ChemPubSoc Europe

DOI: 10.1002/chem.201405662

CHEMISTRY
A European Journal
Full Paper

Zinc Catalysis

Cationic Zinc Organyls as Precatalysts for Hydroamination Reactions

Maren A. Chilleck,[a] Larissa Hartenstein,[b] Thomas Braun,*[a] Peter W. Roesky,*[b] and Beatrice Braun[a]

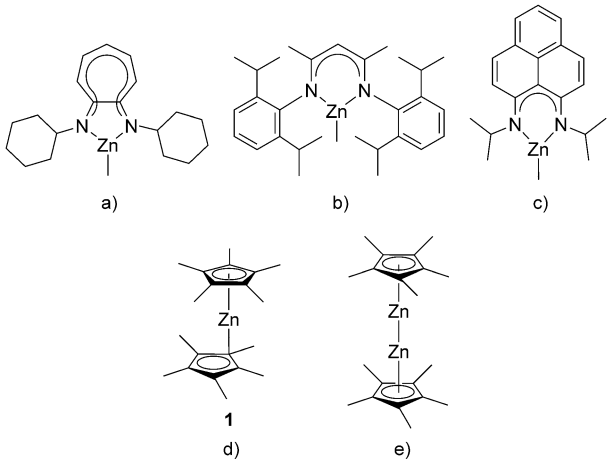
Dedicated to Professor Konrad Seppelt on the occasion of his 70th birthday

Abstract: The cationic zinc triple-decker complex $[Zn_2Cp^*_3]^+$ $[BAr^F_4]^-$ ($BAr^F_4 = B(3,5\text{-}(CF_3)_2C_6H_3)_4$) exhibits catalytic activity in intra- and intermolecular hydroamination reactions in the absence of a cocatalyst. These hydroaminations presumably proceed through the activation of the C–C multiple bond of the alkene or alkyne by a highly electrophilic zinc species, which is formed upon elimination of the Cp* ligands. The reaction of $[Zn_2Cp^*_3]^+[BAr^F_4]^-$ with phenylacetylene gives the hydrocarbonation product $(Cp^*)(Ph)CCH_2$, which might be formed via a similar reaction pathway. Additionally, several other structurally well-defined cationic zinc organyls have been examined as precatalysts for intermolecular hydroamination reactions without the addition of a cocatalyst. These studies reveal that the highest activity is achieved in the absence of any donor ligands. The neutral complex $[ZnCp^{2S}_2]$ ($Cp^{2S} = C_5Me_4(CH_2)_2SMe$) shows a remarkably high catalytic activity in the presence of a Brønsted acid.

Introduction

Hydroamination reactions can be applied to the synthesis of a broad range of nitrogen-containing molecules.[1] A variety of different metal-based catalysts have been employed for hydroamination catalysis,[2] including complexes of main group metals and the lanthanides, as well as early and late transition metals. Various different reaction mechanisms have been discussed. In principle, hydroamination reactions can be classified according to whether they proceed through the activation of the N–H bond or through an olefin or alkyne activation pathway.[1b]

In recent years, zinc complexes have attracted increasing interest as catalysts for hydroamination reactions.[3–8] Zinc has proven to exhibit many favorable properties, and it is a cheap and nontoxic metal. In hydroamination catalysis, zinc complexes often show a high catalytic activity in combination with a high tolerance towards polar functional groups. Zinc triflate was one of the first zinc compounds to be used as catalyst in hydroamination reactions.[3] However, the catalytic activity is limited by the low solubility of zinc triflate in organic solvents. Considerable progress has been made by the use of zinc complexes bearing chelating N,N donor ligands. Thus, zinc alkyl complexes with aminotroponiminato, β-diketiminato, and phenalenyl-based N,N ligands (Scheme 1) have successfully been applied as catalysts.[4–6] However, to achieve considerable catalytic activities, a Brønsted acid has to be added as a cocatalyst. The role of the cocatalyst, which does not show significant catalytic activity, is probably to protonate the alkyl ligand of the zinc precatalyst, which leads to the formation of a cationic species.[4c,d,5a,6] It has been assumed that the N,N donor ligand



Scheme 1. Precatalysts for zinc-catalyzed hydroamination reactions: a) aminotroponiminato zinc complex; b) β-diketiminato zinc complex; c) zinc complex with phenalenyl-based N,N donor ligand; d) zincocene $[ZnCp^*_2]$ (**1**); e) dizincocene $[Zn_2Cp^*_2]$.[4b,5a,6a,7a,b]

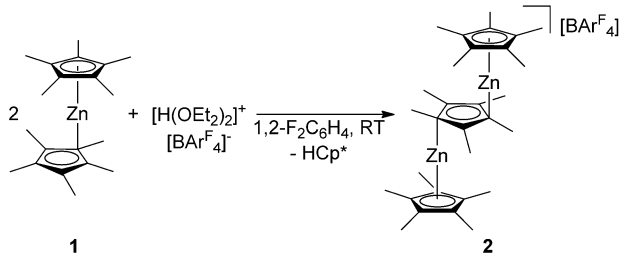
[a] Dr. M. A. Chilleck, Prof. Dr. T. Braun, Dr. B. Braun
Department of Chemistry
Humboldt-Universität zu Berlin
Brook-Taylor-Straße 2, 12489 Berlin (Germany)
E-mail: thomas.braun@chemie.hu-berlin.de

[b] L. Hartenstein, Prof. Dr. P. W. Roesky
Institute of Inorganic Chemistry
Karlsruhe Institute of Technology (KIT)
Engesserstraße 15, 76131 Karlsruhe (Germany)
E-mail: roesky@kit.edu

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201405662.

acts as a spectator ligand during hydroamination catalysis. Mandal et al. conducted experimental and theoretical studies on the intramolecular hydroamination of aminoalkenes catalyzed by zinc complexes with phenalenyl-based N,N donor ligands, which suggested that an olefin activation pathway was favored over the activation of the N–H bond.[6] In situ NMR experiments and DFT calculations performed by this group supported the formation of a catalytically active zinc cation.[6a] Recently, zinc complexes which exclusively feature ligands that are coordinated through zinc–carbon bonds have been applied as hydroamination catalysts. The precatalysts $[ZnCp^*_2]$ (**1**), $[Zn_2Cp^*_2]$ (Scheme 1), and $ZnEt_2$ led to a high catalytic activity for the intermolecular hydroamination of phenylacetylenes with amines in the presence of $[PhNMe_2H]^+[B(C_6F_5)_4]^-$ as cocatalyst.[7] Again, the formation of catalytically active cationic species was suggested.

Apart from hydroamination catalysis, cationic zinc organyls have been proposed to act as catalysts or precatalysts in various catalytic transformations.[9] However, only a few examples of structurally characterized cationic zinc complexes that exhibit zinc–carbon bonds have been reported so far.[9–11] In particular, cationic zinc cyclopentadienyl (Cp) complexes are rare.[11] In a recent study, the synthesis and structural characterization of the cationic triple-decker complex $[Zn_2Cp^*_3]^+[BAr^F_4]^-$ (**2**; $BAr^F_4 = B(3,5\text{-}(CF_3)_2C_6H_3)_4$; Scheme 2), which can serve as a source of the $\{ZnCp^*\}^+$ cation, was described.[11b]



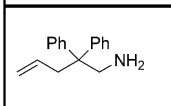
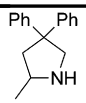
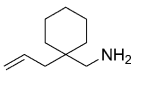
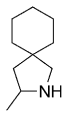
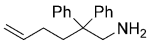
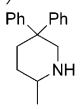
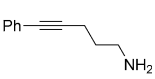
Scheme 2. Formation of the triple-decker complex $[Zn_2Cp^*_3]^+[BAr^F_4]^-$ (**2**).[11b]

Herein, we report on the triple-decker complex **2** and other cationic zinc organyl compounds as precatalysts for intra- and intermolecular hydroamination reactions in the absence of any cocatalyst. Additionally, the use of neutral zinc organyls as catalyst precursors in the presence of a cocatalyst is described. Investigations into the mechanism of the zinc-catalyzed hydroamination reaction show the importance of a highly electrophilic zinc center to achieve a high catalytic activity.

