Palladium(II) Complexes with N-Phosphanyl-N-heterocyclic Carbenes as Catalysts for Intermolecular Alkyne Hydroaminations

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ABSTRACT: The catalytic potential of palladium(II) complexes with chelating N-phosphanyl-N-heterocyclic carbenes featuring a saturated imidazolin-2-ylidene or tetrahydropyrimid-2-ylidene ring has been investigated in intermolecular alkyne hydroamination reactions. The complexes were found to be among the most active Pd-based catalysts for these processes and to enable the use of low reaction temperatures (40 °C) and of solventless conditions. The Pd complexes require activation by 2 equiv of a silver salt to remove chlorido ligands from the metal coordination sphere; they can however also be presynthesized in active form, which allows their use under silver-free conditions. The hydroamination reaction was found to efficiently proceed with terminal alkynes and different ring-substituted, primary arylamine substrates.

INTRODUCTION

The addition of molecules containing an N–H function across multiple C–C bonds of unsaturated organic molecules, commonly termed hydroamination, is a very useful synthetic tool for the preparation of complex nitrogen-containing compounds, including, for example, nitrogen heterocycles featured in several pharmaceuticals and agrochemicals of technological interest.1,2 This reaction is generally run under organometallic catalysis, as at least one of the reaction partners, the N–H containing substrate or the unsaturated substrate, needs to be activated for reaction in order to overcome the electronic repulsion between the C–C multiple bond and the nitrogen-containing functional group, which are both electron-rich moieties. Whereas hard metal centers preferentially coordinate and activate the N–H group, soft ones, typically late-transition metals, interact instead preferentially with the π system of the unsaturated substrate, depleting its electron density and favoring nucleophilic attack by the N–H moiety.1–3 The lower oxophilicity of late transition metal centers renders them also more tolerant toward functional groups present in the substrates. Although gold-based catalysts for this reaction class have become increasingly popular in the course of the last two decades,4,5 other late transition metals, in particular group 10 metals such as Pd and Pt,6–12 have been intensively investigated as well; palladium species that have been successfully employed as catalyst include simple palladium(II) salts and also palladium(II) complexes, such as the Pd(II) complexes with N-heterocyclic carbene (NHC) ligands successfully tested by several research groups.9–11,13

In recent years, we14,15 and others16,17 have reported on Pd complexes with a novel class of ligands, namely, stable carbene ligands N-functionalized with a phosphanyl moiety (Scheme 1). Such ligands, termed N-phosphanyl-N-heterocyclic carbenes (NHCPs) or N-phosphanyl acyclic dianimocarbenes, have been extensively investigated as catalysts for cross-coupling reactions.14,15 They were found to exhibit a high reactivity toward unreactive aryl chlorides but also to undergo decomposition in the course of the reaction. This instability has been tentatively attributed to the fact that these complexes feature small bite angle chelating ligands, which give rise to stable square planar complexes with palladium(II) but do not fit well in the tetrahedral coordination geometry of palladium(0); as the catalytic cycle for cross-coupling reactions relies on a Pd(0)/Pd(II) manifold and expectedly produces palladium(0) complexes, these complexes will be prone to ligand dissociation and decomposition. Consequently, in the frame of this work, we have extended our investigation on the catalytic performance of palladium(II) complexes with NHCP ligands to the intermolecular hydroamination of alkynes, which is generally considered to be a redox-neutral process under Pd catalysis (Figure 1).2

Scheme 1. General Structure of a Stable Carbene Ligand N-Functionalized with a Phosphanyl Moiety

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RESULTS AND DISCUSSION

In order to assess the catalytic potential of complexes with N-phosphanyl carbenes for hydroamination reactions, we have considered complexes \( 1 - 2 \), featuring a saturated imidazolin-2-ylidene or tetrahydropyrimid-2-ylidene ring, which were previously reported and thoroughly characterized by us\(^{14} \) (Scheme 2).

Catalytic tests were run on the hydroamination of phenylacetylene with an aromatic primary amine such as mesitylamine (Scheme 3), and were aimed at establishing the best reaction conditions, particularly in terms of solvent and employed cocatalyst. Indeed, the palladium(II) complexes have to be activated for reaction upon removal of the chlorido ligands from their coordination sphere, which generates the catalytically competent, formally dicationic complex (Figure 1); no reaction is observed employing the starting palladium(II) complexes alone as catalyst. We purposely chose a notoriously rather difficult amine substrate for hydroamination reactions, such as the rather sterically encumbered mesitylamine, in order to have an engaging test reaction against which to optimize our catalytic system. The reaction produced the Markovnikov hydroamination product exclusively, as it is commonly the case with group 10 and 11 metal catalysts.\(^{2} \)

We performed first some blank experiments in acetonitrile in order to ascertain whether the silver salt cocatalyst could promote the reaction by itself, as there have been reports in the literature that hydroamination can be also catalyzed by Ag salts.\(^{18} \) Under the reaction conditions employed herein, though, the Ag salt alone was a poorly effective catalyst for hydroamination (4% yield), whereas it appeared a bit more active for alkyne hydration by traces of water introduced together with the silver salt; indeed, yields in acetophenone (the product of phenylacetylene hydration) were variable (1–10%) and correlated with the hygroscopicity of the silver salt.

