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Efficient palladium catalysts for the carbonylation of alkynes

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Abstract

A class of highly efficient homogeneous palladium catalysts has been developed for the carbonylation of alkynes. One application of interest is the selective production of methyl methacrylate by methoxycarbonylation of propyne. The essential feature of the new catalyst systems is that they are formed by the combination of a ligand containing a 2-pyridylphosphine moiety with a palladium(II) species and a proton source containing weakly coordinating anions. High turn-over numbers of more than 40000 mol (mol Pd)$^{-1}$ h^{-1} and selectivities towards methyl methacrylate of up to 99.95% can be obtained under mild conditions. It is suggested that the 2-pyridylphosphine ligand plays an essential role both as a chelating P–N ligand in the selectivity-determining step and as a monocoordinated ligand in the rate-determining step of the catalytic cycle.

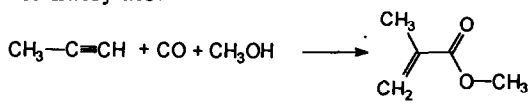
1. Introduction

The transition-metal-catalysed carbonylation of alkynes has been known since the pioneering work of Reppe [1]. Carbonylation of acetylene utilizing Reppe's nickel carbonyl catalyst in the presence of halide promoters is used in the commercial production of acrylic acid and its esters [1]. Methyl methacrylate (MMA), a large-scale chemical intermediate for the production of homopolymers and copolymers (world production 1200 kt year^{-1} in 1990), can in principle be manufactured by similar nickel- or palladium-catalysed carbonylation of propyne [2,3], but this reaction has not so far been applied on a commercial scale, mainly because of the lack of a catalyst with sufficient activity and selectivity.

We now report on the development of a class of highly efficient homogeneous palladium catalysts for the carbonylation of alkynes [4–7]. This reaction proceeds particularly well in the case of propyne, which is available as feedstock from naphtha crackers in amounts of 0.2–1.0 wt.% on intake hydrocarbon feed. The availability of these catalysts will allow for the first time the development of a cost-effective MMA process based on carbonylation technology [8]. Owing to the unprecedented high selectivities achieved, this process possesses the additional advantage of having minimal harmful effects on the environment.

2. Results

Our interest in the carbonylation of alkynes originated from a general study of carbonylation reactions catalysed by transition metal compounds. In particular, our investigations concentrated on the effects of certain bidentate ligands (bis-phosphine and bis-pyridyl ligands L–L) on the course of carbonylation reactions catalysed by cationic (L–L)PdX$_2$ complexes. These investigations have previously resulted in the discovery of very efficient catalysts for the alternating copolymerization of carbon monoxide and olefins [9]. In the course of these studies, mixed bidentate ligands containing a phosphine as well as a pyridyl group (so-called P–N ligands) were also considered for chelation of cationic palladium(II) species. One reaction studied was the methoxycarbonylation of propyne to give methyl methacrylate:



(1)

MMA

2.1. Effects of ligand structure

Tables 1–3 give the results from batch autoclave experiments. The catalysts originally tested were palla-

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TABLE 1. Propyne carbonylation: effect of presence and position of the nitrogen atom in the ligand [a]

Ligand type	Pd acetate intake (mmol)	Temperature (°C)	Average rate (mol (mol Pd)$^{-1}$ h^{-1})	Selectivity (%MMA)
PPh_3	0.10	115	~10	89
4-$PyPPh_2$	0.10	90	~10	90
3-$PyPPh_2$	0.10	70	1000	99.2
2-$PyPPh_2$	0.012	45	40000	98.9

[a] Conditions: batch; intakes 30 ml propyne, 50 ml methanol, 60 bar CO, 3.0 mmol ligand, 2.0 mmol CH_3SO_2OH.

dium systems formed by the combination of palladium acetate with an excess of triphenylphosphine (PPh_3) and a Brønsted acid such as CH_3SO_2OH (MeSA) [10]. Table 1 shows that the reaction proceeded at a low rate but with an acceptable selectivity (89%). However, a remarkable increase in activity and selectivity was observed upon replacement of PPh_3 by 2-pyridyldiphenylphosphine (2-$PyPPh_2$). Even under considerably milder conditions (45°C instead of 115°C), the use of this catalyst resulted in a spectacular rate increase by three orders of magnitude, as well as an increase in selectivity to 98.9% [4]. A much lower rate enhancement was observed with 3-pyridyldiphenylphosphine (3-$PyPPh_2$) as ligand, whereas with 4-pyridyldiphenylphosphine (4-$PyPPh_2$) the results were very similar to those obtained with PPh_3. In all these experiments the only significant byproduct observed was the linear isomer of MMA, *i.e.* methyl crotonate.

