$[b] (mmol)	Selectivity (%)
1	A	60	0.4	1.22	45	0.86	70
2	A	60	0.7	1.50	55	1.05	70
3	A	70	0.7	1.63	60	1.04	64
4	A	90	0.7	2.18	80	1.20	55
5	A	60	1.0	1.90	70	1.14	60
6	A	60	1.2	1.98	73	1.12	56
7	B	60	0.7	1.55	57	1,12	72
8	C	60	0.7	1.47	54	1.00	68
9	E	60	0.7	1.90	70	1.35	71
10[c]	E	60	0.7	1.85	68	1.29	70
11[c]	B	60	0.7	1.51	55	0.60	40

[a] In all the experiments 40 mg of catalyst, 7 ml of methanol and 0.3 ml of phenylacetylene (2.72 mmol), were used. Unless stated otherwise, 0.1 mmol of NEt_3 or NPh_3 (Base/Pd = 5:1) were added; reaction times, 2 h. The catalysts A, B and C were as described in the footnote to Table 1 E = γ-$ZrH_{0.8}Rh_{0.4}(PO_4)2{\cdot}3.5H_2O$.

[b] Double-carbonylation products were the main by-products.

[c] No base was added.

and disappears after the 4–5th cycle, that related to Pd(0) disappears only when the materials are exhausted. These data seem to be in agreement with a carbonylation mechanism involving Pd(0) as the initial active species. It is noteworthy that intercalated metal complexes show a greater stability than Pd(II) ions. Moreover, when the carbonylation is carried out under atmopheric pressure, the catalysts are inactive during the first 4–5 h. These data seem to support the mechanism proposed. It is worth emphasizing that, if the materials are pretreated with CO before their use in catalysis, they do not show an induction time. The pretreatment is carried out by stirring the materials in a 5:2 methanol NEt_3 mixture at 80 °C under CO for 1–2 h. The XPS spectra of pretreated materials show an analogy to those recovered after catalytic cycles and display the Pd(0) and Pd(II) signals at 335.5 and 338.6 eV, respectively. The intensity of Pd(II) decreases as the pretreatment time is prolonged and goes to zero in materials pretreated for 7–8 h.

According to the literature data the reduction of Pd(II) to Pd(0) occurs either at the expense of an alcohol molecule or of CO in the presence of water

Table 4 Catalyst stability under reducing conditions[a]

Entry	No. of cycles	Catalyst	Turnover frequency, tof
1	1	A	0.18
2	2	A	0.14
3	3	A	0.12
4	5	A	0.080
5	8	A	0.041
6	2	C	0.13
7	4	C	0.10
8	7	C	0.075
9	2	A + HCl (1:3)	0.091
10	2	A + HCl (1:5)	0.072
11	2	A + HCl (1:6)	0.052

[a] Reaction conditions: $T = 120$ °C; $p(CO) = 4$ MPa; phenylacetylene, 4.54 mmol; reaction time, 8 h. Catalysts A–C were as described in the footnote to Table 1.

Table 5 Catalyst stability under oxidative conditions[a]

Entry	No. of cycles	Catalyst	Turnover frequency, tof
1	1	A	0.49
2	2	A	0.47
3	5	A	0.45
4	3	B	0.43
5	3	C	0.35
6	3	A + HCl(1:2)	0.47
7	5	A + HCl(1:2)	0.44
8	3	A + HCl(1:5)	0.38
9	2	$A + NEt_3CH_3^+I^-(1:2)$	0.44
10	2	$A + NEt_3CH_3^+I^-(1:6)$	0.33

[a] Reaction conditions: $T = 120$ °C; $p(CO) = 4$ MPa; phenylacetylene, 4.54 mmol.