Next, we evaluated the effect of different solvents on the reaction outcome using catalyst \( 1 \) (Table 1). As it is apparent from the table, the catalytic system exhibits a fair performance in acetonitrile, whereas a more coordinating solvent such as dimethyl sulfoxide (DMSO) suppresses catalytic activity. Activity in a less-coordinating, less-polar solvent such as toluene is also low, possibly because of poor solubility of the dicationic catalyst in this solvent. Use of a standard ionic liquid such as 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide.

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Table 1. Solvent Effect on the Performance of Catalyst \( 1^{a} \)

| entry | solvent         | alkyne conversion (%) | hydroamination yield (%) | hydration yield (%) |
|-------|-----------------|------------------------|--------------------------|--------------------|
| 1     | acetonitrile    | 70                     | 45                       | 7                  |
| 2     | toluene         | 49                     | 24                       | 3                  |
| 3     | IL\(^{b}\)      | 88                     | 62                       | 8                  |
| 4     | DMSO            | 0                      | 0                        | 0                  |
| 5     | neat            | >99                    | 68                       | 3                  |

\(^{a}\)Reaction conditions: 1 mmol mesitylamine, 1 mmol phenylacetylene, 0.01 mmol (1 mol %) catalyst \( 1 \), 2 mol % AgPF\(_6\), 1 mL solvent, 80 °C, 25 h. \(^{b}\)IL = 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide.

Figure 1. Postulated mechanism for a palladium(II)-catalyzed hydroamination of an alkyne; \( S = \) solvent molecules.

Scheme 2. Synthesis of Complexes \( 1 - 2^{a} \)

\(^{a}\)Mes = mesityl; BN = benzonitrile.

Scheme 3. General Hydroamination Reaction Investigated in This Study

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the evaluation of the nature and amount of the silver salt cocatalyst on the catalytic performance (Table 2). Reactions were carried out using catalyst 1 in combination with different silver salts, both in acetonitrile (Table 2, entries 1−6) and under neat conditions (Table 2 entries 7−9); under the latter conditions, catalyst 2 was investigated as well (Table 2, entries 10−13).

The nature of the employed silver salt was found to have little influence on the yield in addition products (hydroamination + hydroamination-derived hydration), whereas it seems to have an influence on the overall conversion of the alkyn reagent, which is however difficult to rationalize. Thus, the yield in addition products appears to be quite insensitive to the different coordinating ability and Bronstedt basicity of the employed anions. This is important for an understanding of the reaction mechanism, as it suggests that the counteranion is not involved in the rate-determining step of the catalytic process, as it has been found to be the case, for example, in related gold(I)-catalyzed reactions such as alkyne hydroamination + hydroamination-derived hydration, whereas it seems to have an influence on the stability of the catalyst. Furthermore, the nature of the cocatalyst seems to play no role, which confirms our findings reported in Table 2 using silver salts. Altogether, use of preactivated, silver-free catalysts appears to bring no significant advantage in the reaction outcome; hence, in the following, catalysts activated in situ by addition of silver salt have been employed.

The complexes 1−SbF$_6$, 2−OTf, and 2−SbF$_6$ turned out to be fairly stable and could be stored for weeks in the solid state under air without noticeable decomposition. The reactivity of these complexes has been extensively evaluated and the results are reported in Table 3.