The results in Table 2 indicate that replacement of the MeSA acid component of the 2-$PyPPh_2$-based catalyst by *p*-toluenesulphonic acid (p-TSA, p-CH_3PhSO_2OH) or other strong acids resulted in similar high reaction rates and selectivities. However, a considerable decrease in rate, but with retention of the high selectivity, was observed when weaker acids such as benzenephosphonic acid and, in particular, acetic acid were used. In the case of HCl, a strong acid, again a low activity was observed, suggesting that the coordinating properties of the conjugate base towards the palladium centre, not just the acidity, influence the catalytic performance. It was observed that in order to obtain high activity, it is necessary to have an excess of acid over and above the 2 mol (mol Pd)$^{-1}$ required for removal of acetate as acetic acid from the palladium coordination sphere. However, once any excess acid was present, the reaction order with respect to the acid concentration was close to zero.

The dramatic effect of ligand structure on activity and specificity, especially the effect of introducing the 2-pyridyl group, prompted a study of the effect of subtle structural variations of substituents on the 2-pyridylphosphine ligands [5–7]. Table 3 shows the effect of varying the type of substituent and the substitution pattern of the 2-pyridyl moiety as well as the effect

TABLE 2. Propyne carbonylation: effect of acid type [a]

Acid type	Acid intake (mmol)	Temperature (°C)	Average rate (mol (mol Pd)$^{-1}$ h^{-1})	Selectivity (%MMA)
CH_3SO_2OH	2.0	45	40000	98.9
p-CH_3PhSO_2OH	2.0	45	20000	99.1
$PhPO(OH)_2$	2.0	50	4000	98.9
CH_3COOH	10	50	100	99.0
HCl	2.0	50	~10	98

[a] Conditions: batch; intakes 30 ml propyne, 50 ml methanol, 60 bar CO, 0.025 mmol Pd acetate, 1.0 mmol 2-$PyPPh_2$.

TABLE 3. Propyne carbonylation: substituent effects in ligands with a 2-pyridylphosphine skeleton [a]

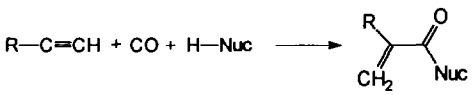
Ligand type	Acid type	Temperature (°C)	Average rate (mol (mol Pd)$^{-1}$ h^{-1})	Selectivity (%MMA)
2-$PyPPh_2$	*p*-CH_3PhSO_2OH	60	40000	98.9
2-(6-CH_3-Py)PPh_2	*p*-CH_3PhSO_2OH	60	40000	99.95
2-(6-CH_3-Py)PPh_2	CH_3SO_2OH	60	50000	99.95
2-(4-CH_3-Py)PPh_2	CH_3SO_2OH	70	20000	98.8
2-(6-OCH_3-Py)PPh_2	CH_3SO_2OH	80	4000	99.85
2-(6-Br-Py)PPh_2	CH_3SO_2OH	90	500	99.65
(2-(6-CH_3-Py))$_2$PPh	CH_3SO_2OH	80	20000	99.9
(2-(6-CH_3-Py))$_3$P	CH_3SO_2OH	80	10000	99.8

[a] Conditions: batch; intakes 30 ml propyne, 30 ml methanol, 30 ml *N*-methylpyrrolidone, 60 bar CO, 0.025 mmol Pd acetate, 1.0 mmol ligand, 2.0 mmol acid.

of the number of 2-pyridyl groups attached to the phosphorus atom. It can be seen that variation in the position of a methyl substituent in the pyridyl group resulted in significant changes in the specificity of the catalyst. Introduction of the methyl substituent at the 6-position of the 2-pyridyl group raised the selectivity to 99.95% (*i.e.* a 20-fold suppression of the formation of methyl crotonate byproduct compared with that for the unsubstituted ligand!), with retention of the high overall activity of the catalyst, whereas substitution at the 4-position had no effect on the selectivity. Methoxy and bromo substitution at the 6-position had virtually the same effect on the selectivity as methyl substitution, although bromo substitution in particular led to a significantly reduced catalytic activity. Increasing the number of 6-methylpyridyl groups of the phosphine ligand resulted in a progressively decreasing catalyst activity, which could only be restored by using a higher reaction temperature. The number of 2-pyridyl groups in the ligand hardly affects the selectivity of the catalyst.

