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Comparison of Decamethyldizincocene $[(\eta^5\text{-Cp*})_2Zn_2]$ versus Decamethylzincocene $[Cp*_2Zn]$ and Diethylzinc Et_2Zn As Precatalysts for the Intermolecular Hydroamination Reaction

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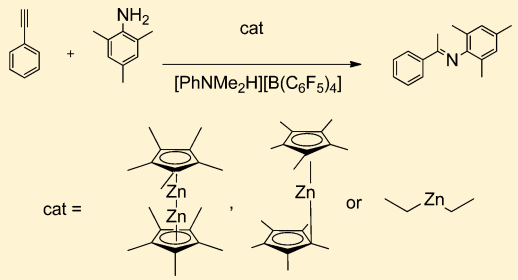
Supporting Information

ABSTRACT: A comparison of the Zn−Zn bonded species $[(\eta^5\text{-Cp*})_2Zn_2]$ versus the related organometallic zinc compound $[Cp*_2Zn]$ and $ZnEt_2$ for the intermolecular hydroamination reaction in the presence of equimolar amounts of $[PhNMe_2H][B(C_6F_5)_4]$ is reported. All compounds show high reaction rates under mild conditions and a good functional group tolerance for the addition of aniline derivatives to primary alkynes. Within this series the metallocene $[Cp*_2Zn]$ is the most active one, whereas the zinc−zinc bonded species $[(\eta^5\text{-Cp*})_2Zn_2]$ shows the best selectivity. Most remarkable is the unexpected excellent catalytic performance of the zinc−zinc bonded species $[(\eta^5\text{-Cp*})_2Zn_2]$.



INTRODUCTION

The hydroamination reaction, which is the direct addition of amine N−H bonds to C−C multiple bonds, has been intensely studied in the last decades.[1−22] Catalytic hydroamination was investigated for a wide range of complexes of various metals, such as main group metals,[2,5,15,23−37] early transition metals,[4,7,9,22] late transition metals,[4,7,9,12,14,15,38−43] and f-elements.[4,7−9,11−13,15−17] Early transition metal and late transition metal catalysts show different forms of substrate activation. Generally complexes of the early transition metals, the lanthanides, and electron-poor main group metals activate the amine function.[20] These systems are highly efficient catalysts for hydroamination, but synthetic application is limited due to their high sensitivity toward moisture and air and their low tolerance to polar functional groups. In contrast, compounds of the late transition metals activate the C−C multiple bond. These kinds of catalysts show normally high polar functional group tolerance, but are usually based on relatively expensive metals. Moreover they show low reaction rates and moderate selectivity for the hydroamination of nonactivated substrates compared to early transition metals. As an alternative we and others introduced zinc compounds as a precatalyst for the hydroamination of alkenes and alkynes.[21,35,44−58] Zinc catalysts show, besides good catalytic activity and selectivity, high tolerance toward polar functional groups. Some of the catalysts show a high stability toward air and moisture, but it seems that a high stability is not beneficial for a high activity. Most of the published zinc catalysts were investigated for the intramolecular hydroamination reaction. We recently communicated on the Zn−Zn bonded compound decamethyldizincocene ($[(\eta^5\text{-Cp*})_2Zn_2]$; Cp* = C_5Me_5) as catalyst for the inter- and intramolecular hydroamination reaction. Many functional groups were tolerated, and high reaction rates under mild conditions were observed.[59]

The discovery of $[(\eta^5\text{-Cp*})_2Zn_2]$ by Carmona et al.[60,61] was the beginning of a broad chemistry dealing with the synthesis and reactivity of low-valent metal−metal bonded organozinc compounds.[62−73] It was shown by Schulz et al. that $[(\eta^5\text{-Cp*})_2Zn_2]$ reacts with the strong Lewis base 4-(dimethylamino)pyridine (dmap), giving the first Lewis acid−base adduct of dizincocene $[(\eta^5\text{-Cp*})Zn\text{-}Zn(dmap)_2(\eta^1\text{-Cp*})]$.[74] Further treatment with $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$ resulted via a protonation of Cp* in the base-stabilized $[Zn_2]^{2+}$ cation $[Zn_2(dmap)_6][Al\{OC(CF_3)_3\}_4]_2$.[75] A similar protonation reaction of $[(\eta^5\text{-Cp*})_2Zn_2]$ with various nitrogen-based ligands (L)[71,73] resulted in the Zn−Zn bonded complexes $[(L)_2Zn_2]$ upon elimination of Cp*H.[69] Carmona et al. revealed the synthesis of $[(\eta^5\text{-Cp*})(OR)(L)_xZn_2]$ (R = 2,6-(2,4,6-$Me_3C_6H_2$)$_2C_6H_3$; x = 2 and Cp*; x = 1; L = 4-pyrrolidinopyridine).[76,77]

Recently, the Zn−Zn bonded compound $[(\eta^5\text{-Cp*})_2Zn_2]$ was investigated by us as a catalyst for the inter- and intramolecular hydroamination reaction.[59,78] High reaction rates under mild conditions for the addition of aniline and some derivatives to arylethynes were observed. This was the first application of a Zn−Zn bonded compound as catalyst. Now we are interested in comparing the catalytic activity of $[(\eta^5\text{-Cp*})_2Zn_2]$ (**1**) with decamethylzincocene $[Cp*_2Zn]$ (**2**) and diethylzinc $ZnEt_2$ (**3**) (Scheme 1).

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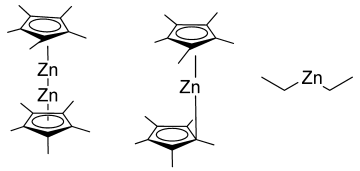
Scheme 1. $[(\eta^5\text{-Cp}^*)_2Zn_2]$ (**1**), $[Cp^*_2Zn]$ (**2**), and $ZnEt_2$ (**3**)



1 2 3

EXPERIMENTAL SECTION[78]

General Considerations. NMR spectra were recorded on a Bruker Avance 400 MHz or Avance II NMR 300 MHz spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Deuterated solvents were obtained from Chemotrade or Euriso-Top GmbH (99 atom % D). Et_2Zn (**3**) was purchased from Aldrich. $[(\eta^5\text{-Cp}^*)_2Zn_2]$ (**1**) and $[Cp^*_2Zn]$ (**2**) were prepared according to literature procedures.[61]

Hydroamination Reactions. The substrates were purchased from Aldrich, AlfaAesar, and Acros.