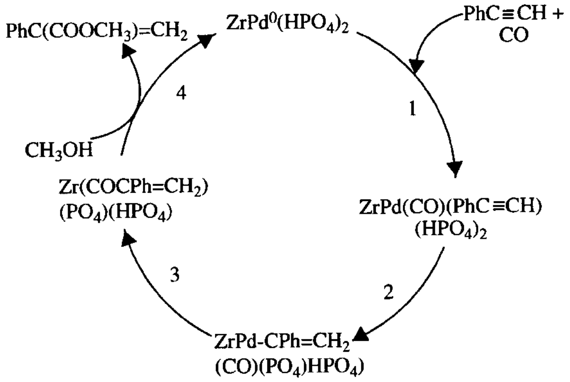


Figure 1

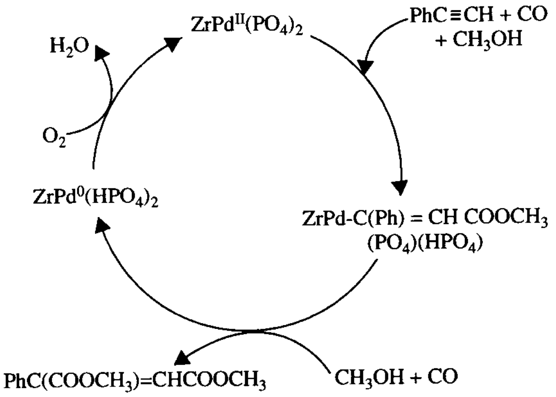


Figure 2

(Eqns [5] and [6]).[18] The monocarbonylation process could probably be initiated by a Pd(0) species that co-ordinates phenylacetylene and CO, then evolves to the final products through a mechanism similar to that proposed by Zarganan and Alper[4] for an unsupported system with a Pd(0)/Pd(II) couple as catalyst (Fig. 1). The conversion of the coordinated phenylacetylene [Pd(RC≡CH)] (step 1) into the corresponding alkenyl complex [Pd(RC=CH$_2$)] (step 2) requires the presence of either an intermediate hydride complex[3–4]

$$\mathrm{Pd(II)} + \mathrm{CH_3OH} \longrightarrow \mathrm{Pd(0)} + 2\mathrm{H}^+ + \mathrm{HCOH} \quad [5]$$

$$\mathrm{Pd(II)} + \mathrm{CO} + \mathrm{H_2O} \longrightarrow \mathrm{Pd(0)} + 2\mathrm{H}^+ + \mathrm{CO_2} \quad [6]$$

or a ‘proton donor’. In our case the ‘H source’ could be the inorganic matrix $\mathrm{ZrH}_{(2-x)}\mathrm{Pd}_x(\mathrm{PO_4})_2$ or $\mathrm{ZrPH}_{(2-x)}\mathrm{Pd}_x\mathrm{L}_y(\mathrm{PO_4})_2$.

In fact, the protons generated in the reductive process of Pd(II) (Eqns [5], [6]) remain in the inorganic matrix bonded to $\mathrm{PO_4}$ groups for the electroneutrality of the system (Eqn [7]). We have already ascertained that Rh(III) ions intercalated in an α-ZrP matrix show the same behaviour.[9]

$$\mathrm{ZrH}_{(2-x)}\mathrm{Pd}_x(\mathrm{PO_4})_2 + x\mathrm{CO} + x\mathrm{H_2O} \longrightarrow \mathrm{ZrPd}_x(\mathrm{HPO_4})_2 + x\mathrm{CO_2} \quad [7]$$

The phosphates are an important sink and source of ‘H’. This transfer could occur either by direct interaction between the alkyne coordinate and the ‘$\mathrm{HPO_4}$’ group, or via a transient hydrido species which forms through the interaction of Pd(0) with ‘$\mathrm{HPO_4}$’. Such an interaction could convert the active Pd(0) species into a hydrido complex, which can also be the generator of the alkenyl complex.

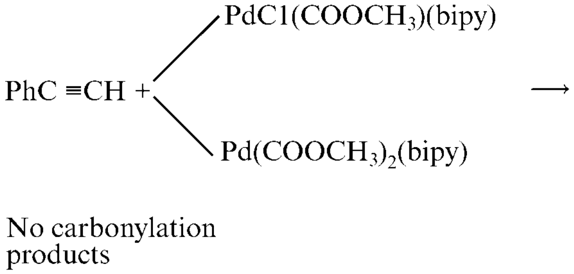
We have investigated the role of an external acid on both the formation of the hydride complex and the catalytic activity.

Interestingly, we have found a moderate beneficial effect up to an H$^+$/Pd molar ratio of 2:1 (Table 1, entries 10–12). Conversely, as the ratio increases, both the activity and stability decrease quickly (Table 4, entries 9–11). A double conflicting effect of H$^+$ can account for such a trend. On one hand the oxidative addition on Pd(0) generates hydride and the alkenyl species; on the other hand an excess of protons takes Pd(II) from the matrix by H$^+$/Pd(II) ionic exchange, which destroys the catalyst. This, again, has been proved for rhodium(III) and palladium(II) intercalated in α-ZrP and γ-TiP.[8,9,21]

The behaviour of materials under oxidative conditions is rather different. The tof values (Table 5) remains almost constant over the cycles, indicating that there is no release of the metal from the support. XPS spectra of materials recovered at the end of each cycle exhibit two signals: one more intense, characteristic of Pd(II) with a binding energy of 338.6 eV, and a second, weaker, one at 336.7 eV. The shape of the spectra as well as the intensity of the signals remain almost constant over the cycles, which is in agreement with the stability of the catalysts.