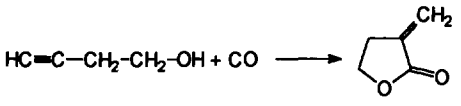
2.2. Scope of the carbonylation reaction

In the above-mentioned experiments the catalytic phenomena were illustrated for propyne and methanol as alkyne substrate and nucleophilic co-reagent respectively. Similar results were obtained with a variety of other alkynes, *e.g.* acetylene and phenylacetylene, as well as with other nucleophilic reagents, *e.g.* water, aliphatic alcohols (primary, secondary and tertiary), aromatic alcohols, thiols, carboxylic acids and amines, thus giving easy access to a variety of unsaturated carboxylic acids, (thiol-)esters and amides. The general reaction catalysed can thus be represented by



(2)

The nucleophilic reagent H–Nuc can also form part of the alkyne substrate, leading to an intramolecular version of eqn. (2) [5], *e.g.*



(2a)

2.3. Continuous experiments

In addition to batch experiments, continuously fed stirred tank reactor (CSTR) experiments were carried out to characterize the catalyst system quantitatively under isothermal, steady state conditions. For these experiments the unsubstituted 2-$PyPPh_2$ ligand was selected. It was observed that a high degree of propyne conversion could be obtained under mild conditions (*i.e.* a temperature of 45°C, a low CO pressure of 11 bar and a low palladium concentration of 18 ppm by weight in methanol feed). The highest rates (propyne conversions of 81% and 95% for residence times of 1.6 and 4.4 h respectively) were found at a ligand/palladium ratio of around 20. These rates correspond to turn-over numbers of 20,000–50,000 mol (mol Pd)$^{-1}$ h^{-1}, thus confirming the results from the batch experiments. The turn-over numbers in the CSTR were surprisingly high considering the relatively low steady state concentration of propyne.

3. Discussion

The above results indicate that the highly efficient palladium(II) catalyst systems for the carbonylation of alkynes have two prominent characteristics in common. These are (i) that the neutral phosphine ligands contain a 2-pyridyl moiety and (ii) that the anionic ligands are weakly or non-coordinating anions.

3.1. Effect of anion type

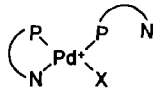
The anions (X) are supplied to the catalyst system as strong acids, displacing the acetate anions via a simple acid–base reaction:

$$Pd(OAc)_2 + 2HX \rightarrow PdX_2 + 2HOAc \qquad (3)$$

The results shown in Table 2 suggest a qualitative correlation between catalyst activity and the acid strength of the anion source, hydrochloric acid excepted. It is suggested that in general the coordination strength of anions towards the cationic palladium(II) centre correlates to a certain extent with the acid strength of the corresponding Brønsted acid, *i.e.* the strength of coordination towards H^+. Exceptions to this rule are provided by halide anions, which, although derived from strong acids, strongly coordinate to palladium(II), giving so-called neutral complexes. Therefore it can be concluded that coordinative rather than acid–base properties determine the effect of anions on catalytic performance. The higher reactivity when weakly coordinating anions are involved is thought to arise in part from the easier access of substrate molecules (alcohol, alkyne and carbon monoxide) as well as the phosphine ligand to the coordination sites around the metal centre. Another factor may be the increased electrophilicity of the palladium centre, which results in lower binding energies with substrate molecules owing to decreased back donation. The intermediate palladium species in the catalytic cycle would then be less stable, with the result that elementary steps would require lower activation energies and so proceed at higher rates [11].

3.2. Effect of phosphine ligands

Although we have not carried out detailed mechanistic studies on the relationship between catalyst activity and selectivity on the one hand and ligand characteristics on the other, we consider it worthwhile to comment on the large difference in catalyst characteristics associated with PPh_3 on the one hand and 2-$PyPPh_2$ and analogous ligands on the other. As described above, the 2-pyridyl moiety of the latter phosphines must play a crucial role in determining the extraordinary activity and high specificity towards the formation of MMA. Recent advances in organometallic chemistry have led to the synthesis and characterization of various transition metal complexes containing 2-$PyPPh_2$ and analogues as ligands [12–15]. Of particular relevance to our discussion are reports of cationic palladium(II) and platinum(II) complexes for which there is clear evidence, in the solid state (X-ray) as well as the liquid state (nuclear magnetic resonance, IR), that the coordination sphere around these cations can accommodate two 2-$PyPPh_2$ ligand molecules that are bonded differently in the square planar configuration expected for the d^8 palladium(II) systems. One of the ligand molecules is chelating palladium(II) through both the phosphorus and nitrogen atom, creating a four-membered ring structure, while the second is monocoordinated via the phosphorus atom only [12–15], as in the following structure in which P–N denotes 2-$PyPPh_2$ or an analogous ligand:



$X^- = [\eta^2\text{-(P-N)Pd(P-N)X}]^+ X^-$

Complex I

We suggest that complexes of type I play a key role in the catalysis of the carbonylation of alkynes. The "P–N ligand" has several functions, such as stabilization of soluble palladium(II) catalyst complexes and adjustment of the electrophilicity of the palladium(II) centre. Moreover, as will be indicated below, it is suggested that the 2-pyridylphosphine moiety plays a crucial role in both the selectivity- and rate-determining step via the chelated and monocoordinated ligand respectively.

3.3. Elementary steps in the catalytic cycle

We suggest that the initiation step of the catalytic cycle probably involves reaction of the above-mentioned palladium complex I with methanol to give a palladium–methoxy species:

$$[\eta^2\text{-(P-N)Pd(P-N)X}]X + CH_3OH \longrightarrow [\eta^2\text{-(P-N)Pd(P-N)OCH}_3]X + HX \quad (4)$$

The next step involves nucleophilic attack by carbon monoxide and displacement of the monocoordinated ligand. It is suggested that this nucleophilic displacement is an easy reaction, since the monocoordinated ligand will be protonated most of the time (by HX generated in eqn. (4) or externally applied) and therefore is expected to coordinate only weakly:

$$[\eta^2\text{-(P-N)Pd(P-N)OCH}_3]X + HX \longrightarrow [\eta^2\text{-(P-N)Pd(P-NH}^+\text{)OCH}_3]X_2 \quad (5)$$

$$[\eta^2\text{-(P-N)Pd(P-NH}^+\text{)OCH}_3]X_2 + CO \longrightarrow [\eta^2\text{-(P-N)Pd(CO)OCH}_3]X + \text{P-NH}^+ X^- \quad (6)$$

Subsequently, migratory insertion of the coordinated carbon monoxide molecule into the palladium–methoxy bond will give a palladium–carbomethoxy species in which the resulting vacant coordination site can now be occupied again by the (probably protonated) P–N ligand:

$$[\eta^2\text{-(P-N)Pd(CO)OCH}_3]X + \text{P-NH}^+ X^- \longrightarrow [\eta^2\text{-(P-N)Pd(P-NH}^+\text{)COOCH}_3]X_2 \quad (7)$$

Owing to the so-called phosphine *trans* effect [16], it is expected that the carbomethoxy group will preferentially occupy the *cis* position with respect to the phosphine group of the chelating P–N ligand.

Now, as in nucleophilic substitution by carbon monoxide as indicated above, propyne displaces the (probably protonated) monocoordinated P–N ligand:

$$[\eta^2\text{-(P-N)Pd(P-NH}^+\text{)COOCH}_3]X_2 + CH_3\text{-C}\equiv\text{CH} \longrightarrow [\eta^2\text{-(P-N)Pd(HC}\equiv\text{CCH}_3\text{)COOCH}_3]X + \text{P-NH}^+ X^- \quad (8)$$

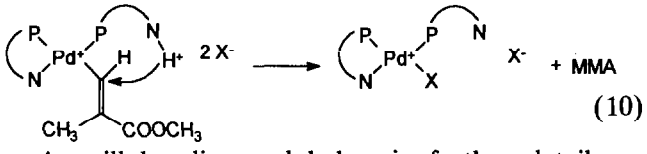
For steric reasons, the most probable mode of coordination of propyne is more or less perpendicular to the square ligand coordination plane. The following step involves the migratory insertion of the coordinated propyne molecule into the palladium–carbomethoxy bond to give palladium–alkenyl species (1-palladium-2-carbomethoxypropene and 2-palladium-1-carbomethoxypropene). This migratory propyne insertion probably involves initial rotation of the coordinated propyne molecule from the preferred coordination perpendicular to the square plane, followed by nucleophilic attack of the carbomethoxy moiety. The resulting vacant coordination site may now again be occupied by the free P–N ligand, probably in its protonated form:

$$[\eta^2\text{-(P-N)Pd(HC}\equiv\text{CCH}_3\text{)COOCH}_3]X + \text{P-NH}^+ X^- \longrightarrow [\eta^2\text{-(P-N)Pd(P-NH}^+\text{)(HC}=\text{C(CH}_3\text{)COOCH}_3\text{)}]X_2 \quad (9a)$$

$$[\eta^2\text{-(P-N)Pd(HC}\equiv\text{CCH}_3\text{)COOCH}_3]X + \text{P-NH}^+ X^- \longrightarrow [\eta^2\text{-(P-N)Pd(P-NH}^+\text{)(CH}_3\text{C}=\text{CHCOOCH}_3\text{)}]X_2 \quad (9b)$$

The relative rates of the reactions represented by eqns. (9a) and (9b), giving eventually MMA and methyl crotonate respectively, determine the (regio-)selectivity of the overall carbonylation reaction. The selectivity is likely to be governed by stereometric constraints determined by the chelated P–N ligand (see Section 3.4).

The final step, resulting in the products MMA and methyl crotonate, involves protonolysis of the palladium–alkenyl bond. We suggest that the protonated monocoordinated ligand (P–NH$^+$) fulfils a key role in this termination reaction by acting as a "proton messenger", bringing the proton in very close proximity to the coordination sphere at the palladium–alkenyl bond, thus facilitating the transfer of this proton to the alkenyl moiety giving MMA (and similarly methyl crotonate) and re-forming the original complex **I**:



(10)

As will be discussed below in further detail, we suggest that this final reaction step is rate determining. The sequence of reaction steps given in eqns. (4–10) constitutes the proposed catalytic cycle for the palladium/2-PyPPh$_2$-catalysed carbonylation of alkynes (see Fig. 1).

3.4. Selectivity-determining step

The observed effects of substituents on the 2-pyridyl group on the course of the propyne carbonylation

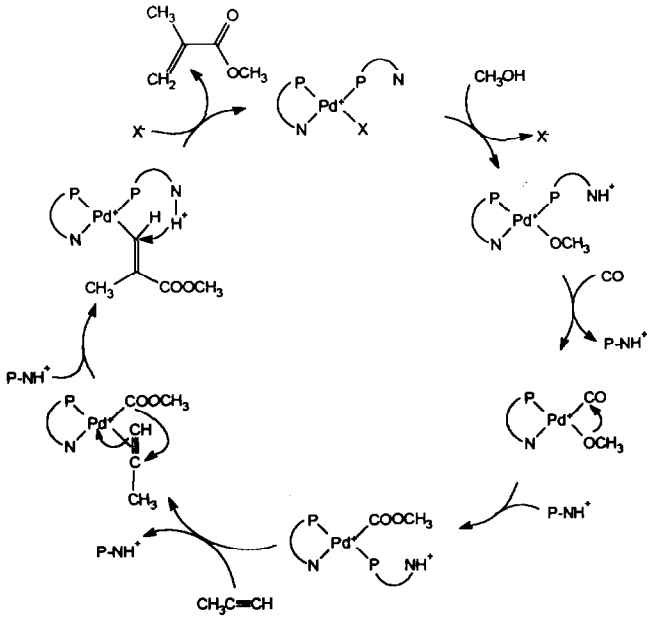
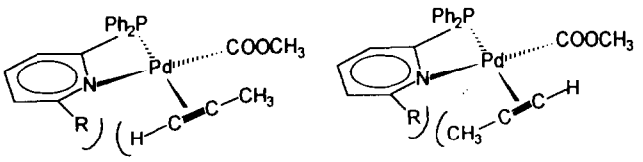


Fig. 1. Proposed catalytic cycle for the palladium–methoxy/2-PyPPh$_2$-catalysed methoxycarbonylation of propyne.



A B

Fig. 2. Spatial configurations in the selectivity-determining step as suggested in eqns. (9a) and (9b).

reaction are instructive with respect to the above proposed catalytic cycle in a number of aspects.