The ^{1}H NMR spectra of *N*-(methylbenzylidene)aniline,[79] methylphenyl(1-phenylvinyl)amine,[80] *N*-(1-phenylethylidene)-4-chloroaniline,[81] *N*-(1-phenylethylidene)-2,4,6-trimethylaniline,[82] *N*-[1-(4-bromophenyl)ethylidene)]benzamine,[83] *N*,*N*-dimethyl-4-[1-(phenylimino)]ethylaniline,[84] *N*-[1-(1-cyclohexene-1-yl)ethylidene]-benzamine,[85] *N*-(1-methylheptylidene)benzamine,[86] 4-chlor-*N*-(1-methylheptylidene)benzamine,[87] and *N*-(1-phenylethylidene)-benzmethanamine[88] conform to the literature.

NMR Scale. The catalyst was weighed under argon in an NMR tube. C_6D_6 (~0.5 mL) was condensed into the NMR tube, and the mixture was frozen at −196 °C. The reactant was injected onto the solid mixture, and the whole sample was melted and mixed just before insertion into the core of the NMR machine (t_0). The ratio between the reactant and the product was calculated by comparison of the integrals of the corresponding signals. Ferrocene was used as an internal standard for kinetic measurements.

Preparative Scale. A 0.23 mL (215 mg, 2.11 mmol) amount of phenylethyne, 0.3 mL (285 mg, 2.11 mmol) of mesidine, 21 mg (0.53 mmol) of **1**, and 42 mg (0.53 mmol) of $[PhNMe_2H][B(C_6F_5)_4]$ were dissolved in 5 mL of toluene. The subsequent mixture was stirred at room temperature. The reaction progress was monitored by TLC. When the reaction was judged to be complete, the mixture was dried in vacuo and purified by column chromatography on alumina as the stationary phase. Hexane/ethyl acetate (4:1) was used as eluent. Finally the solution was concentrated *in vacuo* to give *N*-(1-phenylethylidene)-2,4,6-trimethylaniline as an oil. Yield: 496 mg (99%).

The following NMR spectra were recorded directly from NMR-scale reactions without further purification

***N*-[1-(4-Bromophenyl)vinyl]-*N*-methylaniline.** ^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) 2.86 (s, 3 H, H-4); 4.60 (s, 1 H, H-5); 4.75 (s, 1 H, H-6); 6.69 (t, $^3J_{H-H}$ = 6.0 Hz, 1 H, H-1); 6.75 (d, $^3J_{H-H}$ = 9.0 Hz, 2 H, H-3); 6.95 (m, 2 H, H_{ar}); 7.05−7.15 (m, 4 H, H_{ar}). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) 40.79; 100.05; 121.01; 121.20; 127.39; 128.73; 128.94; 131.27; 133.39; 148.65; 152.53. See also Supporting Information.

***N*-[1-(4-Bromophenyl)ethylidene]-4-chloroaniline.** ^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) 1.61 (s, 3 H, H-3); 6.39 (d, $^3J_{H-H}$ = 9.0 Hz, 2 H, H-2); 7.09 (d, $^3J_{H-H}$ = 9.0 Hz, 2 H, H-1); 7.28 (d, $^3J_{H-H}$ = 9.0 Hz, 2 H, H-5); 7.52 (d, $^3J_{H-H}$ = 9.0 Hz, 2 H, H-4). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) 16.30; 120.72; 125.26; 128.83; 129.00; 131.34; 131.45; 137.79; 149.92; 164.14. See also Supporting Information.

***N*-[1-(4-Bromophenyl)ethylidene]-2,4,6-trimethylaniline.** ^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) 1.63 (s, 3 H, H-4); 1.94 (s, 6 H, H-3); 2.22 (s, 3 H, H-1); 6.83 (s, 2 H, H-2); 7.29 (d, $^3J_{H-H}$ = 9.0 Hz, 2 H, H-6); 7.62 (d, $^3J_{H-H}$ = 9.0 Hz, 2 H, H-5). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) 16.38; 17.72; 20.58; 124.87; 125.07; 128.70; 128.71; 131.32; 131.72; 137.80; 146.59; 163.55. See also Supporting Information.

4-[1-((4-Chlorophenyl)imino)ethyl]-*N*,*N*-dimethylaniline. ^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) 1.89 (s, 3 H, H-3); 2.48 (s, 6 H, H-6); 6.50 (m, 4 H, H-5, H-2); 7.09 (d, $^3J_{H-H}$ = 9.0 Hz, 2 H, H-1); 7.99 (d, $^3J_{H-H}$ = 9.0 Hz, 2 H, H-4). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) 16.20; 39.34; 111.12; 121.39; 128.84; 129.24; 133.17; 151.41; 151.87; 164.16. See also Supporting Information.

***N*-[1-(4-(Dimethylamino)phenyl)ethylidene]-2,4,6-trimethylaniline.** ^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) 1.87 (s, 3 H, H-4); 2.07 (s, 6 H, H-3); 2.24 (s, 3 H, H-1); 2.51 (s, 6 H, H-7); 6.54 (d, $^3J_{H-H}$ = 9.0 Hz, 2 H, H-6); 6.87 (s, 2 H, H-2); 8.08 (d, $^3J_{H-H}$ = 9.0 Hz, 2 H, H-5). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) 16.33; 17.97; 20.63; 39.46; 111.28; 125.65; 128.60; 130.77; 133.16; 147.74; 151.81; 163.42. See also Supporting Information.

3-[1-(Phenylimino)ethyl]phenol. ^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) 1.82 (s, 3 H, H-5); 6.45 (d, $^3J_{H-H}$ = 6.0 Hz, 2 H, H-6); 6.77 (d, $^3J_{H-H}$ = 6.0 Hz, 1 H, H-1); 7.07 (t, $^3J_{H-H}$ = 6.0 Hz, 2 H, H-2, H-8,); 7.15−7.25 (m, 2 H, H-7); 7.32 (d, $^3J_{H-H}$ = 6.0 Hz, 1 H, H-3,); 7.01 (s br, 1 H, OH); 7.56 (s, 1 H, H-4). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) 17.94; 116.44; 120.05; 123.42; 124.17; 129.21; 129.63; 140.31; 149.94; 156.23; 169.49. See also Supporting Information.

3-[1-((4-Chlorophenyl)imino)ethyl]phenol. ^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) 1.69 (s, 3 H, H-5); 6.07 (d, $^3J_{H-H}$ = 9.0 Hz, 1 H, H-1); 6.46 (d, $^3J_{H-H}$ = 9.0 Hz, 2 H, H-6); 6.93 (d, $^3J_{H-H}$ = 9.0 Hz, 1 H, H-3); 7.01 (t, $^3J_{H-H}$ = 9.0 Hz, 1 H, H-2); 7.02 (s br, 1 H, OH); 7.07 (d, $^3J_{H-H}$ = 9.0 Hz, 1 H, H-7); 7.45 (s, 1 H, H-4). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) 17.72; 114.36; 117.13; 119.53; 121.41; 129.04; 129.23; 129.65; 129.73; 148.78; 156.58; 169.19. See also Supporting Information.

