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Invited Lecture

Homogeneous catalysis by cationic palladium complexes. Precision catalysis in the carbonylation of alkynes

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Abstract

A class of highly efficient homogeneous palladium cationic catalysts has been developed for the carbonylation of alkynes. An interesting application 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 turnover numbers of more than 40000 mol/(mol Pd h) and selectivities to methyl methacrylate of up to 99.95% can be obtained under mild conditions. It is hypothesized that the 2-pyridylphosphine ligand plays an essential role both as a chelating P–N ligand in the selectivity-determining step and as a mono-coordinated ligand in the protonolysis step of the catalytic cycle.

Key words: Palladium; Catalysis; Carbonylation; Alkyne; Methyl methacrylate; 2-Pyridylphosphine

1. Introduction

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 [1].

The transition-metal catalysed carbonylation of alkynes has been known since the pioneering work of Reppe [2]. Carbonylation of acetylene utilizing Reppe's nickel carbonyl catalyst in the presence of halide promoters is being commercially applied to produce acrylic acid and its esters [2]. Methyl methacrylate (MMA), a large-scale chemical intermediate for the production of homopolymers and copolymers (world production 1200 ktonnes/annum in 1990) can in principle be manufactured *via* similar nickel- or palladium-catalysed carbonylation of propyne [3,4]. However, this reaction has thus far not been commercialized, 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 [5–8] and will exemplify the catalytic aspects with propyne as substrate, which, together with its isomer propadiene, is available as feedstock from naphtha crackers in amounts of 0.2–1.0 wt% on intake hydrocarbon feed. For the first time, these catalysts will allow the development of a cost-effective MMA process on the basis of carbonylation technology [9]. Due to the unprecedented high selectivities achieved, this process has the extra benefit of exerting minimal negative effects on the environment.

2. Results

In the course of the above-mentioned 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.

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TABLE 1. Propyne carbonylation, the 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 h)	Selectivity (% MMA)
PPh_3	0.10	115	*ca.* 10	89
4-$PyPPh_2$	0.10	90	*ca.* 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.

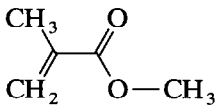
TABLE 2. Propyne carbonylation: the effect of acid type [a]

Acid type	Acid intake (mmol)	Temperature (°C)	Average rate (mol/mol Pd h)	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	*ca.* 10	98

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

One reaction studied was the methoxycarbonylation of propyne to give methyl methacrylate (eqn. (1)):

$$CH_3{-}C{\equiv}CH + CO + CH_3OH \longrightarrow$$



(1)

MMA

2.1. Effects of ligand structure

Tables 1–3 give the results from batch autoclave experiments. The catalysts originally tested were palladium 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-$PyPPh_2$), results were very similar to those obtained with PPh_3. In all these experiments, the only significant by-product observed was the linear isomer of MMA, *i.e.* methyl crotonate.

Table 2 indicates that replacement of the MeSA acid component of the 2-$PyPPh_2$-based catalyst by *p*-toluenesulfonic 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 obtained upon application of weaker acids, such as benzenephosphonic acid and, more particularly, acetic acid. With HCl, being a strong acid, again a low activity was achieved, suggesting that it is also the coordinating properties of the conjugated base to the palladium centre, rather than the acidity alone, that determine the catalytic performance.

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

TABLE 3. Propyne carbonylation, substituent effects in ligand with a 2-pyridyl-phosphine skeleton [a]

Ligand type	Acid type	Temperature (°C)	Average rate (mol/mol Pd h)	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, 50 ml methanol, 30 ml *N*-methylpyrrolidone, 60 bar CO, 0.025 mmol Pd-acetate, 1.0 mmol ligand, 2.0 mmol acid.

specificity of the catalyst. Introduction of the methyl substituent at the 6-position of the 2-pyridyl group resulted in an increase in the selectivity to 99.95% (*i.e.* a 20-fold suppression of the methyl crotonate by-product formation compared with the unsubstituted ligand!) with retention of the high overall activity of the catalyst, whereas substitution at the 4-position did not affect the selectivity at all. Methoxy and bromo substitution at the 6-position had virtually the same effect on the selectivity as the 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 progressively decreasing catalyst activity, which could only be restored by the application of a higher reaction temperature. The number of 2-pyridyl groups in the ligand hardly affects the selectivity of the catalyst.