The dependence of selectivity on the position of the methyl substituent (see Table 3) strongly suggests that steric rather than electronic factors play a key role in the selectivity-determining step. Spatial details of the selectivity-determining step as proposed in eqns. (9a) and (9b) are modelled more clearly in Fig. 2. It was suggested above that the carbomethoxy group will preferentially occupy the *cis* position with respect to the phosphine moiety of the chelated P–N ligand. Consequently, the incoming propyne molecule is bound at the position *cis* to the pyridyl group. In this configuration a substituent at the 6-position of the pyridyl group effectively limits the available space for propyne on its route to migratory insertion into the carbomethoxy group and leads to a preferred insertion pathway in which the methyl group of propyne points away from the palladium centre (position A in Fig. 2). As a consequence, the formation of 2-palladium-1-carbomethoxypropene, *i.e.* the precursor for methyl crotonate, is strongly disfavoured by substituents on the 6-position of the pyridyl group. Thus 6-methyl substitution leads to a 20-fold suppression of the formation of methyl crotonate relative to the unsubstituted analogous ligand. Similar effects on selectivity are observed with 6-methoxy and 6-bromo substituents.

The observation that the introduction of substituents on the 6-position of the 2-pyridyl group leads to an increase in selectivity towards MMA supports our hypothesis that the catalytic cycle starts with a palladium(II)–methoxy species (Fig. 1) instead of the potential alternative of a palladium(II)–hydride species. In the latter case the sequence of catalytic steps would be (i) initiation by propyne insertion into the palladium(II)–hydride bond, (ii) carbon monoxide insertion into the palladium(II)–propenyl group and (iii) termination by methanol to yield unsaturated ester product and the initial palladium(II)–hydride species (see Fig. 3). However, as a consequence of the steric factors discussed above, 6-substitution of the pyridyl group would then give rise to an increase in the extent of

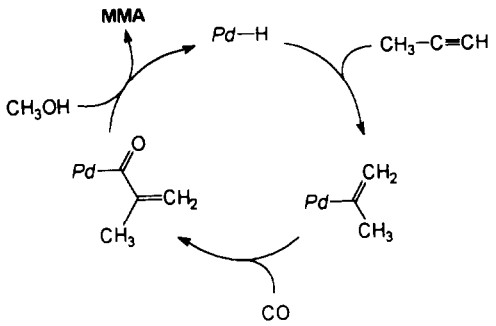


Fig. 3. Potential alternative catalytic cycle: palladium–hydride-catalysed methoxycarbonylation of propyne.

formation of methyl crotonate, which is clearly in contradiction with the experimental facts.

3.5. Activity-determining step

Although 6-methyl substitution of the pyridyl group greatly affects the selectivity, this does not lead to a significantly different catalyst activity, indicating that the steric constraints imposed by substitution at the 6-position of the pyridyl group do not affect the reaction rate. This strongly suggests that the activity-determining step in the catalytic cycle is different from the step that determines the regio-selectivity (eqns. (9a) and (9b)). As a consequence, either formation of the palladium(II)–carbomethoxy species (eqn. (7)) or protonolysis of the palladium(II)–alkenyl species to give the final products MMA and methyl crotonate (eqn. (10)) might determine the overall reaction rate. The most important indication that protonolysis of palladium(II)–alkenyl species is the rate-determining step comes from the observation that some excess of strong acid over and above the stoichiometric amount required to remove the acetate anions from palladium acetate (see eqn. (3)) is necessary for efficient catalysis with 2-pyridylphosphine ligands. Since the reaction is not simply first order in acid concentration, this suggests that pyridyl-protonated phosphine rather than a free proton is the actual protonating reagent ("proton messenger") of the palladium(II)–alkenyl species.

It is tentatively suggested that to be an effective proton messenger, the 2-$PyPPh_2$ ligand must have two essential features: (i) the phosphorus atom is required to act as an anchor for efficient binding to the electrophilic palladium centre; (ii) the distance between the phosphorus atom and protonated nitrogen should not be too large. The low rates observed with ligands containing a 3-pyridyl or, more particularly, a 4-pyridyl group (see Table 1) might be related to too long a P–N distance, with a consequently less efficient proton transfer. Differences in activity caused by different types of substituents are thought to be partly related to subtle electronic effects affecting the electrophilicity of the palladium centre as well as the ligand basicity and therefore the effectiveness of the ligand as a proton messenger (eqn. (10)). Too low a basicity of the ligand might lead to insufficient ligand protonation, whereas too high a basicity might hamper proton transfer from the ligand. The less effective ligands with 6-bromo and 6-methoxy substituents on the 2-pyridyl group could represent examples of these two categories of ligand respectively. The reduced reaction rate observed with phosphine ligands containing more than one 2-pyridyl group (see Table 3) could be due to a less efficient phosphorus anchoring function as a result of double protonation, leading to a reduced nucleophilicity of the phosphine moiety.

