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Co-catalysis between M^{n+} and H^+ in the direct addition of N–H bonds to CC double and triple bonds

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Abstract—A kinetic analysis of the addition of amines to CC double and triple bonds using different transition metal catalysts is presented. It is shown that the reaction is initiated by the Lewis acidic metal centres. In the presence of protons, the rate of reaction is drastically increased. The key role played by the protons in the catalytic system is discussed. Therefore, Brønsted and Lewis acids, and their respective properties, have to be taken into account in the rational design of hydroamination processes mediated by late transition metals.

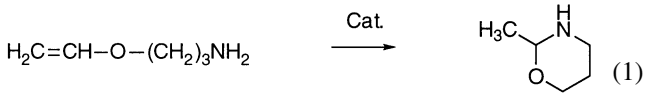
1. Introduction

Amines are typical intermediate products of the chemical industry and their derivatives are of fundamental importance as natural products, pharmacological agents, fine chemicals and dyes. However, their commercial production frequently involves multi-step syntheses, resulting in many amines having a high price. Thus, there is considerable interest in the development of new synthetic protocols for the formation of carbon–nitrogen bonds. In this respect, the direct addition of amine N–H bonds to CC multiple bonds (hydroamination) is a particularly convenient method.[1–3] A specific class of catalysts, based on the late transition-metals, has started to attract considerable interest in the organic and organometallic community.[1] Especially, the metals Ir(I), Rh(I), Pd(II), Cu(I) and Zn(II), in the oxidation states stated, have been identified as suitable catalysts for this reaction.[4] Recent examples are the addition of secondary amines to norbornene using $[Ir_2(\mu\text{-}Cl)_2(PP)_2]$, where PP=bidentate phosphane,[5] and the addition of amines to styrene or vinylpyridine using a $[Rh(COD)_2]BF_4/PPh_3$ catalyst system.[6,7]

We have recently described the first heterogeneous version of the reaction promoted by a catalytic amount of Zn^{2+}, Cu^+ or Rh^+ exchanged beta zeolite.[8] Surprisingly, higher reaction rates were observed with the heterogeneous catalysts than with the corresponding homogeneous catalysts, although transport limitations within the zeolite pores could slow the reaction in case of the heterogeneous catalysts. This prompted us to pursue more detailed studies on homogeneous hydroamination reactions. We report here the results of kinetic studies on the transition metal mediated addition of amines to alkynes and alkenes. On the basis of these results, the respective roles played by Lewis and Brønsted acids in these reactions are suggested. Moreover, we would like to stress how the presence of Brønsted acids can dramatically increase the reaction rate in many transition metal mediated hydroamination reactions.

2. Results

The direct addition of N–H to CC double and triple bonds was studied using the cyclisation of 3-aminopropyl-vinyl-ether (**1**) and 6-aminohex-1-yne (**2**) as specific examples. The vinyl ether structure in **1** allows for a slightly activated carbon–carbon double bond.[9,10] The cyclisation of **1** gives



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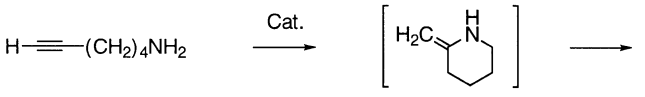
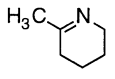
1 **3**



2 **4**



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(2)

Keywords: hydroamination; addition; amine; alkyne; alkene.

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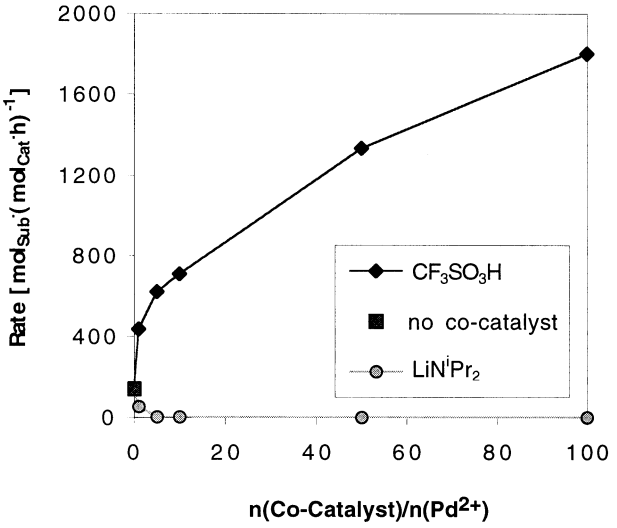


Figure 1. Initial rate of reaction for the cyclisation of 6-aminohex-1-yne using the catalyst [Pd(Triphos)]$(CF_3SO_3)_2$ in the presence of CF_3SO_3H or LiN^iPr_2 as co-catalyst.

the *N,O*-acetal tetrahydro-2-methyl-1,3-oxazine (**3**) (Eq. 1). The intramolecular hydroamination of **2** first generates 2-methylene-piperidine (**4**) with an exocyclic double bond (Eq. 2). Subsequent 1,3-hydrogen-shift occurs in situ and converts the enamine to the more stable isomeric imine 2-methyl-1,2-dehydropiperidine (**5**).