3-(1-(Mesitylimino)ethyl)phenol. ^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) 1.65 (s, 3 H, H-5); 1.95 (s, 6 H, H-6); 2.16 (s, 3 H, H-8); 6.78 (s, 2 H, H-7); 6.20−6.90 (m, 2 H, H-1, OH); 7.00 (t, $^3J_{H-H}$ = 9.0 Hz, 1 H, H-2); 7.33 (d, $^3J_{H-H}$ = 6.0 Hz, 1 H, H-3); 7.44 (s, 1 H, H-4). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) 17.63; 17.79; 20.50; 114.50; 118.48; 119.04; 126.30; 129.00; 129.46; 129.72; 132.85; 145.10; 156.79; 169.62. See also Supporting Information.

4-Chloro-*N*-[1-(cyclohex-1-en-1-yl)ethylidene]aniline. ^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) 1.40−1.61 (m, 4 H, H-3, H-4); 1.61 (s, 3 H, H-6); 1.92−2.09 (m, 2 H, H-5); 2.42−2.55 (m, 2 H, H-2); 6.14−6.23 (m, 1 H, H-1); 6.43 (d, $^3J_{H-H}$ = 9.0 Hz, 2 H, H-7); 7.10 (d, $^3J_{H-H}$ = 9.0 Hz, 2 H, H-8). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) 15.08; 21.27; 22.03; 24.60; 26.04; 120.66; 128.76; 128.85; 133.57; 139.42; 150.97; 166.06. See also Supporting Information.

***N*-(1-(Cyclohex-1-en-1-yl)ethylidene)-2,4,6-trimethylaniline.** ^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) 1.32−1.53 (m, 4 H, H-3, H-4); 1.57 (s, 3 H, H-6); 1.94 (s, 6 H, H-7); 1.97−2.13 (m, 2 H, H-5); 2.20 (s, 3 H, H-9); 2.61−2.70 (m, 2 H, H-2); 6.12−6.26 (m, 1 H, H-1); 6.80 (s, 2 H, H-8). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) 15.15; 17.78; 21.26; 22.03; 22.10; 24.79; 25.96; 128.53; 128.87; 130.93; 132.24; 135.68; 147.27; 165.47.

RESULTS AND DISCUSSION

In this contribution, we present a comparison of the reaction scope and substrate selectivity of $[(\eta^5\text{-Cp}^*)_2Zn_2]$ (**1**) with decamethylzincocene $[Cp^*_2Zn]$ (**2**) and diethylzinc $ZnEt_2$ (**3**) (Scheme 1).[78] Compound **3** was reported by us and others as being active as a catalyst for the intramolecular hydroamination reaction, while compound **2** has not been used as a catalyst so far.[48,54] Generally the reactions we studied were run in benzene with a catalyst loading of 2.5 mol %, with 2.5 mol % of $[PhNMe_2H][B(C_6F_5)_4]$ as a cocatalyst and ferrocene as internal standard. It was shown earlier by us that the addition of one equivalent of $[PhNMe_2H][B(C_6F_5)_4]$ has a beneficial effect on the reactivity of the zinc catalyst.[21,44,52−58] We anticipate the formation of a cationic zinc species that is formed by the protonolysis of the Cp* moiety, because Cp*H could be

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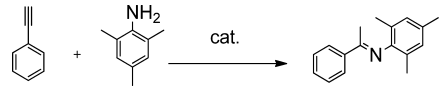
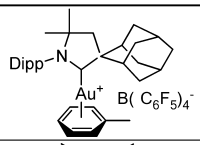
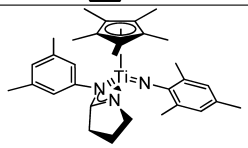
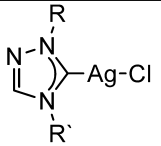
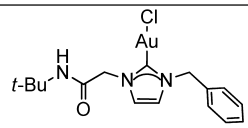
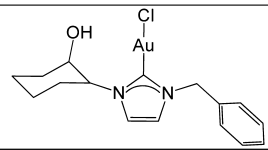
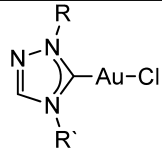
Table 1. Intermolecular Hydroamination of Phenylethyne with 2,4,6-Trimethylaniline[59]



Entry/ Ref.	Cat.	T [°C]	t [h]	Yield [%]	mol% cat.	Ratio amine/ alkyne
1[59]	**[(η^5-Cp*)$_2$Zn$_2$] (1)**	**23**	**11.25**	**quant. (NMR)**	**2.5**	**1:1**
		23	**5.5**	**quant. (NMR)**	**2.5**	**1:2**
2	**[Cp*$_2$Zn] (2)**	**23**	**2**	**quant. (NMR)**	**2.5**	**1:2**
3	**Et$_2$Zn (3)**	**23**	**4.25**	**quant. (NMR)**	**2.5**	**1:2**
4[90]		40	16	81 (NMR)	5	1:1
5[91]		105	24	80 (isolated)	5	1:1
6[96]	 R = CH_2CO*t*Bu, R`= CH_2Ph (**I**)	90	12	7	2	1:1.5
	R = CH_2CONH*t*Bu, R`= CH_2Ph (**II**)	90		0		
	R = CH_2CO*t*Bu, R`= CH_2CO*t*Bu (**III**)	90		16		
	R = $C_6H_{10}OH$, R`= CH_2Ph (**IV**)	90		1		
7[92]	CuSTA[a]	110	4	75 (GC)		2:1
			8	95 (GC)		

Entry/ Ref.	Cat.	T [°C]	t [h]	Yield [%]	mol% cat.	Ratio amine/ alkyne
8[93]	CuAlSBA-15[b]	110	6	37		2:1
9[94]	Cu-K-10[c]	110	20	95 (GC)	10 wt%	2:1
			20	91 (isolated)		
10[95]	$(Ph_3P)AuCH_3$ + $H_3PW_{12}O_{40}$	70	2	93 (NMR)	0.2 : 1	1.1:1
11[96]		90	12	16	2	1:1.5
12[96]		90	12	46	2	1:1.5
13[96]	 R = CH_2CO*t*Bu, R`= CH_2Ph (**V**)	90	12	84	2	1:1.5
	R = CH_2CONH*t*Bu, R`= CH_2Ph (**VI**)	90		75		
	R = CH_2CO*t*Bu, R`= CH_2COtBu (**VII**)	90		80		
	R = $C_6H_{10}OH$, R`= CH_2Ph (**VIII**)	90		58		

detected in the NMR spectrum as a byproduct. As mentioned above, it was shown earlier that [(η^5-Cp*)$_2$Zn$_2$] can be protonated upon elimination of Cp*H with preservation of the Zn−Zn bond.[69,75,76] For [Cp*$_2$Zn] Braun et al. reported on a similar protonation reaction, which gave the base-stabilized [(Cp*)Zn(L)]$^+$ cation (L = $Me_2N(CH_2)_2P$*i*Pr_2, $Cy_2P(CH_2)_2PCy_2$, $Cy_2PCH_2PCy_2$).[89]

