Developing Transition-Metal Catalysts for the Intramolecular Hydroamination of Alkynes

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Group 7−12 transition-metal complexes serve as effective catalysts for the regioselective intramolecular hydroamination of aminoalkynes having the general formula $RC{\equiv}C(CH_2)_n$-NH_2 ($n = 3$, R = H, Ph; $n = 4$, R = H) and of 2-(phenylethynyl)aniline. Primary products are pyrrolidines and piperidines bearing an α-alkylidene functionality and 2-phenylindole, respectively. Isomerization yields the corresponding pyrrolines and 1,2-dehydropiperidines. The catalytic properties of the transition-metal complexes depend on the appropriate choice of ligand, solvent, temperature, and counteranion. Principles for identifying the most active transition-metal catalysts for the hydroamination of alkynes and for optimizing the reaction conditions are developed. The X-ray crystal structure of one catalyst, [PdCl(triphos)](CF_3-SO_3), has been determined.

Introduction

Despite the fundamental importance of C−N bond-forming steps in organic synthesis, their construction remains often challenging and there is considerable interest in new catalytic approaches.[1−9] In particular, the direct addition of an amine N−H bond across a carbon−carbon multiple bond remains a highly desirable reaction. To date, efforts to catalytically effect this transformation in an efficient and general sense have been only modestly successful.[1,10−13] Approaches that have been employed involve activation either of the amine or of the unsaturated carbon−carbon moiety. The amine can be activated by alkali-metal and alkaline-earth-metal bases to generate a highly nucleophilic amide species, which then undergoes addition to C=C bonds.[14−20] This approach affords modest yields and generally exhibits poor selectivity. Similarly, organometallic complexes of lanthanide,[21,22] actinide,[23] and early transition metals[24,25,84,85] activate the amine by converting it into the coordinated imide M=NR, enabling the insertion of carbon−carbon multiple bonds into the M−N bond. Facile intramolecular cyclization of aminoalkenes[26,27] and aminoalkynes[28,29] demonstrate the feasibility of this approach. One drawback is the sensitivity of most of these complexes toward traces of oxygen and water. In contrast, group 7−12 transition metals employed stoichiometrically are known to activate the unsaturated moiety via complexation, rendering it susceptible to attack by amine nucleophiles.[13] So far, catalytic systems based on these metals are limited to nickel, palladium, and gold, exhibiting short catalyst lifetimes and low turnover frequencies.[30−42,86−89]

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Scheme 1. Intramolecular Cyclization of Bifunctional Aminoalkynes

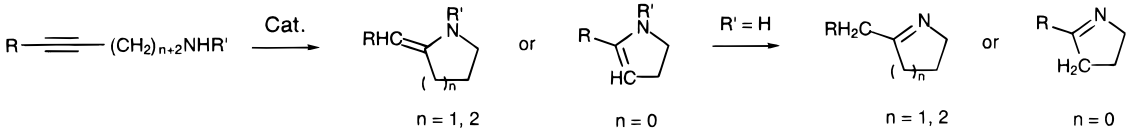
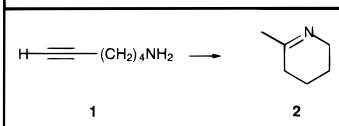
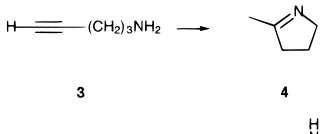
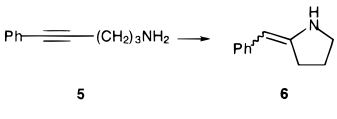
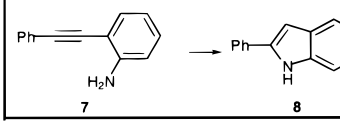


Table 1. Initial Rates *r* (Substrate Molecules per Metal Center per Hour) and Time until Quantitative Conversion (≥99%) for the Cyclization of *γ*- and *δ*-Aminoalkynes with Late Transition Metals (Ratio of Substrate to Catalyst (s/c) = 100)

Catalyst	$[Cu(CH_3CN)_4]PF_6$		$Zn(CF_3SO_3)_2$		$[Pd(triphos)](CF_3SO_3)_2$	
Solvent, Temperature	CH_3CN, 82°C		Toluene, 111°C		Toluene, 111°C	
Reaction	r / h^{-1}	t / h	r / h^{-1}	t / h	r / h^{-1}	t / h
 1 → 2	53.2(5)	8.7	34.2(5)	13	103(1)	12[a]
 3 → 4	211(13)	2.2	604(9)	0.75	≥1686(11)	0.3
 5 → 6	29.4(1.6)	16	55.4(2.2)	8.3	51.0(1.6)	9
 7 → 8	114(13)	4	151(22)	— [b]	117(16)	8.2[c]

[a] After 30 min the reaction rate decreases to about 65.1(5.4) h^{-1} and formation of some brown oil is observed. [b] 34% conversion obtained after 40 min; the catalytic activity is then lost. [c] After 2 h the reaction rate decreases to about 56.4(2.0) h^{-1}.

With the aim of finding new and highly active hydroamination catalysts which combine a long lifetime with high tolerance toward catalyst poisons, the basic principles for catalysis with group 7−12 transition metals were explored. The intramolecular addition of N−H bonds to alkynes was chosen for this study, as the ΔG value is more favorable than for similar reactions.[43−45] The addition generates an enamine with an endo- or exocyclic double bond (Scheme 1). If primary amines are used, a subsequent 1,3-hydrogen shift leads to isomerization of the initially formed enamine to the more stable imine. We have previously reported that all group 8−12 metals are able to catalyze the cyclization of 6-aminohex-1-yne.[46,47] An empirical rule was established that, depending on the metal, a d^8 or d^{10} electronic configuration of the metal is required. In the course of this paper principles for optimization of the catalyst and the reaction conditions are developed. Additionally, it will be demonstrated that Lewis acidic metal centers of rhenium also catalyze the hydroamination of alkynes.

Results and Discussion

A. Catalyst Performance. The transition-metal complexes $[Cu(CH_3CN)_4]PF_6$, $Zn(CF_3SO_3)_2$, and $[Pd(triphos)](CF_3SO_3)_2$ were chosen for a more detailed study on their catalytic properties and applied to a number of representative substrates. In particular, the cyclization of aminoalkynes having the general formula $RC{\equiv}C(CH_2)_nNH_2$ (n = 3, R = H, Ph; n = 4, R = H) and of 2-(phenylethynyl)aniline was studied. As can be seen from the results compiled in Table 1, the catalysis applies to the cyclization of these aminoalkynes to form nitrogen heterocycles. For the closely related substrates 6-aminohex-1-yne (**1**) and 5-aminopent-1-yne (**3**) the formation of the five-membered ring in 2-methyl-1-pyrroline (**4**) is 4−18 times faster than the formation of

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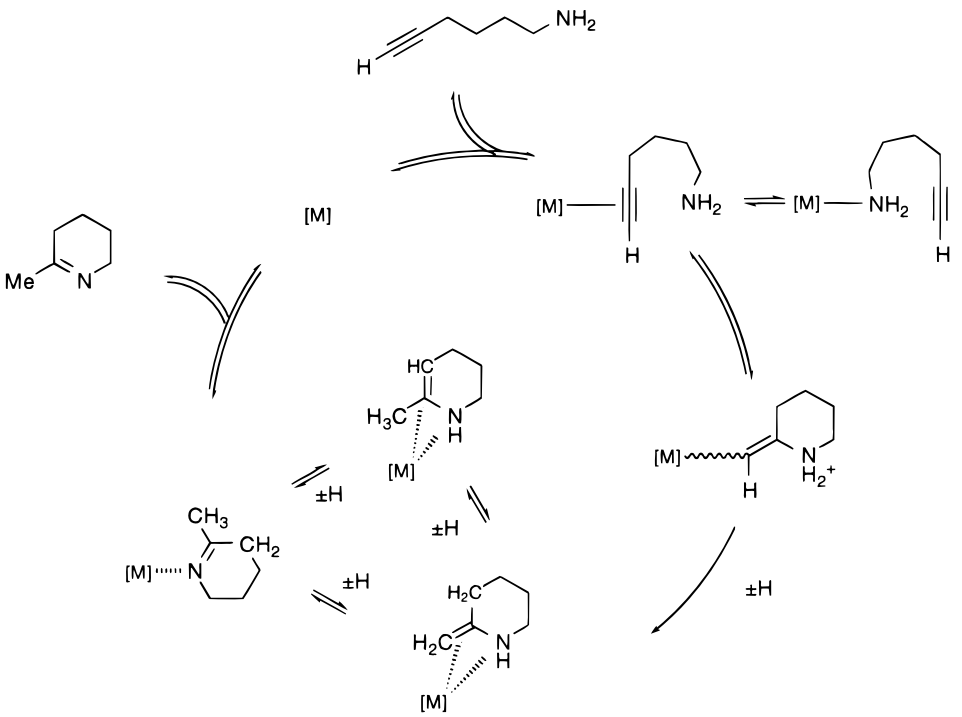
Scheme 2. Mechanism Proposed for the Cyclization of Aminoalkynes by Group 7−12 Transition-Metal Catalysts[a]



[a] Formal [1,3]-hydrogen shifts are indicated by ±H.

the corresponding six-membered ring in 2-methyl-1,2-dehydropiperidine (**2**). Substitution of the alkyne proton by a phenyl group in 5-amino-1-phenylpent-1-yne (**5**) lowers the rate of cyclization by 1 order of magnitude in comparison to **3**, which is probably caused by steric hindrance in the transition state. In contrast, the formation of 2-phenylindole (**8**) from 2-(phenylethynyl)-aniline (**7**) is faster than the cyclization of **5**, which can be explained by the high stability of the 10-π-electron system formed, resulting in a more negative ΔG value, which in turn contributes to a higher reaction rate. The ring closure seems dominated by steric factors, as the formation of the smaller ring is preferred (ring size 5 > 6 > 7).

Other palladium(II) complexes also catalyze the intramolecular addition of amines to alkynes. One example is the complex $[Pd(CH_3CN)_4](BF_4)_2$, which converts **3** into **4** within 3.5 h with 73% yield and **5** into **6** with 48% isolated yield (s/c = 40, THF, 90 °C). Using $[PdCl_2(PPh_3)_2]$ as catalyst compound **7** is converted into the indole **8** with 96% isolated yield (s/c = 20, DMAc, 90 °C).

The catalytic activities of the late-transition-metal catalysts described are comparable to the activity of catalysts based on organolanthanides. Marks et al. have used $[Cp'_2SmCH(SiMe_3)_2]$ ($Cp' = C_5Me_5$) as a precatalyst, which converts to the active catalyst $[Cp'_2SmNHR]$ in situ.[21,28,29] The turnover frequency determined for the conversion of **3** into **4** was 580 h^{-1} at 21 °C, and that for the transformation of **5** into **6** was 2830 h^{-1} at 60 °C. Turnover frequencies for the cyclization of six-membered rings, e.g. the conversion of 6-amino-1-phenylhex-1-yne to 2-benzyl-1,2-dehydropiperidine, are lower (4 h^{-1} at 21 °C and 328 h^{-1} at 60 °C). In a recent publication by Roesky et al. cyclization rates of 0.6 and 1.5 h^{-1} were given for the cyclization of **3** and **5**, respectively, with the yttrium complex $[(^iPr_2ATI)YN(SiMe_3)_2]$ ($^iPr_2ATI$ = *N*-isopropyl-2-(isopropylamino)-troponimine), the first lanthanide catalyst for hydroaminations not containing the cyclopentadienyl ligand.[24]

B. Mechanistic Reflections. The key step for the hydroamination of alkynes probably involves a nucleophilic attack of the nitrogen lone pair on a coordinated alkyne moiety.[13] A catalytic cycle based on this assumption is shown in Scheme 2.[47] In contrast to the mechanism based on oxidative addition of an amine to the metal center, which was suggested for catalysis with rhodium(I) and palladium(II),[48−50] this reaction sequence can explain hydroamination reactions catalyzed by zinc(II) and copper(I), as these metal ions have no oxidation state available for the donation of two electrons. The similar behavior of the catalysts studied indicates that for these metal centers the reaction proceeds according to the same mechanism. Recently, we have tested $[Re(CO)_5(H_2O)]BF_4$ for its catalytic properties toward cyclization of **1**. After 20 h of keeping the reaction mixture in toluene at reflux temperature, 37% of **1** was converted into **2**. This example extends the range of catalytically active metals and demonstrates that the Lewis acidity of the metal is an important factor for its catalytic activity toward hydroaminations.