Results and Discussion

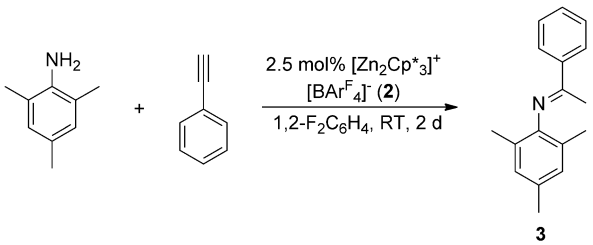
The triple-decker complex $[Zn_2Cp^*_3]^+[BAr^F_4]^-$ (**2**) was tested as a precatalyst for the intramolecular hydroamination of aminoalkenes and aminoalkynes. As compound **2** is already a cationic complex, no additional cocatalyst for the generation of cationic species was added. All catalytic reactions involving complex **2** were performed in 1,2-difluorobenzene, which is a polar and non-coordinating solvent. The reactions led to the selective formation of the corresponding cyclic amines or imines with high regioselectivities (Table 1), with the exception of (4*E*)-2,2-dimethyl-5-phenylpent-4-enylamine, which showed no reaction under the conditions specified. As described below, the triple-decker complex **2** is not the catalytically active species of the hydroamination reaction but a precatalyst.

Table 1. Intramolecular hydroaminations catalyzed by $[Zn_2Cp^*_3]^+[BAr^F_4]^-$ (**2**).[a]

Substrate	Product	Conversion (reaction time)[b]
		98% (5 h)
		93% (63 h)[c]
		99% (6 h)
		98% (16 h)
	no reaction	–

[a] Reagents and conditions: **2** (2 mol%), substrate (0.54 mmol), $[FeCp_2]$ as internal standard (10 mol%), 1,2-difluorobenzene (0.4 mL), 120 °C. [b] The conversion was determined by the integration of the olefin signals of the substrates in the ^1H NMR spectra vs. the internal standard. [c] Reaction at 140 °C.

In addition, the triple-decker complex **2** was used as a precatalyst in intermolecular hydroamination reactions of phenylacetylenes with aniline derivatives (see below, Table 2). The hydroamination of phenylacetylene with 2,4,6-trimethylaniline was chosen as a test reaction because this reaction also proceeds at room temperature using the zinc organyls $[ZnCp^*_2]$ (**1**), $[Zn_2Cp^*_2]$, or $ZnEt_2$ as precatalysts.[7a,b] On applying 2.5 mol% of complex **2** and 40 equivalents each of 2,4,6-trimethylaniline and phenylacetylene, a quantitative conversion of phenylacetylene was achieved after a reaction time of two days in an NMR-scale experiment at room temperature. The reaction led to the selective formation of the imine *N*-(1-phenylethylidene)-2,4,6-trimethylaniline (**3**) with Markovnikov regioselectivity (Scheme 3). The identity of **3** was confirmed by NMR spectros-

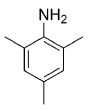
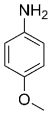
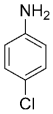
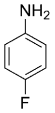
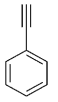
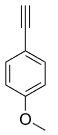
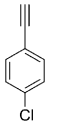
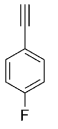


Scheme 3. Hydroamination of phenylacetylene with 2,4,6-trimethylaniline catalyzed by **2**.

copy and GC-MS analysis. Although phenylacetylene was consumed quantitatively after two days, small amounts of residual 2,4,6-trimethylaniline were still present in the reaction mixture. The ratio of 2,4,6-trimethylaniline to the imine **3** was approximately 1:10. The incomplete consumption of 2,4,6-trimethylaniline was also observed using other precatalysts (see below, Table 3). Note that in recent studies with zinc organyls as precatalysts, a 2:1 ratio of phenylacetylene to 2,4,6-trimethylaniline was used, which led to an increase in the reaction rates.[7a,b] However, since we aimed for a full conversion of both substrates, an equimolar amount of the reagents was applied. The reaction rate could be increased by first mixing complex **2** and 2,4,6-trimethylaniline and adding phenylacetylene after a period of 1 h. Thus, the time needed for full conversion of phenylacetylene could be reduced to approximately one day. The hydroamination with 2.5 mol% of **2** was also repeated on a larger scale using 2.86 mmol of each substrate. After a reaction time of 24 h at room temperature, the yield of isolated **3** was 91%.

Moreover, the long-term catalytic activity using complex **2** as precatalyst was investigated. 2.5 mol% of **2** was reacted with 2.86 mmol (40 equiv) each of 2,4,6-trimethylaniline and phenylacetylene. After complete consumption of the substrates (typically after 1–2 days), a fresh batch of substrates was added. Thus, within 12 days 17.2 mmol of both substrates were converted. The yield of the imine **3** isolated was 87%, which corresponds to a turnover number (TON) of 208. This shows the excellent long-term catalytic activity obtained by using **2** as precatalyst.

Table 2. Intermolecular hydroaminations catalyzed by $[Zn_2Cp^*_3]^+[BAr^F_4]^-$ (**2**).[a]

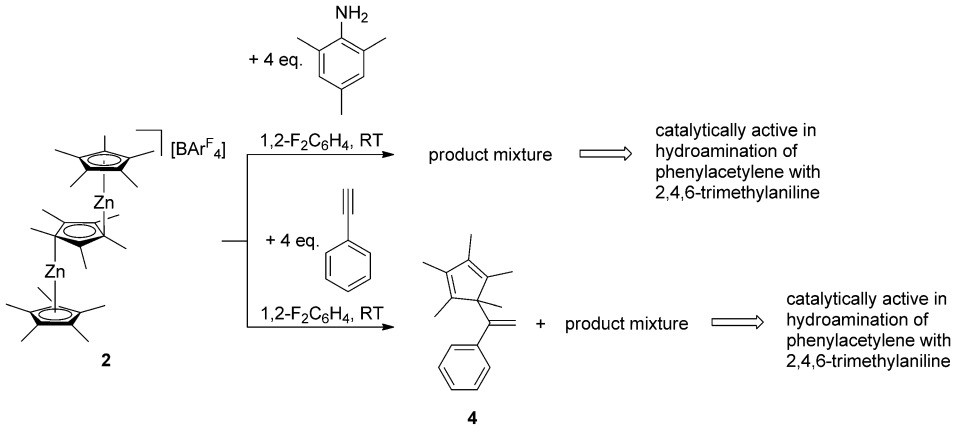
					
	85% (1 h) 32% (7 h)[b] 81% (24 h)[b] 91% (49.5 h)[b,c]	54% (5.5 h) 85% (24 h)	38% (5.5 h) 75% (23.5 h)	62% (4.5 h) 79% (23 h)[c]	65% (4 h) 89% (24.5 h)[c]
	78% (5 h) 92% (23 h)[c]	39% (4.5 h) 84% (21.5 h)	44% (6 h) 81% (25 h)	71% (4.5 h) 100% (23 h)	42% (3.5 h) 81% (20 h)
	100% (5.5 h)	50% (5.5 h) 89% (25.5 h)	21% (4 h) 71% (24 h)	74% (4 h) 91% (24 h)	77% (7 h) 95% (24 h)
	92% (1 h) 100% (5.5 h) 77% (22.5 h)[b]	45% (5.5 h) 81% (24 h)	19% (3.5 h) 85% (29 h)	55% (2.5 h) 84% (19 h)	60% (3.5 h) 96% (22 h)

[a] Conversions (reaction time) of intermolecular hydroamination reactions with **2** as precatalyst. Reagents and conditions: **2** (2.5 mol%), aniline (0.29 mmol), phenylacetylene (0.29 mmol), 1,2-difluorobenzene (0.5 mL), 80 °C; conversion determined by ^{1}H NMR spectroscopy.[12] [b] Reaction at room temperature. [c] The phenylacetylene was totally consumed; conversion thus refers to the aniline.

To investigate the substrate scope of the intermolecular hydroamination reaction catalyzed by **2**, anilines and phenylacetylenes bearing different functional groups were reacted together, employing 2.5 mol% of **2**. All combinations of the aniline derivatives 2,4,6-trimethylaniline, aniline, *p*-methoxyaniline, *p*-chloroaniline, and *p*-fluoroaniline with the phenylacetylene derivatives phenylacetylene, *p*-methoxyphenylacetylene, *p*-chlorophenylacetylene, and *p*-fluorophenylacetylene led to the formation of the corresponding imines with Markovnikov selectivity. The results are summarized in Table 2. Except for the combination of 2,4,6-trimethylaniline with phenylacetylene or *p*-fluorophenylacetylene, the reactions were slow at room temperature and were therefore run at 80 °C. The reaction progress was examined by NMR spectroscopy, and the conversions were determined by integration of the signals of the substrates and the hydroamination products in the ^{1}H NMR spectra of the reaction mixtures.[12] With 2.5 mol% of complex **2**, conversions of at least 70% were reached for all substrate combinations within 24 h. In some cases quantitative conversions of both substrates were achieved. These results show that the triple-decker complex **2** exhibits a high tolerance towards different functional groups at the substrates. The reactions involving 2,4,6-trimethylaniline tend to be faster, which may be ascribed to the electron donating properties of the methyl groups, which enhances the nucleophilicity of the amino group. Apart from that, no clear trends concerning the influence of the functional groups at the substrates on the reaction rates are apparent.