Our results under oxidative conditions are consistent with the literature reports on the double carbonylation of phenylacetylene by homogeneous palladium-based catalysts,[5,6] suggesting Pd(II) as the active species.

The possible reaction pathway leading to the formation of final products is depicted in Fig. 2. The double methoxycarbonylation of phenylacetylene liberates protons that are taken up by the $\mathrm{PO_4}$



Scheme 1

groups. The final step is presumably a reductive elimination of the double-carbonylation product mainly in *Z* form[15] with formation of a Pd(0) species intercalated into the matrix $[ZrPd^0(HPO_4)_2]$. The re-oxidation of Pd(0) to Pd(II) by oxygen restores the initial active catalyst. The matrix plays a fundamental role as an H sink and pH regulator.

An alternative mechanism could be proposed based on Pd(II) ability to stabilize methoxocarbonyl ligand ($—COOCH_3$) formed by direct interaction of methanol with the coordinated CO. In order to ascertain whether the insertion of $—COOCH_3$ in the Pd–carbon bond of the linked alkyne may be operative in our process, we carried out stoichiometric reactions between phenylacetylene and some mono- and dimethoxo-carbonyl complexes of Pd stabilized by the bipyridine ligand[19b] (Scheme 1). We have never observed the carbonylation of phenylacetylene; this rules out the transfer of the methoxocarbonyl as a possible process.

Another aspect which we have examined is the re-oxidation of Pd(0). This can be accomplished either by direct oxidation of Pd(0) by O_2, with the intermediation of a hydroperoxo species[20] (Scheme 2) or, as recently found by us and other groups,[6,21] via interaction with molecular iodine formed *in situ* by iodide oxidation by O_2 (Scheme 3).

In order to shed light on this process, we have investigated the influence of promoters such as HCl, HI and $NR_4^+I^-$ on the performance of catalysts. The results show that when a mineral acid is added in an H^+/Pd molar ratio of 2), the tof values increase slightly (Table 2, entries 15, 16), whereas the selectivity and stability remain constant (Table 5, entries 6, 7). At a higher molar ratio the most evident result is a steady lowering of the catalyst stability and activity (Table 5, entry 8), which can be explained by considering the effect of protons as promoters of the release of the metal from the support (H^+/Pd^{2+} exchange).

Conversely, while the addition of $NEt_3(CH_3)^+I^-$ does not show any influence on the activity of the catalyst, as the I^-/Pd molar ratio increases, the tof values over several cycles decrease in a remarkable way (Table 5, entries 9–10). This negative effect of iodine has been also observed in the oxidative carbonylation of amines catalysed by rhodium intercalated in titanium phosphate.[21] In our case, such an effect can be ascribed to the ability of iodide to form the PdI_4^{2-} species in solution.

These data seem to support the view that the Pd(0) oxidation proceeds via a hydroperoxo species. The signal at 336.9 eV found in the spectra of materials recovered from catalytic cycles could be ascribed to a Pd–(O_2) or Pd–O_2H species. A very similar signal has been found in the oxidative carbonylation of aniline by ZRP–Pd compounds; it has been assigned to a Pd oxygenate species.[17]

The last topic to elucidate is the formation of compound **5**. The presence of a base is necessary in the case of palladium-doped materials, whereas **5** is formed in neutral medium with rhodium systems. The literature reports[16] suggest that the base promotes the formation of the anion $PhC{\equiv}C^-$, which links to palladium and then evolves to the final product through steps very close to those discussed above for the double-carbonylation processes (Fig. 3).

An intriguing question is why with rhodium compounds the addition of the base is not necessary.

$$Pd^\circ + O_2 + 2H^+ \longrightarrow Pd\text{-}OOH + H^+ \longrightarrow Pd(II) + H_2O + \tfrac{1}{2}O_2$$

Scheme 2

$$2I^- + 2H^+ + \tfrac{1}{2}O_2 \longrightarrow I_2 + H_2O \longrightarrow I_2 \xrightarrow{Pd(0)} Pd(II) + 2I^-$$

Scheme 3

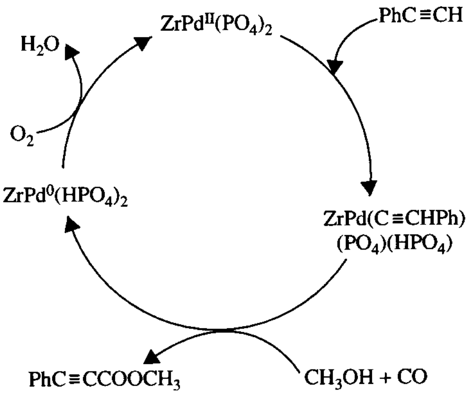


Figure 3

Starting from the observation that ZrP in the γ-phase contains two different phosphate groups, one PO_4 and the other H_2PO_4, in contrast with the α-phase which contains two equal 'HPO_4'[22] groups, we can suggest that a key role could be played by PO_4 groups, which are in higher concentration in the γ- phase. Support for this view comes from the finding that when a palladium material in the γ-phase was used in a catalytic test without the addition of a base (Table 3, entry 10), compound **5** was formed, even if with a lower selectivity than in the presence of a base.