The effectiveness of the catalysts for the cyclization of 2-(phenylethynyl)aniline provides evidence for the reaction pathway involving coordination of the C≡C bond to the metal. Without this coordination, it is

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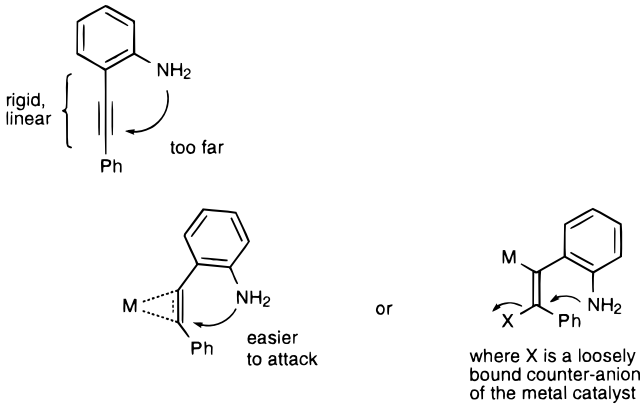
Scheme 3. Facile Cyclization of 2-(Phenylethynyl)aniline Indicating a Reaction Pathway Involving Coordination of the C≡C Bond to the Metal



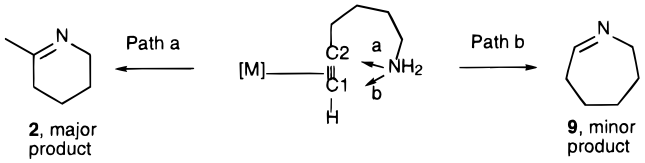
impossible for the amino group to attack the alkyne carbon bonded to the phenyl group, since the molecule is too rigid to bend around. Coordination of C≡C to a metal decreases the bond angles at the alkyne carbons, making it possible for the amino group to attack the alkyne carbon (Scheme 3).

With the aim of obtaining further insight into the mechanism, the triply deuterated substrate $DC{\equiv}C(CH_2)_4ND_2$ (d_3-**1**) was cyclized with various catalysts. For all catalysts employed (e.g., $[Pd(triphos)](BF_4)_2$, $[Cu(CH_3CN)_4]PF_6$, $AgBF_4$, $AuCl_3$, $Zn(CF_3SO_3)_2$) the product d_3-**2** had a random distribution of the three deuterium atoms over the methyl group and the methylene group at C3. Cyclizing **1** with $[Pd(triphos)](BF_4)_2$ in the deuterated solvent CH_3OD gives d_5-**2** with the methyl group and the methylene group at C3 being completely deuterated. In a further experiment **2** was heated in CH_3OD at reflux temperature for 20 h. The last experiment also gave d_5-**2** with complete deuteration at the methyl group and the C3 methylene group. The observations from the deuteration experiments can be explained by an equilibrium between the exo enamine, the endo enamine, and the imine as described in Scheme 2. Coordination of d_3-**2** to the metal center may accelerate the shift of the C=C double bond between the different positions.

Thorough analysis of the product distribution in the cyclization of **1** shows a side product **9** to be formed in quantities below 1%. The ^1H NMR data indicate **9** to be 1-azacycloheptene. The nature of the side product was confirmed by reduction of a typical product mixture with $NaBH_4$ to the corresponding amines 2-methylpiperidine (**10**) and 1-azacycloheptane (**11**). The compounds **10** and **11** were isolated as a mixture of their hydrochlorides and identified by comparison of their NMR spectra with those of authentic samples. Formation of **9** can be explained by an external nucleophilic attack of the nitrogen lone pair on the coordinated triple bond. In principle, this attack is possible at C2 (Scheme 4, path a) or C1 (path b). Reaction according to path a will give the six-membered ring in **2**, whereas path b accounts for the formation of the seven-membered ring in **9**. The steric strain of the linkage between the alkyne moiety and the nitrogen atom will favor an attack at C2 and explains the high regioselectivity of the reaction.

The formation of **2** as the main product from **1** is also expected according to the Markovnikoff rule. However,

Scheme 4. Explanation for the Formation of Side Product 9[a]



[a] Side Product **9** was identified by reduction to **11**. Attack of the nitrogen atom according to path a explains the formation of the six-membered ring in **2**, and that according to path b explains the seven-membered ring in **9**.

the rule cannot explain the conversion of the shorter homologues **3** and **5** to the five-membered heterocycles **4** and **6** with a similar regioselectivity. As the formal *anti*-Markovnikoff products, compounds **4** and **6** should be obtained as the minor products. Their formation as the predominant product (>98%) demonstrates that the intramolecular hydroamination is controlled by steric constraints imposed on the linkage and not by electronic factors.

C. Kinetic Studies. For all transformations described, with exception of those reactions where deactivation of the catalyst is specifically mentioned, the kinetic plots reveal an exponential decrease of aminoalkyne substrate concentration with reaction time over the whole substrate concentration range (3.5×10^{-2} mol dm^{-3} to 0). A more detailed kinetic study of the **1** → **2** transformation was undertaken for the catalyst $[Cu(CH_3CN)_4]PF_6$. The kinetic plots as shown in Figure 1 reveal a linear dependence of $\ln([\mathbf{1}]_t/[\mathbf{1}]_0)$ on time in the concentration range 1.8×10^{-4} to 3.5×10^{-2} mol dm^{-3} in compound **1**. When the initial concentration of compound **1** is held constant at 3.5×10^{-2} mol dm^{-3} and the concentration of the complex $[Cu(CH_3CN)_4]PF_6$ varied in the range 2.7×10^{-6} to 3.5×10^{-4} mol dm^{-3}, a double-logarithmic plot of rate r vs catalyst concentration indicates the reaction to be close to first order in the catalyst. The essentially first-order dependence of the catalytic rate on substrate and catalyst concentration translates into the empirical rate law

$$r = k[\mathbf{1}][[Cu(CH_3CN)_4]PF_6]$$

The rate constant derived from plot in Figure 1a for the **1** → **2** transformation at 82 °C is $k = 0.39$ dm^3 mol^{-1} s^{-1}. The rate law is consistent with nucleophilic attack of a coordinated alkyne by the amine followed by rate-determining protonation of the intermediate β-aminoethynyl complex at the carbon atom attached to the metal.

D. Preequilibrium. The nucleophilic attack of the alkyne requires its prior coordination to the metal center. However, the substrate can bind to the metal center either (a) via the alkyne moiety ($M-(\pi\text{-}HC{\equiv}C(CH_2)_4NH_2)$) or (b) via the amine lone pair ($M-(\sigma\text{-}NH_2(CH_2)_4C{\equiv}CH)$). While (a) is the active species, (b) constitutes a resting state for the catalyst limiting the concentration of the active species. The position of the equilibrium between the two species in the catalytic mixture can be estimated by considering the corresponding stability constant of the silver amine complexes $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$ (2.0×10^3 and $6.9 \times$

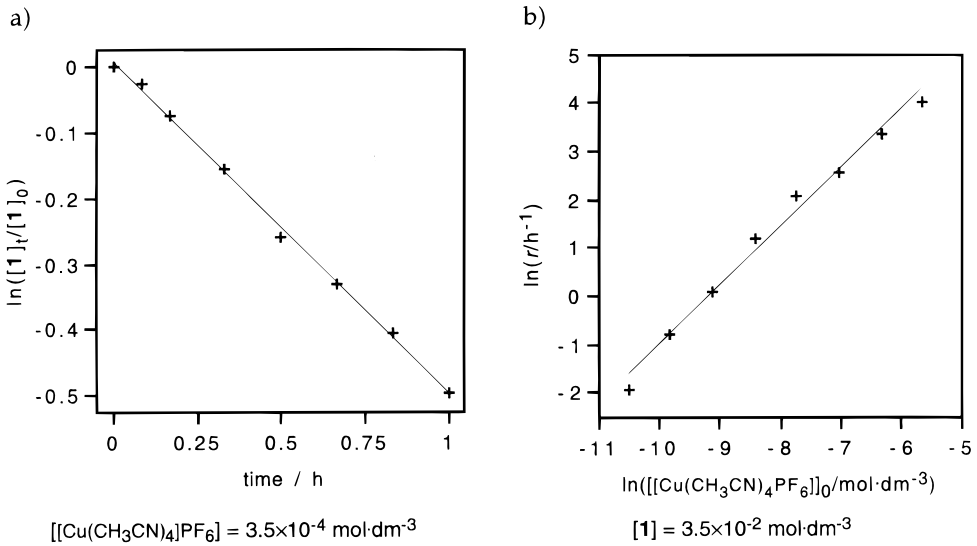


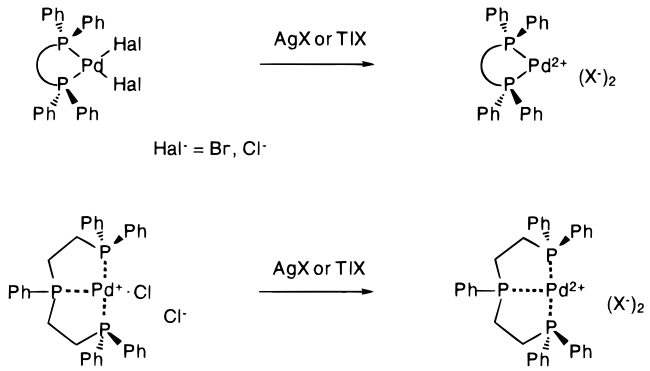
Figure 1. Determination of reaction order in (a) the substrate concentration and (b) the catalyst concentration for the cyclization of **1** → **2**. The straight lines fitted are (a) $\ln([\mathbf{1}]_t/[\mathbf{1}]_0) = -0.49(1) \times$ time/h, $R^2 = 0.998$, and (b) $\ln(r/h^{-1}) = 1.2(1) \times \ln([[Cu(CH_3CN)_4]PF_6]_0/\text{mol dm}^{-3}) - 11(1)$, $R^2 = 0.988$.

10^3 dm^3 mol^{-1} in H_2O)[51] in comparison to the stability constant of $Ag(C_2H_2)^+$ (42.7 dm^3 mol^{-1} in H_2O, 25 °C).[52] The latter is 2−3 orders of magnitude lower, although the formation of the alkyne complex is energetically favorable at ambient temperatures ($\Delta H = -55.2$ kJ mol^{-1} and $\Delta S = -154$ J mol^{-1} K^{-1}). As the stability of neither complex is exceptionally high, the two complexes Ag^+−(σ-$NH_2(CH_2)_4C{\equiv}CH$) and Ag^+−(π-$HC{\equiv}C(CH_2)_4NH_2$) and the free silver cation will be present in the reaction mixture with the σ-amino complex having the highest concentration. The preference to form σ-amino complexes is probably similar for most late-transition-metal centers; however, data which allow us to compare the relative stabilities of σ-amino and π-alkyne complexes are rare. Stabilizing the metal−alkyne complex relative to the metal−amine complex will be one way of optimizing the activity of transition-metal catalysts for the hydroamination of alkynes.

E. Effects of Anions in the Catalytic Cyclization of 1. Palladium catalysts containing at least one weak donor ligand were chosen for a more detailed study because the extensive coordination chemistry of palladium allows tuning of the catalytic properties of the metal center. The weakly complexed palladium salt $[Pd(CH_3CN)_4](BF_4)_2$ is a catalyst with high activity for the hydroamination of alkynes. However, during catalysis the complex tends to decompose when the temperature is raised to accelerate the reaction. The palladium can be stabilized in solution by appropriate addition of phosphine ligands. To study in detail the influence of ligand and anion on the stability and catalytic properties,[53] a number of different palladium complexes [Pd(phosphine)]X_2 with bi- and tridentate phosphines were synthesized.