In situ NMR spectroscopic studies reveal that the triple-decker complex **2** is not the catalytically active species of the intra- and intermolecular hydroamination reactions. Immediately after adding the substrates to complex **2**, quantitative formation of HCp* (3 equivalents based on the amount of applied **2**) was observed. Therefore, it can be excluded that the catalytically active species contains a {ZnCp*} moiety.

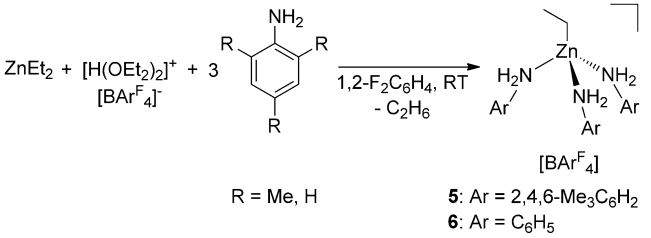
The progress of the reaction of phenylacetylene with 2,4,6-trimethylaniline catalyzed by **2** was monitored by ^{1}H NMR spectroscopy in intervals of 30 min. For up to 80% of the conversion, a linear increase of the conversion with the reaction time was found (see the Supporting Information, Figure S1). Thus, the reaction rate is apparently independent of the concentrations of the substrates, which corresponds to a zero-order rate law. This observation might indicate that the coordination of any substrates at the zinc center is not the rate-determining step of the hydroamination catalysis. Note that a zero-order rate dependence has been reported before for the hydroamination of phenylacetylene with 2,4,6-trimethylaniline applying $[ZnCp^*_2]$ (**1**), $[Zn_2Cp^*_2]$, or $ZnEt_2$ as precatalysts.[7a,b]



Scheme 4. Reactions of **2** with 2,4,6-trimethylaniline or phenylacetylene.

To elucidate the mechanism of the hydroamination reaction with complex **2** as precatalyst, it is essential to determine which of the substrates is activated by the catalytically active species. Compound **2** was separately treated either with 4 equivalents of 2,4,6-trimethylaniline or with 4 equivalents of phenylacetylene, because the occurrence of a reaction may indicate an activation of the substrates by **2**. Both reactions led to the formation of product mixtures (Scheme 4), and the resulting zinc compounds could not be identified. The product mixtures resulting from both reactions proved to be catalytically active in the hydroamination of phenylacetylene with 2,4,6-trimethylaniline when an excess of the substrates was added. In the reaction of **2** with phenylacetylene, one of the products in the reaction mixture was identified as 1-(pentamethylcyclopenta-2,4-dienyl)-1-phenylethene (**4**; Scheme 4). By chromatographic purification of the reaction mixture, **4** could be obtained as the major product, which still contained contamination by small amounts of unidentified byproducts. However, the identity of **4** could unambiguously be determined by ^{1}H, ^{13}C, ^{13}C APT, $^{1}H/^{13}C$ HSQC, and $^{1}H/^{13}C$ HMBC NMR spectroscopy (see the Supporting Information, Figures S2 and S3; APT = attached proton test, HSQC = heteronuclear single quantum coherence, HMBC = heteronuclear multiple bond correlation) as well as by GC-MS analysis. The synthesis of **4** via a different reaction route was reported in the literature and the NMR data of **4** conform to the literature.[13] Compound **4** is the product of the formal hydrocarbonation reaction of phenylacetylene with HCp* and is formed with Markovnikov selectivity. Whether the nucleophilic species that adds to the triple bond of phenylacetylene is a zinc-coordinated or uncoordinated Cp* anion or HCp* remains unclear. The reaction of phenylacetylene with HCp* in the presence of catalytic amounts (2.5 mol%) of **2** also led to the formation of **4**. However, this reaction is not selective, and a variety of different products are formed. It seems reasonable that the formation of **4** and the hydroamination reaction proceed according to similar reaction mechanisms. Probably, the electron density of the triple bond of phenylacetylene is lowered by coordination to the zinc center. Thus, phenylacetylene becomes susceptible to nucleophilic attack by Cp* or the aniline nitrogen atom. Note that for the zinc-catalyzed hydroamination a reaction pathway which proceeds on the activation of the C–C multiple bond has already been proposed in the literature.[3a,b,e,6a,8b] By GC-MS analysis, very small amounts of **4** were also found in the reaction mixture of the hydroamination of phenylacetylene with 2,4,6-trimethylaniline catalyzed by **2**.[14]

The products resulting from the reaction of the triple-decker complex **2** with either phenylacetylene or 2,4,6-trimethylaniline appear to be highly interesting with regard to a mechanism of the hydroamination reactions. As no zinc-containing products could be identified, attempts were made to synthesize structurally defined model complexes. For these studies, diethylzinc was chosen as a starting material. The reaction of $ZnEt_2$ with $[H(OEt_2)_2]^+[BAr^F_4]^-$ in the presence of phenylacetylene did not lead to the formation of a well-defined product. In contrast, the reaction of a slight excess of $ZnEt_2$ with $[H(OEt_2)_2]^+[BAr^F_4]^-$ in the presence of three equivalents of 2,4,6-trimethylaniline or aniline afforded the cationic complexes $[ZnEt(2,4,6\text{-}Me_3C_6H_2NH_2)_3]^+[BAr^F_4]^-$ (**5**) and $[ZnEt(C_6H_5NH_2)_3]^+[BAr^F_4]^-$ (**6**), respectively (Scheme 5). The ^{1}H and ^{13}C NMR spectra of **5** and



Scheme 5. Formation of cationic ethyl zinc complexes **5** and **6**.

6 exhibit the signals of a zinc-coordinated ethyl group, of the $[BAr^F_4]^-$ anion, and of three equivalents of coordinated 2,4,6-trimethylaniline or aniline (see the Supporting Information, Figures S4–S11). In addition, **6** was characterized by single-crystal X-ray diffraction.[15] The solid-state structure of the cation of **6** is shown in Figure 1. The zinc center is coordinated by the ethyl ligand and three aniline ligands in a distorted tetrahedral fashion. There are no short interatomic contacts between the $[ZnEt(C_6H_5NH_2)_3]^+$ cations and the $[BAr^F_4]^-$ anions. The structure of **6** is similar to those of other known cationic ethyl zinc complexes which also exhibit three neutral donor groups that are coordinated to the zinc center.[10d–f] Furthermore, Wehmschulte and Wojtas reported on the zinc aniline complex $[Zn(CB_{11}Cl_{11})(NH_2CH_2CPh_2CH_2CHCH_2)_3]$, which was obtained in a hydroamination experiment.[9d] As the $\{CB_{11}Cl_{11}\}^{2-}$ ligand is dianionic, $[Zn(CB_{11}Cl_{11})(NH_2CH_2CPh_2CH_2CHCH_2)_3]$ is a neutral com-

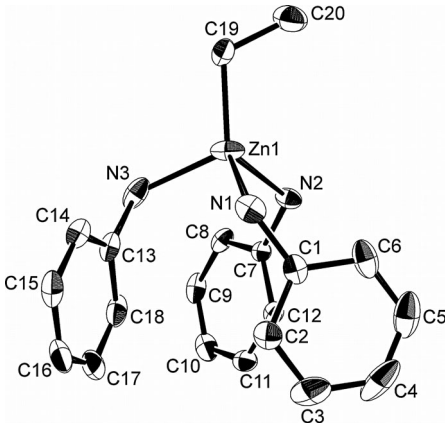


Figure 1. Structure of the $[ZnEt(C_6H_5NH_2)_3]^+$ cation in **6**. Thermal ellipsoids were drawn at the 50% probability level. For clarity, the hydrogen atoms are omitted and only one position of the disordered ethyl ligand is shown. Selected bond lengths [Å] and angles [°]: Zn1–N1 2.1447(19), Zn1–N2 2.1564(18), Zn1–N3 2.128(2), Zn1–C19 1.960(9); N1-Zn1-N2 100.53(7), N1-Zn1-N3 99.87(8), N2-Zn1-N3 99.62(7), N1-Zn1-C19 118.9(3), N2-Zn1-C19 121.7(3), N3-Zn1-C19 112.5(2).

plex. Although the zinc centers in **5** and **6** are probably highly electrophilic due to the cationic nature of the complexes, no deprotonation of the amino groups was observed, which is not supportive of an amine activation pathway. So far it could not be ruled out that the zinc-catalyzed hydroamination proceeds via an initial deprotonation of a coordinated amino group, which would yield a zinc amido species.