As catalysts, the metal complexes $[Rh(NOR)_2]ClO_4$, where NOR=norbornadiene, [Pd(Triphos)]$(CF_3SO_3)_2$, where Triphos=bis-(2-diphenylphosphinoethyl)-phenylphosphane, $[Cu(CH_3CN)_4]PF_6$ and $Zn(CF_3SO_3)_2$ were used. Different metals were chosen to explore whether principles developed for one metal would also be valid for the other late transition metals. Coordination of palladium(II) with a phosphane ligand was necessary to prevent precipitation of metallic palladium during catalysis. The cyclisation of **1** and **2** was performed in toluene at reflux temperature (111°C) and a substrate to catalyst ratio of 20 and 100, respectively. For both substrates and for all catalysts, the reaction is highly regioselective yielding only (>99%) the 6-*endo* product. Close to quantitative product yields (>99%) were obtained after sufficient time, e.g. 40 and 30 min for the cyclisation of **1** and **2**, respectively, using the catalyst system [Pd(Triphos)]$(CF_3SO_3)_2$ and 10 equiv. CF_3SO_3H.

For a catalytic mixture of **2** and [Pd(Triphos)]$(CF_3SO_3)_2$ in a molar ratio of 100:1, the initial rate of reaction was 1.4×10^2 mol$_{Sub}$ (mol$_{Cat}$ h)$^{-1}$. Upon addition of 1 equiv. of CF_3SO_3H, with respect to the catalyst, the reaction rate more than tripled to 4.4×10^2 h^{-1} (Fig. 1). Upon addition of 5 and 10 equiv. CF_3SO_3H, the rate of reaction increased to 6.2×10^2 and 7.1×10^2 h^{-1}, respectively. Even higher amounts of acid led to higher rates, but the relative increase in activity became less. In a catalytic mixture of equimolar amounts of **2** and CF_3SO_3H and 1 mol% [Pd(Triphos)]$(CF_3SO_3)_2$, the reaction was complete within 10 min and the rate of reaction could only be estimated (ca. 1.8×10^3 h^{-1}). In contrast, when a base like LiN^iPr_2 was added to the catalytic mixture, the initial rate of reaction declined sharply. Upon addition of 5 equiv. LiN^iPr_2, the catalytic activity of [Pd(Triphos)]$(CF_3SO_3)_2$ was close to zero.

A similar co-catalytic effect upon addition of acid was also observed for catalysts based on the other late transition metals (Fig. 2a). For $[Cu(CH_3CN)_4]PF_6$, the rate increased from 18 h^{-1} for the parent catalyst to 30, 88, 1.3×10^2 and 2.1×10^2 h^{-1} upon addition of 1, 5, 10 and 15 equiv. CF_3SO_3H, respectively. For $Zn(CF_3SO_3)_2$ and $[Rh(NOR)_2]ClO_4$, the rate of reaction also increased when an acid was added; however, the effect was less pronounced. When 10 equiv. CF_3SO_3H were employed, the catalytic activity of the zinc catalyst doubled from 19 to 41 h^{-1} and increased by a factor of 7 for the rhodium catalyst (from 4.1 to 29 h^{-1}). These results clearly demonstrate that, for each of the catalysts, addition of CF_3SO_3H leads to higher reaction rates. In contrast, when CF_3SO_3H was used without a metal catalyst no significant conversion of **2** to **5** was observed.