Synthesis and Characterization of Palladium Catalysts. The palladium complexes [Pd(phosphine)]X_2, with the exception of the corresponding acetate salts, were prepared from the respective halide precursor by halide abstraction with the appropriate silver or thallium salts (Scheme 5). With $TlCF_3SO_3$ and Ag_2CO_3 only one halide was removed from the palladium and complexes with two different anions were isolated. To study the steric requirements of the triphos ligand, an X-ray analysis of the complex $[PdCl(triphos)](CF_3SO_3)$ was performed. Suitable crystals were grown by slow diffusion of *n*-pentane into a solution of the complex in dichloromethane. A perspective view of the complex, which has approximate C_s symmetry but no crystallographic symmetry, is shown in Figure 2. The metal is coordinated by three phosphorus atoms and the chlorine atom in a square-planar fashion. The palladium−phosphorus and palladium−chlorine distances are Pd−P1 = 2.211(1), Pd−P2 = 2.332(1), Pd−P3 = 2.314(1), and Pd−Cl = 2.341(1) Å (Table 2). These distances are within the range of those in 12 similar palladium complexes with a square-planar $Pd^{II}(ClP_3)$ coordination geometry (average Pd−Cl = 2.36(1) Å).[54] The bond

Scheme 5. Preparation of Palladium Catalysts with Various Anions X = $CH_3C_6H_4SO_3^-$, $CF_3SO_3^-$, CF_3COO^-, and BF_4^- [a]



[a] The bidentate phosphine used is 1,1′-bis(diphenylphosphino)ferrocene (dppf).

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(54) Cambridge Structural Database 1999, 197481 entries. Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187.

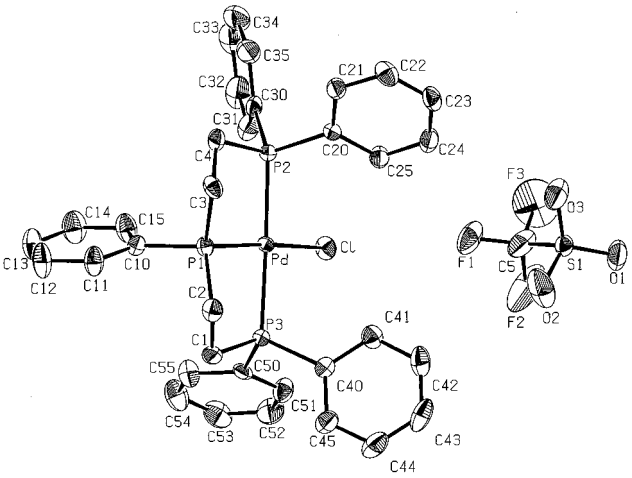

Figure 2. Molecular structure of the complex [PdCl(triphos)](CF_3SO_3).

Table 2. Selected Bond Lengths (Å) and Angles (deg)

Pd−P1	2.211(1)	Pd−P2	2.332(1)
Pd−P3	2.314(1)	Pd−Cl	2.341(1)
P1−C1	1.822(6)	P2−C3	1.820(6)
P2−C4	1.849(6)	P3−C2	1.848(6)
C1−C2	1.530(8)	C3−C4	1.520(8)
P1−C10	1.816(5)	P2−C20	1.817(5)
P3−C40	1.812(5)		
Cl−Pd−P2	99.3(1)	Cl−Pd−P3	92.4(1)
P1−Pd −P2	84.8(1)	P1−Pd−P3	84.0(1)
P2−Pd−P3	165.9(1)	Pd−P1−C1	108.5(2)
Pd−P1−C3	109.0(2)	C1−P1−C3	114.3(3)
Pd−P2−C4	106.3(2)	Pd−P3−C2	108.3(2)
P1−C1−C2	106.8(4)	P1−C3−C4	106.8(4)
P3−C2−C4	106.8(4)	C2−P3−C50	109.4(3)
Pd−P1−C10	112.0(2)	Pd−P3−C50	114.8(2)
Cl−Pd−P1	175.0(1)		

lengths from palladium to P2 and P3 which are opposite to each other are significantly longer than Pd−P1, clearly demonstrating the stronger *trans* influence of phosphorus relative to chlorine.[55] Two ethylene bridges connect P1 with P2 and P3, respectively, to form two five-membered metallacycles. The angles P1−Pd−P2 (84.89(5)°) and P1−Pd−P3 (83.98(5)°) are significantly smaller than 90°, indicating steric strain to be present in the metallacycles. The angles Cl−Pd−P2 (99.34(5)°) and Cl−Pd−P3 (92.39(5)°) are consequently larger than 90°.

Both metallacycles have a nearly perfect envelope configuration. The carbon atoms C1 and C3 which make up the flaps are oriented *cis* to each other and *trans* to the phenyl group at P1. The two planes constituting the bodies of the envelopes are flat within 2σ. The carbon atoms C1 and C3 have distances of 0.73(1) and 0.70(1) Å from the respective planes consisting of C2/P3/Pd/P1 and C4/P2/Pd/P1. The overall geometry of the complex is determined by the coordination of three different ligands (Cl, PPh, 2 PPh_2) to the palladium and the steric requirement of the phenyl group.

Two sharp signals in the $^{31}P\{^1H\}$ NMR spectra of the complexes [Pd(triphos)]X_2 can be assigned to P1 and P2/P3 due to their ratio 1:2 and show that the PPh_2 groups of the triphos ligand remain attached to the palladium center on the ^{31}P NMR time scale. The different relationship to the phenyl ring on P1 renders the four hydrogen atoms on each ethylene bridge inequivalent, which is also maintained in solution, as can be seen by ^1H NMR spectroscopy (Table 3). Similar ^1H NMR spectra were obtained for all related palladium complexes [Pd(triphos)]X_2 (X = $CH_3C_6H_4SO_3^-$, $CF_3SO_3^-$, CF_3COO^-, BF_4^-, Ac^-, Cl^-) and [PdCl(triphos)]X (X = $CF_3SO_3^-$, 0.5 CO_3^{2-}). A septet in the range 3.31−4.08 ppm (H_a) and a doublet of doublets ($H_{a'}$) can be assigned to the protons attached to C1 and C3. A quintet at 2.65−2.90 ppm and a triplet at ca. 2.2 ppm can be assigned to the protons attached to C2 and C4.

Table 3. ^1H NMR Data for the Methylene Protons in the Complexes [Pd(triphos)]X_2 (X = $CH_3C_6H_4SO_3^-$, $CF_3SO_3^-$, CF_3COO^-, BF_4^-, Ac^-, Cl^-) and [PdCl(triphos)]X (X = Tf^-, 0.5 CO_3^{2-}) in $CDCl_3$[a]

complex	$\delta(H_a)$	$\delta(H_{a'})$	^2J, ^3J	$\delta(H_b)$	$\delta(H_{b'})$
[Pd(triphos)](CF_3SO_3)$_2$	3.37	3.11	55, 15	3.00	2.25
[Pd(triphos)]($CH_3C_6H_4SO_3$)$_2$	3.70	3.14	55, 15	2.90	2.15
[Pd(triphos)](CF_3CO_2)$_2$	3.60	3.12	58, 12	2.75	2.17
[Pd(triphos)](BF_4)$_2$[b]	(3.11)	(3.38)	54, 15	(3.02)	(2.44)
[Pd(triphos)](CH_3CO_2)$_2$	4.08	3.13	58, 15	2.75	2.22
[PdCl(triphos)]Cl	3.87	3.14	58, 12	2.75	2.23
[PdCl(triphos)]CF_3SO_3	3.45	3.13	57, 14	2.57	2.16
[PdCl(triphos)]$_2CO_3$	3.96	3.06	57, 13	2.68	2.15

[a] Conditions and definitions: in CD_3CN solution, δ in ppm, J in Hz, $^2J = {}^2J(^1H_{a'},^{31}P)$, $^3J = {}^3J(^1H_{a'},^{31}P)$.

The chemical shift of H_a varies over a rather large range (3.31−4.08 ppm), which can be related to the coordination properties of the anion. Weakly coordinating anions such as $CF_3SO_3^-$ lead to a shift of $\delta(H_a)$ toward high field (3.31 ppm), whereas the strongly coordinating chloride leads to a downfield shift of $\delta(H_a)$ (4.03 ppm). In the solid state no interaction between the complex cation $[PdCl(triphos)]^+$ and the second anion was observed in [PdCl(triphos)]CF_3SO_3 or [PdCl(triphos)]Cl.[56] For the related complexes [PdX(PR_3)$_3$]X ($X^- = Cl^-$, Br^-), the distances d(Pd···X) indicate cation−anion contacts (Table 4). For these complexes the most striking feature is the large difference between the two Pd−Hal bond lengths. The best description for their geometry is therefore as a tight ion pair between a four-coordinate $[PdX(PR_3)_3]^+$ fragment and the second halide.

Effect of the Anion on the Cyclization of 1 with Palladium Catalysts. To investigate the anion effects systematically, the complexes [Pd(triphos)]X_2 and [PdCl(triphos)]X synthesized with various combinations of anions were employed for the catalytic cyclization of **1**. The rate was determined at 25 °C, anticipating that the complexes with the highest activity at 25 °C are also the most active at higher temperatures. The highest rates for the series [Pd(triphos)]X_2 were measured for the anions $CH_3C_6H_4SO_3^-$ with 0.57(1) h^{-1} and $CF_3SO_3^-$ with 0.55(1) h^{-1} (Figure 3a). For the anions CF_3COO^- and BF_4^- cyclization rates are less than half of the former (0.25(1) and 0.19(1) h^{-1}, respectively). The presence of chloride is unfavorable for the catalytic activity, as can be seen for the complexes [PdCl(triphos)]X with the anions X = $CF_3SO_3^-$ and 0.5 CO_3^{2-} (0.22(1) and 0.12(1) h^{-1}, respectively). Even lower rates are observed for [Pd(triphos)](CH_3COO^-)$_2$ (0.076(1) h^{-1}) and [PdCl(triphos)]Cl (0.065(1) h^{-1}).

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Table 4. Distances d(M−Hal) and Angles ∠(Hal_{basal}−M−Hal_{apical}) for the Complexes $[PdX(PR_3)_3]X$ ($X^- = Hal^-$)[a]

complex	d(M−Hal_{basal}) /Å	d(M−Hal_{apical}) /Å	∠(Hal_{basal}−M− Hal_{apical})/deg	ref
$[PdCl(triphos)]CF_3SO_3$	2.341(1)			this paper
[PdCl(triphos)]Cl	2.355(2)			56
$[PdCl(PMe_2Ph)]Cl{\cdot}CH_2Cl_2$	2.434(3)	2.956(3)	96.3	79
$[PdBr(PPhC_8H_8)_3]Br{\cdot}C_3H_6O$	2.529	3.017	99.2	80
$[PdBr(PPhC_8H_8)_3]Br$	2.544	2.923	104.8	80
$[PdBr(PEtC_{13}H_9)_3]Br{\cdot}C_6H_5Cl$	2.555(5)	2.936(4)	103.4	81

[a] Definitions: $PEtC_{13}H_9$ = 5-ethyl-5*H*-dibenzophosphole, $PPhC_8H_8$ = 2-phenylisophosphindoline.

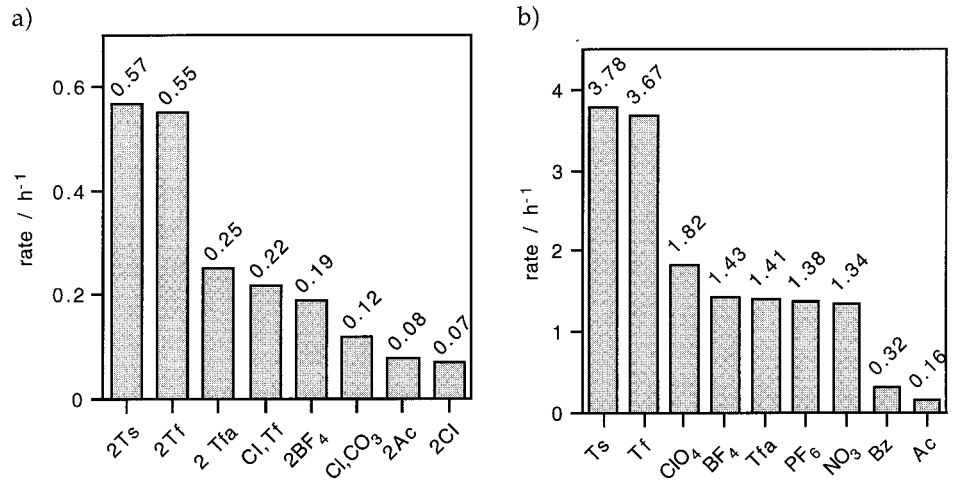

Figure 3. Rates observed for the cyclization of **1** using (a) the palladium catalysts $[Pd(triphos)]X_2$ and [PdCl(triphos)]X (solvent CH_2Cl_2, temperature 25 °C) and (b) silver salts AgX (solvent CH_3CN, temperature 25 °C) with X = $CH_3C_6H_4SO_3^-$ (Ts^-), $CF_3SO_3^-$ (Tf^-), CF_3COO^- (Tfa^-), BF_4^-, 0.5 CO_3^{2-}, CH_3COO^- (Ac^-), ClO_4^-, PF_6^-, NO_3^-, $C_6H_5COO^-$ (Bz^-).