Complex **5** is catalytically active in the hydroamination of phenylacetylene with 2,4,6-trimethylaniline, and the catalytic activity is comparable to the activity of **2** (Table 3, entry 5). After addition of the substrates to **5**, the characteristic signals of the zinc-bound ethyl ligand disappear in the ^1H and ^{13}C NMR spectra, whereas a new signal appears, which is assigned to ethane. Therefore, there is probably no ethyl ligand coordinated to the central zinc atom in the catalytically active species.

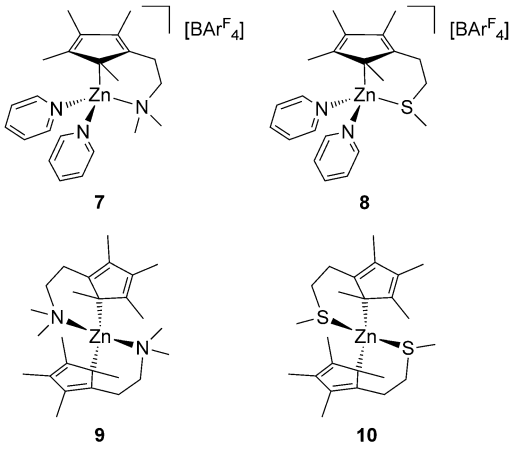
Moreover, the catalytic activities of several cationic and neutral zinc Cp complexes were compared in the test reaction of phenylacetylene with 2,4,6-trimethylaniline (Table 3). The reactions were performed in 1,2-difluorobenzene at room temperature applying a 1:1 molar ratio of 2,4,6-trimethylaniline and phenylacetylene. Note that for the comparison of catalytic activities, each triple-decker cation in **2** was considered to be the source of only one catalytically active cationic zinc center. For all precatalysts, the formation of the respective protonated cyclopentadienes was observed during catalysis. $[ZnCp^*_2]$ (**1**) has been reported to be the zinc complex with the highest catalytic activity in the hydroamination of phenylacetylene with 2,4,6-trimethylaniline to date.[7a] Using 5 mol% of **1** in the presence of 5 mol% of the cocatalyst $[H(OEt_2)_2]^+[BAr^F_4]^-$, a conversion to the imine **3** of 66% was achieved within a reaction time of 3.5 h (Table 3, entry 4). After the same reaction time under the same reaction conditions, a conversion of 25% was reached with the triple-decker complex **2** as precatalyst (Table 3, entry 2). Thus, **2** exhibits a lower catalytic activity in the test reaction than a combination of complex **1** and $[H(OEt_2)_2]^+[BAr^F_4]^-$. It has to be noted, however, that **2** can be used without an additional cocatalyst, whereas **1** is catalytically inactive in the absence of a cocatalyst.

In addition, the structurally defined cationic complexes $[ZnCp^{2N}(py)_2]^+[BAr^F_4]^-$ (**7**; $Cp^{2N}=C_5Me_4(CH_2)_2NMe_2$, py = pyridine) and $[ZnCp^{2S}(py)_2]^+[BAr^F_4]^-$ (**8**; $Cp^{2S}=C_5Me_4(CH_2)_2SMe$; Scheme 6), which were published recently,[11d] were examined as precatalysts in the test reaction. However, the catalytic activities were low (Table 3, entries 6 and 7). This may be ascribed to the presence of the pyridine ligands in **7** and **8**, which proved to be essential to stabilize the electrophilic zinc center.[11d] The inhibiting effect of pyridine on the catalytic activity can also be seen when two equivalents of pyridine are added to complex **2**, which effectively suppresses the catalytic activity (Table 3, entry 3). Pyridine can inhibit hydroamination catalysis

Table 3. Hydroamination of phenylacetylene with 2,4,6-trimethylaniline with different zinc precatalysts.[a]

Entry	Precatalyst (amount)	Cocatalyst/pyridine (amount)	Conversion (reaction time)	TON[c] (reaction time)
1	**2** (2.5 mol%, 0.007 mmol)	–	32% (7 h) 81% (24 h) 91% (49.5 h)[b]	13 (7 h) 32 (24 h) 36 (49.5 h)
2	**2** (5 mol%, 0.022 mmol)	–	25% (3.5 h) 80% (25 h)[b]	5 (3.5 h) 16 (25 h)
3	**2** (2.5 mol%, 0.007 mmol)	pyridine (5 mol%)	<3% (24.5 h)	<1 (24.5 h)
4	**1** (5 mol%, 0.022 mmol)	$[H(OEt_2)_2]^+[BAr^F_4]^-$ (5 mol%)	66% (3.5 h) 84% (7 h) 90% (24.5 h)[b]	13 (3.5 h) 17 (7 h) 18 (24.5 h)
5	**5** (2.5 mol%, 0.007 mmol)	–	34% (6 h) 79% (27 h)	14 (6 h) 32 (27 h)
6	**7** (5 mol%, 0.016 mmol)	–	<3% (26 h)	<1 (26 h)
7	**8** (5 mol%, 0.016 mmol)	–	19% (27 h)	4 (27 h)
8	**9** (5 mol%, 0.022 mmol)	$[H(OEt_2)_2]^+[BAr^F_4]^-$ (5 mol%)	10% (3.5 h) 34% (24.5 h)	2 (3.5 h) 7 (24.5 h)
9	**10** (5 mol%, 0.022 mmol)	$[H(OEt_2)_2]^+[BAr^F_4]^-$ (5 mol%)	61% (3.5 h) 73% (7 h) 85% (25 h)[b]	12 (3.5 h) 15 (7 h) 17 (25 h)

[a] Reagents and conditions: molar ratio 2,4,6-trimethylaniline/phenylacetylene = 1:1, 1,2-difluorobenzene (0.5 mL), RT; conversion determined by ^1H NMR spectroscopy. [b] Phenylacetylene was totally consumed; conversion thus refers to 2,4,6-trimethylaniline. [c] TON = turnover number. The TON values for **2** are based on the assumption that each molecule is the source of only one catalytically active cationic zinc center.



Scheme 6. Zinc precatalysts **7**-**10**.[11d,16]

either by occupying coordination sites at the zinc center of the catalytically active species or by acting as a Brønsted base. Due to the adverse effect of pyridine on the catalytic activity, the neutral complexes [ZnCp$^{2N}_2$] (**9**) and [ZnCp$^{2S}_2$] (**10**; Scheme 6) were employed as precatalysts in the presence of [H(OEt$_2$)$_2$]$^+$[BAr$^F_4$]$^-$ to generate a catalytically active cationic species in situ. Complex **9** is a relatively poor catalyst (Table 3, entry 8). Although upon addition of the cocatalyst and the substrates the quantitative formation of HCp^{2N} was observed, the presence of the potentially coordinating and basic amino functions of HCp^{2N} in solution may inhibit catalytic activity. In contrast, **10** exhibits a high catalytic activity (Table 3, entry 9), which is comparable to that of **1**. In addition, **1** and **10** showed similar activities in the hydroamination of *p*-fluorophenylacetylene with *p*-methoxyaniline. Therefore, both **1** and **10** are excellent precatalysts for the intermolecular hydroamination of phenylacetylenes with anilines.

Conclusion

The cationic triple-decker complex [Zn$_2$Cp*$_3$]$^+$[BAr$^F_4$]$^-$ (**2**) was successfully applied as a precatalyst in intra- and intermolecular hydroamination reactions, without the addition of a cocatalyst. In addition, the catalytic activities of different cationic and neutral zinc organyls were compared. The organyl ligands proved beneficial for a high catalytic activity because the catalytically active species are probably generated by protonation of the Zn–C bonds. To preserve the high electrophilicity of the zinc center, all other reagents in the reaction mixture (e. g., the anion and the solvent) had to be weakly coordinating.