2.2. 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 high propyne conversion could be obtained under mild conditions (*i.e.* a temperature of 45°C, a low CO pressure (11 bar) and a low palladium concentration of 18 ppmw/methanol feed). The highest rates (propyne conversions of 81 and 95% at residence times of 1.6 and 4.4 h, respectively) were found at ligand/palladium and acid/ligand molar ratios of around 20 and 1, respectively. These rates correspond to turnover numbers of 20 000–50 000 mol/(mol Pd h), thus confirming the results from the batch experiments. It was observed that, in order to obtain high activity, some excess of acid over the 2 mol/mol Pd, required for removal of acetate as acetic acid from the palladium coordination sphere, is essential. However, once some extra acid was used, the reaction order in the acid concentration was close to zero. Moreover, it was concluded that the carbonylation rate was first order with respect to the concentrations of palladium, methanol and propyne at the above-mentioned catalyst composition.

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 so-called weakly or non-coordinating anions.

3.1. Effect of anion type

The anions (X) are supplied to the catalyst system as strong acid to displace the acetate anions from palladium acetate *via* a simple acid-base reaction, thus generating cationic palladium(II) species (eqn. (2)):

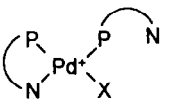
$$Pd(OAc)_2 + 2\,HX \longrightarrow PdX_2 + 2\,HOAc \qquad (2)$$

The results shown in Table 2 suggest a qualitative correlation between catalyst activity and the acid strength of the anion source, with the exception of hydrochloric acid. 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 acids, *i.e.* the strength of coordination towards H^+. Exceptions to this rule comprise halide anions, which, although derived from strong acids, strongly coordinate to palladium(II), giving so-called neutral complexes. Therefore, it is concluded that coordinative, rather than acid/base properties, determine the effect of anions on catalytic performance. The higher reactivity with weakly coordinating anions is thought to arise, in part, from the easier access of substrate molecules (alcohol, alkyne and carbon monoxide) as well as 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 due to decreased back-donation. The intermediate palladium species in the catalytic cycle would then be less stable, with the result that elementary steps would demand lower activation energies and therefore would proceed at higher rates [11].

3.2. Effect of phosphine ligands

The difference in catalyst characteristics displayed by PPh_3 on the one hand and 2-$PyPPh_2$ and analogues on the other is extreme. As described above, the 2-pyridyl moiety of the latter phosphines must play a crucial role in determining the extraordinary activity and high specificity to give 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 ligand [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 in the liquid state (NMR, IR), that the coordination sphere around these cations can accommodate two 2-$PyPPh_2$ ligand molecules which 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) with both the phosphorus and the nitrogen atom creating a four-

membered ring structure, while the second is mono-coordinated *via* the phosphorus atom only [12–15]:



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

P–N in this structure symbolizes the 2-$PyPPh_2$ ligand or an analogue.

We propose 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 in the following paragraphs, it is proposed that the 2-pyridylphosphine moiety plays a crucial role in both selectivity and rate enhancement, *via* the chelated and the mono-coordinated ligand, respectively.

3.3. Elementary steps in the catalytic cycle

We suggest that the initiation step of the catalytic cycle probably involves the reaction of the above-mentioned palladium complex I with methanol to give a palladium-methoxy species (eqn. (3)):

$$[\eta^2\text{-(P-N)Pd(P-N)X}]X + CH_3OH \longrightarrow [\eta^2\text{-(P-N)Pd(P-N)OCH}_3]X + HX \quad (3)$$

The next step involves the nucleophilic attack by carbon monoxide and displacement of the mono-coordinated ligand. It is suggested that this nucleophilic displacement is an easy reaction, since the mono-coordinated ligand will be protonated most of the time (by HX generated in eqn. (3) or externally applied) and therefore is expected to coordinate only weakly (eqns. (4) and (5)):

$$[\eta^2\text{-(P-N)Pd(P-N)OCH}_3]X + HX \longrightarrow [\eta^2\text{-(P-N)Pd(P-NH}^+\text{)OCH}_3]X_2 \quad (4)$$

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

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, probably protonated, P–N ligand (eqn. (6)):

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

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

Now, similar to nucleophilic substitution by carbon monoxide as indicated above, propyne displaces the, probably protonated, mono-coordinated P–N ligand (eqn. (7)):

$$[\eta^2\text{-(P-N)Pd(P-NH}^+\text{)COOCH}_3]X_2 + CH_3\text{-C}\equiv\text{CH} \longrightarrow [\eta^2\text{-(P-N)Pd(HC}\equiv\text{CCH}_3\text{)COOCH}_3]X + \text{P-NH}^+X^- \quad (7)$$