Effect of Anions on the Cyclization of 1 with Other Metal Catalysts. To establish if the trends described are generally valid, various silver salts were employed in acetonitrile. The activity observed varied by more than 1 order of magnitude from 0.16(1) h^{-1} for $AgCH_3COO$ to 3.78(6) h^{-1} for $AgCH_3C_6H_4SO_3$. As can be seen from Figure 3b, the anions can be classified into three groups. The highest rates are observed when derivatives of the sulfonic acid are used ($CH_3C_6H_4SO_3^-$, 3.78(6) h^{-1}; $CF_3SO_3^-$, 3.67(10) h^{-1}). Medium rates are observed for the anions ClO_4^-, BF_4^-, CF_3COO^-, PF_6^- and NO_3^- (1.82(3), 1.43(2), 1.41(2), 1.38(2), and 1.34(1) h^{-1}, respectively), whereas very low rates are observed for the anions $C_6H_5COO^-$ and CH_3COO^- (0.32(1) and 0.16(1) h^{-1}, respectively). These trends are equivalent to those observed for palladium complexes.

A strong influence of the anion on the catalytic activity was also observed for group 12 metal salts. When the salts $HgCl_2$, $Hg(NO_3)_2{\cdot}H_2O$, $Hg(ClO_4)_2{\cdot}3H_2O$, and $Hg(CF_3SO_3)_2$ were employed as catalysts (1 mol %) in CH_3CN at reflux temperature, **1** was quantitatively converted into **3** within 20 h. In contrast, only 4% conversion was observed with $Hg(CH_3CO_2)_2$. With the catalyst $HgBr_2$ 50% of **1** is converted to **3**, with the remaining 50% of **1** being transformed to a different product which could not yet be identified. Using $Cd(NO_3)_2{\cdot}4H_2O$ as catalyst, full conversion of **1** to **2** was achieved, whereas with the salt $Cd(CO_3)_2$ only traces of **2** were obtained. Employing $Zn(CF_3SO_3)_2$ as catalyst in toluene gives full conversion of **1**. In CH_3CN no conversion is observed at 82 °C, whereas 50% conversion is achieved at 150 °C. In contrast, using $Zn(CH_3CO_2)_2{\cdot}2H_2O$ in CH_3CN 10% conversion is obtained after keeping the catalytic mixture at reflux temperature for 20 h.

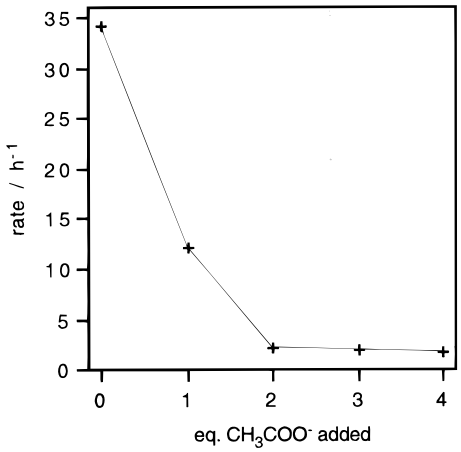

Figure 4. Effect of acetate ions added to $Zn(CF_3SO_3)_2$ on the catalytic activity for the cyclization of **1** (solvent toluene, temperature 111 °C).

The catalytic activity seems to be generally inhibited by acetate ions. This effect was studied in further detail for zinc(II). In a series of experiments 0, 1, 2, 3, and 4 equiv of tetrabutylammonium acetate was added to a suspension of the catalyst $Zn(CF_3SO_3)_2$ in refluxing toluene. The zinc salt dissolves as soon as the substrate is added. The initial rate of the catalysis measured for the parent catalyst (34.2(5) h^{-1}) drops to 12.1(8) h^{-1} when 1 equiv of acetate is added and to 2.3(1) h^{-1} when 2 equiv of acetate is added (Figure 4). Addition of more acetate gives an insignificant further decrease in catalytic activity of the zinc catalyst (2.0(1) for 3 equiv and 1.9(1) h^{-1} for 4 equiv). These experiments clearly

Table 5. pK_a Values of the Anions[82,83] and Their Partial Molal Volume ($\bar{V}$) in Water at 25 °C[60,61]

anion	abbrev	pK_a	$\bar{V}$
$CH_3C_6H_4SO_3^-$	Ts	1.7	120
$CF_3SO_3^-$	Tf	−4.7[a]	80.4
ClO_4^-		−2.1	48.6
BF_4^-			44.2
CF_3COO^-	Tfa	0.5	
PF_6^-			
NO_3^-		−1.4	29.0
Br^-		−9.0	24.7
Cl^-		−6.1	17.8
$C_6H_5COO^-$	Bz	4.19	
CH_3COO^-	Ac	4.75	40.5
CO_3^{2-}		10.25	

[a] Determined in CH_3COOH.

demonstrate that acetate has a negative effect on catalytic rates.

From these experiments the anions can be classified into four groups.

(i) Inhibition of the catalytic activity is observed when basic anions (pK_a above 4) such as CH_3COO^-, $C_6H_5COO^-$, and CO_3^{2-} are present (Table 5). One possible explanation is that bases inhibit the formal 1,3-hydrogen shifts described before in Mechanistic Reflections. As these 1,3-hydrogen shifts are orbital-forbidden, they are likely to occur as intermolecular reactions. Basic anions remove the proton from the catalytic cycle, and the activity of the corresponding metal salt will decrease. Inhibition by basic anions seems surprising, as the substrate itself contains a basic amino group with a pK_a comparable to that of *n*-hexylamine (pK_a = 10.6).[51] The strong influence of basic anions on the catalytic rates indicates the formation of close ion pairs which allow the anion to bind intermediate protons that occur with a short lifetime.

(ii) In the case of the complexes $[Pd(triphos)]^{2+}$ chloride ions are also unfavorable. The high σ-donor strength of chloride results in a strong coordination to the palladium center blocking the only available coordination site. However, the catalytic activity of the complexes with mixed anions X = Tf^- and 0.5 CO_3^{2-} is higher than for the complex [PdCl(triphos)]Cl. Thus, the second anion also seems important. This can be explained by the weaker ion pairing between large ions of low nucleophilicity which makes it easier for the substrate to approach the metal center.[57]

(iii) The third group of anions are the classic noncoordinating anions (ClO_4^-, BF_4^-, PF_6^-), which are all highly symmetrical species whose ability to coordinate to soft metals is extremely limited. As the substrate competes with the anions for coordination to the metal center, those anions which coordinate least should lead to the highest catalytic activities. However, neither the σ-donor strength which is often used as a guide to the ability of these anions to coordinate to a metal ($Cl^- \gg ClO_4^- > CF_3SO_3^- > BF_4^- > PF_6^-$)[58] nor the rates of acid aquation which have been reported for the replacement of weakly coordinating anions from their respective pentaamminecobalt(III) complexes ($ClO_4^- > CF_3SO_3^- \gg NO_3^- > Cl^- > CH_3COO^-$)[59] correlates with the catalytic activities observed ($CH_3C_6H_4SO_3^- > CF_3SO_3^- \gg ClO_4^- > BF_4^- \approx CF_3COO^- \approx PF_6^- \approx NO_3^- \gg C_6H_5COO^- > CH_3COO^- > Cl^-$). In contrast, when the anions are ordered according to their partial molal volume ($CH_3C_6H_4SO_3^- > CF_3SO_3^- \gg ClO_4^- > BF_4^- > NO_3^- > Cl^-$),[60,61] a good correlation with the catalytic activity of their respective metal salts is obtained. Apparently, large anions with low nucleophilicity are favorable.

(iv) The highest activities are observed for salts containing derivatives of the sulfonic acid as $CF_3SO_3^-$ and $CH_3C_6H_4SO_3^-$. As they combine a large volume ($\bar{V}$ = 80.4 and 120 $cm^3\ mol^{-1}$) with a relatively low σ-donor strength, their metal salts will be essentially dissociated in solution. Amines readily replace anions such as $CF_3SO_3^-$.[62] However, nucleophilicity and volume cannot fully explain the higher reaction rates observed with anions RSO_3^- in comparison to other weakly coordinating anions. Possibly, the anions are involved in the initial coordination of the alkyne to the metal center, as described in Scheme 3.

F. Studies of the Effect of Ligand and Solvent for Group 9−12 Catalysts. Ligands, solvent, and temperature also have a strong influence on the catalytic activity of the metal complexes; for example, 1 mol % of [Rh(cod)(dipamp)]BF_4 employed in toluene at reflux temperature results in 80% conversion of **1** into **2**. Changing the solvent to CH_2Cl_2 gives only 3% conversion at reflux temperature. An increase of temperature to 150 °C in both examples gives a slightly increased conversion (86%) in toluene, whereas in CH_2Cl_2 no product was observed. The stabilizing effect of added phosphines is apparent for nickel(0) complexes, which in solution are especially prone to decomposition. In a refluxing catalytic mixture of **1** and the weakly complexed $[Ni(cod)_2]$ in THF a precipitate rapidly develops. Only 2% conversion is obtained after 20 h. Stabilizing the nickel(0) as $[Ni(CO)_2(PPh_3)_2]$ gives a slightly improved conversion (11%) in EtOH and no conversion in toluene. With $[Ni(PPh_3)_4]$ prepared in situ from $[Ni(cod)_2]$ 28% conversion is achieved in THF. In contrast, for $[(Ni(triphos))_2(cod)]$ full conversion of **1** into **3** was observed in toluene within 20 h. In this complex the nickel center is stabilized with the tridentate phosphine, whereas the weakly bound cod ligand is easily replaced by the substrate.

Similar trends were observed for palladium(II) complexes. During catalysis employing $[Pd(CH_3CN)_4](BF_4)_2$ in MeOH or CH_3CN at reflux temperature, the salt decomposed to varying degrees, although catalytic activity was observed (43% and 83%, respectively). To study the influence of phosphines more systematically, PPh_3 was added to a solution of the catalyst $PdCl_2$ in CH_3CN in a molar ratio between 0:1 and 4:1. The substrate **1** was added to the refluxing mixture and the initial rate of catalysis determined (Figure 5). With increasing phosphine concentration the initial rate of catalysis decreased exponentially from 11.6(1.3) h^{-1} (ratio 0:1) to 0.9(1) h^{-1} (ratio 4:1). This can be explained by the preferential formation of *trans*-$[PdCl_2(PPh_3)_2]$,[63,64] which has a low catalytic activity (Scheme 6). Because

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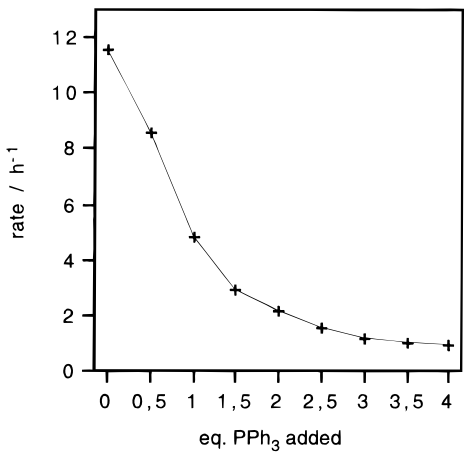
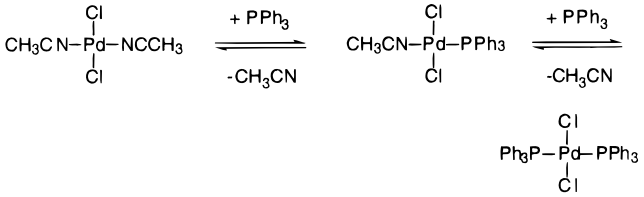


Figure 5. Dependence between the initial rate of cyclization of **1** and the ratio $PdCl_2/PPh_3$.