Experimental Section

Reagents and General Methods

Unless stated otherwise, the experiments were performed with a Schlenk line under an atmosphere of argon or in an argon-filled glovebox with oxygen levels below 10 ppm. All solvents were purified and dried by conventional methods and distilled under an atmosphere of argon. 1,2-Difluorobenzene was purchased from ABCR and dried over CaH_2 before use. $ZnEt_2$ was obtained from Sigma-Aldrich as a 1 M solution in hexane. The reagents for the intermolecular hydroamination experiments (2,4,6-trimethylaniline, aniline, *p*-methoxyaniline, *p*-chloroaniline, *p*-fluoroaniline, phenylacetylene, *p*-methoxyphenylacetylene, *p*-chlorophenylacetylene, *p*-fluorophenylacetylene) were purchased from Sigma–Aldrich, ABCR, or Acros Organics and stored in an argon-filled glovebox. 2,4,6-Trimethylaniline, aniline, and *p*-fluoroaniline were dried over NaH prior to use. [ZnCp*$_2$] (**1**), [Zn$_2$Cp*$_3$]$^+$[BAr$^F_4$]$^-$ (**2**), [ZnCp^{2N}(py)$_2$]$^+$[BAr$^F_4$]$^-$ (**7**), [ZnCp^{2S}(py)$_2$]$^+$[BAr$^F_4$]$^-$ (**8**), [ZnCp$^{2N}_2$] (**9**), [ZnCp$^{2S}_2$] (**10**), and [H(OEt$_2$)$_2$]$^+$[BAr$^F_4$]$^-$ were prepared according to literature procedures.[17,11b,d,16,18] The NMR spectra were recorded on a Bruker Avance 400, a Bruker DPX 300, a Bruker Avance III 300, a Bruker Avance III 500, or a Bruker Avance II 300 spectrometer. For NMR experiments in 1,2-difluorobenzene, the NMR tubes were equipped with a glass capillary filled with C_6D_6. ^{1}H NMR chemical shifts were referenced to the residual proton signals of the deuterated solvents (C_6D_5H: $\delta = 7.15$ ppm; $CHCl_3$: $\delta = 7.26$ ppm). $^{13}C\{^1H\}$ NMR shifts were referenced to the ^{13}C NMR signal of the solvent (C_6D_6: $\delta = 128.06$ ppm; $CDCl_3$: $\delta = 77.16$ ppm). ^{19}F NMR shifts were referenced to external C_6F_6 ($\delta = -162.9$ ppm). The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of compounds **4**–**6** are depicted in the Supporting Information. GC-MS (EI) spectra were recorded on an Agilent Technologies 6890/5973N GC-MS system. Liquid injection field desorption ionization (LIFDI) mass spectra were measured at a Micromass Q-TOF 2 mass spectrometer equipped with a LIFDI 700 (Linden CMS) ion source. Microanalyses were measured at a HEKAtech Euro EA 3000 elemental analyzer. The NMR and GC-MS analytical data of the following imines are given in the Supporting Information: *N*-(1-(*p*-methoxyphenyl)ethylidene)-2,4,6-trimethylaniline, *N*-(1-(*p*-chlorophenyl)ethylidene)-2,4,6-trimethylaniline, *N*-(1-(*p*-fluorophenyl)ethylidene)-2,4,6-trimethylaniline, *N*-(1-phenylethylidene)aniline, *N*-(1-(*p*-methoxyphenyl)ethylidene)aniline, *N*-(1-(*p*-chlorophenyl)ethylidene)aniline, *N*-(1-(*p*-fluorophenyl)ethylidene)aniline, *N*-(1-phenylethylidene)-*p*-methoxyaniline, *N*-(1-(*p*-methoxyphenyl)ethylidene)-*p*-methoxyaniline, *N*-(1-(*p*-chlorophenyl)ethylidene)-*p*-methoxyaniline, *N*-(1-(*p*-fluorophenyl)ethylidene)-*p*-methoxyaniline, *N*-(1-phenylethylidene)-*p*-chloroaniline, *N*-(1-(*p*-methoxyphenyl)ethylidene)-*p*-chloroaniline, *N*-(1-(*p*-chlorophenyl)ethylidene)-*p*-chloroaniline, *N*-(1-(*p*-fluorophenyl)ethylidene)-*p*-chloroaniline, *N*-(1-phenylethylidene)-*p*-fluoroaniline, *N*-(1-(*p*-methoxyphenyl)ethylidene)-*p*-fluoroaniline, *N*-(1-(*p*-chlorophenyl)ethylidene)-*p*-fluoroaniline, and *N*-(1-(*p*-fluorophenyl)ethylidene)-*p*-fluoroaniline.

General procedure for the intramolecular hydroamination with precatalyst 2

In an NMR tube, [Zn$_2$Cp*$_3$]$^+$[BAr$^F_4$]$^-$ (**2**; 15 mg, 0.011 mmol, 2 mol%) and [FeCp$_2$] (10 mg, 0.054 mmol, 10 mol%) as an internal standard were dissolved in 1,2-difluorobenzene (0.4 mL). After addition of the aminoalkene or aminoalkyne (0.535 mmol; see Table 1), the reaction mixture was warmed to 120 or 140 °C and the reaction progress was monitored by NMR spectroscopy. The conversion was determined by the integration of the olefin signals of the substrates in the ^{1}H NMR spectra vs. the internal standard.

General procedure for the intermolecular hydroamination with precatalyst 2

An NMR tube was charged with [Zn$_2$Cp*$_3$]$^+$[BAr$^F_4$]$^-$ (**2**; 10 mg, 0.007 mmol, 2.5 mol%). A premixed solution of the aniline derivative (0.29 mmol) and the phenylacetylene derivative (0.29 mmol) in 1,2-difluorobenzene (0.5 mL) was added at room temperature (see

Table 2). The NMR tube was sealed and heated at 80 °C, if appropriate (see Table 2). The reaction progress was monitored by ^{1}H, ^{13}C, and, if suitable, ^{19}F NMR spectroscopies. The conversion was determined by integration of ^{1}H NMR signals of the substrates and the corresponding hydroamination product.[12] After termination of the catalysis, the identity of the resulting imine was confirmed by GC-MS analysis under non-inert conditions.

Synthesis of *N*-(1-phenylethylidene)-2,4,6-trimethylaniline (3)

In a Schlenk tube $[Zn_2Cp^*_3]^+[BAr^F_4]^-$ (**2**; 100 mg, 0.071 mmol, 2.5 mol%) was dissolved in 1,2-difluorobenzene (2 mL), and a premixed solution of 2,4,6-trimethylaniline (401 μL, 2.86 mmol) and phenylacetylene (314 μL, 2.86 mmol) in 1,2-difluorobenzene (3 mL) was added at room temperature. The resulting yellow solution was stirred for 24 h at room temperature. The volatiles were then removed under reduced pressure and the resulting oily residue was purified by column chromatography on silica gel (eluent = petroleum ether/ethyl acetate 4:1 + 2% triethylamine) under non-inert conditions to give **3** as a yellow oil (0.62 g, 91% yield). ^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K): $\delta = 8.03$ (m, 2H, ArH), 7.48 (m, 3H, ArH), 6.88 (s, br, 2H, ArH), 2.29 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.00 ppm (s, 6H, CH_3); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6, 298 K): $\delta = 164.7$ ($NCCH_3$), 147.4 (C_{Ar}), 139.6 (C_{Ar}), 131.8 (C_{Ar}), 130.5 (C_{Ar}), 129.0 (C_{Ar}), 128.5 (C_{Ar}), 127.5 (C_{Ar}), 125.6 (C_{Ar}), 20.9 (CH_3), 18.1 (CH_3), 16.9 ppm (CH_3); GC-MS (70 eV): *m/z*: 237 [M^+], 222 [$M^+ - CH_3$], 207 [$M^+ - 2CH_3$].

Investigation of the long-term catalytic activity of 2

In a Schlenk tube, $[Zn_2Cp^*_3]^+[BAr^F_4]^-$ (**2**; 100 mg, 0.071 mmol, 2.5 mol%) was dissolved in 1,2-difluorobenzene (3 mL), and a premixed solution of 2,4,6-trimethylaniline (401 μL, 2.86 mmol) and phenylacetylene (314 μL, 2.86 mmol) in 1,2-difluorobenzene (4 mL) was added at room temperature. The resulting solution was stirred at room temperature, and the progress of the reaction was examined by GC-MS analysis of small samples. After consumption of the substrates, which typically took 1–2 days, a fresh batch of 2,4,6-trimethylaniline and phenylacetylene (each 2.86 mmol) was added. In total, 17.2 mmol each of 2,4,6-trimethylaniline and phenylacetylene reacted within 12 days. Purification by column chromatography under non-inert conditions gave **3** as a yellow oil (3.53 g, 87% yield; TON = 208).