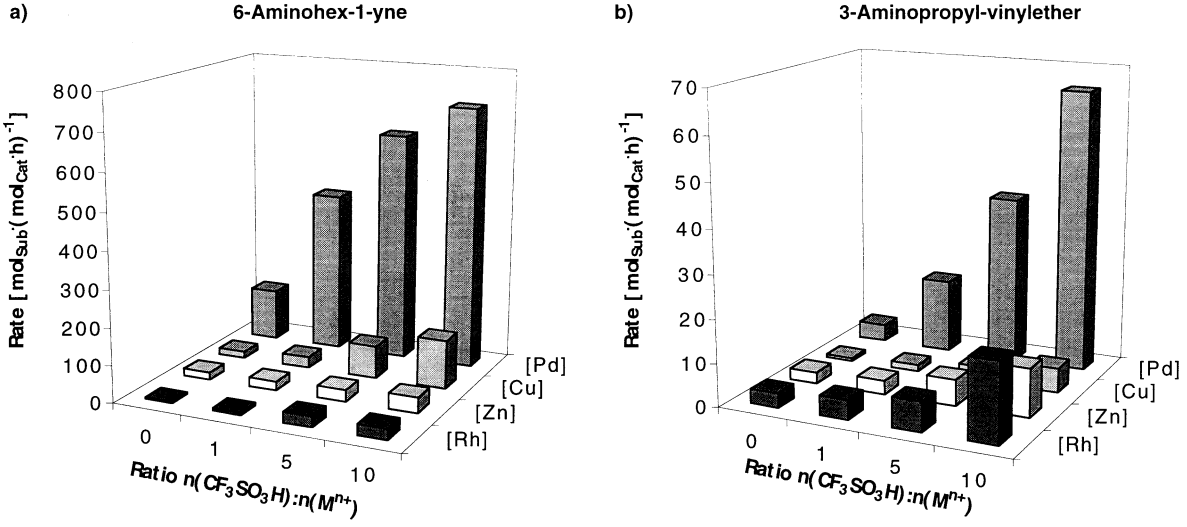
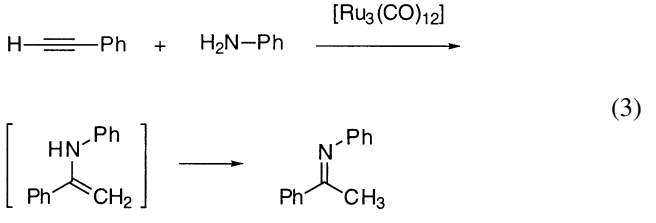


Figure 2. Reaction rates for the cyclisation of (a) 6-aminohex-1-yne and (b) 3-aminopropyl-vinylether using the catalysts [Pd(Triphos)]$(CF_3SO_3)_2$, $[Cu(CH_3CN)_4]PF_6$, $Zn(CF_3SO_3)_2$ and $[Rh(NOR)_2]ClO_4$ in the presence of different amounts of CF_3SO_3H. Solvent toluene at 111°C (a) and 60°C (b).

To explore whether the same catalysts are also active for the addition of an amine N–H bond to a CC double bond, the cyclisation of **1** was tested. However, when the reaction was performed at the reflux temperature of the solvent (toluene, 111°C), a brown oil formed, whereas the desired product was not found. Upon lowering the temperature to 60°C, the reaction proceeded smoothly with $[Pd(Triphos)](CF_3SO_3)_2$ as catalyst, but was much slower than the cyclisation of **2**. To compensate for the longer reaction time, a lower substrate to catalyst ratio (20) was used. Upon addition of CF_3SO_3H to the catalytic mixture, the initial rate of reaction increased sharply from 4.0 h^{-1} for the parent catalyst to 17, 39 and 65 h^{-1} upon addition of 1, 5 and 10 equiv. of acid (Fig. 2b). The latter corresponds to an increase in the rate by a factor of 16. Thus, while the cyclisation of **1** with $[Pd(Triphos)](CF_3SO_3)_2$ is slower than that of **2**, the effect of addition of acid is much stronger.

The complexes based on the other late transition metals were also active for the cyclisation of **1**. The salt $Zn(CF_3SO_3)_2$ and the complex $[Rh(NOR)_2]ClO_4$ showed catalytic activity (2.6 and 3.3 h^{-1}, respectively) similar to $[Pd(Triphos)](CF_3SO_3)_2$, whereas $[Cu(CH_3CN)_4]PF_6$ showed a lower activity (0.7 h^{-1}). Thus, the order in intrinsic activity of the four catalysts is different for the cyclisation of **1** (Pd≈Rh≈Zn>Cu) and **2** (Pd>Zn≈Cu>Rh). Upon addition of acid to the catalytic mixtures, the rate of cyclisation of **1** increased considerably. For $[Cu(CH_3CN)_4]PF_6$, the increase (factor of 8 upon addition of 10 equiv. CF_3SO_3H) was similar to the increase observed for the cyclisation of **2**. For $Zn(CF_3SO_3)_2$, the initial reaction rate increased from 2.6 to 11 h^{-1} (factor of 4) and for $[Rh(NOR)_2]ClO_4$ from 3.3 to 18 h^{-1} (factor of 6), upon addition of 10 equiv. of CF_3SO_3H. In the presence of acid, the order in activity was approximately the same as without acid: for the cyclisation of **1** (Pd>Rh>Zn>Cu) and **2** (Pd>Cu>Zn>Rh). Thus, the addition of acid leads to higher reaction rates, but does not alter the relative activity of the four catalysts.