Scheme 6. Equilibrium between Free and Complexed Palladium Centers in an in Situ Mixture of $PdCl_2(CH_3CN)_2$ and PPh_3



of the strong *trans* effect[65] of PPh_3, the complex $[PdCl_2(CH_3CN)(PPh_3)]$ exists in the reaction mixture only in small concentrations. Thus, by addition of 0.5 equiv (1 equiv) of PPh_3 approximately 0.25 (0.5) palladium centers are inactivated, which causes a decrease in rate by 25% (50%). At higher concentrations the catalytic activity in the mixture approaches that of $[PdCl_2(PPh_3)_2]$.

Use of bidentate phosphines leads to a drop in catalytic activity; e.g., with $[PdBr(dppf)]NO_3$ in toluene only 3% conversion of **1** was observed. $[Pd(dppf)](NO_3)_2$ is not soluble in toluene, whereas in CH_2Cl_2 5% conversion and in CH_3CN 59% conversion of **1** is achieved (Table 6). This solvent effect is in agreement with reports for the complex $[Pd(dppe)](ClO_4)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$), which shows a very low molar conductance in dichloromethane but behaves as a 1:2 electrolyte in such solvents as THF, MeCN, and MeOH,[66] obviously owing to displacement of coordinated perchlorates by solvent molecules. Similarly, the complex $[Pd(dppf)](NO_3)_2$ is probably much more dissociated in CH_3CN, which can explain the higher catalytic activity compared to CH_2Cl_2. Another general feature of the chemistry of organonitrile complexes of palladium is the ease of replacement of the nitrile ligand. In contrast to catalytic systems for olefin hydrogenation based on $[Pd(dppe)(solvent)_2]^{2+}$, which are ineffective when the coordinated solvent is acetonitrile,[67,68] the hydroamination does not seem to be inhibited by the use of acetonitrile as ligand or as the solvent. With triphos as tridentate ligand, the metal complex $[Pd(triphos)](BF_4)_2$ is catalytically active (69% conversion in refluxing toluene) and sufficiently stable to higher temperatures (93% conversion at 150 °C).

Table 6. Catalytic Activity of Various Late-Transition-Metal Complexes[a]

complex	solvent	temp/°C	conversn/%	r/h^{-1}
$[Rh(cod)(dipamp)]BF_4$	toluene	111	80	
	toluene	150	86	
	CH_2Cl_2	40	3	
	CH_2Cl_2	150	0	
$[Ni(cod)_2]$	THF	66	2	
$[Ni(CO)_2(PPh_3)_2]$	EtOH	78	11	
	toluene	111	0	
$[Ni(PPh_3)_4]$	THF	66	28	
$[(Ni(triphos))_2(cod)]$	toluene	111	100	
$[Pd(CH_3CN)_4](BF_4)_2$	MeOH	65	43	
	CH_3CN	82	83	
$[Pd(triphos)](BF_4)_2$	toluene	111	69	
	toluene	150	93	
$[PdBr(dppf)]NO_3$	toluene	111	3	
$[Pd(dppf)](NO_3)_2$	CH_2Cl_2	40	5	
	CH_3CN	82	59	
$[Cu(CH_3CN)_4]PF_6$	CH_3CN	82	100	53(1)
$[Cu(PPh_3)_2]NO_3$	toluene	111	9	
	CH_2Cl_2	40	18	
$[Cu(triphos)]PF_6$	CH_3CN	82	100	17(2)
$AgCH_3C_6H_4SO_3$	CH_3CN	25		3.8(1)
	CH_2Cl_2	25		1.3(1)
	toluene	25		0.021(1)
$AgCF_3SO_3$	CH_3CN	25		3.7(1)
	CH_2Cl_2	25		0.42(2)
	toluene	25		0.48(1)
$AuCl_3$	CH_3CN	82	57	
$AuCl_3/PPh_3$	CH_3CN	82	91	
$AuCl_3/_2PPh_3$	CH_3CN	82	28	
$AuCl_3$/dppf	CH_3CN	82	21	
$AuCl_3$/triphos	CH_3CN	82	14	
$[AuCl(triphos)](NO_3)_2$	CH_3CN	82	100	ca. 212
	CH_2Cl_2	40	35	

[a] The conversion of **1** after 20 h is given.

In the case of copper(I) the weakly complexed metal salt $[Cu(CH_3CN)_4]PF_6$ in CH_3CN gives full conversion of **1** within 8 h ($r = 53.2(5)\ h^{-1}$); the complex $[Cu(PPh_3)_2]NO_3$ gives 9% and 18% conversion after 20 h in toluene and CH_2Cl_2, respectively, whereas the complex $[Cu(triphos)]PF_6$ has an intermediate catalytic activity in CH_3CN, giving full conversion within 20 h ($r = 17.2(2.2)\ h^{-1}$). The importance of the solvent for the catalytic activity of the metal complexes was studied in further detail for the most active silver salts, $AgCH_3C_6H_4SO_3$ and $AgCF_3SO_3$. Initial rates were measured in the solvents CH_3CN, CH_2Cl_2, and toluene at 25 °C. Both silver salts display similar catalytic activities in CH_3CN (3.78(6) and 3.67(10) h^{-1}, respectively). The initial rate decreases in CH_2Cl_2 to 1.28(2) and 0.42(2) h^{-1}, whereas in toluene the catalytic activity of $AgCH_3C_6H_4SO_3$ nearly vanishes (0.021(1) h^{-1}). For $AgCF_3SO_3$ the rates are similar in CH_2Cl_2 and toluene (0.48(1) h^{-1}). It is known that two-coordinate silver(I) complexes of the type $Ag(PR_3)ClO_4$ (R = ^{t}Bu, Cy, *o*-tolyl, ClC_6H_4) are un-ionized in dichloromethane.[69] The higher catalytic activity of silver salts in CH_3CN is probably due to a breakup of the ion pairs.

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A similar stabilizing effect of phosphines as described before was also observed for gold(III). Employing $AuCl_3$ in CH_3CN as catalyst for the cyclization of **1** gives 57% conversion within 20 h; however, decomposition of the catalyst to the parent metal is observed. Addition of 1 equiv of PPh_3 increases the conversion to 91% without observing decomposition of the gold complex. Addition of further equivalents of phosphine leads to lower conversions (28% for 2 equiv of PPh_3, 21% for 1 equiv of dppf and 14% for 1 equiv of triphos). However, when two of the chloride ions are replaced by nitrate in [AuCl(triphos)]$(NO_3)_2$, and the reaction is carried out in CH_3CN, 88% of **1** is converted into **2** within 1 h and 100% in 24 h, corresponding to an initial rate of ca. 212 h^{-1}. In contrast, in CH_2Cl_2 the same catalyst gives only 35% conversion within 24 h.

G. Studies of the Effect of Water on the Cyclization of 1. To test the sensitivity of group 7−12 catalysts toward traces of water, a series of five experiments was performed in which 0, 1, 2, 3, and 4 equiv of water were added to the reaction mixture ($Zn(CF_3SO_3)_2$ and 100 equiv of **1**). Initial rates determined are 33(1), 36(1), 39(1), 33(2), and 31(2) h^{-1}. There is a slight maximum at the ratio $H_2O/Zn(CF_3SO_3)_2 = 2$; however, this is close to the experimental error. Thus, the catalytic activity of $Zn(CF_3SO_3)_2$ is not significantly influenced by up to 4 equiv of H_2O. Similarly, most of the complexes described, with the exception of nickel(0) complexes, tolerate traces of catalyst poisons.

H. Principles for Identifying the Most Active Catalysts. From the observations on the cyclization of **1** under different reaction conditions the following rules arise. (i) At the metal center a single free coordination site is required for catalytic activity. However, a ligand exchange which proceeds via the coordination of a further ligand, resulting in a five-coordinate transition state, cannot be excluded.[70,71] (ii) Metal centers which are only coordinated by solvent molecules have a high activity, but for the noble metals and nickel, the complexes tend to decompose to the parent metal. Comparable activities are observed for complexes containing a ligand with a high *trans* effect, e.g., a phosphine, opposite to the empty coordination site where catalysis is taking place. (ii) All of the catalysts described, with exception of nickel(0) complexes, are cationic. To dissolve these salts, a strongly polar solvent is required. Although solvents such as CH_3CN compete with the substrate for coordination to the metal, little inhibition of the catalysis by CH_3CN is observed. Additionally, coordinating solvents are able to stabilize the nickel(0) and cationic noble metal complexes in solution which have a tendency to decompose. (iii) The anion has a strong influence on the catalytic activity of the metal salt. Most favorable are derivatives of the sulfonic acid which can be attributed to their large volume in combination with a low nucleophilicity. A good choice is $CF_3SO_3^-$ because of its chemical inertness and the good solubility of its complexes in organic solvents. In contrast, catalysis is inhibited by basic anions such as CH_3COO^- and, for the complexes [Pd(triphos)]X_2, by the strongly coordinating chloride.

Conclusions

The intramolecular addition of an amine R_2N-H bond across an alkyne C≡C moiety can efficiently be catalyzed by transition-metal complexes of group 7−12. The aminoalkynes $RC{\equiv}C(CH_2)_nNH_2$ ($n = 3$, R = H, Ph; $n = 4$, R = H) and 2-(phenylethynyl)aniline are cyclized with rates up to ≥1686(11) h^{-1}. Although these rates are comparable to those observed with early-transition-metal catalysts, the main advantage of the catalysts described is their higher tolerance toward poisons such as water and oxygen. Catalytically active are complexes with d^8 or d^{10} electronic configuration and $[Re(CO)_5(H_2O)]BF_4$—the most active are $[Cu(CH_3CN)_4]PF_6$, $Zn(CF_3SO_3)_2$, and [Pd(triphos)]$(CF_3SO_3)_2$. One molecule of $[Cu(CH_3CN)_4]PF_6$ converts ≥1280 substrate molecules without deactivation of the catalyst. In summary, the intramolecular addition of amines to alkynes constitutes an easy access to enamines, imines, and indoles. The α-alkylidene functionality of the enamines and the C=N double bond of the imines allows easy derivatization[72] and opens access to a large number of nitrogen heterocycles.

Experimental Section

Materials and Methods. All reactions involving air- and/or water-sensitive compounds were performed using standard Schlenk techniques. Solvents were obtained dry from Aldrich. Catalysts and other chemicals not described in the Experimental Section were purchased from Aldrich, Fluka, and Strem and used as received. The hydrochlorides of 6-aminohex-1-yne (**1**), **1**·HCl, and 2-methyl-1,2-dehydropiperidine (**2**), **2**·HCl, $Ni(PPh_3)_4$, $Pd(dppf)(NO_3)_2{\cdot}CH_2Cl_2$, [Pd(triphos)]$(BF_4)_2{\cdot}CH_3CN$,[47] and $[Re(CO)_5(H_2O)]BF_4$[73] were prepared as described in the respective references.

Physical and Analytical Methods. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AM 400 instrument and referenced in ppm relative to the solvent shift[74] or tetramethylsilane. GC analyses were performed on a HP 5730A gas chromatograph equipped with a Supelco Amin (3 m × $^1/_8$ in. S.S., 25% CW-400 + 2.5% KOH on Chrom-W-AW) or Supelco Carbowax (6 ft × $^1/_8$ S.S., 10% Carbowax 30M on 80/100 Chromosorb WAW) column. Infrared spectra were obtained on a Perkin-Elmer 1600 or 2000 FT-IR spectrometer as KBr disks if not stated otherwise. Mass spectroscopic analyses were performed on a Finnigan MAT 311A by chemical ionization (CI) or the fast atom bombardment (FAB) method. Elemental analyses were performed by the Microanalytical Laboratory of the Technische Universität München.