In situ NMR spectroscopic investigation of the hydroamination of phenylacetylene with 2,4,6-trimethylaniline catalyzed by 2

$[Zn_2Cp^*_3]^+[BAr^F_4]^-$ (**2**; 20 mg, 0.014 mmol, 2.5 mol%) was dissolved in 1,2-difluorobenzene (0.5 mL), and 2,4,6-trimethylaniline (80 μL, 0.57 mmol) was added at room temperature. The resulting solution was stirred for 1 h at room temperature, after which phenylacetylene (63 μL, 0.57 mmol) was added. The progress of the reaction was monitored by recording ^{1}H NMR spectra at intervals of 30 min. The conversion was determined by integration of a signal of the imine **3** ($\delta = 7.92$ ppm; m, 2H, ArH), using the signal of the *ortho* protons of the $[BAr^F_4]^-$ anion ($\delta = 8.12$ ppm; m, br, 8H) as an internal standard.

Reaction of 2 with 2,4,6-trimethylaniline and subsequent hydroamination

$[Zn_2Cp^*_3]^+[BAr^F_4]^-$ (**2**; 400 mg, 0.29 mmol) was dissolved in 1,2-difluorobenzene (4 mL), and 2,4,6-trimethylaniline (160 μL, 1.14 mmol) was added at room temperature. The resulting orange solution was stirred for 30 min at room temperature. The volatiles were then removed under reduced pressure. The resulting oily residue was washed with hexane (3×5 mL) at −70 °C and dried under vacuum, which gave 306 mg of a beige solid. The ^{1}H and ^{13}C NMR spectra indicated that a mixture of various products was obtained, which except for HCp* could not be identified. For a hydroamination experiment, an NMR tube was charged with the thus-obtained product mixture (50 mg) and a premixed solution of 2,4,6-trimethylaniline (70 μL, 0.50 mmol) and phenylacetylene (55 μL, 0.50 mmol) in 1,2-difluorobenzene (0.5 mL) was added at room temperature. After a reaction time of 4 days at room temperature, the ^{1}H and ^{13}C NMR spectra showed that phenylacetylene was completely consumed, whereas **3** and 2,4,6-trimethylaniline were present in a molar ratio of about 1:0.4.

Reaction of 2 with phenylacetylene and subsequent hydroamination

$[Zn_2Cp^*_3]^+[BAr^F_4]^-$ (**2**; 758 mg, 0.54 mmol) was dissolved in 1,2-difluorobenzene (6 mL). Phenylacetylene (238 μL, 2.17 mmol) was added at room temperature, upon which the color of the solution immediately changed to dark brown and, within the next minutes, to orange. The resulting solution was stirred for 1 h, and the volatiles were removed under reduced pressure. The oily residue was washed with hexane (10 mL, then 2×5 mL), lyophilized, washed with hexane (4×5 mL), and lyophilized again, which gave 318 mg of a brown solid. The ^{1}H and ^{13}C NMR spectra exhibited the signals of **4** and a variety of unidentified products. For a hydroamination experiment, a sample of the product mixture (50 mg) was placed in an NMR tube and dissolved in 1,2-difluorobenzene (0.6 mL). 2,4,6-trimethylaniline (28 μL, 0.20 mmol) and phenylacetylene (22 μL, 0.20 mmol) were added to the solution at room temperature. After 3 days at room temperature, the ^{1}H and ^{13}C NMR spectra showed that both substrates were consumed and that the imine **3** had quantitatively been formed.

Synthesis of (Cp*)(Ph)CCH_2 (4)

$[Zn_2Cp^*_3]^+[BAr^F_4]^-$ (**2**; 300 mg, 0.21 mmol) was dissolved in 1,2-difluorobenzene (3 mL), and phenylacetylene (94 μL, 0.86 mmol) was added at room temperature, upon which the solution turned dark brown. Over the following minutes, the color changed to orange. The resulting solution was stirred for 2 h at room temperature. The volatiles were then removed under reduced pressure and the oily residue was purified by column chromatography on silica gel (eluent = petroleum ether + 1% ethyl acetate) under non-inert conditions to give a colorless oil. According to the ^{1}H and ^{13}C NMR spectra, the product contained **4** as the main product and minor amounts of various unidentified byproducts. ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): $\delta = 7.10$–7.01 (m, 5H, ArH), 5.26 (m, 2H, CH_aH_b), 1.72 (s, 6H, CH_3), 1.60 (s, 6H, CH_3), 1.18 ppm (s, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR (100.6 MHz, C_6D_6, 298 K): $\delta = 152.6$ (C), 142.9 (C), 140.8 (C), 135.9 (C), 127.6 (CH), 127.2 (CH), 127.1 (CH), 115.6 (CH_2), 62.1 (C), 20.6 (CH_3), 11.2 (CH_3), 10.5 ppm (CH_3); GC-MS (70 eV): *m/z*: 238 [M^+], 223 [$M^+ - CH_3$], 208 [$M^+ - 2CH_3$], 193 [$M^+ - 3CH_3$], 103 [$M^+ - Cp^*$].

Synthesis of $[ZnEt(2,4,6\text{-}Me_3C_6H_2NH_2)_3]^+[BAr^F_4]^-$ (5)

$ZnEt_2$ (1 M solution in hexane, 3.0 mL, 3.0 mmol) was added to a solution of 2,4,6-trimethylaniline (832 μL, 5.93 mmol) in 1,2-difluorobenzene (10 mL) at room temperature. Solid $[H(OEt_2)_2]^+[BAr^F_4]^-$ (2.00 g, 1.98 mmol) was then added, which led to the evolution of gas. The resulting solution was stirred for 15 min at room tempera-

ture, and the volatiles were removed under reduced pressure. The residue was washed with hexane (4×10 mL). Upon drying under vacuum, **5** was obtained as a colorless solid (2.49 g, 92% yield). ^{1}H NMR (400.1 MHz, 1,2-$F_2C_6H_4$, C_6D_6 capillary, 298 K): δ = 8.10 (m, br, 8H, *o*-H, $BAr^F{}_4^-$), 7.45 (m, br, 4H, *p*-H, $BAr^F{}_4^-$), 6.63 (s, 6H, 2,4,6-$Me_3C_6H_2NH_2$), 3.76 (s, br, 6H, NH_2), 2.00 (s, 9H, *p*-CH_3, 2,4,6-$Me_3C_6H_2NH_2$), 1.82 (s, 18H, *o*-CH_3, 2,4,6-$Me_3C_6H_2NH_2$), 0.92 (t, ^3J(H,H) = 8.1 Hz, 3H, CH_2CH_3), 0.11 ppm (q, ^3J(H,H) = 8.1 Hz, 2H, CH_2CH_3); ^{13}C{^{1}H} NMR (100.6 MHz, 1,2-$F_2C_6H_4$, C_6D_6 capillary, 298 K): δ = 162.5 (q, ^1J(C,^{11}B) = 50 Hz, *i*-C, $BAr^F{}_4^-$), 135.6 (s, C_{Ar}, 2,4,6-$Me_3C_6H_2NH_2$), 135.1 (s, *o*-C, $BAr^F{}_4^-$), 133.1 (s, C_{Ar}, 2,4,6-$Me_3C_6H_2NH_2$), 130.6 (s, C_{Ar}, 2,4,6-$Me_3C_6H_2NH_2$), 129.7 (q, br, ^2J(C,F) = 32 Hz, *m*-C, $BAr^F{}_4^-$), 126.1 (s, C_{Ar}, 2,4,6-$Me_3C_6H_2NH_2$), 124.9 (q, ^1J(C,F) = 272 Hz, CF_3, $BAr^F{}_4^-$), 117.6 (m, *p*-C, $BAr^F{}_4^-$), 19.5 (s, *p*-CH_3, 2,4,6-$Me_3C_6H_2NH_2$), 16.3 (s, *o*-CH_3, 2,4,6-$Me_3C_6H_2NH_2$), 11.4 (s, CH_2CH_3), 1.5 ppm (s, CH_2CH_3); LIFDI-TOF-MS (1,2-$F_2C_6H_4$): *m/z*: 363 $[ZnEt(2,4,6\text{-}Me_3C_6H_2NH_2)_2]^+$, 228 $[ZnEt(2,4,6\text{-}Me_3C_6H_2NH_2)]^+$; elemental analysis calcd (%) for $C_{61}H_{56}N_3BF_{24}Zn$: C 53.74, H 4.14, N 3.08; found: C 53.90, H 4.04, N 2.63.