These results are in agreement with a report on the ruthenium catalysed addition of aniline to phenylacetylene (Eq. 3).[11] Rate enhancement was observed when small amounts of an acid were employed together with the catalyst $[Ru_3(CO)_{12}]$. Most effective were the strong acids HPF_6 and HBF_4, or their ammonium salts, whereas only a small rate enhancement was observed for HCl, probably due to the strong tendency of the Cl^- ion to coordinate to the metal centre. The maximum rate was obtained when a ratio of additive to ruthenium cluster of 2:1 was employed. Addition of more acid did not give higher rates for this reaction. The co-catalytic effect of Brønsted acids observed here also concur with corresponding reports on the palladium catalysed addition of amines to alkenes.[12–15]



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3. Discussion

Here, the potential role of metal ions and protons as the catalytically active species will be discussed. For the reaction sequence, as depicted in Fig. 3a, it is necessary that the reactant coordinates to the metal centre. Despite the preference for coordination at the amine end of the molecule, about 1% of the 6-aminohex-1-yne molecules are coordinated via the alkyne bond. In this respect, the complex formation constant K for coordination of alkynes to late transition metal centres[16] is about 100 times lower than for coordination of amines.[17] The interaction of the alkyne with the metal centre reduces the electron density in the π-system and allows the nucleophilic attack of the amine nitrogen atom at the secondary carbon atom of the CC triple bond.[18] The intermediate 2-ammonio alkenyl complex formed in this way requires a proton for the protolytic cleavage of the metal–carbon bond. The enamine **4** is released and isomerises in situ to **5**.

The protons are involved in three elementary steps, suggesting that Brønsted and Lewis acid sites may be necessary in an ideal catalyst.

(A) As the amine group in **2** is the strongest base in the reaction mixture, added acids will protonate it in situ to the ammonium salt which has a much lower tendency to coordinate to the metal centre. Thus, the probability of coordination of the alkyne group to the metal centre is increased in acidic reaction media.
(B) The protolytic cleavage of the metal–carbon bond in the intermediate 2-ammonio alkenyl complex is facilitated in acidic conditions. The 1,3-hydrogen shift from the ammonium group to the α-carbon atom could occur as suprafacial [1,3] sigmatropic rearrangement, however, is orbital-forbidden.[19] A recent theoretical study confirms that an intermolecular proton transfer is more likely.[20] In this case, an additional proton acceptor acts as proton shuttle.
(C) The isomerisation of **4** to **5** is accelerated in the presence of protons. If dissociation of **4** from the coordination sphere is slow, the lower transient concentration of **4** in acidic conditions would result in a higher overall rate of reaction. In this respect, it is known that enamines are coordinated more strongly to late transition metal centres than the corresponding imines.[21]

To explore which of the three possibilities contributes most to the co-catalytic effect of protons, the cyclisation of **2** was followed in situ with NMR spectroscopy. When using the catalyst $[Pd(Triphos)](CF_3SO_3)_2$, the ^{31}P chemical shift of the phosphane groups is a sensitive measure of the electronic density at the palladium centre. This allows one to observe even small changes in the coordination sphere of the metal. Surprisingly, the $^{31}P\{^1H\}$ NMR spectra taken during the cyclisation of **2** showed only two signals. These can be assigned to the two distinct phosphane groups of one palladium complex, which is the predominant (≥98%) metal species in the catalytic mixture. The high concentration of this species suggests that the subsequent step in the catalytic cycle could be rate limiting. To identify the species, heptyne and triethylamine were added in stoichiometric amounts to a solution of