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 afford formation of palladium–alkenyl species (1-palladium-2-carbomethoxy-propene and 2-palladium-1-carbomethoxypropene). The details of this migratory propyne insertion probably involve first 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 free P–N ligand, probably in its protonated form (eqns. (8a) and (8b)):

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

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

The relative rates of the reactions represented by eqns. (8a) and (8b) determine the (regio)selectivity of the overall carbonylation reaction giving eventually MMA and methyl crotonate, respectively. The selectivity is likely to be governed by stereometric constraints determined by the chelated P–N ligand (see further discussion in the next paragraph).

The final step, resulting in the products MMA and methyl crotonate, involves the protonolysis of the palladium–alkenyl bond. We suggest that the protonated mono-coordinated ligand ($P\text{–}NH^+$) fulfils a key role in this termination reaction by acting as "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

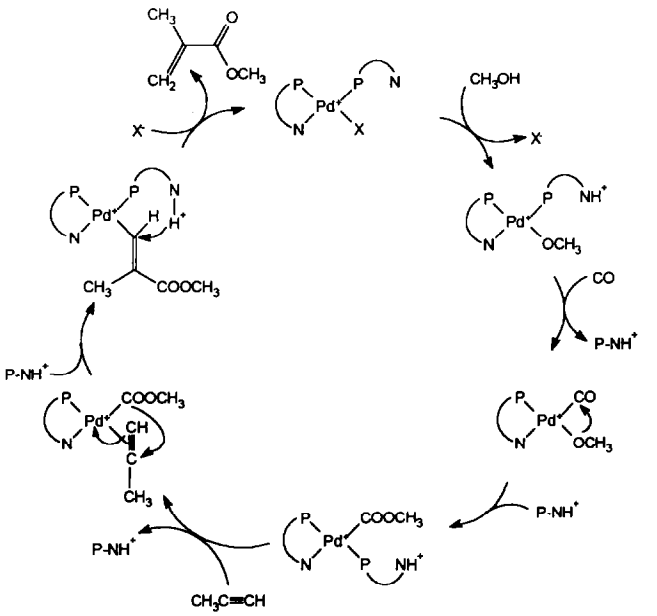
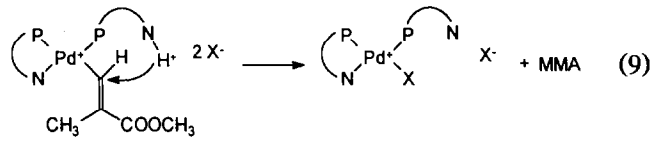


Fig. 1. Proposed catalytic cycle for the palladium–methoxy/2-PyPPh$_2$-catalysed methoxycarbonylation of propyne.

alkenyl moiety giving MMA (and similarly methyl crotonate) and reforming the original complex **I** (eqn. (9)):



(9)

The sequence of the reaction steps given in eqns. (3)–(9) constitutes the proposed catalytic cycle for the palladium/2-PyPPh$_2$-catalysed carbonylation of alkynes (see Fig. 1).

3.4. *Effect of ligand structure on selectivity*

The observed effects of substituents of the 2-pyridyl group on the course of the propyne carbonylation reaction are instructive with respect to the catalytic cycle proposed above 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. (8a,b) are modelled more clearly in Fig. 2. It has been 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 in its

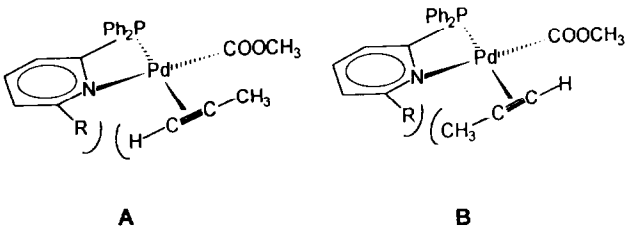


Fig. 2. Spatial configurations in the selectivity-determining step as proposed in eqns. (8a) and (8b).