Synthesis of $[ZnEt(C_6H_5NH_2)_3]^+[BAr^F{}_4]^-$ (6)

$ZnEt_2$ (1 M solution in hexane, 0.74 mL, 0.74 mmol) was added to a solution of aniline (135 μL, 1.48 mmol) in 1,2-difluorobenzene (5 mL) at room temperature. $[H(OEt_2)_2]^+[BAr^F{}_4]^-$ (500 mg, 0.49 mmol) was added as a solid, which led to the formation of gas. The resulting solution was stirred for 30 min at room temperature. The volatiles were then removed under reduced pressure, and the residue was washed with hexane (10 mL + 2×5 mL). After drying under vacuum, **6** was obtained as a colorless solid (535 mg, 88% yield). Single-crystals that were suitable for X-ray diffraction were obtained by slow evaporation of a solution of **6** in 1,2-difluorobenzene at −30 °C. ^{1}H NMR (400.1 MHz, 1,2-$F_2C_6H_4$, C_6D_6 capillary, 298 K): δ = 8.09 (m, br, 8H, *o*-H, $BAr^F{}_4^-$), 7.45 (m, br, 4H, *p*-H, $BAr^F{}_4^-$), 7.14 (m, br, 6H, ArH, $C_6H_5NH_2$), 6.96 (m, br, 3H, ArH, $C_6H_5NH_2$), 6.62 (m, br, 6H, ArH, $C_6H_5NH_2$), 4.05 (s, br, 6H, NH_2), 1.09 (t, ^3J(H,H) = 8.2 Hz, 3H, CH_2CH_3), 0.26 ppm (q, ^3J(H,H) = 8.2 Hz, 2H, CH_2CH_3); ^{13}C{^{1}H} NMR (100.6 MHz, 1,2-$F_2C_6H_4$, C_6D_6 capillary, 298 K): δ = 162.5 (q, ^1J(C,^{11}B) = 50 Hz, *i*-C, $BAr^F{}_4^-$), 138.8 (s, C_{Ar}, $C_6H_5NH_2$), 135.1 (s, *o*-C, $BAr^F{}_4^-$), 130.7 (s, C_{Ar}, $C_6H_5NH_2$), 129.7 (q, br, ^2J(C,F) = 32 Hz, *m*-C, $BAr^F{}_4^-$), 125.7 (s, C_{Ar}, $C_6H_5NH_2$), 124.9 (q, ^1J(C,F) = 272 Hz, CF_3, $BAr^F{}_4^-$), 119.0 (s, C_{Ar}, $C_6H_5NH_2$), 117.6 (m, *p*-C, $BAr^F{}_4^-$), 11.9 (s, CH_2CH_3), −2.5 ppm (s, CH_2CH_3).

General procedure for the hydroamination of phenylacetylene with 2,4,6-trimethylaniline using different precatalysts

An NMR tube was charged with the zinc precatalyst (see Table 3). If appropriate, an equimolar amount of $[H(OEt_2)_2]^+[BAr^F{}_4]^-$ was added. A premixed solution of 2,4,6-trimethylaniline and phenylacetylene in a 1:1 molar ratio and, if appropriate, pyridine in 1,2-difluorobenzene (0.5 mL) were added at room temperature (see Table 3). The NMR tube was sealed, and the progress of the reaction was examined by ^{1}H and ^{13}C NMR spectroscopy. The conversion was determined by integration of a ^{1}H NMR signal of 2,4,6-trimethylaniline (δ = 2.01 ppm; s, 3H, CH_3) and the imine **3** (δ = 2.10 ppm; s, 3H, CH_3).

Hydroamination of *p*-fluorophenylacetylene with *p*-methoxyaniline using 1 or 10 as precatalysts

The respective zinc complex, $[ZnCp^*_2]$ (**1**; 7 mg, 0.022 mmol) or $[ZnCp^{2S}_2]$ (**10**; 10 mg, 0.022 mmol), was placed in an NMR tube, and solid $[H(OEt_2)_2]^+[BAr^F{}_4]^-$ (22 mg, 0.022 mmol) was added. A premixed solution of *p*-methoxyaniline (54 mg, 0.44 mmol) and *p*-fluorophenylacetylene (53 mg, 0.44 mmol) in 1,2-difluorobenzene (0.5 mL) was added. The NMR tube was sealed and heated at 80 °C. The reaction progress was monitored by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, and the conversion was determined by integration of a ^{1}H NMR signal of *p*-methoxyaniline (δ = 3.46 ppm; s, 3H, OMe) and the imine *N*-(1-(*p*-fluorophenyl)ethylidene)-*p*-methoxyaniline (δ = 3.53 ppm; s, 3H, OMe). Conversions with **1** as precatalyst: 56% (3.5 h), 83% (23.5 h; *p*-fluorophenylacetylene was totally consumed). Conversions with **10** as precatalyst: 56% (3.5 h), 78% (23.5 h; *p*-fluorophenylacetylene was totally consumed).

Acknowledgements

We are grateful to Dipl.-Chem. Anne-Kristin Trützschler and Dipl.-Chem. Stefan Scheifler for experimental support.

Keywords: alkynes · homogeneous catalysis · hydroamination · zinc organyls

[1] a) T. E. Müller, K. C. Hultzsch, M. Yus, F. Foubelo, M. Tada, *Chem. Rev.* **2008**, *108*, 3795–3892; b) T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675–703; c) F. Pohlki, S. Doye, *Chem. Soc. Rev.* **2003**, *32*, 104–114; d) R. Severin, S. Doye, *Chem. Soc. Rev.* **2007**, *36*, 1407–1420.

[2] For some recent examples, see: a) E. Bernoud, P. Oulié, R. Guillot, M. Mellah, J. Hannedouche, *Angew. Chem. Int. Ed.* **2014**, *53*, 4930–4934; *Angew. Chem.* **2014**, *126*, 5030–5034; b) C. Brinkmann, A. G. M. Barrett, M. S. Hill, P. A. Procopiou, *J. Am. Chem. Soc.* **2012**, *134*, 2193–2207; c) S. Pan, K. Endo, T. Shibata, *Org. Lett.* **2012**, *14*, 780–783; d) K. Manna, S. Xu, A. D. Sadow, *Angew. Chem. Int. Ed.* **2011**, *50*, 1865–1868; *Angew. Chem.* **2011**, *123*, 1905–1908; e) A. Mukherjee, S. Nembenna, T. K. Sen, S. P. Sarish, P. K. Ghorai, H. Ott, D. Stalke, S. K. Mandal, H. W. Roesky, *Angew. Chem. Int. Ed.* **2011**, *50*, 3968–3972; *Angew. Chem.* **2011**, *123*, 4054–4058; f) J. Koller, R. G. Bergman, *Chem. Commun.* **2010**, *46*, 4577–4579; g) M. R. Crimmin, M. Arrowsmith, A. G. M. Barrett, I. J. Casely, M. S. Hill, P. A. Procopiou, *J. Am. Chem. Soc.* **2009**, *131*, 9670–9685; h) D. C. Leitch, P. R. Payne, C. R. Dunbar, L. L. Schafer, *J. Am. Chem. Soc.* **2009**, *131*, 18246–18247; i) Z. Liu, J. F. Hartwig, *J. Am. Chem. Soc.* **2008**, *130*, 1570–1571; j) B. D. Stubbert, T. J. Marks, *J. Am. Chem. Soc.* **2007**, *129*, 6149–6167.

[3] a) T. E. Müller, M. Grosche, E. Herdtweck, A.-K. Pleier, E. Walter, Y.-K. Yan, *Organometallics* **2000**, *19*, 170–183; b) V. Neff, T. E. Müller, J. A. Lercher, *Chem. Commun.* **2002**, 906–907; c) K. Alex, A. Tillack, N. Schwarz, M. Beller, *ChemSusChem* **2008**, *1*, 333–338; d) A. Pews-Davtyan, M. Beller, *Chem. Commun.* **2011**, *47*, 2152–2154; e) G.-Q. Liu, Y.-M. Li, *Tetrahedron Lett.* **2011**, *52*, 7168–7170.