Preparations. Substrates and Products. 1-Aminopent-4-yne (3). The compound 4-cyanobut-1-yne (4.8 g, 60 mmol) was dissolved in Et_2O (75 cm^3) and added over a period of 60 min to a magnetically stirred mixture of $LiAlH_4$ (2.75 g, 72.4 mmol) in Et_2O (100 cm^3) at 0 °C. The mixture was stirred at room temperature overnight and then refluxed for 10 h, the excess $LiAlH_4$ destroyed by addition of H_2O (10.6 cm^3), the mixture filtered, and the solid residue extracted with Et_2O (3 × 20 cm^3). Addition of HCl in Et_2O (1 M, 160 cm^3, 0.16 mol) to the combined ethereal solution precipitated the product as the hydrochloride, which was filtered off and dried in vacuo. The

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hydrochloride (7.37 g) was dissolved in methanol (50 cm^3), 8.33 g of K_2CO_3 (60.3 mmol) added, and the mixture stirred at room temperature overnight. The solvent was removed and the product distilled (30−32 °C at 90 Torr).

Yield: 0.99 g, 20%. Anal. Found: C, 69.8; H, 10.9; N, 16.5. Calcd for C_5H_9N: C, 72.2; H, 10.9; N, 16.9. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 84.3 (s, C4), 68.8 (s, C5), 41.4 (s, C1), 32.6 (s, C2), 15.9 (s, C3). ^1H NMR (C_6D_6): δ 2.58 (t, J = 6.8 Hz, 2H, CH_2N), 2.12 (m, 2H, $CH_2C{\equiv}C$), 2.04 (m, 1H, $HC{\equiv}C$), 1.46 (m, 2H, CH_2), 0.86 (s, br, 2H, NH_2). IR (film): 3295 vs, 2946 vs, 2870 m, 2116 m, 1710 s, 1662 s, 1436 s, 1363 s, 1246 m, 1222 m, 1009 m, 1022 w, 634 vs cm^{-1}. MS (EI): m/z 83 (M^+).

2-Methyl-1-pyrroline (4). Compound **3** (0.2 g, 2.4 mmol) and $Pd(CH_3CN)_4(BF_4)_2$ (27 mg, 60 μmol) were dissolved in THF (15 cm^3), and the mixture was heated to 90 °C for 3.5 h. The solvent was removed and the product obtained pure by vacuum distillation.

Yield: 0.15 g, 73%. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 172.8 (s, C2), 61.7 (s, C4), 38.7 (s, C3), 23.4 (s, C4), 19.6 (s, Me). ^1H NMR (C_6D_6): δ 3.84 (m, 2H, $CH_2C{=}N$), 2.02 (t, J = 8.1 Hz, 2H, CH_2N), 1.89 (s, 3H, CH_3), 1.55 (m, 2H, CH_2). IR (film): 3284 m, 2954 vs, 2867 s, 1652 vs, 1432 s, 1377 s, 1314 s, 1228 w, 1032 m, 1011 m, 938 s, 806 s cm^{-1}. MS (EI): m/z 83 (M^+).

1-Amino-5-phenylpent-4-yne (5). The compounds 1-chloro-5-phenylpent-4-yne (52 g, 0.29 mol) and potassium phthalimide (60 g, 0.32 mol) were dissolved in DMF (300 cm^3), and the mixture was heated to 148 °C for 16 h. After it was cooled, the solution was poured into CH_2Cl_2−water (1:1, 1 dm^3), the organic phase separated, and the polar phase extracted with CH_2Cl_2 (6 × 40 cm^3). The combined organic phase was washed (3 × 100 cm^3 of 0.2 N KOH, 2 × 200 cm^3 of water) and dried over $MgSO_4$. Removal of the solvent yielded white crystals of *N*-(5-phenyl-4-pentynyl)phthalimide which were washed with Et_2O (2 × 80 cm^3) and dried in vacuo. The phthalimide (55 g, 0,19 mol) and 20.0 g of $N_2H_4{\cdot}H_2O$ (0.40 mol) were dissolved in MeOH (450 cm^3), and the mixture was refluxed for 1 h. The methanol was removed and the residue extracted with Et_2O (6 × 30 cm^3). The fractions were combined, and the Et_2O was distilled off to yield a colorless oil.

Yield: 12.6 g, 27%. Anal. Found: C, 82.1; H, 8.4; N, 8.6. Calcd for $C_{11}H_{13}N$: C, 82.9; H, 8.2; N, 8.8. d = 0.93 g cm^{-3}. ^1H NMR (CD_3OD): δ 7.36 (m, 2H, H_{ortho}), 7.26 (m, 3H, H_{meta}), 4.69 (s, 2H, NH_2), 2.71 (s, 2H, CH_2N), 2.43 (s, 2H, $CH_2C{\equiv}C$), 1.70 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_3OD): δ 132.3 (C_{ortho}), 129.2 (C_{meta}), 128.5 (C_{para}), 125.1 (C_{ipso}), 90.4 ($C{\equiv}CPh$), 81.8 ($C{\equiv}CPh$), 41.6 (CH_2N), 33.9 (CH_2), 17.4 ($CH_2C{\equiv}C$). IR (film): 3458 vs, 3365 vs, 3027 m, 2205 s, 1615 s, 1495 s, 1455 s, 1308 s, 1251 m, 1157 m, 916 m, 750 vs, 691 vs cm^{-1}. MS (CI): m/z 158 (M^+ − H).

2-Benzyl-1-pyrroline (6). Compound **5** (0.2 g, 1.3 mmol) and $Pd(CH_3CN)_4(BF_4)_2$ (14 mg, 31 μmol) were dissolved in THF (15 cm^3), and the mixture was heated to 90 °C for 3.5 h. The solvent was removed and the product obtained pure by vacuum distillation.

Yield: 96 mg, 48%. ^1H NMR ($CDCl_3$): δ 7.0−6.8 (m, 5H, Ph), 3.61 (t, $J(^1H,^1H)$ = 7.2 Hz, 2H, CH_2N), 3.41 (s, 2H, CH_2-Ph), 1.83 (t, $J(^1H,^1H)$ = 8.1 Hz, 2H, $CH_2{=}N$), 1.23 (m, 2H, CH_2). MS (EI): m/z 159 (M^+).

2-(Phenylethynyl)aniline (7). A solution of 2-bromonitrobenzene (16 g, 80 mmol), phenylacetylene (9.8 g, 90 mmol), $Pd(PPh_3)_2Cl_2$ (1.3 g, 2 mmol), and CuI (0.60 g, 30 mmol) in NEt_3 (160 cm^3) was stirred at 70 °C for 3 h. After the reaction mixture was cooled to room temperature, a mixture of H_2O and Et_2O (1:1, 160 cm^3) was added, the solution filtered over Celite, and the organic phase separated. The aqueous phase was extracted with Et_2O, the combined organic phase dried over $MgSO_4$, and the solvent distilled off. The residue was dissolved in EtOH (160 cm^3), $SnCl_2$ (75 g, 0.39 mol) added slowly, and the mixture stirred for 1 h. Aqueous KOH (1 N, 350 cm^3) was added and the mixture extracted with CH_2Cl_2 (3 × 100 cm^3). The combined organic phase was dried over $MgSO_4$ and filtered and the solvent removed. The orange crystals obtained were purified by column chromatography on silica gel and recrystallization from hexane−MeCOOEt (4:1).

Yield: 9.3 g, 60%. Anal. Found: C, 86.8; H, 5.8; N, 7.2. Calcd for $C_{14}H_{11}N$: C, 87.0; H, 5.7; N, 7.3. ^1H NMR (CD_3OD): δ 7.53 (m, 2H, H10,14), 7.35 (m, 3H, H11−13), 7.25 (m, 1H, H6), 7.09 (td, 1H, H4), 6.75 (dd, 2H, H3), 6.64 (td, 1H, H5), 4.86 (s, 2H, NH_2).$^{13}C\{^1H\}$ NMR (CD_3OD): δ 150.1 (C2), 132.9 (C6), 132.3 (C10,14), 129.8 (C4), 129.2 (C11−13), 124.9 (C9), 118.5 (C5), 115.7 (C3), 108.9 (C1), 95.3 (C7), 87.1 (C8). IR: 3459 (vs), 3366 (vs), 3028 (m), 2205 (s), 1613 (s), 1495 (s), 1455 (vs), 1310 (s), 1251 (m), 1151 (m), 916 (m), 750 (vs), 691 (vs) cm^{-1}. MS (CI): m/z 193 [M^+].

2-Phenylindole (8). Compound **7** (0.2 g, 1.0 mmol) and $Pd(PPh_3)_2Cl_2$ (36 mg, 52 μmol) were dissolved in DMAc (15 cm^3), and the mixture was heated to 90 °C for 3.5 h. The solvent was removed and the product obtained pure by sublimation (30 Torr, 120 °C bath temperature).

Yield: 0.19 g, 96%. Anal. Found: C, 86.7; H, 5.7; N, 7.2. Calcd for $C_{14}H_{11}N$: C, 87.0; H, 5.7; N, 7.3. $^{13}C\{^1H\}$ NMR (CH_3OD): δ 129.9 (Ph), 126.2 (Ph), 122.7 (Ph), 121.2 (Ph), 120.5 (Ph), 112.1 (Ph), 99.7 (Ph). ^1H NMR (CH_3OD): δ 7.77 (dd, 2H, Ph), 7.40−7.38 (m, 3H, Ph), 7.28 (m, 1 H, Ph), 7.07 (m, 1 H, Ph), 6.99 (m, 1 H, Ph), 4.86 (s, 2H, NH_2). IR: 3438 (s), 3046 (m), 2856 (s), 1600 (m), 1637 (s), 1453 (s), 1037 (s), 754 (vs), 692 (vs). MS (CI): m/z 193 [M^+].

Complexes. [AuCl(triphos)]$(NO_3)_2$. The salt $AuCl_3$ (45 mg, 0.15 mmol) was dissolved in CH_3CN (3 cm^3) and a solution of triphos (79 mg, 0.15 mmol) in CH_2Cl_2 (3 cm^3) added, followed by a solution of $AgNO_3$ (75 mg, 0.44 mmol) in MeOH (25 cm^3). The mixture was stirred overnight and filtered and the filtrate taken to dryness. The residue was suspended in CH_3CN, the suspension filtered through Celite, and the filtrate concentrated under a partial vacuum. The product was precipitated with Et_2O, recrystallized from CH_3CN/Et_2O, and dried in vacuo.

Yield: 67 mg, 49%. Anal. Found: C, 45.5; H, 3.9; N, 2.4. Calcd for $C_{34}H_{33}AuClN_2O_6P_3$: C, 45.8; H, 3.7; N, 3.1. $^{13}C\{^1H\}$ NMR (CD_3CN): 136.1−129.3 (mm, Ph), 25.7 (m, CH_2), 23.7 (m, CH_2). ^1H NMR (CD_3CN): 7.8−7.2 (mm, 25H, Ph), 3.0 (b, 8H). IR: 3052 (m), 2900 (m), 1436 (s), 1384 (vs, NO_3^-), 1182 (s), 1104 (s), 738 (s), 693 (s), 514 (s) cm^{-1}. MS (FAB): m/z 731 (M^+ − Cl − $2NO_3$).

[AuCl(triphos)]Cl_2. A solution of triphos (0.25 g, 0.47 mmol) in CH_2Cl_2 (10 cm^3) was added to a mixture of $AuCl_3$ (0.14 g, 0.47 mmol) in CH_2Cl_2 (25 cm^3). The volume of the solution was reduced and the product precipitated with pentane and recrystallized from CH_2Cl_2/pentane.