### Table 2. Counteranion Effect on the Catalytic Performance of Catalysts 1 and 2$^{a}$

| entry | catalyst | cocatalyst | solvent  | conv.$^{b}$ (%) | HA$^{c}$ (%) | HY$^{d}$ (%) |
|-------|----------|------------|----------|----------------|-------------|-------------|
| 1     | AgPF$_6$ | Acetonitrile | 100      | 62            | 0           | 38          |
| 2     | AgPF$_6$ | Acetonitrile | 90       | 58            | 0           | 42          |
| 3     | AgNTf$_6$ | Acetonitrile | 84       | 45            | 0           | 55          |
| 4     | AgOTf   | Acetonitrile | 77       | 31            | 0           | 69          |
| 5     | AgOTf   | Acetonitrile | 71       | 28            | 0           | 72          |
| 6     | AgSbF$_6$ | Acetonitrile | 60       | 23            | 0           | 77          |
| 7     | AgSbF$_6$ | Neat       | 54       | 22            | 0           | 78          |
| 8     | AgPF$_6$ | Neat       | 45       | 20            | 0           | 75          |
| 9     | AgOTf   | Neat       | 40       | 18            | 0           | 82          |

$^{a}$Reaction conditions: 1 mmol mesitylamine, 1 mmol phenylacetylene, 0.01 mmol (1 mol %) catalyst, 2 mol % AgX, 1 mL solvent, 80 °C, 25 h. $^{b}$Alkyne conversion. $^{c}$Yield in hydroamination product. $^{d}$Yield in hydration product.

### Table 3. Catalytic Performance of Preformed Pd Complexes without Halide Ligands$^{a}$

| entry | catalyst | AgX  | solvent  | conv.$^{b}$ (%) | HA$^{c}$ (%) | HY$^{d}$ (%) |
|-------|----------|------|----------|----------------|-------------|-------------|
| 1     | AgSbF$_6$ | Acetonitrile | 84      | 56            | 0           | 48          |
| 2     | AgSbF$_6$ | Acetonitrile | 100     | 50            | 0           | 50          |
| 3     | AgOTf   | Neat  | 90       | 60            | 0           | 40          |
| 4     | AgOTf   | Acetonitrile | 60     | 40            | 0           | 60          |
| 5     | AgOTf   | Acetonitrile | 45     | 28            | 0           | 72          |
| 6     | AgOTf   | Neat  | 94       | 83            | 0           | 11          |
| 7     | AgOTf   | Neat  | 97       | 64            | 0           | 36          |
| 8     | AgOTf   | Acetonitrile | 77    | 41            | 0           | 59          |
| 9     | AgSbF$_6$ | Acetonitrile | 53     | 29            | 0           | 74          |
| 10    | AgSbF$_6$ | Acetonitrile | 95    | 89            | 0           | 11          |
| 11    | AgSbF$_6$ | Neat  | 100     | 62            | 0           | 38          |

$^{a}$Reaction conditions: 1 mmol mesitylamine, 1 mmol phenylacetylene, 0.01 mmol (1 mol %) catalyst, 2 mol % AgX, 80 °C, 25 h.

Generally speaking, the catalytic performance of preformed catalysts in terms of yield of hydroamination product is comparable to (in the case of complex 1) or lower than (in the case of complex 2) that of systems formed in situ, which again rules out a possible catalytic role of the introduced Ag(I) beside halide removal from Pd, at least in the case of complex 1. The extent of formation of the formal alkyne hydration product is decreased, as expected, as no hygroscopic silver salt is introduced in the system. Furthermore, the nature of the counteranion seems to play no role, which confirms our findings reported in Table 2 using silver salts. Altogether, use of preactivated, silver-free catalysts appears to bring no significant advantage in the reaction outcome; hence, in the following, catalysts activated in situ by addition of silver salt have been employed.
We then considered the effect of changes in the reaction time and temperature on the outcome of the reaction (Table 4). We first established that 25 h of reaction time was not necessary in order to reach good hydroamination yields, and that respectable amounts of imine product were produced already after only 4 h of reaction time (Table 4, entries 1–5). Furthermore, use of silver triflate or hexafluoroantimonate as catalyst activator has a slight effect on the conversion of alkyne and on the incidence of formal alkyne hydration (probably due to the higher hygroscopicity of the hexafluoroantimonate salt) but not on the yield in the hydroamination product, which remains the same irrespective of the silver salt employed (Table 4, entries 2 and 3); this corroborates our previous assumption about the negligible influence of the nature of the non-coordinating anion on the performance of the catalyst.

Gratifyingly, significant catalytic activity was recorded with both complexes also at 40 °C (Table 4, entries 6–9), which to the best of our knowledge represents the lowest temperature ever reported for an intermolecular alkyne hydroamination reaction promoted by a Pd-based catalyst. Furthermore, comparing the performance of our catalysts with that of other NHC–Pd catalysts previously reported in the literature for the same reaction,9–11 it is evident that the latter require significantly higher temperatures, in the range 100–120 °C, as well as an excess of alkyne (1.2–2 equiv) in order to operate efficiently, which highlights the advantage of using our compounds.