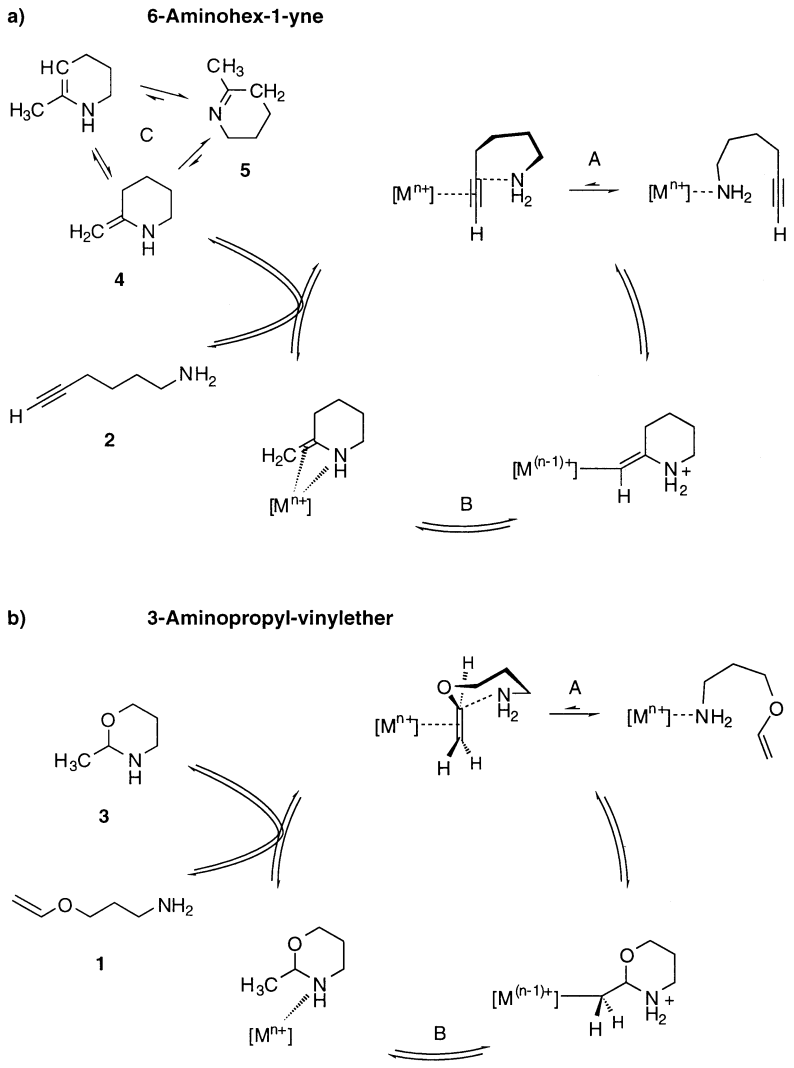
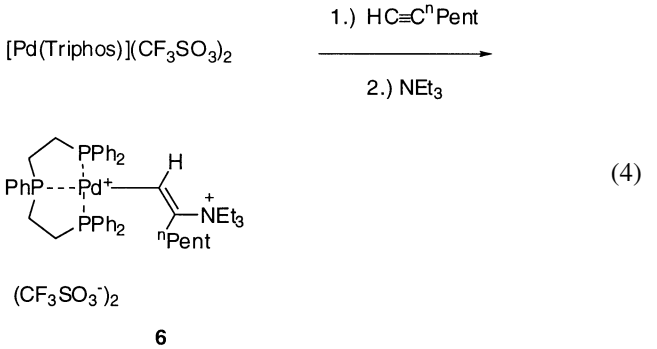


Figure 3. Mechanism proposed for the cyclisation of (a) 6-aminohex-1-yne and (b) 3-aminopropyl-vinylether.

$[Pd(Triphos)](CF_3SO_3)_2$ forming the 2-ammonio alkenyl complex **6** (Eq. 4). For this mixture, the ^{31}P chemical shift of the two different phosphane groups was identical to the shift in the catalytic mixture (Table 1). This indicates that the palladium is in a very similar chemical environment. It is concluded that the predominant metal species in the catalytic mixture is complex **7** and that cleavage of the palladium–carbon bond is rate limiting. As added protons have a very strong influence on the reaction rate, their main effect seems to be to accelerate step B.



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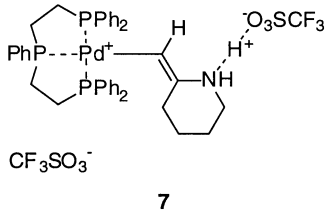

For the cyclisation of **1**, a similar mechanism to that for **2** seems likely (Fig. 3b). However, for the addition of amine N–H bonds to alkenes, no subsequent isomerisation of the

Table 1. Chemical shift of the phosphane groups in the palladium complexes observed during the in situ NMR experiments

Complex	$^{31}P\{^1H\}$ signals observed (ppm)[a]	
	PPh group	PPh_2 groups
$[Pd(Triphos)](CF_3SO_3)_2$	116.4	52.2
6[b]	102.6	45.1
7	102.8	45.2

[a] Relative intensity: PPh group/PPh_2 groups=1:2.
[b] ca. 91% **6**, remainder $[Pd(Triphos)](CF_3SO_3)_2$ and $[Pd(Triphos)(NEt_3)](CF_3SO_3)_2$.

product occurs. Thus, the protons can only be involved in steps A and B.

4. Conclusions

In summary, complexes of four different late transition metals (Rh, Pd, Cu, Zn) have been shown to be efficient catalysts for the intramolecular addition of N–H to CC double and triple bonds. In particular, the cyclisation of 3-aminopropyl-vinylether (**1**) and 6-aminohex-1-yne (**2**) was explored. For both reactions, the catalyst [Pd(Triphos)]$(CF_3SO_3)_2$ had a higher catalytic activity than $[Rh(NOR)_2]ClO_4$, $[Cu(CH_3CN)_4]PF_6$ or $Zn(CF_3SO_3)_2$. In each reaction, the addition of a Brønsted acid as co-catalyst dramatically increased the rate of reaction. Although different for the two substrates, the order in the intrinsic activity of the catalysts remained unchanged in acidic reaction conditions. The equal behaviour of the different catalytic systems indicates a similar reaction mechanism.