route to migratory insertion into the carbomethoxy group and thus leads to a preferred insertion pathway involving the methyl group of propyne pointing away from the palladium centre (position A in Fig. 2). As a consequence, formation of 2-palladium-1-carbomethoxypropene, *i.e.* the precursor for methyl crotonate as product, is thus strongly disfavoured by substituents at 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 introduction of substituents at the 6-position of the 2-pyridyl group leads to a *decrease* in the formation of methyl crotonate 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 in the palladium(II)–hydride bond, (ii) carbon monoxide insertion in 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, due to the same steric factors as discussed above, 6-substitution of the pyridyl group would then predict an *increase* in the formation of

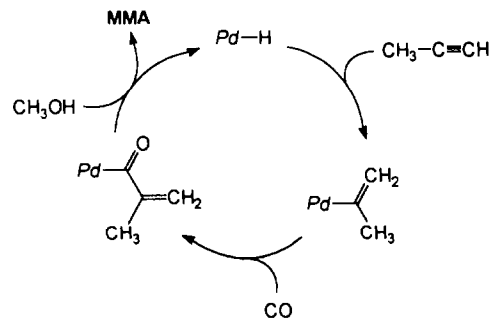


Fig. 3. Potential alternative catalytic cycle: palladium–hydride-catalysed methoxycarbonylation of propyne.

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

3.5. Effect of ligand on protonolysis step

The data of Table 1 show that the introduction of a nitrogen atom in the ligand has not only an effect on selectivity, but also on carbonylation rate. It is therefore suggested that this nitrogen atom plays an important role in the protonolysis step (eqn. (9)), as a so-called proton messenger. In the absence of a nitrogen atom or if the nitrogen atom is wrongly positioned, protonolysis is assumed to be slow and rate-limiting. Using the 2-$PyPPh_2$ ligand and its analogues, however, efficient, rapid protonolysis is achieved. However, at low concentrations of strong acid the carbonylation rate is affected, pointing to protonolysis as the rate-determining step. Kinetic measurements at higher concentration of strong acid (acid/Pd > 10) indicate a zero order in strong acid and first order in palladium, propyne and methanol. These data point to propyne insertion as the rate-determining step, making the likely assumption that this reaction is irreversible. Apparently protonolysis has become so fast that it is no longer rate-determining. Moreover, the preceding elementary steps of the catalytic cycle (eqns. (3)–(5)) can be considered to be rapid equilibrium reactions: the palladium-carbomethoxy species is "trapped" by irreversible propyne insertion.

To be an effective proton messenger, several properties of the 2-$PyPPh_2$ ligand are tentatively proposed to be essential: (i) the phosphorus atom might be required as an anchor for efficient binding to the electrophilic palladium centre and (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 and, more in particular, 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, at least in part, 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 proton messenger (eqn. (9)). 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 anchor function as a result of double protonation which leads to a reduced nucleophilicity of the phosphine moiety.

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

4. Conclusions

The class of cationic palladium catalysts described above shows unprecedented activity and precision 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- and rate-determining step of the catalytic cycle, and at the same time as a mono-coordinating ligand, functioning as a proton messenger to the active palladium centre in the protonolysis step. Although this proposal makes many of the observations plausible, it is clear that further detailed studies of the elementary steps of the catalytic cycle are required to gain full insight into the factors that control these very selective and fast reactions.

5. Experimental details

5.1. Analytical equipment

Routine gas chromatographic analysis was performed on a Perkin Elmer 8500 gas chromatograph fitted with a Chrompack 25 m CP-sil-5 capillary column. Gas-chromatographic/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, solvent (*N*-methylpyrrolidone) and palladium acetate were obtained from Merck. 4-Methoxyphenol originated from Jansen Chimica. Carbon monoxide was obtained from Air Products or Matheson (purity > 99%). Propyne was purchased from Intermar (Breda, The Netherlands). The propyne feeds applied contained propadiene in concentrations below 0.4% and butane in concentrations varying between 1 and 3%, as measured by gas chromatography. Preparation of all ligands applied has been described in detail [6,7]. Generally, coupling reactions of a phoshine 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 has been carried out with 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 whereupon propyne was added 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 gas chromatography from which selectivities and average catalyst activities were determined. Activity data were also obtained from registration of pressure (recorded by a Transamerica Instruments pressure transducer, series 2000) versus reaction time. Reaction rates can vary over time; the rate data in the tables are averages over the period when actual reaction takes place, up to 80% propyne conversion.

5.4. Continuous autoclave carbonylation experiments

Accurate kinetic data were obtained using a continuously fed stirred tank reactor (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 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 was 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 feeding rates. Activity and selectivity data were obtained *via* gas chromatographic analysis of the continuously withdrawn product stream.

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