In order to prove that a combination of catalyst and cocatalyst is needed, both zinc catalysts **1** and **2** were separately used without cocatalyst in the reaction of phenylethine with anilines. In these reactions only polymers were obtained by using **1**, and no reaction was observed by using **2** without cocatalyst. Similar results were reported earlier by us using compound **3** without cocatalyst. The cocatalyst alone or another proton source such as benzoic acid did not catalyze the reaction at all under the described conditions. Thus, a proton-catalyzed conversion can be excluded.[54]

As test reaction we used the addition of 2,4,6-trimethylaniline to phenylethyne because this reaction has also been studied with many other reported catalysts (Table 1).[59,90−96] Most reported catalysts for this reaction shown in Table 1 are based on group 11 metals, although there are some exceptions such as a titanium catalyst (Table 1, entry 5). All three zinc catalysts (**1**−**3**) (Table 1, entries 1−3) catalyze the transformation at room temperature, whereas most of the other systems operate in the range 90−110 °C (Table 1, entries 4−9 and 11−13). With typical catalyst and cocatalyst loading of 2.5 mol % each, the isolated yield was 99% for the test reaction by using compounds **1**−**3**. Since we could show that the reaction rate of **1** could even be further increased by applying an amine to

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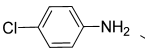
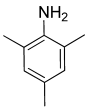
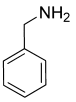
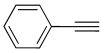
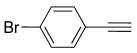
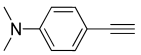
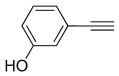
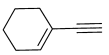
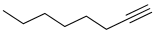
Table 2. Intermolecular Hydroamination of Anilines and Alkynes Catalyzed by $[Cp^*_2Zn]$[a]

Entry	Substrates	A	B	C	D	E
						
1[b]		9 h, quant. (9 % bypr)[c]	2 h, quant. (5 % bypr2)[h]	6 h, quant. (21 % bypr)[c]	2 h, quant.[e]	168 h, 81 %[d]
2		14 h, quant. (7 % bypr)[c]	2 h, quant.	8 h, quant. (5 % bypr)[c]	14 h, quant.[e] 30 min, quant.	-[g]
3		8 h, quant.[e] (20 % bypr)[c]	1 h, 14 % 20 h, 16 %	2 h, 96 % (15 % bypr)	18.75 h, quant. (17 % bypr)[c,e] 2 h, 85 % (9 % bypr)[c]	-[g]
4		4 h, quant.	-[g]	4 h, quant.	47 h, 69 %[e] 6 h, quant.	-[g]
5		12 h, 90 % 19 h, 93 %	mixture of products	12 h, 85 % 19 h, 88 %	7.5 h, 97 %	-[g]
6		14 h, 78 %[d] 20 h, quant.[f]	12 h, 72 %[d]	19 h, quant.[d]	4 h, quant.[e]	

[a]Reagents and conditions: catalyst (2.5 mol %), $[PhNMe_2H][B(C_6F_5)_4]$ (2.5 mol %), C_6D_6, 60 °C, conversion determined by ^1H NMR, ferrocene as internal standard. Amine (0.5 mmol), alkyne (0.75 mmol). [b]Amine (0.5 mmol), alkyne (1 mmol). [c]bypr = byproduct: the corresponding enamine. [d]Reaction at 80 °C. [e]Reaction at room temperature. [f]Reaction at 120 °C. [g]No conversion. [h]Unknown byproduct.

alkyne ratio of 1:2, we adapted these conditions also by using compounds **2** and **3** as catalysts. Among the series of the three zinc compounds **1**–**3**, compound **2** showed the most rapid conversion (Table 1, entries 1–3). Compound **3** is slightly more active than compound **1**, but, as seen from the kinetics (see below), both catalysts show almost the same rate for the first 90% of conversion. By performing a full screening (see below) **1** and **3** roughly showed the same activity. Although the reaction temperature for the zinc compounds **1**–**3** was significant lower, the time needed for a full conversion was comparable or even shorter than the other catalysts shown in Table 1. Therefore, in the whole series shown in Table 1 compound **2** is the most active system for the test reaction. Surprisingly, even certain sophisticated gold and silver catalysts (Table 1, entries 4 and 10–13) could not compete. The good performance of compounds **1**–**3** is not limited to 2,4,6-trimethylaniline to phenylethyne but can also be extended to the addition other anilines to arylethynes. The addition of aniline to phenylethyne, which is also shown in Tables 2–4 (entry 1A, each), was evaluated with 32 other published catalysts. Although very different reaction conditions were reported, it clearly can be seen from Table S1 that the performance of compounds **1**–**3** is excellent for this reaction.

We then investigated catalytic activities of compounds **1**–**3** in various intermolecular hydroamination reactions by using substituted primary and secondary amines (mostly anilines) with different functional groups and different arylethynes and aliphatic alkynes (Tables 2–4). In this screening we applied an amine to alkyne ratio of 1:1.5 because for all substrates other than phenylacetylene the rates were comparable to that of a 1:2 ratio. In general, for all catalysts quantitative Markovnikov regioselectivity was observed for all reactions (Tables 2–4). For comparison, in Table 4 the recently communicated results of our screening with compound **1** as catalyst are given, although slightly different conditions were used in the earlier studies.[59,97] To these data, which were covering only aromatic substrates, we now add the results of the intermolecular hydroamination reactions by using different aliphatic alkynes (see below, Table 4).