Yield: 0.13 g, 35%. Anal. Found: C, 48.4; H, 4.5. Calcd for $C_{34}H_{33}AuCl_3P_3$: C, 48.7; H, 4.0. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 133.8 (Ph), 133.0 (Ph), 130.1 (Ph), 129.9 (Ph), 14.5 (CH_2). ^1H NMR ($CDCl_3$): δ 8.10−7.40 (m, 25H, Ph), 3.50 (m, 2H, $PhPCH_a$), 3.13 (m, 2H, $PhPCH_{a'}$), 2.85 (m, 2H, Ph_2PCH_b), 2.33 (m, 2H, $Ph_2PCH_{b'}$). IR: 3416 (s), 3049 (s), 2923 (s), 2360 (s), 1624 m, 1435 (vs), 1181 (s), 1099 (vs), 1103 (s), 739 (vs), 692 (vs), 514 (s) cm^{-1}. MS (FAB): m/z 731 (M^+ − 3Cl).

[Cu(triphos)]$PF_6{\cdot}0.5CH_3CN$. The phosphine triphos (0.29 g, 0.54 mmol) was dissolved in CH_2Cl_2 (4 cm^3) and the solution added to a magnetically stirred suspension of $[Cu(CH_3CN)_4]$-PF_6 (0.20 g, 0.54 mmol) in CH_2Cl_2 (50 cm^3). The mixture was heated to reflux for 2 h and filtered, the volume reduced under a partial vacuum, and the product precipitated with Et_2O (15 cm^3). The product was recrystallized from CH_3CN/Et_2O and dried in vacuo.

Yield: 0.32 g, 80%. Anal. Found: C, 54.7; H, 4.7; N, 0.8. Calcd for $C_{35}H_{34.5}CuF_6N_{0.5}P_4$: C, 55.0; H, 4.6; N, 0.9. $^{31}P\{^1H\}$ NMR (CD_3CN): δ 7.6 (b), −2.3 (b). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 133.7 (t), 133.1 (t), 131.6 (m), 131.1 (s), 130.1−129.9 (mm), 26.5 (m, CH_2), 25.5 (m, CH_2). ^1H NMR (CD_3CN): δ 7.7−7.2 (mm,

25H, Ph), 2.6 (b, 2H, CH_2), 2.4 (b, 2H, CH_2), 2.2 (s, 4H, CH_2), 1.9 (s, 1.5 H, CH_3CN). IR: 3054 (m), 1484 (m), 1436 (s), 1101 (m), 839 (vs), 742 (s), 695 (s), 558 (s), 516 (m) cm^{-1}. MS (FAB): *m*/*z* 598 ($M^+ - PF_6$).

[(Ni(triphos))$_2$(cod)]. The compound [Ni(cod)$_2$] (0.13 g, 0.45 mmol) was dissolved in THF (25 cm^3), triphos (0.24 g, 0.45 mmol) added, and the mixture stirred until the phosphine had dissolved. The solvent was removed under a partial vacuum and the residue washed with pentane, dried in vacuo, and used without further characterization.

[PdBr(dppf)](NO$_3$). The complex $PdBr_2$(cod) (0.16 g, 0.43 mmol) was dissolved in CH_2Cl_2, a solution of dppf (0.36 g, 0.43 mmol) added, and the solvent removed in vacuo. The residue was redissolved in CH_2Cl_2, $TlNO_3$ (0.22 g, 0.85 mmol) added, and the mixture stirred for 3 days. The white precipitate formed was removed by filtration, the volume reduced under a partial vacuum, and the product precipitated with hexane, recrystallized from CH_2Cl_2/hexane, and dried in vacuo.

Yield: 0.29 g, 85%. Anal. Found: C, 50.1; H, 3.5; N, 1.9. Calcd for $C_{34}H_{28}BrFeNO_3P_2Pd$: C, 50.9; H, 3.5; N, 1.7. $^{31}P\{^1H\}$ NMR (CD_3CN): δ 36.7 (s), 34.7 (s). ^1H NMR (CD_3CN): δ 7.7 (b, 8H, Ph), 7.5 (m, 4H, Ph), 7.4 (b, 8H, Ph), 4.5 (b, 8H, cp). IR: 3054 (m), 1480 (s), 1467 (s), 1436 (s), 1384 (vs), 1272 (vs), 1096 (s), 999 (m), 746 (s), 694 (s), 494 (s), 467 (s) cm^{-1}. MS (FAB): *m*/*z* 741 ($M^+ - NO_3$), 722 ($M^+ - Br$), 660 ($M^+ - Br - NO_3$).

[Pd(triphos)](CH$_3$CO$_2$)$_2$. The salt $Pd(CH_3CO_2)_2$ (42 mg, 0.19 mmol) was dissolved in CH_3CN (5 cm^3) and a solution of triphos (0.10 g, 0.19 mmol) in CH_2Cl_2 (15 cm^3) added. The volume was reduced under a partial vacuum. Addition of Et_2O yielded an orange solid which was recrystallized two times from CH_2Cl_2/pentane and dried in vacuo.

Yield: 85 mg, 60%. Anal. Found: C, 55.9; H, 5.0. Calcd for $C_{39}H_{41}Cl_2O_4P_3Pd$: C, 55.5; H, 4.9. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 110.3 (s, 1P, PPh), 45.3 (s, 2P, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 134.6−125.0 (mm, Ph), 30.3 (td, $^1J(^{13}C,^{31}P) = 33$ Hz, $^{2/3}J(^{13}C,^{31}P) = 6$ Hz, $PhPCH_2$), 28.6 (dt, $^{1/3}J(^{13}C,^{31}P) = 16$ Hz, $^2J(^{13}C,^{31}P) = 8$ Hz, Ph_2PCH_2). ^1H NMR ($CDCl_3$): 8.34 (dd, 2H, Ph), 7.85 (quart, 4H, Ph), 7.70 (quart, 4H, Ph), 7.60−7.44 (mm, 15H, Ph), 5.30 (s, 2H, CH_2Cl_2), 4.08 (sept, 2H, CH_a), 3.13 (dd, $^2J(^1H,^{31}P) = 58$ Hz, $^3J(^1H,^{31}P) = 15$ Hz, $CH_{a'}$), 2.75 (m, 2H, CH_b), 2.22 (b, 2H, $CH_{b'}$). IR: 3051 (m), 2911 (m), 1572 (m), 1483 (m), 1435 (vs), 1410 (s), 1324 (m), 1188 (m), 1103 (vs), 998 (s), 828 (s), 746 (s), 724 (s), 690 (vs), 656 (m) cm^{-1}.

[PdCl(triphos)]Cl·0.5CH$_2$Cl$_2$. The complex [$PdCl_2$(cod)] (0.38 g, 1.3 mmol) was dissolved in CH_2Cl_2 (90 cm^3) at 30 °C and a solution of triphos (0.71 g, 1.3 mmol) in CH_2Cl_2 (15 cm^3) added. The volume was reduced under a partial vacuum. Addition of pentane yielded a slightly yellow precipitate which was recrystallized from CH_2Cl_2/pentane and dried in vacuo.

Yield: 0.86 g, 91%. Anal. Found: C, 54.5; H, 4.3. Calcd for $C_{34.5}H_{34}Cl_3P_3Pd$: C, 54.9; H, 4.5. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 110.9 (s, 1P, PPh), 45.5 (s, 2P, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 134.5−125.0 (mm, Ph), 29.6 (d, CH_2), 28.6 (m, CH_2). ^1H NMR ($CDCl_3$): 8.24 (dd, 2H, Ph), 7.85 (quart, 4H, Ph), 7.70 (quart, 4H, Ph), 7.60−7.44 (mm, 15H, Ph), 5.73 (b, 1H, CH_2Cl_2), 3.87 (sept, 2H, CH_a), 3.14 (dd, $^2J(^1H,^{31}P) = 58$ Hz, $^3J(^1H,^{31}P) = 12$ Hz, $CH_{a'}$), 2.75 (b, 2H, CH_b), 2.23 (b, 2H, $CH_{b'}$). IR: 3049 (m), 2890 (m), 2806 (w), 1483 (s), 1435 (vs), 1411 (s), 1308 (w), 1189 (w), 1102 (vs), 998 (s), 827 (s), 746 (s), 725 (s), 708 (s), 689 (vs), 656 (m) cm^{-1}. MS (FAB): *m*/*z* 677 ($M^+ - Cl$).

[PdCl(triphos)](CF$_3$SO$_3$). The complex [PdCl(triphos)]Cl (0.65 g, 0.91 mmol) was dissolved in CH_2Cl_2 (25 cm^3), $Tl(CF_3SO_3)$ (0.64 g, 1.8 mmol) added, and the mixture stirred for 48 h. The solids were removed by filtration and extracted with CH_2Cl_2 (10 cm^3), and the volume of the combined filtrates was reduced under a partial vacuum. Addition of pentane (25 cm^3) yielded a yellow solid which was filtered off, recrystallized from CH_2Cl_2/pentane, and dried in vacuo.

Yield: 0.27 g, 37%. Anal. Found: C, 50.5; H, 3.9. Calcd for $C_{35}H_{33}ClF_3O_3P_3PdS$: C, 50.9; H, 4.0. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 133.8 (Ph), 133.0 (Ph), 130.1 (Ph), 129.9 (Ph), 28.8 (CH_2). ^1H NMR ($CDCl_3$): δ 8.10 (dd, 2H, Ph), 7.85 (dd, 4 H, Ph), 7.69 (dd, 4 H, Ph), 7.61−7.45 (mm, 15H, Ph), 3.45 (sept, 2H, CH_a), 3.13 (dd, $^2J(^1H,^{31}P) = 57$ Hz, $^3J(^1H,^{31}P) = 14$ Hz, $CH_{a'}$), 2.57 (quint, 2H, CH_b), 2.16 (m, 2H, $CH_{b'}$). IR: 3486 (m), 3054 (m), 2965 (m), 2918 (m), 1436 (vs), 1263 (vs), 1223 (s), 1154 (s), 1029 (vs), 998 (s), 731 (s), 690 (vs), 637 (vs), 522 (vs) cm^{-1}. MS (FAB): *m*/*z* 677 ($M^+ - CF_3SO_3$).

X-ray Crystal Structure Determination. Crystals were grown by slow diffusion of *n*-pentane into a solution of [PdCl(triphos)](CF_3SO_3) in CH_2Cl_2. A yellow crystal of dimensions 0.30 × 0.18 × 0.18 mm was mounted on the tip of a glass fiber. Cell constants were determined by least-squares refinement of 5000 reflections in the interval 6.9° < 2θ < 22.0° with the program CELL.[75] Preliminary examination and data collection were carried out on an imaging plate diffraction system (IPDS; Stoe&Cie) equipped with a rotating anode (Nonius FR591; 50 kV; 80 mA equipped with an Oxford cryosystem) and graphite monochromator. The data were collected at 193 K with an exposure time of 3.0 min per image (rotation scan modus from φ = 0.0° to 360° with $\Delta\varphi$ = 1°). A total of 24 709 reflections were collected (1.9° < θ < 25.6°), of which 6289 were unique (R_{merge} = 0.0512). Final full-matrix least-squares refinement (on F^2) based on 6289 unique reflections converged with 556 variable parameters. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically. The data analysis and the drawing were made using the programs SIR-92,[76] SHELXL-97[77] and PLATON.[78] The experimental conditions are summarized in Table 7; details are given in the Supporting Information.

[PdCl(triphos)]$_2$CO$_3$. The complex [PdCl(triphos)]Cl (0.25 g, 0.35 mmol) was dissolved in CH_2Cl_2 (25 cm^3), Ag_2CO_3 (97 mg, 0.35 mmol) added, and the mixture stirred for 48 h in the dark. The solids were removed by filtration and extracted with CH_2Cl_2 (10 cm^3), and the volume of the combined filtrates was reduced under a partial vacuum. Addition of pentane (25 cm^3) yielded a yellow solid which was filtered off, recrystallized from CH_2Cl_2/pentane, and dried in vacuo.