The common feature of the four metal catalysts is their Lewis acidity. Coordination of the CC π-bond to the metal centre enables nucleophilic attack by the amine. The resulting formal amphoteric ion rearranges to release the product. In the cyclisation of **2**, the intermediate 2-methylene-piperidine (**4**) isomerises subsequently to the final product 2-methyl-1,2-dehydropiperidine (**5**). The specific role of the Brønsted acid in the catalytic cycle is only partially understood at present. Three possibilities exist, i.e. (A) a higher probability of coordination of the CC double or triple bond group to the metal centre by reversible protonation of the amine group; (B) the promotion of the formal 1,3-proton shift which leads to cleavage of the metal–carbon bond in the intermediate 2-ammonio alkenyl complex; and (C) for the cyclisation of **2**: faster isomerisation of the enamine to the imine. In summary, the simultaneous presence of a Brønsted and Lewis acid seems necessary for a fast and efficient catalysis of hydroamination reactions with late transition metal compounds.

5. Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane with the solvent resonance as the internal standard.[22] Infrared spectra were obtained on a Perkin Elmer 1600 spectrometer. Mass spectroscopic analyses were performed on a Finnigan MAT 311A by Chemical Ionisation (CI). Elemental analyses were performed by the Microanalytical Laboratory of the Technische Universität München. Analytical gas chromatography was performed on a Hewlett–Packard HP 5890 gas chromatograph with a flame ionisation detector, using a crosslinked 5% diphenyl- 95% dimethyl-polysiloxane column (30 m, Restek GmbH, Rtx-5 Amine) and helium with a column head pressure of 69 kPa as carrier gas. All reactions were carried out under a nitrogen atmosphere using standard inert techniques. All commercially obtained reagents were used as received; toluene was purchased anhydrous from Aldrich. 6-Aminohex-1-yne and [Pd(Triphos)]$(CF_3SO_3)_2$ were prepared according to the published procedures.[5,23]

5.1. Kinetic studies

5.1.1. Cyclisation of 3-aminopropyl-vinylether (1). In a typical experiment, the catalyst (4.4×10^{-2} mmol) was weighed into a sample tube, dry toluene (15 cm^3) added, the mixture heated to 60°C and the catalytic reaction started by addition of 3-aminopropyl-vinylether (0.1 cm^3, 0.9 mmol). The acid CF_3SO_3H was added within of the first 2 min of the reaction. During the reaction, samples were taken for GC-analysis. Separation of **1**, **3** and toluene was achieved using the following temperature program: 4 min at 40°C, 15°C/min to 200°C, 5 min at 200°C; the retention times were 8.78 and 8.41 min for **1** and **3**, respectively. The substrate and the product concentrations were determined against an external standard. For the experiments, the following amounts of catalyst and acid were used: 21 mg $[Rh(NOR)_2]ClO_4$, 42 mg [Pd(triphos)]$(CF_3SO_3)_2$, 17 mg $[Cu(CH_3CN)_4PF_6$ or 16 mg $Zn(CF_3SO_3)_2$; 0, 3.9×10^{-3}, 1.9×10^{-2}, 3.9×10^{-2} cm^3 CF_3SO_3H (0, 4.4×10^{-2}, 2.2×10^{-1}, 4.4×10^{-1} mmol, respectively).

For characterisation of the product, the catalyst was removed by vacuum transfer, an excess of HCl (1 M solution in Et_2O) added and the volatiles removed in vacuo. The product was obtained as the hydrochloride **3**·HCl. Yield: 0.10 g, 85% white powder. Found: C, 43.7; H, 8.9; N, 9.8%. Calcd for $C_5H_{12}ClNO$: C, 43.6; H, 8.8; N, 10.2%. ^1H NMR (CD_3OD): δ 4.8 (s, 2H, NH_2), 4.4 (s, 1H, CH), 3.9 (s, 1H), 3.6 (s, 1H), 3.3 (s, 1H), 3.1 (s, 1H), 1.8 (s, 1H), 1.6 (s, 1H), 1.2 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_3OD): δ 85.7 (s, CH), 68.2 (s, CH_2O), 44.0 (s, CH_2N), 23.0 (s, CH_2), 19.6 (s, CH_3) ppm. *m/z* (FAB) 102 (M^+-Cl).