The results of the tests reported in Table 4 allow also to make a comparison between the performances of catalysts 1 and 2. A pictorial view of the same data is reported in the graph in Figure 2. It can be appreciated that at a lower temperature (40 °C) catalyst 1 appears slightly more active than catalyst 2 at the beginning of the reaction and that both catalysts remain active for several hours. On the other hand, at 80 °C catalytic activity decreases markedly for both catalysts after the first hours of reaction, and the decrease is much more pronounced for catalyst 1 compared to catalyst 2. We conclude that catalyst 1 is a more active catalyst for the intermolecular alkyne hydroamination reaction, but at the same time it is also less stable under the reaction conditions, especially at a higher temperature. The reason for this lower stability, which has been recorded also using the same complexes as catalysts for cross-coupling reactions, is in our opinion explained by the more strained nature of the chelate ring in complex 1 compared to complex 2.

Finally, the generality of the intermolecular alkyne hydroamination reaction employing catalysts 1 and 2 has been evaluated with several different alkynes and aromatic amines. The yields in hydroamination product are reported in Table 5; they have been recorded after a 4 h reaction time at 80 °C and are therefore not optimized. It can be appreciated that the reactivity of the two Pd complexes is not limited to phenylacetylene and mesitylamine; other terminal alkyynes and differently ring-substituted primary arylamines can be employed. Yields are somewhat lower with the p-substituted anilines compared with mesitylamine, and are found not to significantly depend on the nature of the para-substituent. This influence that the electronic properties of the amine do not significantly influence the reaction yield to a great extent, whereas steric effects are more important; possibly the steric bulk of the amine promotes faster protonolysis of the vinylpalladium intermediate and/or dissociation of the coordinated enamine product, thereupon accelerating the reaction. On the other hand, the reaction fails altogether when internal alkyynes (such as phenylpropyne) or secondary arylamines (such as N-methyl-N-nitrosopyridine) are employed as substrates. Consequently, the substrate scope of these catalysts appears somewhat narrower compared with the Pd complex with an iminophosphane ligand recently reported by us,12 which exhibits notable reactivity also with internal alkyynes.

**CONCLUSIONS**

NHCP palladium(II) complexes 1 and 2 have been found to be among the most active Pd-based catalysts reported to date for the intermolecular hydroamination of alkyynes. Use of these catalysts enables the use of low reaction temperatures (40 °C) and of solventless conditions, and allows to carry out the reaction with stoichiometric quantities of the reagents, thus rendering the whole process very sustainable. The complexes can be activated in situ by addition of 2 equiv of a silver salt, or prepared in advance in active, silver-free form. Finally, the complexes were able to activate terminal alkyynes and different ring-substituted primary arylamines substrates for the reaction. Work in progress aims at extending the application of these complexes as catalysts to other reactions, and to further optimize the catalytic performance of the complexes by acting on the NHCP ligand structure.

**EXPERIMENTAL SECTION**

All manipulations of air- and moisture-sensitive compounds were carried out using standard Schlenk techniques or in a glovebox under an atmosphere of dinitrogen. The reagents

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**Table 4. Effect of the Reaction Temperature and Time on the Catalytic Performance of the Pd Complexes**

| entry | catalyst | cocatalyst | T (°C) | time (h) | conv. (%) | HA (%) | HY (%) |
|-------|----------|------------|--------|----------|-----------|--------|--------|
| 1     | 1        | AgOTf     | 80     | 25       | 97        | 68     | 4      |
| 2     | 1        | AgOTf     | 80     | 8        | 79        | 57     | 4      |
| 3     | 1        | AgSbF6    | 80     | 4        | 89        | 58     | 11     |
| 4     | 2        | AgOTf     | 80     | 25       | 99        | 83     | 7      |
| 5     | 2        | AgOTf     | 80     | 4        | 80        | 66     | 7      |
| 6     | 2        | AgSbF6    | 40     | 4        | 48        | 24     | 4      |
| 7     | 2        | AgSbF6    | 40     | 25       | 97        | 65     | 9      |
| 8     | 1        | AgSbF6    | 40     | 4        | 43        | 41     | 4      |
| 9     | 1        | AgSbF6    | 40     | 25       | 99        | 71     | 8      |

*Reaction conditions: 1 mmol mesitylamine, 1 mmol phenylacetylene, 0.01 mmol (1 mol %) catalyst, 2 mol % AgX. Alkyne conversion. Yield in hydroamination product. Yield in hydration product.*
were purchased from Aldrich as high-purity products and generally used as received. All solvents were purified and dried by standard methods. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AVANCE spectrometers working at 300 MHz (300.1 MHz for \(^1\)H, 75.5 MHz for \(^{13}\)C, and 121.5 MHz for \(^{31}\)P); chemical shifts (\(\delta\)) are reported in units of ppm relative to the residual solvent signals and to external 85% H₃PO₄ (for \(^{31}\)P). Elemental analyses were carried out with a Fisons EA 1108 CHNS−O apparatus or with a Carlo Erba analyzer.