Yield: 0.18 g, 68%. Anal. Found: C, 58.5; H, 4.6. Calcd for $C_{69}H_{66}Cl_2O_3P_6Pd_2$: C, 58.7; H, 4.7. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 133.8 (Ph), 133.0 (Ph), 130.1 (Ph), 129.9 (Ph), 28.8 (CH_2). ^1H NMR ($CDCl_3$): δ 8.25 (dd, 2H, Ph), 7.78 (dd, 4 H, Ph), 7.63 (dd, 4 H, Ph), 7.55−7.37 (mm, 15H, Ph), 3.96 (sept, 2H, CH_a), 3.06 (dd, $^2J(^1H,^{31}P) = 57$ Hz, $^3J(^1H,^{31}P) = 13$ Hz, $CH_{a'}$), 2.68

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Table 7. Crystal Data, Data Collection Conditions, and Solution Refinement Details for [PdCl(triphos)](CF$_3$SO$_3$)

empirical formula	$C_{34}H_{33}ClP_3Pd\cdot CF_3O_3S$
color, habit	yellow block
space group	$P\bar{1}$
cryst syst	triclinic
a, Å	11.4668(11)
b, Å	11.7293(12)
c, Å	15.6012(13)
α, deg	99.248(11)
β, deg	111.178(10)
γ, deg	106.744(11)
V, Å^3	1789.4(3)
Z	2
d_{calcd}, g cm^{-3}	1.532
fw	825.46
abs coeff, mm^{-1}	0.80
radiation	Mo Kα (λ = 0.710 73 Å)
temp, K	193
final *R* indices ($I > 2\sigma(I)$)[a]	R1 = 0.0395, wR2 = 0.0867
R indices (all data)[a]	R1 = 0.0637, wR2 = 0.0906
no. of data/params	6289/556
no. of rflns obsd ($F^2 > 2\sigma(F^2)$)	4498

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

(m, 2H, CH_b) 2.15 (m, 2H, $CH_{b'}$). IR: 3421 (s), 3049 (m), 2891 (m), 2348 (m), 1629 (m), 1585 (m), 1435 (vs), 1263 (s), 1102 (s), 998 (m), 731 (s), 690 (vs), 520 (vs) cm^{-1}. MS (FAB): *m*/*z* 677 (0.5(M − CO_3)$^+$).

[Pd(triphos)](CF$_3$SO$_3$)$_2$. The complex [PdCl(triphos)]Cl (0.10 g, 0.14 mmol) was dissolved in CH_2Cl_2 (10 cm^3), a solution of $AgCF_3SO_3$ (72 mg, 0.28 mmol) in CH_3CN (2 cm^3) added, and the mixture stirred at room temperature for 1 month. A white precipitate formed, which was removed by filtration, and the volume of the filtrate reduced under a partial vacuum. Addition of Et_2O yielded a light yellow solid which was recrystallized from CH_2Cl_2/pentane and dried in vacuo.

Yield: 0.11 g, 85%. Anal. Found: C, 46.2; H, 3.5. Calcd for $C_{36}H_{33}F_6O_6P_3PdS_2$: C, 46.2; H, 3.5. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 115.1 (s, 1P, PPh), 52.0 (s, 2P, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 134.7−123.9 (mm, Ph), 29.8 (d, $^1J(^{13}C,^{31}P)$ = 35 Hz, CH_2), 28.4 (t, $^{1/3}J(^{13}C,^{31}P)$ = 17 Hz, CH_2). ^1H NMR ($CDCl_3$): 8.19 (dd, 2H, Ph), 7.74−7.48 (mm, 23H, Ph), 3.37 (sept, 2H, CH_a), 3.11 (dd, $^2J(^1H,^{31}P)$ = 55 Hz, $^3J(^1H,^{31}P)$ = 15 Hz, $CH_{a'}$), 3.00 (m, 2H, CH_b), 2.25 (b, 2H, $CH_{b'}$). IR: 3058 (m), 2965 (w), 2920 (w), 1485 (m), 1437 (s), 1324 (m), 1266 (vs), 1158 (s), 1105 (s), 1030 (vs), 999 (m), 830 (m), 747 (m), 725 (m), 709 (m), 690 (m), 637 (vs), 572 (m) cm^{-1}. MS (FAB): *m*/*z* 789 ($M^+ - CF_3SO_3$), 640 ($M^+ - 2CF_3SO_3$).

[Pd(triphos)](CF$_3$CO$_2$)$_2$. The compound was prepared in the same way as for [Pd(triphos)](CF_3SO_3)$_2$, employing [PdCl(triphos)]Cl (0.10 g, 0.14 mmol) and $AgCF_3CO_2$ (62 mg, 0.28 mmol).

Yield: 65 mg, 53%. Anal. Found: C, 52.2; H, 3.7. Calcd for $C_{38}H_{35}F_6O_4P_3Pd$: C, 52.5; H, 4.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 107.9 (t, 1P, $^2J(^{31}P,^{13}C)$ = 9 Hz, PPh), 48.2 (d, 2P, $^2J(^{31}P,^{13}C)$ = 9 Hz, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 134.4−124.7 (mm, Ph), 29.0 (td, $^1J(^{13}C,^{31}P)$ = 35 Hz, $^{2/3}J(^{13}C,^{31}P)$ = 6 Hz, PhP−CH_2), 27.5 (dt, $^{1/3}J(^{13}C,^{31}P)$ = 16 Hz, $^2J(^{13}C,^{31}P)$ = 7 Hz, Ph_2PCH_2). ^1H NMR ($CDCl_3$): 8.46 (dd, 2H, Ph), 7.75−7.39 (mm, 23H, Ph), 3.60 (sept, 2H, CH_a), 3.12 (dd, 2H, $^2J(^1H,^{31}P)$ = 58 Hz, $^3J(^1H,^{31}P)$ = 12 Hz, $CH_{a'}$), 2.75 (b, 2H, CH_b), 2.17 (b, 2H, $CH_{b'}$). IR: 3056 (m), 2946 (m), 2908 (m), 1678 (vs), 1484 (m), 1437 (s), 1408 (s), 1311 (m), 1194 (vs), 1114 (vs), 998 (m), 836 (s), 801 (s), 753 (s), 724 (vs), 689 (vs), 660 (m), 616 (w) cm^{-1}. MS (FAB): *m*/*z* 753 ($M^+ - CF_3CO_2$), 640 ($M^+ - 2CF_3CO_2$).

[Pd(triphos)](CH$_3$C$_6$H$_4$SO$_3$)$_2$·CH$_2$Cl$_2$. The compound was prepared in the same way as [Pd(triphos)](CF_3SO_3)$_2$, employing [PdCl(triphos)]Cl (0.10 g, 0.14 mmol) and $AgCH_3C_6H_4SO_3$ (78 mg, 0.28 mmol).

Yield: 99 mg, 72%. Anal. Found: C, 56.8; H, 4.7. Calcd for $C_{49}H_{49}Cl_2O_4P_3Pd$: C, 56.8; H, 4.8. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 112.8 (t, 1P, $^2J(^{31}P,^{13}C)$ = 9 Hz, PPh), 48.2 (d, 2P, $^2J(^{31}P,^{13}C)$ = 9 Hz, PPh_2). ^1H NMR ($CDCl_3$): 8.46 (dd, 2H, Ph), 7.83−7.37 (mm, 23H, Ph), 5.30 (s, CH_2Cl_2), 3.70 (sept, 2H, CH_a), 3.14 (dd, 2H, $^2J(^1H,^{31}P)$ = 55 Hz, $^3J(^1H,^{31}P)$ = 15 Hz, $CH_{a'}$), 2.90 (m, 2H, CH_b), 2.15 (b, 2H, $CH_{b'}$). IR: 3052 (m), 2959 (w), 2920 (w), 1484 (m), 1436 (s), 1252 (s), 1218 (vs), 1197 (vs), 1119 (s), 1032 (s), 1011 (s), 982 (s), 891 (m), 816 (m), 730 (m), 711 (m), 689 (s), 679 (vs), 568 (s) cm^{-1}.

Catalyses. In a typical procedure, a mixture of 6-amino-1-hexyne[47] (**1**; 0.10 cm^3, 0.88 mmol), [Cu(CH_3CN)$_4$]PF_6 (3.2 mg, 8.8 μmol), and acetonitrile (25 cm^3) was heated at reflux for 20 h. The product, 2-methyl-1,2-dehydropiperidine (**2**), was isolated together with the remaining starting material as a mixture of their hydrochlorides (0.11 g, 93% yield). The product distribution was analyzed by ^1H NMR spectroscopy using the following signals for the integration: at 3.0, 2.3, and 1.6 ppm for the starting material (**1**·HCl) and at 3.6, 2.8, 2.4 ppm for the product (**2**·HCl).[47] For [Cu(CH_3CN)$_4$]PF_6 a quantitative conversion to the product was observed.

Catalyst Concentration. The catalyst [Cu(CH_3CN)$_4$]PF_6 (8.0 mg, 22 μmol) was dissolved in toluene (25 cm^3). The solution was diluted with toluene (1:2, 1:4, 1:8, 1:16, 1:32, 1:64, 1:128, 1:256, 1:512, and 1:1024) and 8 cm^3 of each sample mixed with a solution (2 cm^3) of 6-aminohex-1-yne (0.50 cm^3, 4.4 mmol) in toluene (25 cm^3). The samples were heated at reflux and GC samples taken over 20 h.

Inhibition by Acetate Ions and by Water. For solution A, the catalyst Zn(CF_3SO_3)$_2$ (16 mg, 44 μmol) and 6-aminohex-1-yne (0.50 cm^3, 4.4 mmol) were dissolved in toluene (50 cm^3). For solution B, the compound Bu_4NAc (26 mg, 88 μmol) was dissolved in toluene (25 cm^3). For solution C, water (4.2×10^{-3} cm^3, 0.23 mmol) was dissolved in toluene (100 cm^3). Inhibition by acetate: samples were prepared by mixing 4 cm^3 of solution A with 0, 1, 2, 3, and 4 cm^3 of solution B, respectively, and addition of toluene to a volume of 10 cm^3. Each sample was heated at reflux, and GC samples were taken over 20 h. Inhibition by water: samples were prepared by mixing 4 cm^3 of solution A with 0, 1.5, 3, 4.5, and 6 cm^3 of solution C, respectively, and addition of toluene to a volume of 10 cm^3. Each sample was heated at reflux, and GC samples were taken over 20 h.

Inhibition by PPh$_3$. For solution A, the catalyst $PdCl_2$(CH_3CN)$_2$ (23 mg, 88 μmol) was dissolved in CH_3CN (25 cm^3). For solution B, the substrate 6-aminohex-1-yne (0.50 cm^3, 4.4 mmol) was dissolved in CH_3CN (50 cm^3). For solution C, the phosphine PPh_3 (47 mg, 0.40 mmol) was dissolved in CH_3CN (50 cm^3). Samples were prepared by mixing 4 cm^3 of solution A with 1 cm^3 of solution B and 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4 cm^3 of solution C, respectively, and addition of toluene to a volume of 10 cm^3. Each sample was heated at reflux, and GC samples were taken over 20 h.

Anion Effect in Ag Salts. The silver salt (19 μmol) was dissolved in CH_3CN (5 cm^3). A 1 cm^3 portion of the solution was added to a solution of 6-aminohex-1-yne (0.39 mmol, 44 mm^3) in CH_3CN (10 cm^3). The resulting solution was mixed thoroughly (for at least 30 s) and left to react at room temperature.

Kinetic Studies. In a typical experiment, GC samples were prepared by taking samples from the catalytic experiments described above, maintaining each sample at −30 °C until the GC measurements were begun. The kinetics were monitored over at least 10 half-lives; the more rapid reactions were monitored until quantitative conversion was achieved. The substrate concentration, c_S, and the product concentration, c_P, were measured against an external standard. All data collected could be convincingly fit (R = 0.96−0.99) to eq 1, where $F_m(t)$ is defined by eq 2 and t = time (h). The catalytic rate r (h^{-1}) is then obtained according to eq 3, where $c_{S,0}$ is the initial substrate concentration and c_{cat} is the catalyst concentration.

$$F_m(t) = 1 - e^{-at} \quad (1)$$

$$F_m(t) = \left(\frac{c_P}{c_P + c_S}\right)_t \quad (2)$$

$$r = \left(\frac{d[F_m(t)]}{dt}\right)_{t\to 0} \frac{c_{S,0}}{c_{cat}} \quad (3)$$

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Supporting Information Available: Table S1, containing crystal data, data collection conditions, and solution and refinement details of [PdCl(triphos)](CF_3SO_3), and Tables S2−S6, giving atomic coordinates and equivalent isotropic displacement parameters, hydrogen atom coordinates and isotropic parameters, anisotropic displacement parameters, bond lengths, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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