First we discuss the hydroamination reactions by using compound **2** as catalyst. As functional groups on the substrates, halides and even OH were tolerated in the catalysis by using compound **2** as catalyst. The reactions were run in benzene at 60 °C with the exception of 2,4,6-trimethylaniline (Table 2, entry D), which already reacted in acceptable rates at room temperature and 1-octyne (Table 2, entry 6) which mostly was converted at higher temperatures. Besides anilines and

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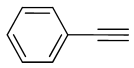
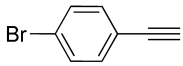
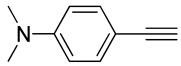
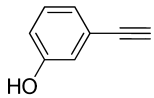
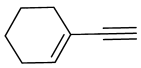
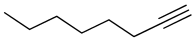
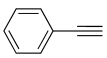
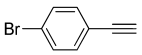
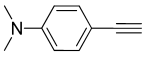
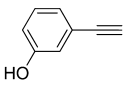
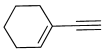
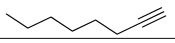
Table 3. Intermolecular Hydroamination of Anilines and Alkynes Catalyzed by Et_2Zn[a]

Entry	Substrates	A	B	C	D
1[b]		31 h, 88% (3% bypr)[c]	2 h, 89% (+ bypr2)[d]	11 h, quant. (12% bypr)[c]	4.25 h, quant.[f]
2		26 h, 85% (2% bypr)[c]	15 h, 95%	6 h, quant. (7% bypr)[c]	33 min, quant.
3		15 h, 96%	1 h, 11% 20 h, 15%	2 h, 94% (7% bypr)[c]	56.5 h, quant.[f] (10% bypr)[c]
4		4 h, 54%	-[g]	16 h, 75%	20 h, 78% (10% bypr)[c] 6 h, 98%
5		19 h, 90%	mixture of products	29 h, 93%	23 h, 91%
6		41 h, 69%[e]	mixture of products	14 h, 83%[e]	14.75 h, 98%[f]

[a]Reagents and conditions: catalyst (2.5 mol %), $[PhNMe_2H][B(C_6F_5)_4]$ (2.5 mol %), C_6D_6, 60 °C, conversion determined by ^1H NMR, ferrocene as internal standard. Amine (0.5 mmol), alkyne (0.75 mmol). [b]Amine (0.5 mmol), alkyne (1 mmol). [c]bypr = byproduct: the corresponding enamine. [d]Unknown byproduct. [e]Reaction at 80 °C. [f]Reaction at room temperature. [g]No conversion at 80 °C.

Table 4. Intermolecular Hydroamination of Anilines and Alkynes Catalyzed by $[(\eta^5\text{-Cp}^*)_2Zn_2]$[a,59]

Entry	Substrates	A	B	C	D
1		9 h, 95%	3.5 h, 82%	5 h, 87%. (22% bypr)[d]	11.25 h, quant.[e] 99 %[c, e]
2		9 h, 96%	15 h, 99%	4 h, 88% 10 h, quant.	19.66 h, 93%[e] 21.66 h, 95%[e]
3		5 h, quant.	1 h, 20%	5 h, quant.	19.75 h, 93%[e] 21.75 h, 96%[e]
4		6.5 h, 82% 30 h, 97%	-[f]	34 h, 99%	41.75 h, 69%[e] 43.75 h, 70%[e]
5[b]		19 h, 84%	mixture of products	50 h, 75%	6 h, 87%
6[b]		37 h, 99%	mixture of products	6 h, 97% 12 h, quant.	24 h, quant.

[a]Reagents and conditions: catalyst (2.5 mol %), $[PhNMe_2H][B(C_6F_5)_4]$ (2.5 mol %), C_6D_6, 60 °C, conversion determined by ^1H NMR, ferrocene as internal standard. Amine (0.5 mmol), alkyne (0.5 mmol). [b]Amine (0.5 mmol), alkyne (0.75 mmol). [c]Isolated yield. [d]bypr = byproduct: the corresponding enamine. [e]Reaction at room temperature. [f]No conversion.

arylethynes also benzylamine (Table 2, entry E), 1-ethynylcyclohexene (Table 2, entry 5), and 1-octyne (Table 2, entry 6) were used as substrates. With the exception of benzylamine (Table 2, entry E) all reactions of the primary amines achieved a conversion of 90−100% by using compound **2** as catalyst. Reactions of the secondary amine *N*-methylaniline

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are less favored. Thus reaction of *N*-methylaniline with 4-ethynyldimethylaniline, 3-ethynylphenol, and ethynylcyclohexene showed poor results (Table 2, entries 3B−5B). In contrast to the amines, aliphatic substituents on the alkyne function did not have any negative influence on the reactions. The primary alkynes 1-ethynylcyclohexene (Table 2, entry 5) and 1-octyne (Table 2, entry 6) were transformed to the corresponding imines by using compound **2** as catalyst. Thus, the nature of the amine and its pK_a value seem to have a major influence on the catalysis, whereas the substituents on the terminal alkynes are less important. The rates and the yields were substrate dependent. We also tried to introduce an OH group as functional group onto the aliphatic chain of the alkyne by using 4-pentyne-1-ol as substrate, but only product mixtures could be obtained.

As second catalyst we investigated the commercially available $ZnEt_2$ (**3**). The ease of accessibility of compound **3** is an advantage compared to the metallocene compounds **1** and **2**. For comparing the catalytic performance, a similar range of substrates and reaction conditions to that for compound **2** were chosen (Table 3). In general compound **3** is slower than compound **2** not only in the test reaction (Table 1, entries 2 and 3) but also for all reactions shown in Tables 2 and 3. Moreover, the amount of the enamine, which is the byproduct of the mainly formed Schiff base, is higher for most of the investigated reactions in which the byproduct is formed. As observed for compound **2**, also compound **3** catalyzes most of the reactions in high conversions. The exceptions are the secondary amine *N*-methylaniline (Table 3, entry B) and 3-ethynylphenol (Table 3, entry 4). The reasons for these hampered conversions might be the steric hindrance of *N*-methylaniline and the phenolic OH group of 3-ethynylphenol, which might react with the catalysts to form a zinc phenoxide. In contrast to compound **2**, which obviously tolerates the OH group of 3-ethynylphenol (Table 2, entry 4), compound **3** is more sensitive. 1-Octyne was completely transformed by using compound **3** as catalyst, but higher reaction temperatures (80 °C) were needed for this aliphatic alkyne for most of the reactions (Table 3, entry 6). In the case of the aliphatic alkynes 1-octyne and 1-ethynylcyclohexene compounds **2** and **3** are less efficient than other easily accessible catalysts. Thus, the $[Ti(NMe_2)_4]$-catalyzed addition of aniline to 1-hexyne proceeds already in 2 h, but 10 mol % of catalysts and a reaction temperature of 75 °C were needed.[98]

We then compared the catalytic activity of compounds **2** and **3** with that of Zn−Zn bonded complex **1** (Table 4). Parts of the results shown in Table 4 were communicated by us earlier.[59] We now added new results for the aliphatic alkynes shown in Table 4, entries 5 and 6. As observed for compounds **2** and **3**, the aliphatic alkynes were mostly converted in high yield. As seen from Tables 1−4 compound **1** shows a slower catalytic rate in most of the investigated reactions than those observed for compounds **2** and **3**. On the other hand, the relative amount of byproduct (enamine) formed by using compound **1** as catalyst is significantly lower than that by the other two catalysts. Thus, Zn−Zn bonded complex **1** shows a better selectivity. During our catalytic experiments we did not observe the formation of any elemental zinc. This observation together with the different selectivity of complex **1** in comparison to complex **2** indicates that compound **1** does not simply disproportionate to elemental Zn and **2** during the reaction.