Acknowledgement The authors thank MURST for financial support (no. 9803026360, 1998).

REFERENCES

1. Pino P Braca G. In *Organic Synthes via Metal Carbonyl*, Vol. 2. Wender I, Pino P. (eds): John Wiley, New York, 1997; 419.
2. Brick LG, Oshshina IV, Kozlova AP, Vorontsov EV, Temkin ON. *J. Mol. Catal.* 1995; **104**: 9.
3. Drent E, Arnoldy P, Budrelaar PHM. *J. Organomet. Chem.* 1993; **455**: 247.
4. Zargarian D, Alper H. *Organometallics* 1993; **12**: 712.
5. Zargarian D, Alper H. *Organometallics* 1991; **10**: 2919.
6. Gabriele B, Costa M, Salerno G, Chiusoli GP. *J. Chem. Soc., Perkin Trans.* 1994; 83.
7. El Ali B, Vasapollo G, Alper H. *J. Org. Chem.* 1993; **58**: 4739.
8. Giannoccaro P, Nobile CF, Moro G, LA Ginestra A, Ferragina C, Massucci MA, Patrono P. *J. Mol. Catal.* 1989; **53**: 349.
9. Giannoccaro P, La Ginestra A, Massucci MA, Ferragina C, Mattogno G. *J. Mol. Catal.* 1996; **111**: 135.
10. Giannoccaro P, Ferragina C, Doronzo S. *Studies in Surface and Catalysis*. Vol. 108. *Heterogeneous Catalysis and Fine Chemicals IV.* Blaser HU, Baiker A, Prins R. (eds). Elsevier: Amsterdam, 1997; 633–640.
11. Giannoccaro P, Ferragina C, Degiglio E, Doronzo S. *XIth FECHEM Conf. on Organometallic Chemistry, Prague, 1997*. Giannoccaro P, Valentino MA, Ferragina C, Cafarelli P. *XIth FECHEM Conf. on Organometallic Chemistry, Parma, 1995*. 244.
12. Ferragina C, La Ginestra A, Massucci AM, Mattogno G, Patrono P, Giannoccaro P, Cafarelli P, Arfelli M. *Mater. Chem.* 1995; **5**(3): 461.
13. Ferragina C, Cafarelli P, Giannoccaro P. *Mater. Res. Bull.* 1998; **33**: 1635–1652. Ferragina C, Cafarelli P, Di Rocco R. *Mater. Res. Bull.*, 1998; **33**: 305–311.
14. Pouchert CJ. *The Aldrich Library of Infrared Spectra*. Aldrich Chemical Co., Inc: 1970.
15. Carderazzo F. *Angew. Chem.* 1977; **16**: 299.
16. Tsuji J, Takahashi M, Takahashi T. *Tetrahedron Lett.* 1980; **21**: 849. Zung TT, Bruk IG, Temkin OM. *Mendeleev Commun.* 1994; 2. Zung TT, Bruk LG, Temkin ON, Malashkevich AV. *Mendeleev Commun.* 1995; 4.
17. Ferragina C, Giannoccaro P, La Ginestra A, Massucci MA, Mattogno G, Patrono P. *Catal Today* 1989; **6**: 133.
18. Calderazzo F, Ercoli R, Natta G. In *Organic Synthesis via Metal Carbonyls*, Wender I, Pino G. (eds). Interscience: New York, 1968.
19. (a) Hiday M, Kokura M, Uchida Y. *J. Organomet. Chem.* 1973; **52**: 431. (b) Giannoccaro P, Ravasio N, Aresta M. *J. Organomet. Chem.* 1993; **451**: 243.
20. Hosokava T, Murahashi SI. *Acc. Chem. Res.* 1990; 23, and references therein.
21. Giannoccaro P, De Giglio E, Gargano M, Aresta M. *J. Mol. Catal. A: Chemical* 1999; 2543.
22. Troup JM, Clearfield A. *Inorg. Chem.* 1977; **16**: 3311. Poojary DM, Shpeizer B, Clearfield A. *J. Chem. Soc., Dalton Trans.* 1995; 111.