5.1.2. Cyclisation of 6-aminohex-1-yne (2). In a typical catalytic experiment, a mixture of 6-aminohex-1-yne (6.0×10^{-2} cm^3, 0.5 mmol), metal complex (5.3×

Table 2. Amounts of acid and base used in the cyclisation of **2**

Ratio, n(co-cat.)/$n(M^{n+})$	CF_3SO_3H		LiN^iPr_2 (1 M solution)	
	Volume (cm^3)	Amount (mmol)	Volume (cm^3)	Amount (mmol)
0	0	0	0	0
1	4.7×10^{-4}	5.3×10^{-3}	5.3×10^{-3}	5.3×10^{-3}
5	2.3×10^{-3}	2.1×10^{-2}	2.1×10^{-2}	2.1×10^{-2}
10	4.7×10^{-3}	5.3×10^{-2}	5.3×10^{-2}	5.3×10^{-2}
15	7.0×10^{-3}	8.0×10^{-2}	–	–
50	2.3×10^{-2}	2.1×10^{-1}	2.1×10^{-1}	2.1×10^{-1}
100	4.7×10^{-2}	5.3×10^{-1}	5.3×10^{-1}	5.3×10^{-1}

10^{-3} mmol) and dry toluene (15 cm^3) was heated at reflux temperature (111°C). The acid CF_3SO_3H or base LiN^iPr_2 was added within the first two minutes of the reaction (amount see Table 2). During the reaction, samples were taken for GC-analysis at regular intervals. Separation of **2**, **5** and toluene was achieved using the following temperature program: 10°C/min from 120 to 160°C, 3 min at 160°C; the retention times were 3.67 and 3.84 min for **2** and **5**, respectively. The substrate and the product concentrations were determined against an external standard. The kinetics was monitored over at least ten half-lives, for the more rapid reactions until quantitative conversion was achieved. The following amounts of catalyst were used: 2.4 mg $[Rh(NOR)_2]ClO_4$, 4.8 mg $[Pd(triphos)](CF_3SO_3)_2$, 2.0 mg $[Cu(CH_3CN)_4]PF_6$ or 1.9 mg $Zn(CF_3SO_3)_2$.

For characterisation of the product, the catalyst was removed by vacuum transfer, an excess of HCl (1 M solution in Et_2O) added and the volatiles removed in vacuo. The product was obtained as the hydrochloride **5**·HCl. Yield: 66 mg, 93% white powder. Found: C, 53.5; H, 9.1; N, 10.4%. Calcd for $C_6H_{12}ClN$: C, 53.9; H, 9.1; N, 10.5%. ^1H NMR (CD_3OD): δ 4.8 (s, 1H, NH^+), 3.64 (s, 2H, CH_2–N), 2.83 (t, 2H, CH_2–C═N), 2.39 (s, 3H, CH_3), 1.89 (m, 2H, CH_2–C–C═N), 1.85 (m, 2H, CH_2–C–N) ppm. $^{13}C\{^1H\}$ NMR (CD_3OD): δ 191.8 (s, C2), 45.7 (s, C6), 32.1 (s, C3), 24.9 (s, CH_3), 20.2 (s, C5), 17.9 (s, C4) ppm. IR: 2960 (s), 2876 (s), 1696 (vs), 1637 (s), 1450 (s), 1026 (s) cm^{-1}. *m/z* (FAB) 98 (M^+-Cl).

Compound **5** was obtained by addition of K_2CO_3 to a methanolic solution of **5**·HCl (0.24 g, 1.8 mmol). The mixture was stirred overnight and the solid removed by filtration. The methanol was removed at normal pressure and the product distilled in a partial vacuum (22 mmHg, 58–60°C). Yield: 0.16 g, 91% colourless liquid. ^1H NMR (CD_3OD): δ 3.45 (m, 2H, CH_2N), 3.31 (m, 2H, CCH_2), 2.02 (s, 3H, CH_3), 1.66 (br, 2H, CH_2), 1.58 (br, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (CD_3OD): δ 172.3 (s, C═N), 58.3 (s, NCH_2), 30.4 (s, CH_2CN), 22.4 (s, CH_3), 20.5 (s, CH_2), 18.4 (s, CH_2) ppm. IR: 3378 (s), 2927 (s), 2856 (vs), 1666 (s), 1637 (s), 1444, 1037 (s) cm^{-1}. *m/z* (CI) 97 (M^+).

5.2. In situ NMR experiments

(a) The complex $[Pd(triphos)](CF_3SO_3)_2$ (5.2 mg, 5.5×10^{-3} mmol) was dissolved in $CDCl_3$ (0.5 cm^3), 6-aminohex-1-yne (6.3×10^{-2} cm^3, 5.5×10^{-1} mmol) in $CDCl_3$ (0.1 cm^3) added and a ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectrum taken. ^1H NMR ($CDCl_3$): δ 2.73 (t, 2H, **2**, CH_2–N), 2.21 (dt, 2H, **2**, CH_2–C≡C), 1.96 (t, 1H, **2**, HC≡C), 2.32 (s, 2H, **2**, NH_2), 1.58 (q, 4H, **2**, CH_2–CH_2), small signals due to **4**, **5** and **7**. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 84.6 (s, **2**, C2), 68.8 (s, **2**, C1), 41.7 (s, **2**, C6), 32.6 (s, **2**, C5), 26.1 (s, **2**, C4), 18.5 (s, **2**, C3), small signals due to **4**, **5** and **7**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 102.8 (t, $J(^{31}P, ^{31}P)$=17 Hz, 1P, PPh), 45.2 (d, $J(^{31}P, ^{31}P)$=17 Hz, 1P, PPh_2).