Recently the hydroamination of phenylethyne with aniline catalyzed by $Zn(OTf)_2$ followed by a reduction was reported (98% yield, in 24 h at 120 °C; Figure S1, Table S1).[45] It can be clearly seen from Tables 2−4 (entry 1A, each) that the organometallic catalysts **1**−**3** are superior. Compound **2** catalyzes the same reaction in 9 h in quantitative conversion at only 60 °C reaction temperature.

Kinetic investigations have shown a substrate dependence of the rate. For the addition of 2,4,6-trimethylaniline to phenylethyne a zero-order kinetics in substrate was observed for the initial 80% of conversion (Figure 1). This kinetic data supports

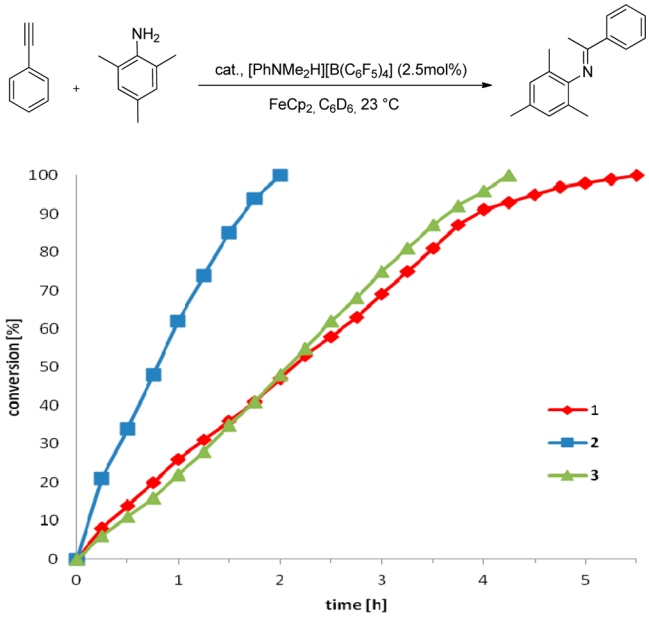

Figure 1. Conversions vs time diagram of the catalytic hydroamination of 2,4,6-trimethylaniline to phenylethyne in a 1:2 ratio using compounds **1**−**3** as catalysts and $[PhNMe_2H][B(C_6F_5)_4]$ as cocatalyst; [aniline] = 1 mol·L^{-1}. The rate constants are k = 0.065 × 10^{-3}·mol·L^{-1}·s^{-1} (**1**), 0.172 × 10^{-3}·mol·L^{-1}·s^{-1} (**2**), and 0.086 × 10^{-3}·mol·L^{-1}·s^{-1} (**3**) for the first 80% of the reaction (concentration 1 mol·L^{-1}).

the results given in Table 1. Compound **2** catalyzes the hydroamination most rapidly, whereas compounds **1** and **3** show similar rates in this reaction. The kinetic data of other transformations such as the addition of 2,4,6-trimethylaniline to 1-octyne (Figure S2; Tables 2 and 3, entry 6D each) and 1-bromo-4-ethynylbenzene (Figure S3; Tables 2 and 3, entry 2D each) also show that compound **2** is the fastest catalyst, but a clear zero-order kinetics cannot be extracted from the first reaction. Nevertheless, both kinetic measurements show neither any induction period nor an unstable conversion. Obviously a stable catalytic species is formed *in situ* for all three catalysts, but at the present stage we do not know the exact nature and the oxidation state of the catalytically active species. Based on the results of other research groups, we propose a cationic complex as the active species.[75]

CONCLUSIONS

In conclusion, we have shown that the three organometallic zinc compounds **1**−**3** are remarkably good catalysts for the intermolecular hydroamination reaction in the presence of equimolar amounts of $[PhNMe_2H][B(C_6F_5)_4]$. Many functional groups are tolerated.

The addition of 2,4,6-trimethylaniline to phenylethyne catalyzed by all three compounds proceeds at room temper-