The 2-$PyPPh_2$ ligand thus combines all the properties needed to function as an ideal proton messenger. This proton transfer is reminiscent of that in enzyme-catalysed reactions, where basic groups that are part of the enzyme assist by proton delivery on an atomic scale, *e.g.* in hydrolysis reactions.

4. Conclusions

The class of cationic palladium catalysts described above shows unprecedented activity and selectivity for the carbonylation of alkynes, in particular propyne. These features are attributed to the unique ability of the applied 2-pyridylphosphine ligands to function both as a chelating P–N ligand, playing a crucial role in the selectivity-determining step of the catalytic cycle, and as a monocoordinating ligand, functioning as a proton messenger to the active palladium centre in the activity-determining step of the catalytic cycle. Although this proposal accounts for many of the observations, it is clear that further detailed studies of the elementary steps of the catalytic cycle are required to gain full insight to the factors that control these very selective and fast reactions.

5. Experimental details

5.1. Analytical equipment

Routine gas–liquid chromatographic (GLC) analysis was performed on a Perkin–Elmer 8500 gas chromatograph fitted with a Chrompack 25 m CP-sil-5 capillary column. GLC–mass spectroscopic analysis was performed on a Finnigan-9610 gas chromatograph fitted with the same column and coupled to a Finnigan-4000 triple-stage mass spectrometer; electron impact ionization was used. This technique was applied to identify reaction products by comparison with authentic samples.

5.2. Materials

Methanol (p.a.), palladium acetate, several Brønsted acids and solvent (*N*-methylpyrrolidone) were obtained from Merck. 4-Methoxyphenol originated from Jansen Chimica. Carbon monoxide was obtained from Air Products of Matheson (purity greater than 99%). Propyne was purchased from Intermar (Breda, Netherlands). The applied propyne feeds contained propadiene in concentrations below 0.4% and butane in concentrations varying between 1% and 3%, as measured by gas chromatography. Preparations of all ligands applied have been described in detail [6,7]. Generally, coupling reactions of a phosphine and a pyridine moiety are involved. Both moieties can be used as nucleophile or electrophile, using *e.g.* chlorodiphenylphosphine with lithiated pyridines, or alternatively the sodium diphenylphosphide can be coupled with bromopyridines. These reactions are rapid under mild conditions. Purification by recrystallization is generally easy and yields are high.

5.3. Batch autoclave carbonylation experiments

Screening of catalyst systems and reaction conditions was carried out in batch autoclave experiments. Use was made of a 250 or 300 ml magnetically stirred Hastelloy™ C autoclave. In a typical experiment this autoclave was filled with the catalyst components (palladium acetate, phosphine ligand, protonic acid), reacting nucleophile (generally methanol) and, optionally, solvent (*N*-methylpyrrolidone). Subsequently, air was evacuated from the autoclave and propyne was introduced up to a pressure of 2 bar, followed by carbon monoxide up to a pressure of 20–60 bar. The autoclave was sealed and the temperature was raised to the desired level (45–115°C). After reaction times of typically 0.25–5 h the autoclave was opened and the contents were analysed by means of GLC, from which selectivities and averaged catalyst activities were determined. Activity data were also obtained by recording the pressure (using a Transamerica Instruments pressure transducer, series 2000) continuously. Reaction rates can vary over time; the rate data in the tables are numbers averaged over the period during which the actual reaction takes place, up to 80% propyne conversion.

5.4. Continuous autoclave carbonylation experiments

Accurate kinetic data were obtained using a CSTR. A 300 ml Hastelloy™ autoclave was equipped with a heating mantle and cooling spiral to control the temperature and with a hollow shaft stirrer to improve the carbon monoxide mass transport. Catalyst components and MMA stabilizer (4-methoxyphenol, 1000 ppm) were dissolved in the methanol feed. Propyne was introduced via syringe pumps. The reactor was filled with this solution and pressurized with carbon monoxide. Subsequently, methanol–catalyst solution, propyne and carbon monoxide were fed continuously into the reactor. The liquid reactor content was kept constant at 220 ml by a level control system. Steady states were obtained at various residence times (1–5 h) by varying the feed rates. Activity and selectivity data were obtained by GLC analysis of the continuously withdrawn product stream.

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