(b) The complex $[Pd(triphos)](CF_3SO_3)_2$ (5.2 mg, 5.5×10^{-3} mmol) was dissolved in $CDCl_3$ (1 cm^3), hept-1-yne (7.3×10^{-4} cm^3, 5.5×10^{-3} mmol), triethylamine (7.7×10^{-4} cm^3, 5.5×10^{-3} mmol) added and a ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectrum taken. ^1H NMR ($CDCl_3$): δ 7.94–7.85 (m, 9H, Ph), 7.46–7.36 (m, 16H, Ph), 3.28 (m, 4H, PCH_2), 3.11 (q, $J(^1H, ^1H)$=7.2 Hz, 6H, NCH_2), 2.20 (m, 4H, PCH_2), 2.10 (m, 2H, CH_2), 1.94 (s, 1H, CH), 1.31 (t, $J(^1H, ^1H)$=7.5 Hz, 9H, NCH_3), 1.11 (m, 4H, CH_2), 0.81 (q, $J(^1H, ^1H)$=7.7 Hz, 2H, CH_2), 0.67 (t, $J(^1H, ^1H)$=7.1 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 132.2–129.5 (mm, Ph), 47.2 (s, NCH_2), 31.4 (s, CH_2), 30.0 (s, CH_2), 22.7 (s, CH_2), 21.7 (s, CH_2), 14.4 (s, CH_3), 9.1 (s, NCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 102.6 (t, $J(^{31}P, ^{31}P)$=15 Hz, 1P, PPh), 45.1 (d, $J(^{31}P, ^{31}P)$=15 Hz, 2P, PPh_2).

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References

1. Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675.
2. Taube, R. In *Applied Homogenous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, 1996; pp 507.
3. Roundhill, D. M. *Chem. Rev.* **1992**, *92*, 1.
4. Müller, T. E.; Grosche, M.; Herdtweck, E.; Pleier, A.-K.; Walter, E.; Yan, Y.-K. *Organometallics* **2000**, *19*, 170.
5. Dorta, R.; Egli, P.; Zürcher, F.; Togni, A. *J. Am. Chem. Soc.* **1997**, *119*, 10857.
6. Beller, M.; Trauthwein, H.; Eichberger, M.; Breindl, C.; Herwig, J.; Müller, T. E.; Thiel, O. R. *Chem. Eur. J.* **1999**, *5*, 1306.
7. Beller, M.; Trauthwein, H.; Eichberger, M.; Breindl, C.; Müller, T. E. *Eur. J. Inorg. Chem.* **1999**, 1121.
8. Penzien, J.; Müller, T. E.; Lercher, J. A. *J. Chem. Soc., Chem. Commun.* **2000**, *18*, 1753.
9. Baig, T.; Jenck, J.; Kalck, P. *J. Chem. Soc., Chem. Commun.* **1992**, 1552.
10. Vogels, C. M.; Hayes, P. G.; Shaver, M. P.; Westcott, S. A. *J. Chem. Soc., Chem. Commun.* **2000**, 51.
11. Tokunaga, M.; Eckert, M.; Wakatsuki, Y. *Angew. Chem. Int. Ed.* **1999**, *38*, 3222.
12. Pugin, B.; Venanzi, L. M. *J. Organomet. Chem.* **1981**, *214*, 125.
13. Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 9546.
14. Seligson, A. L.; Trogler, W. C. *Organometallics* **1993**, *12*, 744.
15. Kiji, J.; Nishimura, S.; Yoshikawa, S.; Sasakawa, E.; Furukawa, J. *Bull. Chem. Soc. Jpn* **1974**, *47*, 2523.
16. Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163.
17. Högfeldt, E. *Stability Constants of Metal–Ion Complexes, Part A: Inorganic Ligands*; *IUPAC Chemical Data Series, No. 21*, Pergamon: Oxford, 1982.
18. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, 1987, 7.4, p 409.
19. Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: Chichester, 1976 p 99.

20. Senn, H. M.; Blöchl, P. E.; Togni, A. *J. Am. Chem. Soc.* **2000**, *122*, 4098.
21. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, 1987, 3.2d, p 64.
22. Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512.
23. Müller, T. E.; Pleier, A.-K. *J. Chem. Soc., Dalton Trans.* **1998**, *4*, 583.