[4] a) A. Zulys, M. Dochnahl, D. Hollmann, K. Löhnwitz, J.-S. Herrmann, P. W. Roesky, S. Blechert, *Angew. Chem. Int. Ed.* **2005**, *44*, 7794–7798; *Angew. Chem.* **2005**, *117*, 7972–7976; b) M. Dochnahl, J.-W. Pissarek, S. Blechert, K. Löhnwitz, P. W. Roesky, *Chem. Commun.* **2006**, 3405–3407; c) M. Dochnahl, K. Löhnwitz, J.-W. Pissarek, M. Biyikal, S. R. Schulz, S. Schön, N. Meyer, P. W. Roesky, S. Blechert, *Chem. Eur. J.* **2007**, *13*, 6654–6666; d) J. Jenter, A. Lühl, P. W. Roesky, S. Blechert, *J. Organomet. Chem.* **2011**, *696*, 406–418.

[5] a) M. Biyikal, K. Löhnwitz, N. Meyer, M. Dochnahl, P. W. Roesky, S. Blechert, *Eur. J. Inorg. Chem.* **2010**, 1070–1081; b) S. P. Sarish, D. Schaffner, Y. Sun, W. R. Thiel, *Chem. Commun.* **2013**, *49*, 9672–9674.

[6] a) A. Mukherjee, T. K. Sen, P. K. Ghorai, P. P. Samuel, C. Schulzke, S. K. Mandal, *Chem. Eur. J.* **2012**, *18*, 10530–10545; b) A. Mukherjee, T. K. Sen, P. K. Ghorai, S. K. Mandal, *Organometallics* **2013**, *32*, 7213–7224.

[7] a) A. Lühl, L. Hartenstein, S. Blechert, P. W. Roesky, *Organometallics* **2012**, *31*, 7109–7116; b) A. Lühl, H. P. Nayek, S. Blechert, P. W. Roesky, *Chem. Commun.* **2011**, *47*, 8280–8282; c) J.-W. Pissarek, D. Schlesiger, P. W. Roesky, S. Blechert, *Adv. Synth. Catal.* **2009**, *351*, 2081–2085.

[8] Heterogeneous zinc-containing catalysts have also been applied in hydroamination catalysis: a) J. Penzien, T. E. Müller, J. A. Lercher, *Chem.*

Commun. **2000**, 1753 – 1754; b) G. V. Shanbhag, S. B. Halligudi, *J. Mol. Catal. A* **2004**, *222*, 223 – 228; c) G. V. Shanbhag, S. M. Kumbar, T. Joseph, S. B. Halligudi, *Tetrahedron Lett.* **2006**, *47*, 141 – 143.

[9] a) M. D. Hannant, M. Schormann, M. Bochmann, *J. Chem. Soc. Dalton Trans.* **2002**, 4071 – 4073; b) Y. Sarazin, M. Schormann, M. Bochmann, *Organometallics* **2004**, *23*, 3296 – 3302; c) C. A. Wheaton, B. J. Ireland, P. G. Hayes, *Organometallics* **2009**, *28*, 1282 – 1285; d) R. J. Wehmschulte, L. Wojtas, *Inorg. Chem.* **2011**, *50*, 11300 – 11302; e) C. Lichtenberg, T. P. Spaniol, J. Okuda, *Angew. Chem. Int. Ed.* **2012**, *51*, 8101 – 8105; *Angew. Chem.* **2012**, *124*, 8225 – 8229; f) C. Romain, V. Rosa, C. Fliedel, F. Bier, F. Hild, R. Welter, S. Dagorne, T. Avilés, *Dalton Trans.* **2012**, *41*, 3377 – 3379.

[10] a) R. M. Fabicon, A. D. Pajerski, H. G. Richey, *J. Am. Chem. Soc.* **1991**, *113*, 6680 – 6681; b) H. Tang, M. Parvez, H. G. Richey, *Organometallics* **2000**, *19*, 4810 – 4819; c) R. M. Fabicon, H. G. Richey, *Organometallics* **2001**, *20*, 4018 – 4023; d) M. Haufe, R. D. Köhn, R. Weimann, G. Seifert, D. Zeigan, *J. Organomet. Chem.* **1996**, *520*, 121 – 129; e) M. Haufe, R. D. Köhn, G. Kociok-Köhn, A. C. Filippou, *Inorg. Chem. Commun.* **1998**, *1*, 263 – 266; f) D. A. Walker, T. J. Woodman, D. L. Hughes, M. Bochmann, *Organometallics* **2001**, *20*, 3772 – 3776; g) M. D. Hannant, M. Schormann, D. L. Hughes, M. Bochmann, *Inorg. Chim. Acta* **2005**, *358*, 1683 – 1691; h) C. A. Wheaton, P. G. Hayes, *Chem. Commun.* **2010**, *46*, 8404 – 8406; i) C. A. Wheaton, P. G. Hayes, *Dalton Trans.* **2010**, *39*, 3861 – 3869; j) H. Sun, J. S. Ritch, P. G. Hayes, *Inorg. Chem.* **2011**, *50*, 8063 – 8072.

[11] a) D. A. Walker, T. J. Woodman, M. Schormann, D. L. Hughes, M. Bochmann, *Organometallics* **2003**, *22*, 797 – 803; b) M. A. Chilleck, T. Braun, B. Braun, *Chem. Eur. J.* **2011**, *17*, 12902 – 12905; c) K. Freitag, H. Banh, C. Ganesamoorthy, C. Gemel, R. W. Seidel, R. A. Fischer, *Dalton Trans.* **2013**, *42*, 10540 – 10544; d) M. A. Chilleck, T. Braun, B. Braun, S. Mebs, *Organometallics* **2014**, *33*, 551 – 560.

[12] The conversions of the intermolecular hydroamination reactions were determined by calculating the substrate/product ratios by integration of the ^{1}H NMR signals of the substrates and products. For this purpose, an appropriate resonance of one of the substrates and the signal of the methyl group on the imine function of the product were applied. This procedure is applicable because all intermolecular hydroaminations lead to the quantitative formation of the corresponding imines. In cases in which the phenylacetylene derivative was completely consumed, the conversion refers to the aniline derivative.

[13] T. Hosokawa, P. M. Maitlis, *J. Am. Chem. Soc.* **1973**, *95*, 4924 – 4931.

[14] In all intermolecular hydroamination reactions of phenylacetylenes with anilines catalyzed by **2**, the corresponding hydrocarbonation products (p-XC_6H_4)(Cp*)CCH_2 (X = H, OMe, Cl, F) were formed as byproducts according to GC-MS analysis of the reaction mixtures. However, the hydrocarbonation products were formed only in very small amounts, so they could not be detected in the NMR spectra of the product mixtures.

[15] Data for the X-ray structure analysis of **6**: $C_{52}H_{38}N_3BF_{24}Zn{\cdot}C_6H_4F_2$, M_r = 1351.13; crystal size 0.46 × 0.36 × 0.25 mm^3; triclinic; $P\bar{1}$; a = 12.8998(5), b = 14.7138(6), c = 16.5320(6) Å; α = 96.875(3), β = 107.163(3), γ = 106.784(3)°; V = 2797.46(19) Å^3; Z = 2; ρ_{calcd} = 1.604 g cm^{-3}; STOE IPDS 2T diffractometer, $2\theta_{max}$ = 53.66°; $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), T = 90(2) K; 39680 reflections measured; 11788 unique reflections (R_{int} = 0.0391); multiscan (PLATON) absorption correction (min./max. transmission 0.7798/0.8708);[19] μ = 0.569 mm^{-1}; final R_1, wR_2 values on all data: 0.0609, 0.1022; R_1, wR_2 values for 8805 reflections with $I_o > 2\sigma(I_o)$: 0.0403, 0.0964; residual electron density +0.88/−1.29 e Å^{-3}. The structures were solved by direct methods and refined with full-matrix least-squares procedures based on F^2 with all measured reflections (SHELX-97).[20] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their idealized positions and refined as riding. CCDC 1013871 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] M. A. Chilleck, T. Braun, R. Herrmann, B. Braun, *Organometallics* **2013**, *32*, 1067 – 1074.

[17] R. Blom, J. Boersma, P. H. M. Budzelaar, B. Fischer, A. Haaland, H. V. Volden, J. Weidlein, *Acta Chem. Scand. A* **1986**, *40*, 113 – 120.

[18] M. Brookhart, B. Grant, A. F. Volpe, *Organometallics* **1992**, *11*, 3920 – 3922.

[19] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7 – 13.

[20] a) G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen (Germany), **1997**; b) G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen (Germany), **1997**.

Received: October 15, 2014
Published online on December 17, 2014