**Synthesis of Catalysts 1−SbF₆, 2−OTf, 2−SbF₆.** Complex 1 or 2 (50 mg) was placed in a Schlenk tube under an inert atmosphere and dissolved in 2 mL of anhydrous acetonitrile. A solution of 2 equiv silver(I) triflate or hexafluoroantimonate in 2 mL of anhydrous acetonitrile was added in one portion, and the resulting mixture was stirred at room temperature for 30 min. The reaction mixture was filtered over Celite and the resulting clear solution was evaporated to dryness. The product was washed with diethylether and dried under vacuum. Isolated yields were in the range 45−55%.

**Table 5. Substrate Screening for the Catalytic Performance of the Pd Complexes in Hydroamination**

| Entry | Catalyst | Alkyne | Amine | Yield (%) |
|-------|----------|--------|-------|-----------|
| 1     | 1        | Ph≡     | NH₂   | 57        |
| 2     | 2        | Ph≡     | NH₂   | 66        |
| 3     | 1        | Ph≡     | NH₂   | 25        |
| 4     | 2        | Ph≡     | NH₂   | 41        |
| 5     | 1        | Ph≡     | NH₂   | 33        |
| 6     | 2        | Ph≡     | NH₂   | 37        |
| 7     | 1        | Ph≡     | NH₂   | 39        |
| 8     | 2        | Ph≡     | NH₂   | 34        |
| 9     | 1        | CH₃₂≡   | NH₂   | 29        |
| 10    | 2        | CH₃₂≡   | NH₂   | 19        |

*Reaction conditions: 1 mmol alkyne, 1 mmol amine, 0.01 mmol (1 mol %) catalyst, 2 mol % AgOTf, 80 °C, 4 h.*
Hz, CH₃), 52.8 (d, J = 4 Hz, CH₃), 129.7 (s, CH), 135.9 (s, C), 140.8 (s, C), 137.5; carbene carbon not detected. ¹³P NMR (CD₃CN): δ 99.1. Anal. Calcd (%) for C₉₂H₃₁₃N₃P₂P₂S₂CH₂CN-H₂O: C, 24.94; H, 4.57; N, 3.97. Found: C, 24.71; H, 4.37; N, 4.57.

2–OfY. ¹H NMR (CD₃CN): δ 1.63 (d, J = 19 Hz, 18H, Bu), 2.27 (s, 6H, Me), 2.29 (m, 2H, CH₂), 2.32 (s, 3H, Me), 3.67 (m, 2H, CH₂), 3.72 (m, 2H, CH₂), 7.08 (s, 2H, CH), 1.98 (s, 6H, CH₃), 2.19 (s, 3H, CH₃), 2.27 (s, 3H, CH₃), 2.48 (m 2H, CH₂), 2.48 (s, 2H, ArH).

2–Sbf₉. ¹H NMR (CD₃CN): δ 1.63 (d, J = 19 Hz, 18H, Bu), 2.26 (s, 6H, Me), 2.29 (m, 2H, CH₂), 2.32 (s, 3H, Me), 3.66 (m, 2H, CH₂), 3.71 (m, 2H, CH₂), 7.07 (s, 2H, CH). ¹³C NMR (CD₃CN): δ 17.0 (s, CH), 20.2 (s, CH₂), 20.3 (d, J = 2 Hz, CH₂), 27.8 (d, J = 4 Hz, CH₂), 40.5 (d, J = 12 Hz, CP), 44.9 (d, J = 6 Hz, CH₂), 49.9 (s, CH₂), 129.8 (s, CH), 135.0 (s, C), 138.8 (s, C), 140.3 (s, C), 158.2 (d, J = 13 Hz, NCN). ¹³P NMR (CD₃CN): δ 58.5. Anal. Calcd (%) for Cₙ₂H₂₃F₆N₂O₆PPdS₂: C, 28.30; H, 3.33; N, 4.56.

**General Procedure for Catalytic Hydroaminations.** In a Schlenk tube equipped with a magnetic stirring bar were placed under an inert atmosphere 10 mmol Pd complex and optionally 2 mL of dry solvent degassed and put under an inert atmosphere. Aniline (1.00 mmol) and optionally 20 mmol), 1.00 mmol alkyne, and optionally 1 mL of dry solvent was diluted in CDCl₃ for the measurement.

**Notes**

The authors declare no competing financial interest.

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