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ature. Also the addition of other aniline compounds and their derivatives to arylethynes proceeds smoothly. For some of these reactions, compounds **1**−**3** are more active than any other catalyst. On the other hand terminal aliphatic alkynes are better converted by other catalysts. Within the series of compounds **1**−**3** the metallocene **2** is the most active one, whereas the zinc−zinc bonded species **1** shows the best selectivity. Since diethylzinc (**3**) is commercially available, it is the catalyst that is the most easily accessible. Thus, each of the three investigated compounds has its advantages. Most remarkable is the broad catalytic application of the zinc−zinc bonded species **1**.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, NMR spectra, kinetic plots, and Table S1 are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Johannsen, M.; Jorgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689−1708.
(2) Roundhill, D. M. *Chem. Rev.* **1992**, *92*, 1−27.
(3) Nobis, M.; Drießen-Hölscher, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3983−3985.
(4) Brunet, J.-J.; Neibecker, D. In *Catalytic Heterofunctionalization*; Togni, A., Grützmacher, H., Eds.; 2001; pp 91−141.
(5) Seayad, J.; Tillack, A.; Hartung, C. G.; Beller, M. *Adv. Synth. Catal.* **2002**, *344*, 795−813.
(6) Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2003**, 935−946.
(7) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104−114.
(8) Roesky, P. W.; Müller, T. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 2708−2710.
(9) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079−3160.
(10) Hartwig, J. F. *Pure Appl. Chem.* **2004**, *76*, 507−516.
(11) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673−686.
(12) Hultzsch, K. C. *Adv. Synth. Catal.* **2005**, *347*, 367−391.
(13) Hultzsch, K. C. *Org. Biomol. Chem.* **2005**, *3*, 1819−1824.
(14) Widenhoefer, R. A.; Han, X. *Eur. J. Org. Chem.* **2006**, *2006*, 4555−4563.
(15) Aillaud, I.; Collin, J.; Hannedouche, J.; Schulz, E. *Dalton Trans.* **2007**, 5105−5118.
(16) Hunt, P. A. *Dalton Trans.* **2007**, 1743−1754.
(17) Müller, T. E.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. *Chem. Rev.* **2008**, *108*, 3795−3892.
(18) Roesky, P. W. *Angew. Chem., Int. Ed.* **2009**, *49*, 4892−4894.
(19) Li, T.; Jenter, J.; Roesky, P. W. *Struct. Bonding (Berlin)* **2010**, *137*, 165−228.
(20) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675−704.
(21) Jenter, J.; Luhl, A.; Roesky, P. W.; Blechert, S. *J. Organomet. Chem.* **2011**, *696*, 406−418.
(22) Eisenberger, P.; Schafer, L. L. *Pure Appl. Chem.* **2010**, *82*, 1503−1515.
(23) Hill, M. S. *Annu. Rep. Prog. Chem. Sect. A: Inorg. Chem.* **2007**, *103*, 39−53.
(24) Koller, J.; Bergman, R. G. *Chem. Commun.* **2010**, *46*, 4577−4579.
(25) Koller, J.; Bergman, R. G. *Organometallics* **2010**, *29*, 3350−3356.
(26) Arrowsmith, M.; Hill, M. S.; Kociok-Köhn, G. *Organometallics* **2009**, *28*, 1730−1738.
(27) Barrett, A. G. M.; Brinkmann, C.; Crimmin, M. R.; Hill, M. S.; Hunt, P.; Procopiou, P. A. *J. Am. Chem. Soc.* **2009**, *131*, 12906−12907.
(28) Buch, F.; Harder, S. *Z. Naturforsch., B: Chem. Sci.* **2008**, *63*, 169−177.
(29) Crimmin, M. R.; Arrowsmith, M.; Barrett, A. G. M.; Casely, I. J.; Hill, M. S.; Procopiou, P. A. *J. Am. Chem. Soc.* **2009**, *131*, 9670−9685.
(30) Crimmin, M. R.; Casely, I. J.; Hill, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 2042−2043.
(31) Datta, S.; Gamer, M. T.; Roesky, P. W. *Organometallics* **2008**, *27*, 1207−1213.
(32) Datta, S.; Gamer, M. T.; Roesky, P. W. *Dalton Trans.* **2008**, 2839−2843.
(33) Datta, S.; Roesky, P. W.; Blechert, S. *Organometallics* **2007**, *26*, 4392−4394.
(34) Dunne, J. F.; Fulton, D. B.; Ellern, A.; Sadow, A. D. *J. Am. Chem. Soc.* **2010**, *132*, 17680−17683.
(35) Horrillo-Martínez, P.; Hultzsch, K. C. *Tetrahedron Lett.* **2009**, *50*, 2054−2056.
(36) Neal, S. R.; Ellern, A.; Sadow, A. D. *J. Organomet. Chem.* **2011**, *696*, 228−234.
(37) Zhang, X.; Emge, T. J.; Hultzsch, K. C. *Organometallics* **2010**, *29*, 5871−5877.
(38) Kang, J.-E.; Kim, H.-B.; Lee, J.-W.; Shin, S. *Org. Lett.* **2006**, *8*, 3537−3540.
(39) Nishina, N.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 3314−3317.
(40) Nishina, N.; Yamamoto, Y. *Synlett* **2007**, 1767−1770.
(41) Zhang, J.; Yang, C.-G.; He, C. *J. Am. Chem. Soc.* **2006**, *128*, 1798−1799.
(42) Zhang, Y.; Donahue, J. P.; Li, C.-J. *Org. Lett.* **2007**, *9*, 627−630.
(43) Zhang, Z.; Lee, S. D.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2009**, *131*, 5372−5373.
(44) Meyer, N.; Löhnwitz, K.; Zulys, A.; Roesky, P. W.; Dochnahl, M.; Blechert, S. *Organometallics* **2006**, *25*, 3730−3734.
(45) Alex, K.; Tillack, A.; Schwarz, N.; Beller, M. *ChemSusChem* **2008**, *1*, 333−338.
(46) Okuma, K.; Seto, J.-I.; Sakaguchi, K.-I.; Ozaki, S.; Nagahora, N.; Shioji, K. *Tetrahedron Lett.* **2009**, *50*, 2943−2945.
(47) Prior, A. M.; Robinson, R. S. *Tetrahedron Lett.* **2008**, *49*, 411−414.
(48) Yin, Y.; Ma, W.; Chai, Z.; Zhao, G. *J. Org. Chem.* **2007**, *72*, 5731−5736.
(49) Biyikal, M.; Löhnwitz, K.; Roesky, P. W.; Blechert, S. *Synlett* **2008**, 3106−3110.
(50) Biyikal, M.; Lohnwitz, K.; Meyer, N.; Dochnahl, M.; Roesky, P. W.; Blechert, S. *Eur. J. Inorg. Chem.* **2010**, 1070−1081.
(51) Biyikal, M.; Porta, M.; Roesky, P. W.; Blechert, S. *Adv. Synth. Catal.* **2010**, *352*, 1870−1875.
(52) Dochnahl, M.; Lohnwitz, K.; Luhl, A.; Pissarek, J. W.; Biyikal, M.; Roesky, P. W.; Blechert, S. *Organometallics* **2010**, *29*, 2637−2645.
(53) Löhnwitz, K.; Molski, M. J.; Lühl, A.; Roesky, P. W.; Dochnahl, M.; Blechert, S. *Eur. J. Inorg. Chem.* **2009**, 1369−1375.
(54) Pissarek, J. W.; Schlesiger, D.; Roesky, P. W.; Blechert, S. *Adv. Synth. Catal.* **2009**, *351*, 2081−2085.
(55) Zulys, A.; Dochnahl, M.; Hollmann, D.; Löhnwitz, K.; Herrmann, J.-S.; Roesky, P. W.; Blechert, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7794−7798.

(56) Dochnahl, M.; Löhnwitz, K.; Pissarek, J.-W.; Biyikal, M.; Schulz, S. R.; Schön, S.; Meyer, N.; Roesky, P. W.; Blechert, S. *Chem.—Eur. J.* **2007**, *13*, 6654−6666.
(57) Dochnahl, M.; Löhnwitz, K.; Pissarek, J.-W.; Roesky, P. W.; Blechert, S. *Dalton Trans.* **2008**, 2844−2848.
(58) Dochnahl, M.; Pissarek, J.-W.; Blechert, S.; Löhnwitz, K.; Roesky, P. W. *Chem. Commun.* **2006**, 3405−3407.
(59) Lühl, A.; Pada Nayek, H.; Blechert, S.; Roesky, P. W. *Chem. Commun.* **2011**, *47*, 8280−8282.
(60) Resa, I.; Carmona, E.; Gutierrez-Puebla, E.; Monge, A. *Science* **2004**, *305*, 1136−1138.
(61) Grirrane, A.; Resa, I.; Rodriguez, A.; Carmona, E.; Alvarez, E.; Gutierrez-Puebla, E.; Monge, A.; Galindo, A.; del Río, D.; Andersen, R. A. *J. Am. Chem. Soc.* **2006**, *129*, 693−703.
(62) del Río, D.; Galindo, A.; Resa, I.; Carmona, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 1244−1247.
(63) del Rio, D.; Resa, I.; Rodriguez, A.; Sánchez, L.; Köppe, R.; Downs, A. J.; Tang, C. Y.; Carmona, E. *J. Phys. Chem. A* **2008**, *112*, 10516−10525.
(64) Wang, Y.; Quillian, B.; Wei, P.; Wang, H.; Yang, X.-J.; Xie, Y.; King, R. B.; Schleyer, P. v. R.; Schaefer, H. F.; Robinson, G. H. *J. Am. Chem. Soc.* **2005**, *127*, 11944−11945.
(65) Zhu, Z.; Brynda, M.; Wright, R. J.; Fischer, R. C.; Merrill, W. A.; Rivard, E.; Wolf, R.; Fettinger, J. C.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2007**, *129*, 10847−10857.
(66) Yang, P.; Yang, X.-J.; Yu, J.; Liu, Y.; Zhang, C.; Deng, Y.-H.; Wu, B. *Dalton Trans.* **2009**, 5773−5779.
(67) Yang, X.-J.; Yu, J.; Liu, Y.; Xie, Y.; Schaefer, H. F.; Liang, Y.; Wu, B. *Chem. Commun.* **2007**, 2363−2365.
(68) Tsai, Y.-C.; Lu, D.-Y.; Lin, Y.-M.; Hwang, J.-K.; Yu, J.-S. K. *Chem. Commun.* **2007**, 4125−4127.
(69) Schulz, S.; Schuchmann, D.; Westphal, U.; Bolte, M. *Organometallics* **2009**, *28*, 1590−1592.
(70) Fedushkin, I. L.; Eremenko, O. V.; Skatova, A. A.; Piskunov, A. V.; Fukin, G. K.; Ketkov, S. Y.; Irran, E.; Schumann, H. *Organometallics* **2009**, *28*, 3863−3868.
(71) Schulz, S.; Gondzik, S.; Schuchmann, D.; Westphal, U.; Dobrzycki, L.; Boese, R.; Harder, S. *Chem. Commun.* **2010**, *46*, 7757−7759.
(72) Gondzik, S.; Bläser, D.; Wölper, C.; Schulz, S. *Chem.—Eur. J.* **2010**, *16*, 13599−13602.
(73) Nayek, H. P.; Lühl, A.; Schulz, S.; Köppe, R.; Roesky, P. W. *Chem.—Eur. J.* **2011**, *17*, 1773−1777.
(74) Schuchmann, D.; Westphal, U.; Schulz, S.; Flörke, U.; Bläser, D.; Boese, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 807−810.
(75) Schulz, S.; Schuchmann, D.; Krossing, I.; Himmel, D.; Bläser, D.; Boese, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 5748−5751.
(76) Carrasco, M.; Peloso, R.; Rodríguez, A.; Álvarez, E.; Maya, C.; Carmona, E. *Chem.—Eur. J.* **2010**, *16*, 9754−9757.
(77) Li, T.; Schulz, S.; Roesky, P. W. *Chem. Soc. Rev.* **2012**, *41*, 3759−3771.
(78) Lühl, A. *Dissertation*, Karlsruher Institut für Technologie (KIT), 2010.
(79) Torregrosa, R.; Pastor, I. M.; Yus, M. *Tetrahedron* **2005**, *61*, 11148−11155.
(80) Barluenga, J.; Fernández, M. A.; Aznar, F.; Valdés, C. *Chem.—Eur. J.* **2004**, *10*, 494−507.
(81) Imamoto, T.; Iwadate, N.; Yoshida, K. *Org. Lett.* **2006**, *8*, 2289−2292.
(82) Shanbhag, G. V.; Halligudi, K. P., S. B. *Open Org. Chem. J.* **2008**, *2*, 52−57.
(83) Han, Z.; Wang, Z.; Zhang, X.; Ding, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 5345−5349.
(84) Katritzky, A. R.; Lan, X.; Lam, J. N. *Chem. Ber.* **1991**, *124*, 1431−1434.
(85) Kuninobu, Y.; Nishina, Y.; Matsuki, T.; Takai, K. *J. Am. Chem. Soc.* **2008**, *130*, 14062−14063.
(86) Tillack, A.; Khedkar, V.; Jiao, H.; Beller, M. *Eur. J. Org. Chem.* **2005**, 5001−5012.
(87) Leyva, A.; Corma, A. *Adv. Synth. Catal.* **2009**, *351*, 2876−2886.
(88) Naeimi, H.; Salimi, F.; Rabiei, K. *J. Mol. Catal. A: Chem* **2006**, *260*, 100−104.
(89) Chilleck, M. A.; Braun, T.; Braun, B. *Chem.—Eur. J.* **2011**, *17*, 12902−12905.
(90) Zeng, X.; Frey, G.; Kousar, S.; Bertrand, G. *Chem.—Eur. J.* **2009**, *15*, 3056−3060.
(91) Weitershaus, K.; Ward, B. D.; Kubiak, R.; Müller, C.; Wadepohl, H.; Doye, S.; Gade, L. H. *Dalton Trans.* **2009**, 4586−4602.
(92) Shanbhag, G. V.; Palraj, K.; Halligudi, S. B. *Open Org. Chem. J* **2008**, *2*, 52−57.
(93) Shanbhag, G. V.; Joseph, T.; Halligudi, S. B. *J. Catal.* **2007**, *250*, 274−282.
(94) Shanbhag, G. V.; Kumbar, S. M.; Joseph, T.; Halligudi, S. B. *Tetrahedron Lett.* **2006**, *47*, 141−143.
(95) Mizushima, E.; Hayashi, T.; Tanaka, M. *Org. Lett.* **2003**, *5*, 3349−3352.
(96) Dash, C.; Shaikh, M. M.; Butcher, R. J.; Ghosh, P. *Inorg. Chem.* **2010**, *49*, 4972−4983.
(97) In the earlier studies we used an amine to alkyne ratio of 1:1, since we aimed to have full conversion without any byproduct or starting material. Now we are more focused on higher rates.
(98) Shi, Y.; Ciszewski, J. T.; Odom, A. L. *Organometallics* **2001**, *20*, 3967−3969.